The Effect of Cooling Rate on the Microstructure and Macroscopic Properties of Rice Bran Wax Oleogels

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Abstract: The main purpose of this paper is to study the microstructure and macroscopic characteristics of rice bran wax (RBW) oleogels at a cooling rate of 1°C/min and 10°C/min by polarized light microscopy, X-ray diffraction, differential scanning calorimetry, texture analyzer, and micro rheometer. The oleogels of soybean oil were prepared by RBW in concentrations of 5%, 7.5%, 10%, 15% and 20% (wt/wt). The results of this study indicated that the concentration of RBW and cooling rates were affected by the crystal size and spatial distribution of these crystals. For the same RBW concentration, oleogels contained smaller crystals when cooled at 10°C/min compared to 1°C/min. And the oleogels obtained at a rate of 10°C/min exhibited a tighter crystal network, lower melting point, harder texture, and energy storage modulus. These results demonstrated the impact of cooling rate on the rheological behavior, nucleation, and crystallization process.

Key words: oleogels, rice bran wax, cooling rate, microstructure, macroscopic characteristics

1 Introduction

Oleogels are lipophilic and solid mixtures obtained with an organogelator such as ethylcellulose, 12-hydroxystearic acid, and rice bran wax (RBW) at levels below 10% of oils. The functions of oleogels are included in (1) stabilizing water-in-oil emulsion; (2) controlling and slow-releasing of drugs and nutrients; (3) restricting the flow and migration of oil phase; (4) replacing the traditional saturated margarine. In food processing, oleogels have been applied to the production of butter and cream sandwich biscuits. Besides, it is used to produce powdered meat products and minced meat products to provide emulsifying stability and instead of saturated and trans-fats, thereby improving the intake of fatty acids¹. The widespread use of oleogels will help us to reduce saturated fatty acids and eliminate trans-fatty acids from the diet, thereby providing beneficial health effects⁵.

Some researchers reported that RBW was more suitable for making oleogels¹⁻⁴. Thermal behavior, crystal structure, and crystal morphology of RBW and oil mixtures were compared with candelilla wax (CLW) and carnauba wax (CRW). These results showed that the dispersion of RBW crystals in these liquid oils was much better than that of CRW and CLW crystals⁷⁻⁹. However, Botega et al. used RBW oleogels instead of solid fat to make ice cream, they found that RBW oleogels did not mix well with air, so ice cream did not have a good shape¹⁰. Thus, there are certain limitations of RBW oleogels instead of solid fat¹⁰⁻¹².

In addition, RBW crystals formed a dense crystal network in oleogels depending on the van der Waals interactions as gelator–gelator interacter. The network structure is strongly correlated to macroscopic. But the network structure can be modulated by the cooling process, which could affect the nucleation and crystallization kinetics. Several studies reported that a rapid cooling rate could decrease crystal length and network pore area fraction, increase the fractal dimension of the crystal network, and lead to an increase in the oil binding capacity¹³. Slower cooling allowed for the growth of larger and consistently shaped crystals, while faster cooling incongruently shaped small crystals. However, the effect of the cooling rate on the microstructure and macroscopic properties of RBW oleogels is still incomplete.

Therefore, the objective of this study was to investigate the effect of cooling rate and RBW concentration on the microstructure (domain size and shape), macroscopic properties, texture characteristics, thermal properties, rheological properties, and microrheological information of RBW oleogels crystals. The results will help us to under-
2 Materials and Methods

2.1 Materials and RBW oleogels preparation

Soybean oil (SBO) (C14:0 0.1%, C16:0 7.6%, C18:0 0.2%, C18:1 27.6%, C18:2 63.5%, C20:0 0.5%, C22:0 0.6%) was purchased from the local market (China Agri-Industries Holdings Limited, Hong Kong, China). RBW (99% purity) was obtained from Tianxing Grain and Oil Co. Ltd. (Hubei, China).

Soybean oil was heated at 90°C and RBW was evenly dispersed in soybean oil at 5 levels (5%, 7.5%, 10%, 15%, and 20% w/w) to prepare the RBW oleogels. The mixture was stirred at 90°C for 30 min using a magnetic stirring apparatus (Model EM300T, Labotech Inc., Berlin, Germany) at 50 × g until completely dissolved. Then, the mixture was cooled down to 20°C at different rates (10°C/min and 1°C/min) and kept for 24 h before observation.

