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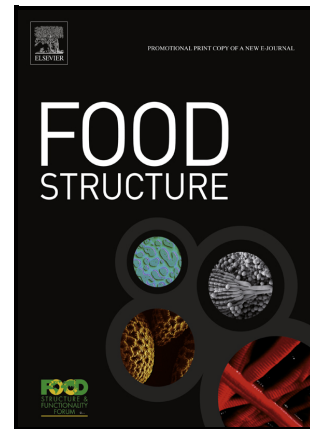
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Composite Oleogels Formed by Cellulose Particles and Sorbitan Acid Esters

Cellulose particles could be used to form an oleogels

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Abstract:

Developing a facile method to prepare edible oleogels under moderate conditions would be of great interest. In this research, oleogels were obtained directly from the mixtures of cellulose particles (average particle size $\approx 25\mu\text{m}$), sorbitan fatty acid esters (Span60 and Span40) and medium chain triglycerides (MCT). Results showed that 6% (w/w) cellulose particles combined with 9% (w/w) sorbitan fatty acid esters could form a strong network to trap the oil phase through ultra-sonic treating. The strength of the oleogels could be regulated by the cellulose particles content and its

ratio to surfactant. XRD, DSC and SEM data revealed that there was synergetic effect between the cellulose particles and fatty acid esters during the gelation. The cellulose particles covered with Span60 could associate with each other to form a network in the oil phase, in the similar way to the Span60 micelles. These findings would be significant for the development and application of food grade oleogels.

Keywords:

oleogels, cellulose particles, edible polymers, synergetic effect

Introduction

Solid-like lipids were widely used in food industry due to their elastic properties for producing texture, spreadability, mouth-feel, and so on. However, most of the solid-like lipids used today are obtained from fat crystal networks comprised primarily of *trans*- and saturated fats (Rogers, 2009). Considering their harmful effects (Islam, *et al.*, 2019) and regulations of banning them in foods, many new approaches have been made for the preparation of solid-like lipids in recent years (Martins, Vicente, Cunha & Cerqueira, 2018). One of which is oleogel, which using small molecular weight gelators to trap the oil phase (Patel, 2017). Various gelators have been used successfully on oleogel preparation, such as hydroxylated fatty acids, fatty acids, fatty alcohols, phytosterol, oryzanol, sorbitan monostearate, lecithin, or their mixtures. (Pernetti, Malssen, Eckhard & Bot, 2007; Pakseresht & Tehrani, 2021). During the gelation, the small molecular weight gelators firstly assemble into micelles or fibrils and then associate or stack into a three-dimensional structure (Patel & Dewettinck, 2016). However, these gelators are uneconomic when they are massively used in food products, because high concentrations of them are usually required. Moreover, high concentrations of some gelators are harmful to the consumer's health (Glynn, *et al.*, 2017).

Using healthy materials, such as natural polymers, to form oleogel has attracted more and more attention of researchers (Suzuki & Hanabusa, 2010). Indirect approaches were usually adopted because most of them had poor solubility in the oil phase (Rogers, 2009). The indirect methods for oleogels preparation mainly include

emulsion-template approach, solvent exchange procedure, and others (Bascuas, Morell, Hernando & Quiles, 2021). The emulsion template was made by evaporation of water after the emulsion formation (Gao, *et al.*, 2014; Pan, *et al.*, 2021; Tavernier, Patel, van der Meeren & Dewettinck, 2017). In the solvent exchange method, the internal aqueous phase of the hydrogel was replaced with an intermediate solvent followed by liquid oil (de Vries, Hendriks, Van Der Linden & Scholten, 2015). These polymer-based indirect approaches exhibited a prospect to be used in food products (Luo, *et al.* 2019), but the complexity of the procedures would seriously limit their industrial-scale applications. In contrast, the direct procedure for oleogels preparation is more convenient, because the polymers just need to be melted in oil under heating and form an oleogel through physical interaction during cooling (Ceballos, *et al.*, 2016; Fu, *et al.*, 2020; Giacintucci, *et al.*, 2018). However, the food grade polymers suitable for the direct procedure are scarce, and high temperature is necessary to melt them. For example, ethylcellulose (EC) needs to be heated to over 130°C to melt in the oil (Laredo, Barbut & Marangoni, 2011; Zetzl, Marangoni & Barbut, 2012), which might be harmful for the heat sensitive components in food.

Therefore, developing a facile method to prepare oleogels under moderate conditions would be of great significance. However, such methods are still lacking. Nikiforidis & Scholten (2015) used chitosan whiskers and nanocrystals to prepare oleogels through a direct approach, with the auxiliary effect from surfactant (such as phospholipids). The mixtures of chitin-surfactant and oil were heated at 85 °C with stirring for 30 minutes and then cooled down at room temperature to obtain the oleogels. A combination of chitin nanocrystal and surfactant causes uniform and very stable gel (Nikiforidis & Scholten, 2015). However, the related mechanism of the synergetic effect between the chitin and surfactant was still unclear.

The aim of this research is to develop a facial method to prepare oleogel under a moderate environment and further reveal the synergetic mechanisms between polymer and surfactant in the gelation process. Crude material of α -cellulose particles (average particle size $\approx 25\mu\text{m}$) was used, and sorbitan fatty acid esters (sorbitan monopalmitate and sorbitan monostearate) were chosen as the surfactant. Medium chain triglyceride (MCT) was chosen as the oil in this research to avoid any other possible surfactant

contamination, although vegetable oils are often used to produce oleogels in real cases. The chemical structures of the α -cellulose and the sorbitan fatty acid esters used in this research are presented in Figure 1. The oleogels were obtained directly by ultra-sonic treating the mixtures of cellulose particles, sorbitan fatty acid esters and MCT. Our results will provide useful information for the application of hydrophilic polymers in edible oleogels preparation through a simple approach.