2.2 Analysis of the fatty acids and fatty alcohols of RBW

A mixture of 20 mg of RBW with 20 mL of 30% KOH in isopropanol was placed in a 100 mL flask. The mixture was refluxed for 6 h in an oil bath at 100°C. Then, the isopropanol was evaporated under reduced pressure until the residue was completely dry. 50 mL of ethyl acetate was added to this residue under stirring at 50°C for 2 h. The mixture was filtered, giving a filtrate and a solid residue. The solid residue was washed with ethyl acetate (3 × 20 mL). All filtrates (fatty alcohols included) were collected and dried over anhydrous sodium sulfate. Fatty alcohols were identified by high-temperature GC.

The solid residue was further washed with ethyl acetate (3 × 20 mL), and the solid portion was acidified with 20 mL of 30% HCl for 1 h at 50°C. 20 mL distilled water was added, and fatty acids were extracted with ethyl acetate (3 × 20 mL). The combined extract was washed with water to neutral pH, and the ethyl acetate layer was then dried over anhydrous sodium sulfate. The solvent was removed in a vacuum rotary evaporator, and fatty acids were obtained. Fatty acids were converted to fatty acid methyl esters by heating with 2 mL of 5% methanolic sulfuric acid at 70°C for 2 h for GC analysis. The compositions of fatty acids and fatty alcohols of RBW were listed in Table 1.

2.3 RBW crystal morphology

The crystallization of RBW oleogels was observed by Leica DM4000M polarizing microscope (Leica Microsystems, Wetzlar, Germany). Oleogels of different concentrations (5 µL) were placed on a glass microscope. The slides were heated at 90°C for 30 min to erase the crystal memory, then cooled to 20°C at different rates (10°C/min or 1°C/min) by a temperature-controlled microscope stage (Linkam Scientific Instruments, Surrey, U.K.).

2.4 RBW crystal structure

The X-ray diffractometer (XRD) (D8 Advance, Bruker, Germany) was operated at 40 kV and 40 mA with Cu Kα radiation (λ = 0.154 nm). For testing, samples were melted at 90°C and then cooled to 20°C at different rates (10°C/min or 1°C/min). The samples were kept at 20°C for 24 h before testing. Jade 6 software was used to analyze the X-ray diffraction image of oleogels to calculate the grain size of oleogels, and to analyze the physical properties of oleogels by comparing the size of the grain.

2.5 RBW oleogels crystallization and melting

Thermal behavior of RBW oleogels was determined by differential scanning calorimeter (DSC) (200 F3, Netzsch, Germany). The oleogel sample is accurately weighed 5 mg into the pan of DSC. The samples were heated from 20°C to 90°C at 10°C/min and held for 5 min. Then the sample was cooled to 20°C at a different rate (10°C/min or 1°C/min) and reheated to 90°C at 5°C/min.

2.6 RBW oleogels texture characteristics

Prepared RBW oleogels were placed in a petri dish with 90 mm diameter for testing. The texture Analyzer (TA-XT plus Stable Micro Systems, UK) was used to detect the hardness, cohesiveness, gumminess, chewiness, and resilience of the oleogels. The sample was extruded with the cylinder probe P/50 at a rate of 1 mm/s and a compression

| Carbon number | Fatty acids (%) | Fatty alcohols (%) |
|---------------|----------------|-------------------|
| 16            | 4.2 ± 0.5      | -                 |
| 18            | 7.9 ± 0.7      | -                 |
| 20            | 10.7 ± 1.3     | 1.6 ± 0.3         |
| 22            | 20.4 ± 2.2     | 4.9 ± 0.1         |
| 24            | 28.7 ± 1.2     | 2.6 ± 0.2         |
| 26            | 12.2 ± 0.8     | 1.4 ± 0.3         |
| 28            | 4.6 ± 0.4      | 27.7 ± 1.2        |
| 30            | 2.3 ± 0.1      | 19.3 ± 0.6        |
| 32            | -              | 16.2 ± 0.9        |
| 34            | -              | 11.6 ± 1.1        |
| 36            | -              | 3.2 ± 0.1         |
| 38            | -              | 11.6 ± 0.4        |
| 40            | -              | 3.6 ± 0.1         |

* - *, Not detected.

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ratio of 50%.

2.7 RBW oleogels microehology

The RBW oleogels were placed in a sample bottle, equilibrated at 30°C for 1 h, and then placed in a micro rheometer (Rheolaser Master, Formulaction inc., France). The test was carried out at 30°C and the test mode was fully characterized. The G’ and G” values were obtained by software (Rheosoft Master) using EI (Elasticity Index) and MVI (Macroscopic Viscosity Index). G’ represents the storage modulus and G” represents the loss modulus of the RBW oleogels. When G’ ≈ G” the sample mainly undergoes elastic deformation, so the sample is in a solid state; when G’<G”, the sample mainly undergoes viscous deformation, so the sample is in a liquid state. When G’ ≈ G”, the sample is semi-solid.

2.8 Statistical analysis

The samples were analyzed in triplicate and the results were expressed as mean ± standard deviation. A one-way ANOVA analysis of variance was performed to test if statistically significant differences were existed. The equality of variances were verified using Levene’s test prior to usage of Tukey’s test to compare the mean values at p<0.05 significance level.

3 Results and Discussion

3.1 Crystal morphology

Crystal morphology of RBW oleogels (the concentrations of RBW were 5%, 7.5%, 10%, 15% and 20% (wt/wt)) prepared at a rate of 10°C/min and 1°C/min were shown in Fig. 1. Micrographs show that these crystals displayed as dendritic. The morphology of RBW crystals in SBO contrasted with those previously reported where the appearance of RBW described as needle-like and fibrous. But our results were similar to RBW-rice bran oil oleogels. The morphology characteristic of RBW was an ideal state for oleogels because these crystals could capture a greater amount of liquid oil than other crystalline forms.

It can be seen from Fig. 1 (A, C, E, G, I) with the increase of the content of RBW, the crystals in the oleogels were larger, the relative motion space between the crystals was smaller, and the network structure was more closely constructed. For the same concentration of RBW, the crystal network formed by the slow cooling rate (1°C/min) was incompact. The length of the crystal is more than 200 μm, which weakens the binding ability of liquid oil. So the crystal network is very fragile and instability. But the crystal network formed by the fast cooling rate (10°C/min) is more uniform and dense. The crystals interact well, forming a tight three-dimensional network and strong gel properties. This result was consistent with the previous researches. Dassanayake reported that when the olive oleogels with the same RBW content under different cooling rates compared to the organic gel network crystal, the smaller cooling rate of the organic gel formed the crystal network is larger and more space. The reason may be that the RBW crystal in the slow cooling rate has been fully grown compared with rapid crystallization. During the cooling process of 10°C/min, the ambient temperature drops too fast and the crystal does not have enough time to grow. Thus, the size of the crystal is less than 200 μm. RBW crystals have longer morphology (20-50 μm), which is an ideal characteristic for gel formation. Combine the results of Fig. 1, we can conclude that at least 20% content of RBW is needed for slow crystallization to form the ideal crystal morphology, while only 10% of RBW is needed for fast crystallization. As expected, a faster cooling rate results in an earlier onset of crystallization and the formation of the relatively smaller crystals than a slower cooling rate. In principle, a higher thermodynamic drive (related to a lower cooling rate) affects the nucleation rate, resulting in the formation of finer crystals. However, a slower cooling rate causes the primary nucleus to grow into a relatively larger crystal. Therefore, we can see that we need to use a fast cooling rate to achieve a better gel effect with the minimum amount of RBW. This also provides a reference for industrialized production of RBW oleogels.

3.2 Crystal structure

XRD diagrams of oleogels provided the information about crystal morphology. The polymorphism of oleogel samples was shown in Fig. 2. Two diffraction peaks were observed in the diffraction patterns of the oleogel samples, which were 4.1 Å, and 3.7 Å. They were corresponding to the forms of wax crystals. The very weak signal at 4.6 Å indicated the β form of triglyceride crystals, which reflects triglycerides with poor crystallization. Similar peaks (β’ form) had been observed for other wax oleogel samples such as beeswax, candellilla, carnauba, and sunflower wax. Irrespective of RBW concentration, all oleogels exhibited similar diffraction. Some researchers also indicated that the effect of wax concentration on the crystal form is less compared with other factors such as molecular composition, preparation conditions (e.g. stirring or cooling rate), and storage conditions. In addition, the XRD patterns were less influenced by the types and compositions of the triglycerides.

The peak intensity of oleogels crystallized at 10°C/min was stronger than the oleogels crystallized at 1°C/min (Fig. 2). Previous studies have shown that the short spacing patterns were significantly more intensely than the long spacing patterns. Generally speaking, the contrast of the peak intensity in X-ray diffraction image is related to the strong anisotropy of the crystal growth rate perpendicular.

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Fig. 1  The micrographs of RBW oleogels formed at cooling rates of 1°C/min and 10°C/min. White bars indicate 200 µm.

Fig. 2  XRD patterns of the oleogels with different concentrations of RBW (5, 7.5, 10, 15, 20 wt%) crystallized at 1°C/min and 10°C/min.
to and parallel to the layered plane. If the growth rate parallel to the layered plane is slower than that perpendicular to the layered plane, needle-like or sheet-like thin crystals will be formed, showing a weaker long-distance type and a stronger short-distance type\(^6\). This property can explain the difference of peaks in X-ray diffraction image between fast and slow cooling rate crystallized for RBW crystals\(^28\). This means that the content of RBW and the cooling rate are not affected by the crystal form but affected by the nanostructure.