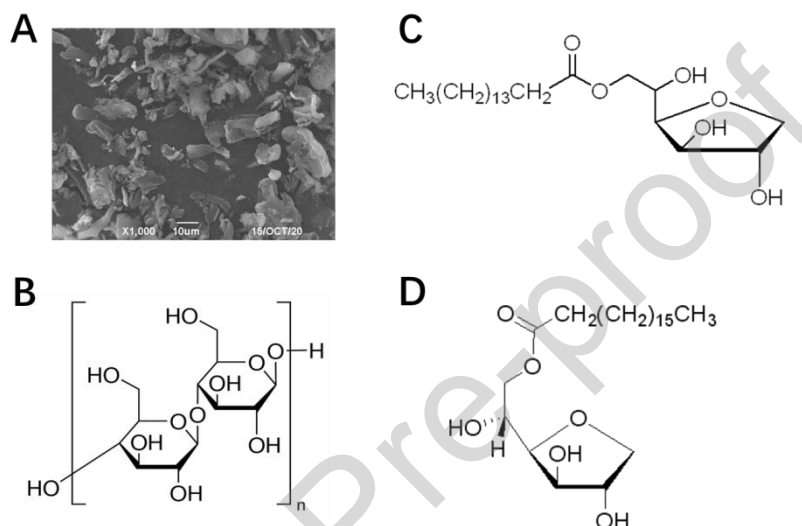


Figure 1: Scanning electron micrograph of α -cellulose particles used in this research (A) and the molecular structures of α -cellulose (B), sorbitan monopalmitate (Span40) (C) and sorbitan monostearate (Span60) (D).

Materials and method

Materials.

α -cellulose particles with average particle size of 25 μ m, sorbitan monopalmitate (Span40, with purity of 94%, and melting point of 46-47°C) and sorbitan monostearate (Span60, with purity of 97%, and melting point of 56-58°C) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). MCT (glyceryl tridecanoate) was purchased from Merck KGaA (T7517, Purity \geq 99%, Shanghai, China).

Preparation of oleogels.

Certain amounts of cellulose particles and sorbitan fatty acid esters were weighed and added into 10 g MCT. The concentration of cellulose particles in MCT varied from 4% (w/w) to 10% (w/w), and the concentration of sorbitan fatty acid esters varied from 2% (w/w) to 20% (w/w), to make the weight ratio between sorbitan fatty acid esters and cellulose particles to be in the range of 0.5 to 2. Then the mixtures were subjected to an ultra-sonic treatment (Sonic Ruptor 400 Ultrasonic Homogenizer, OMNI, USA) for 2 min at room temperature (25 ± 1 °C), where the probe diameter was 0.6 mm and the frequency and power were 40 KHz and 480 W, respectively. The temperature of the samples was about 75°C after the ultra-sonic treatment. Then, the samples were naturally cooled down to room temperature (25 ± 1 °C) and left for 3 days. The formation of oleogels under various precursor concentrations was summarized by a phase diagram, which was made by photographs of the samples in the inverted tubes.

Optical micrograph observation.

To observe the microstructure of the oleogels, an optical microscope was used (C-Li, Nikon, Japan). A drop of the ultra-sonic treated liquid sample before its gelation was put on the glass slide and covered with a coverslip. Then the sample was naturally cooled at room temperature (25 ± 1 °C) for 3 days before subjecting to microscopic observation. A magnification of 10 times was applied.

X-ray diffraction (XRD) measurement.

XRD patterns were obtained using a D/Max-3B diffractometer (Rigaku Corporation, Japan) with Cu K α radiation (40 kV, 100 mA), at a scanning rate of 5°/min. Oleogel samples were mounted on a vitreous sample holder and scanned with a step size of $2\theta = 0.02^\circ$ between $2\theta = 10^\circ$ and 60° .

Differential scanning calorimetry (DSC) analysis.

Thermograms of oleogels were collected on a DSC system (DSC1, METTLER TOLEDO, Swiss). The oleogel samples (12 mg) were weighed into aluminium pans that were then hermetically sealed. They were heated at a temperature increasing from

20°C to 90°C at a rate of 1°C/min. The transition temperatures were determined by endothermic peak maxima during the heating process. The samples before and after DSC analysis were weighted to promise no liquid leaked from the pan during the measurement.

Centrifugal treatment of the samples.

To evaluate the gelation behavior of the surface modified cellulose particles, ultra-sonic treated cellulose particles/Span60/MCT mixtures were centrifuged at 5,000 g for 2 minutes immediately before their solidification. This centrifugal treatment would lead to the separation of the surface modified cellulose particles (the sediments) from the Span60/MCT mixtures. The centrifuge tube was then inverted and photographed. Then the sediment was collected and subjected to rheological analysis.

Rheological analysis.

Rheological properties of the oleogels were measured using a HAAKE Rheostress 6000 rheometer (Thermo Scientific) with parallel plate geometry (diameter of 35 mm). The samples were loaded between the parallel plates (with 1 mm gap) before their gelation. After cooling down to 25 ± 1 °C for 3 hours, the oleogels were formed, and the measurement was commenced. The frequency sweeps were taken in the range from 0.01 to 10 Hz at strain of 0.001%.