Figure 3 showed the domain size of RBW crystals and triglyceride crystals crystallized at 1°C/min and 10°C/min based on the d001 long spacing. The crystallite domain size was 8.21-80.36 nm (2.81-72.55 nm) between 5 and 20 wt% RBW at 1°C/min (10°C/min) cooling rate, which is larger than the triglyceride crystallites. It can be seen that at the same crystallization rate, the domain sizes of RBW and triglyceride crystals increased with the increase of RBW concentration. These results may be due to the increased solubilization of the RBW in the SBO. At the same concentration, different cooling rates have a large effect on the size of the crystal domains. When the cooling rate is 1°C/min compared to 10°C/min, the domain sizes of RBW and triglyceride crystals in the 5% RBW oleogels are reduced from 8.21 nm to 2.81 nm and 0.77 nm to 0.32 nm, respectively. The domain sizes of RBW and triglyceride crystals formed under the cooling rate at 10°C/min were smaller than 1°C/min at other concentrations (7.5, 10, 15, 20 wt%). These cooling rate-dependent differences of domain sizes were interpreted as faster rates of nucleation (more crystallographic mismatches and branching) arising from the fast cooling rate.

3.3 Thermal behavior

The cooling and heating thermograms of the different concentrations of RBW oleogels after cooling at 1 and 10°C/min, and then melting at 5°C/min were shown in Fig. 4.
And the melting temperature ($T_m$), crystallization temperature ($T_c$), melting enthalpy ($\Delta H_m$) and crystallization enthalpy ($\Delta H_c$) were summarized in Table 2 to characterize the melting and crystallization behavior of RBW oleogels. Independent of the cooling rate used, the $T_m$, $T_c$, and enthalpy were increased as the RBW concentration increased. The $T_m$ and $T_c$ of 5% RBW oleogels crystallized at 1°C/min increased from 65.4 and 57.5°C to 71.8 and 69.4°C in the oleogels with 20% RBW. The oleogels with higher RBW concentrations had the higher $\Delta H_m$ and $\Delta H_c$ values at different cooling rates (Table 2). The hysteresis was also observed in the thermograms for 5-20% RBW dispersion in SBO. This phenomenon was consistent with the result of Toro-Vazquez et al. that more gel was developed as the concentration of the gelator increased.

The cooling rate changed the crystallization behavior of RBW oleogels (Fig. 4). When the cooling rate was increased from 1 to 10°C/min of the oleogels prepared by 5-20% RBW, the $T_m$ and $T_c$ of RBW oleogels were moved from 65.4-71.8°C and 57.5-69.4°C to 62.8-71.6°C and 57.3-67.5°C. For a given RBW concentration (5-20%), the $\Delta H_c$ was increased from 0.3 (24.4) to 2.1 (27.9) J/g (Table 2). This means that when the cooling rate is increased, the $T_m$ and the $T_c$ of RBW oleogels are moved to a lower temperature region and an increase of $\Delta H_c$. A similar result was reported by Pérez-Monterroza in the crystallization of beeswax and avocado oil. In principle, higher thermodynamic driving forces (associated with lower cooling rates) will affect the nucleation rate, resulting in the formation of finer crystals. At the same time, slower cooling rates will cause the pronuclei to grow into larger crystals. This was in agreement with the polarized light microphotographs (Fig. 1). Thus, RBW had less time to be crystallized at 10°C/min than 1°C/min, requiring a lower crystallization temperature to achieve the crystal formation. However, the cooling rate effect on $\Delta H_m$ was different at each RBW concentration. This result might be related to the high temperature (20°C) during isothermal gelation of oleogels. Toro-Vazquez indicated that the other minor components ($\alpha$-alkanes) presented in RBW might develop a mix of molecular packing with the subsequent effect on melting enthalpy.