Scanning electron microscope (SEM) observation.

To observe the microstructure of the oleogels by SEM, petroleum ether was used as the oil phase to prepare the samples, because it could be removed easily by volatilization. 10% (w/w) Span60 or 10% (w/w) cellulose particles/10% (w/w) Span60 mixture was added into the petroleum ether, then the mixture was ultra-sonic treated at the conditions mentioned above. Next, the samples were cooled down to 25 ± 1 °C and left for 3 days in the fume hood to let the petroleum ether to volatilize. Then, the samples were fixed to a SEM aluminum stub through double sided conductive carbon tapes. After coating with gold in an E-1010 ion sputter (Hitachi,

Tokyo, Japan), the samples were observed using a JSM-6390LV SEM (JEOL, Japan) at an accelerating voltage of 15 kV.

Statistical analysis.

Unless otherwise specified, three independent trials were carried out for each measurement, and the results were given as mean \pm standard deviation. Statistical analysis was done using a software of Origin Pro v8.0 (OriginLab Corp., USA).

Results and analysis

Formation of the composite oleogel.

The appearance of the Span60/MCT, cellulose particles/MCT and cellulose particles/Span60/MCT mixtures after ultra-sonic treatment is shown in Figure 2A. The 10% (w/w) cellulose particles alone or 10% (w/w) Span60 alone did not form a solid-like oleogel (10% w/w Span60 formed a flowable semi-solid mixture). However, their mixtures (10% w/w cellulose particles and 10% w/w Span60) could solidify the oil phase, indicating the synergetic effect between the cellulose particles and Span60. Various concentrations of cellulose particles (from 4% to 10% w/w) and sorbitan acid esters (from 2% to 20% w/w) (the weight ratios of sorbitan acid esters to cellulose particles varied from 0.5 to 2.0) were applied to prepare the oleogels, and results were shown in Figures 2B and 2C. The cellulose particles could trap the oil phase through the synergetic effect with both of Span40 and Span60. It could be observed that the concentration of cellulose particles and the ratio of Span60/cellulose particles could affect the formation of oleogels. The minimum requirement for the cellulose particles content was 6% (w/w). As increasing cellulose particles content, the minimum requirement for Span60/cellulose particles ratio decreased.

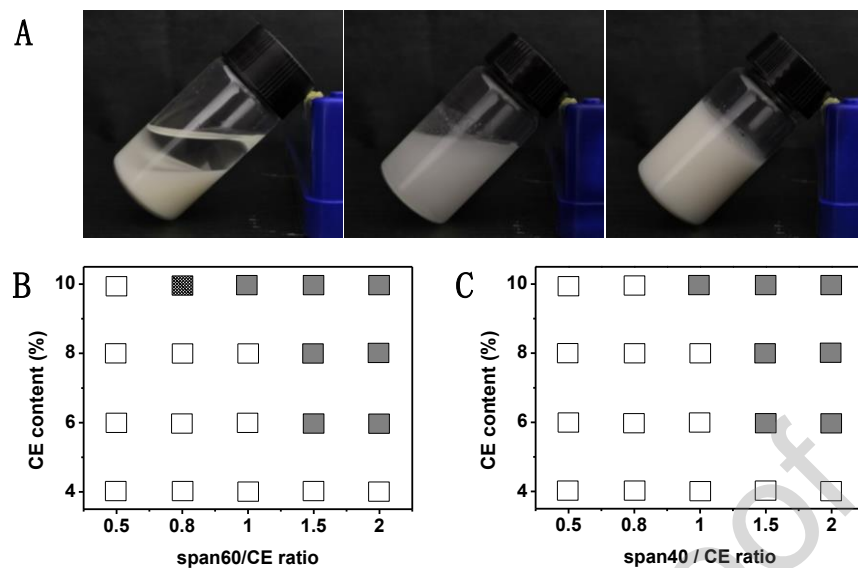


Figure 2: (A) is the appearance of cellulose particles/MCT, Span60/MCT and cellulose particles/Span60/MCT mixtures after ultra-sonic treatment; (B) and (C) showed the phase diagrams of the mixtures of cellulose particles and Span60 or Span40, where “CE” means cellulose particles. The empty squares represent liquid mixture, the filled gray squares represent a solid-like oleogel and the square filled with spots stands for a flowable semi-solid mixture.

The optical micrographs of the cellulose particles/MCT mixture and cellulose particles/surfactant/MCT mixtures after ultra-sonic treatment are presented in Figure 3. It could be observed that with the absence of surfactant, cellulose particles showed a serious aggregation state in MCT (Figure 3, left), due to their hydrophilicity. Previous report also showed that the chitin particles extensively aggregated in sunflower oil with absent of surfactant (Nikiforidis & Scholten, 2015). However, with the presence of 10% (w/w) Span40 or 10% (w/w) Span60, cellulose particles could be well dispersed in MCT (Figure 3, middle and right). It should be attributed to the binding of surfactant on the surface of cellulose particles *via* hydrophilic interactions, which improved the dispersibility of cellulose particles in MCT and benefited their functionality in the formation of the oleogels. Similar results were observed by Nikiforidis & Scholten (2015) where modified phosphatidylcholine and Span 60 apparently led to a better dispersibility of chitin in the hydrophobic medium. It was speculated that due to the interactions, phospholipid molecules in their work were

probably anchored on the chitin strands and their fatty acid chains created a lipophilic surface that penetrated into the more hydrophobic solvent.

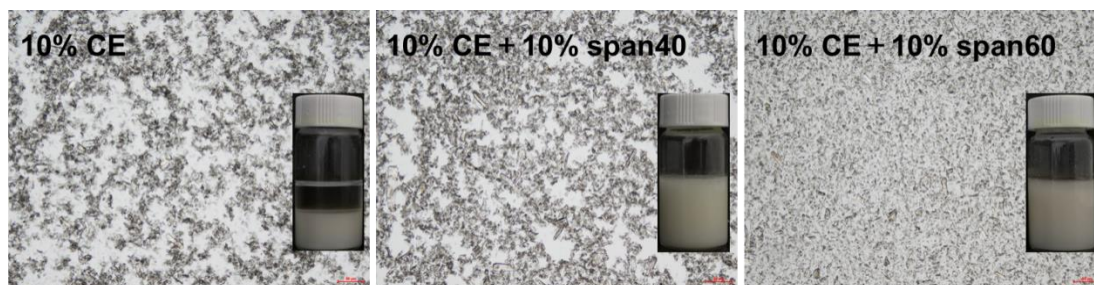


Figure 3: Micrographs of the mixtures of cellulose particles/MCT (left), cellulose particles/Span40/MCT (middle), and cellulose particles/Span60/MCT (right) after ultrasonic treatment. “CE” means cellulose particles. Scale bar = 50 μm .

Mechanisms of the composite oleogel formation.

The XRD measurement showed that at low concentration of Span60 (*e.g.* 1% w/w or 3% w/w), the Span60/MCT composites only produced a diffraction peak at $2\theta = 21.5^\circ$ (Figure 4A), indicating the formation of micelle by Span60 in MCT. With increasing the Span60 concentration (5% or 10% w/w), another very weak diffraction peak at $2\theta = 22.1^\circ$ arose, suggesting the stacking of the Span60 micelles and the formation of networks. Our XRD results were similar to the oleogels of Span60/mustard oil obtained by Sagiri, *et al.* (2016). The fluctuation of the diffraction signals was well matched with the formation of micelles and oleogels.

Cellulose has a main diffraction peak at $2\theta = 22.5^\circ$, as shown in Figure 4B. With the addition of 1% (w/w) Span60, another weak diffraction peak at $2\theta = 21.5^\circ$ arose, the same as the Span60 oleogels (Figure 4A), indicating the formation of Span60 micelles. When the span60 concentration increased to 5% (w/w), the signal of micelles diffraction also increased, and the diffraction peak of cellulose was sheltered. With further increase of Span60 concentration to 10% (w/w) or above (*e.g.* 20% w/w), the diffraction peak of the micelle clusters ($2\theta = 22.1^\circ$) arose and solid-like oleogels formed (as observed in Figure 2B). The XRD patterns of cellulose particles/Span60 oleogels were consistent with those of sole Span60 oleogels.

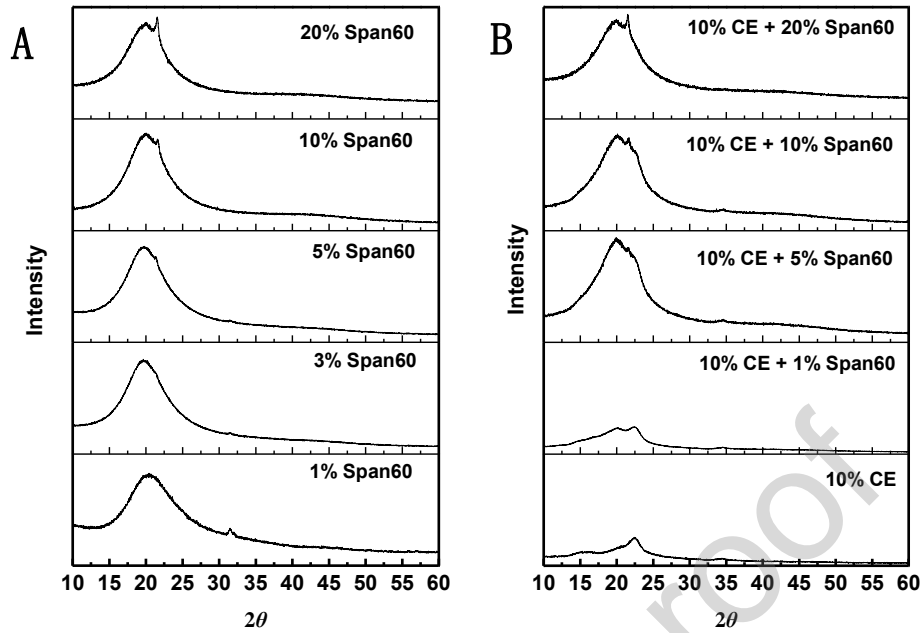


Figure 4: X-ray diffraction spectra of the Span60/MCT mixtures (A) and cellulose particles/Span60/MCT mixtures (B) after ultra-sonic treatment and storage at room temperature (25°C) for 3 days. “CE” means cellulose particles.