### 3.4 Texture analysis

The texture-profile analysis (TPA) results were shown in Fig. 5. Hardness indicated the compactness of the gel network and the strength of the oleogels. The content of RBW is a major factor in changing the physical properties of the oleogels. Under the same cooling rate, the hardness force of the oleogels increased as the concentration of RBW increased. Besides, a significant difference between the samples that crystallized at 10°C/min and 1°C/min was existed. When the RBW concentrations were above 5% (the critical concentration), the hardness was at least twice higher than that at a lower cooling rate. These results were in agreement with the other studies, which reported that the hardness enhanced with a faster cooling rate. The hardness values of 20% RBW oleogels cooling at 10°C/min were similar to the hydrogenated coconut oil (381.14 N). Cohesiveness indicated the ability of the oleogels to resist the second deformation after the first deformation. The cooling rate did not significantly affect the cohesiveness of oleogels. In the case of gumminess, the RBW oleogels cooling at 10°C/min was higher than that at 1°C/min. And the value of gumminess increased with the RBW content increased due to their hard texture. These results

| Crystallization rate (°C/min) | RBW (wt%) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) |
|-----------------------------|-----------|------------|-------------------|------------|-------------------|
|                             |           |            |                   |            |                   |
|                             | 5         | 57.5 ± 0.2$^d$ | 0.3 ± 0.1$^c$ | 65.4 ± 1.0$^d$ | 3.1 ± 0.3$^d$ |
| 7.5                         | 10        | 66.0 ± 1.0$^b$ | 8.2 ± 1.5$^e$ | 69.3 ± 0.4$^b$ | 17.0 ± 1.3$^b$ |
| 15                          | 15        | 66.3 ± 1.0$^b$ | 11.8 ± 1.6$^b$ | 69.3 ± 0.4$^b$ | 18.0 ± 2.5$^b$ |
| 20                          | 20        | 69.4 ± 0.2$^b$ | 24.4 ± 1.1$^e$ | 71.8 ± 0.5$^e$ | 36.5 ± 4.9$^e$ |
|                             | 5         | 57.3 ± 0.3$^d$ | 2.1 ± 0.1$^d$ | 62.8 ± 0.6$^d$ | 3.1 ± 0.2$^d$ |
| 7.5                         | 7.5       | 59.3 ± 2.1$^c$ | 8.3 ± 0.7$^e$ | 66.3 ± 1.5$^c$ | 8.9 ± 1.9$^c$ |
| 15                          | 10        | 64.0 ± 0.5$^a$ | 12.0 ± 1.4$^a$ | 68.3 ± 0.5$^a$ | 14.3 ± 2.2$^a$ |
| 20                          | 15        | 64.2 ± 0.8$^a$ | 14.0 ± 1.6$^a$ | 69.0 ± 0.6$^a$ | 16.1 ± 0.2$^a$ |
| 20                          | 20        | 67.5 ± 0.3$^b$ | 27.9 ± 1.9$^b$ | 71.6 ± 0.4$^b$ | 36.3 ± 3.9$^b$ |
showed that the cooling rate played the main role in the texture of oleogels.

3.5 Rheological measurements

The $G'_{\text{LVP}}$ and $G''_{\text{LVP}}$ profiles of RBW oleogels that formed under high (10°C/min) and low (1°C/min) cooling rates were shown in Fig. 6. It is indicated that the $G'$ values were higher than $G''$ in all RBW oleogels and the values of $G'$ and $G''$ increased with the increasing concentration of RBW. In all cases, the $G'$ value was higher than $G''$, showing more elastic properties. When the RBW at an equivalent concentration, the $G'$ values cooled at 10°C/min were larger than 1°C/min. In general, the $G'$ is usually associated with the
amount or the size of crystals. A higher difference between $G'$ and $G''$ indicates a stronger gel and a more stable network\cite{2013}. These results were consistent with that the smaller crystal size and the more compact crystal morphology were presented in the RBW oleogels developed at 10°C/min than 1°C/min (Fig. 1). The thermodynamic driving force for RBW gel formation increased faster led to that the RBW molecules had less time to organize at the 10°C/min cooling rate. Consequently, the smaller crystal size and stronger network in the RBW oleogels crystallized at 10°C/min than 1°C/min. Patel et al. explained from the fact that the formation of finer crystals promoted stronger network formation due to the higher crystal-crystal interactions (probably due to an increase in the total effective surface area of crystals)\cite{2016}. Therefore, we can conclude that the rapidly cooling RBW oleogels have better rheological properties, which is conducive to the development of oleogel products.

4 Conclusion

In conclusion, the crystallization characteristics of RBW oleogels crystallized at 10°C/min and 1°C/min rate were thoroughly investigated. The results show that there is a significant difference between RBW oleogels crystallized at different cooling rates. It can be concluded that the RBW crystals crystallized at 1°C/min is larger than 10°C/min at the same concentration of RBW in SBO. Due to the influence of the size of crystals, the thermal properties are also markedly different, and the slow-crystallized oleogels melt at a higher temperature and lower hardness than the rapidly crystallized oleogels.

Conflicts of Interest

The authors declare no competing financial interest.

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