Furthermore, we measured the DSC profiles of the Span60/MCT and cellulose particles/Span60/MCT composites, as presented in Figure 5. There are two endothermic peaks in 10% (w/w) Span60 system (flowable semi-solid mixture) at 42.2 °C (peak I) and 55 °C (peak II). The endothermic peak I might indicate the dissociation of the micelle clusters of Span60, and endothermic peak II might be related to the collapse of the Span60 micelles under heating. The melting temperature (42.2 °C) was very close to the oleogels formed by Span60 in soybean oil (43.0 °C) (Godoi *et al.*, 2019). For the mixture of 10% (w/w) cellulose particles and 1% (w/w) Span60, there was a negligible signal of peak I and no signal of micelle (peak II) detected, suggesting there might exist the “micelle cluster-like” association. It seems to be conflicting with the observation in Figure 4B where there is apparent XRD signal for micelles in the 10% cellulose particles/1% Span60 mixture, possibly because the endothermic signal of micelle was too weak to be detected by our DSC instrument. With further addition of Span60 to 5% (w/w) or above (*e.g.* 10% w/w), the endothermic peak II began to arise, indicating more micelles were formed. Note that in the endothermic profile of 10% cellulose particles/10% Span60 system, the endothermic peak I is stronger than peak II, which is different to the DSC profile of 10% (w/w) Span60. This phenomenon suggests that the presence of cellulose particles enhanced the “micelle cluster-like” association. Considering that after surface modification, the alkyl chains of Span60 on the

surface of cellulose particles would have a high affinity with the Span60 micelles in MCT, it is reasonable to speculate that there existed at least three types of “micelle cluster-like” association, including micelle-micelle association, particle-particle association, and particle-micelle association.

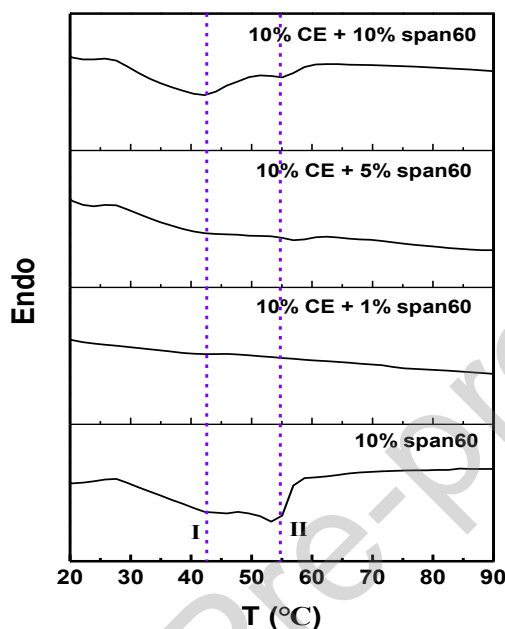


Figure 5: The differential scanning calorimetry (DSC) profiles of Span60/MCT and cellulose particles/Span60/MCT mixtures after ultra-sonic treatment and storage at room temperature (25°C) for 3 days. “CE” means cellulose particles.

Theoretically, with the presence of cellulose particles in the mixtures, part of the Span60 molecules would bind with the particles *via* hydrophilic interaction, which induced the reduction of the number of Span60 micelles and the micelle-micelle dissociation heat quantity. Therefore, the strengthening of the micelle cluster endothermic signal in 10% (w/w) cellulose particles/10% (w/w) Span60 mixture might be contributed by the particle-particle and particle-micelle associations. In another word, the surface modified cellulose particles might play a similar role to the Span60 micelles during the oleogels formation. After centrifugal treatment of the samples at 5,000 g for 2 minutes before solidification, cellulose particles were deposited at the bottom of the centrifuge tube, and the upper layer of the samples could not solidify (Figure 6A). This phenomenon further confirmed the reduction of Span60 micelles in the continuous phase with the presence of cellulose particles, and simultaneously proved the surface modified cellulose particles contributed to the

endothermic peak I of 10% cellulose particles/10% Span60 system (in Figure 5). The modulus of the sediment of 30% (w/w) cellulose particles and 1% w/w, 2% w/w and 3% w/w Span60 mixtures were analyzed, respectively (Figure 6B). At these concentration conditions, Span60 micelles formed networks could be avoided. All the storage modul of the sediments was greater than their loss modul, indicating the formation of viscoelastic gels. These results confirmed the associations between the surface modified cellulose particles. With increasing Span60 concentration, the association between the cellulose particles was enhanced.

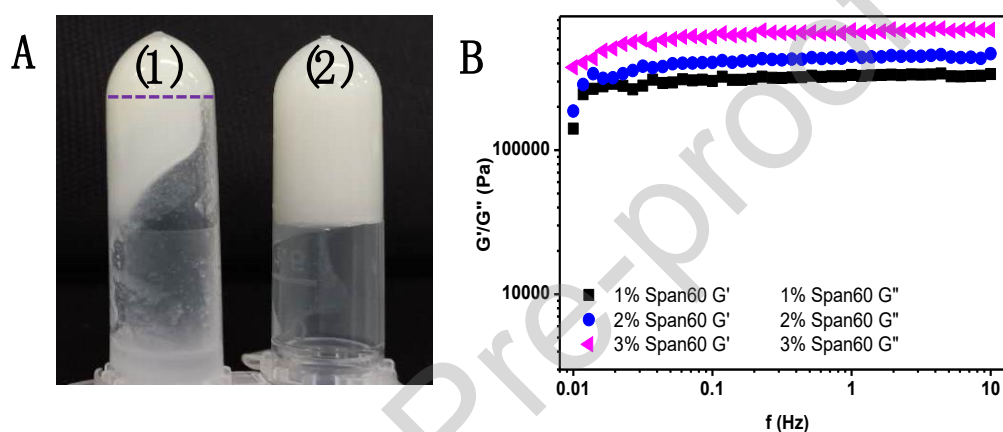


Figure 6: Inverted samples (A) of the 10% (w/w) cellulose particles/10 % (w/w) Span60 mixed oleogels with (1) or without (2) centrifuge at 5,000 g and 2 min before solidification; the modulus (B) of the sediment of the mixtures of 30% (w/w) cellulose particles and 1%, 2% and 3% w/w Span60 in MCT, after the centrifuge treatment at 5,000 g and 2 min.

Scanning electron microscope observation was taken for the oleogels, as showed in Figure 7. A fibrillar network could be observed from the Span60 formed gels (Figure 7A), similar to the previous reports (Trujillo-Ramírez, Lobato-Calleros, Vernon-Carter & Alvarez-Ramirez, 2019; Swe & Asavapichayont, 2018). Murdan *et al.* (1999) revealed that Span60 molecules self-assembled into toroidal inverse vesicles at the gelation temperature. Further cooling resulted in the conversion of the toroids into rod-shaped tubules. Once formed, the tubules associated with others, resulting in a three-dimensional network which immobilized the solvent. With the presence of cellulose particles (Figure 7B), the composite oleogel was mainly formed

by the associated cellulose particles, and the fibrillar network of Span60 could hardly be found from the magnified picture ($\times 3000$, inset in Figure 7B). It was reported that with the increase of sorbitan monopalmitate content, ethylcellulose oleogels had more compact gel networks with evenly distributed smaller pores (Liu, *et al.*, 2020). The sorbitan monopalmitate was consumed to reinforce the gel strength. Our observations suggest that most of the association between Span60 micelles was displaced by the association between the surface modified cellulose particles in the composite gel formation.

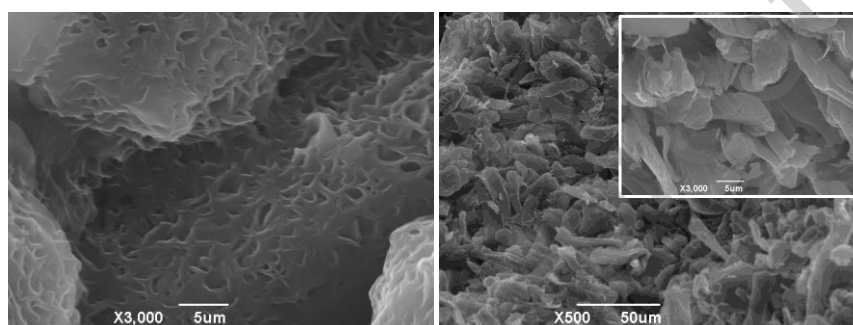


Figure 7: Scanning electronic micrographs of the oleogels formed by 10% (w/w) Span60 (A) or 10% Span60/10% (w/w) cellulose particles (B) in petroleum ether.

In the previous research, the presence of the surfactants limited chitin aggregation so that they were more able to participate in the formation of a stable network (Nikiforidis & Scholten, 2015). Surfactants are inferred to be anchored through their hydrophilic head onto the chitin, and their hydrophobicity determines the interaction of the polymer-surfactant complex with the solvent. Based on our observations, a proposed mechanism of the cellulose particle/Span60 synergetic oleogels formation is presented in Figure 8. With the absence of cellulose particles, the Span60 molecules firstly assembled into fibrillar micelles, and then the micelles stacked to form a classical oleogel. If the celluloses particles were present in the system, they were firstly surface modified by the Span60, then the modified particles associated *via* the alkyl chain of Span60 and formed a composite oleogel.

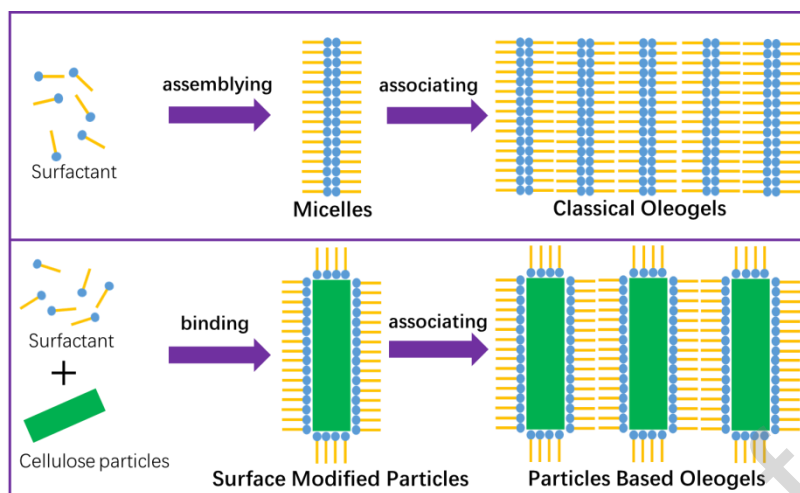


Figure 8: The schematic diagram of the formation of oleogel by sole Span60 and cellulose particles/Span60 mixture.

Effect of cellulose particles on the composite oleogels.

In practice, the use of high concentration surfactants in foods should be avoided as far as possible. Here, to clarify the effect of cellulose particles on the sorbitan fatty acid esters formed network, high concentration (20%, w/w) of Span60 and Span40 was used to prepare oleogels, and 6% (w/w) and 10% (w/w) cellulose particles were incorporated, respectively. Results are presented in Figures 9A and 9B. All the samples showed a viscoelastic profile during the frequency sweeping and the modulus was almost independent of frequency, suggesting very strong networks formed. With the presence of 6% (w/w) cellulose particles, the strength of the 20% (w/w) Span40 or 20% (w/w) Span60 oleogels were increased, confirming that the surface modified cellulose particles have participated in and enhanced the networks. With the same cellulose particles content, the cellulose particles/Span60 oleogels showed higher modulus. This might be related to the alkyl chain of the sorbitan acid esters, where the longer alkyl chain of Span60 was beneficial for the association or stacking of the modified cellulose particles. By further increasing the cellulose particles content to 10% (w/w), the enhancement on the networks was weakened. Tian and co-workers (2010) have evaluated the effect of single-walled carbon nanotubes (SWNTs) on the N,N'-bis (octadecyl)-L-(1-pyrenebutyric acid)-glutamic diamide (LPG) formed oleogels. They found that incorporation of 4% SWNTs considerably prolonged linear

viscoelastic regime (LVE) of the LPG oleogels. The well dispersed SWNTs in the LPG oleogels made the organization of the nanocomposite harder than the one-component LPG oleogels. However, the effect of SWNTs concentration was not evaluated. In our experiments, the 20% (w/w) Span40 or Span60 could form a stable network in MCT with the absence of cellulose particles. In this case, the network of the oleogels was dominated by the fibrillar micelles of the surfactant. With the presence of cellulose particles, the effect of cellulose particle on the oleogels formation should be evaluated from two aspects. On one hand, the surface modified cellulose particles could bridge the fibrillar micelles, which could enhance the network. On the other hand, the modified cellulose particles could interact with each other and form a second network when their content reached a certain value. This secondary network might destroy the surfactant formed main network, and weaken the strength of the oleogels. Therefore, the effect of cellulose particles on the strength of the oleogels should depend on their concentration. When the cellulose particle content was low (such as 6% w/w), their positive effect might be preferential. By further increasing the cellulose particle content (such as 10%, w/w), the negative effect arose. As a result, the increase of the oleogel strength was showed to be less significant.

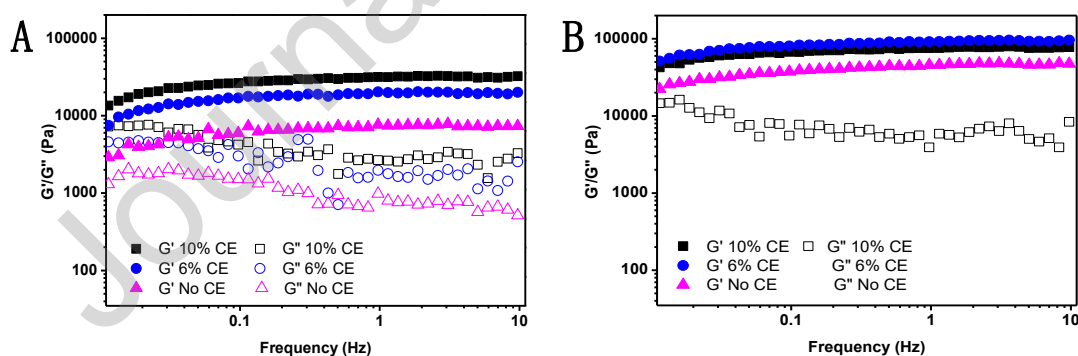


Figure 9: Frequency sweeping modulus of the oleogels composited by 20% (w/w) Span40 (A), 20% (w/w) Span60 (B) and their mixtures with 6% (w/w) or 10% (w/w) cellulose particles. “CE” means cellulose particles.

Conclusion

Cellulose particles could be surface modified by the surfactant (such as Span60), which gave them the dispersibility in organic solvents. After surface modification, cellulose particles possessed similar surface characteristics to the Span60 micelles, and they could associate with each other, just like the surfactant micelles in the oil phase, to form a network and trap the oil phase. These procedures could be achieved facily by ultra-sonic treating the mixtures of cellulose particles, surfactant, and MCT. Both the content of cellulose particles in the oil phase and the surfactant/cellulose particles ratio could affect the formation and strength of the networks. However, it should be noted that the oil type would affect the assembly behavior of Span40 or Span60, and further the network formation of the oleogels. Therefore, in order to adapt to practical application, this method should be further tested with other hydrocolloids, surfactants, and oil types. There is reason to believe that the convenience and economy of this method would give it a great potential in food industry.

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Reference

- Bascuas, S., Morell, P., Hernando, I., Quiles, A. (2021). Recent trends in oil structuring using hydrocolloids. *Food Hydrocolloids*, 2021, 118, 106612.
- Ceballos, M., Bierbrauer, K., Faudone, S., *et al.* (2016). Influence of ethylcellulose -Medium chain triglycerides blend on the flow behavior and β -V polymorphretention of dark chocolate. *Food Structure*, 10: 1-9.

- de Vries, A., Hendriks, J., Van Der Linden, E., Scholten, E. (2015). Protein oleogels from protein hydrogels *via* a stepwise solvent exchange route. *Langmuir*, 31(51), 13850-13859.
- Fu, H., Lo, Y., Yan, M., *et al.* (2020). Characterization of thermo-oxidative behavior of ethylcellulose oleogels. *Food Chemistry*, 305(1), 125470.
- Gao, Z., Yang, X., Wu, N., *et al.* (2014). Protein-Based Pickering Emulsion and Oil Gel Prepared by Complexes of Zein Colloidal Particles and Stearate. *Journal of Agricultural and Food Chemistry*, 62(12), 2672-2678.
- Giacintucci, V., Di Mattia, C., Sacchetti, G., *et al.* (2018). Ethylcellulose oleogels with extravirgin olive oil: the role of oil minor components on microstructure and mechanical strength. *Food Hydrocolloids*, 84, 508-514.
- Glynn, A., Igra, A., Sand, S., *et al.* (2017). Are additive effects of dietary surfactants on intestinal tight junction integrity an overlooked human health risk? -A mixture study on Caco-2 monolayers. *Food & Chemical Toxicology*, 106, 314-323.
- Godoi, K., Basso, R., Ming, C., Silva, V., Cunha, R., Barrera-Arellano, D., Ribeiro, A. (2019). Physicochemical and rheological properties of soybean organogels: Interactions between different structuring agents, *Food Research International*, 124: 108475.
- Islam, M., Amin, M., Siddiqui, S., *et al.* (2019). Trans fatty acids and lipid profile: A serious risk factor to cardiovascular disease, cancer and diabetes. *Diabetes & Metabolic Syndrome Clinical Research & Reviews*. 13(2), 1643-1647.
- Laredo, T., Barbut, S., Marangoni, A. (2011). Molecular interactions of polymer oleogelation. *Soft Matter*, 7(6): 2734-2743.
- Liu, N., Lu, Y., Zhang, Y., Gao, Y., Mao, L. (2020). Surfactant addition to modify the structures of ethylcellulose oleogels for higher solubility and stability of curcumin. *International Journal of Biological Macromolecules*, 165: 2286-2294.

- Luo, S., Hu, X., Jia, Y., *et al.* (2019). Camellia oil-based oleogels structuring with tea polyphenol-palmitate particles and citrus pectin by emulsion-templated method: preparation, characterization and potential application. *Food Hydrocolloids*, 95, 76-87.
- Martins, A., Vicente, A., Cunha, R., Cerqueira, M. (2018). Edible oleogels: an opportunity for fat replacement in foods. *Food & function*, 9(2), 758-773.
- Murdan, S., Gregoriadis, G., Florence, A. (1999). Novel sorbitan monostearate organogels. *Journal of Pharmaceutical Sciences*, 88(6): 608-614.
- Nikiforidis, C., Scholten, E. (2015). Polymer organogelation with chitin and chitin nanocrystals. *Rsc Advances*, 5(47), 37789-37799.
- Pakseresht, S., Tehrani, M. (2021). Advances in Multi-component Supramolecular Oleogels-a Review. *Food Reviews International*, 2021, 37: 1525-6103.
- Pan, H., Xu, X., Qian, Z., *et al.* (2021). Xanthan gum-assisted fabrication of stable emulsion-based oleogel structured with gelatin and proanthocyanidins. *Food Hydrocolloids*, 2021, 115, 106596.
- Patel, A. (2017). A colloidal gel perspective for understanding oleogelation. *Current Opinion in Food Science*, 15, 1-7.
- Patel, A., Dewettinck, K. (2016). Edible oil structuring: an overview and recent updates. *Food & Function*, 7(1), 20-29.
- Pernetti, M., Malssen, K., Eckhard, F., Bot, A. (2007). Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science*, 12, 221-231.
- Rogers, M. (2009) Novel structuring strategies for unsaturated fats-meeting the zero-trans, zero-saturated fat challenge: a review. *Food Research International*. 42 (7), 747-753.

- Sagiri, S., Kasiviswanathan, U., Shaw, G., Singh, M., Anis, A., Pal, K. (2016). Effect of sorbitan monostearate concentration on the thermal, mechanical and drug release properties of oleogels[J]. *Korean Journal of Chemical Engineering*, 33(5): 1720-1727.
- Suzuki, M., Hanabusa, K. (2010). Polymer organogelators that make supramolecular organogels through physical cross-linking and self-assembly. *Chemical Society Reviews*, 39(2), 455-463.
- Swe, M., Asavapichayont, P. (2018). Effect of silicone oil on the microstructure, gelation and rheological properties of sorbitan monostearate-sesame oil oleogels. *Asian Journal of Pharmaceutical Sciences*, 13(5), 485-497.
- Tavernier, I., Patel, A., van der Meeren, P., Dewettinck, K. (2017). Emulsion-templated liquid oil structuring with soy protein and soy protein: kappa-carrageenan complexes. *Food Hydrocolloids*, 2017, 65, 107-120.
- Tian, Y., Zhang, L., Duan, P., *et al.* (2010) Fabrication of organogels composed from carbon nanotubes through a supramolecular approach. *New Journal of Chemistry*, 34(12): 2847-2852.
- Trujillo-Ramírez, D., Lobato-Calleros, C., Vernon-Carter, E., Alvarez-Ramirez, J. (2019). Cooling rate, sorbitan and glyceryl monostearate gelators elicit different microstructural, viscoelastic and textural properties in chia seed oleogels. *Food Research International*, 119, 829-838.
- Zetzl, A., Marangoni, A., Barbut, S. (2012). Mechanical properties of ethylcellulose oleogels and their potential for saturated fat reduction in frankfurters. *Food & Function*, 3(3): 327-337.

Declaration of Interest Statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled “Composite Oleogels Formed by Cellulose Particles and Sorbitan Acid Esters”.

Highlights

- Cellulose particles combined with surfactant could be used to prepare oleogels.
- Oleogels was formed by ultra-sonic treating the mixture of gelators and oil phase.
- The cellulose particles were surface modified by the surfactants in oil phase.
- The surface modified cellulose particles could form a network in oil phase.