Retardation Effects of Polyglycerol Fatty Acid Esters on the Crystallization of \( n \)-Hexadecane

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Abstract: In this study, we investigated the effects of two types of polyglycerol fatty acid esters, both of which were made from the same polar group of polymerized 10 glycerols, on the crystallization of \( n \)-hexadecane (\( n \)-HD). One of the emulsifiers, known as THL-17, consists of three different saturated fatty acid chains with different carbon numbers between 8 and 18. Another emulsifier, known as 10G10S, contains a stearic acid chain only. The two emulsifiers were added to retard the crystallization rate of \( n \)-HD, which has melting point of 18.0\( ^\circ \)C, and was chosen as a model fat material. Visual and optical microscopic observations showed that the growth of \( n \)-HD seed crystals in bulk liquid was significantly retarded by the addition of 1.0 wt.\% THL-17 at 17.0\( ^\circ \)C. The DSC cooling peaks of \( n \)-HD with and without the addition of THL-17 showed that the crystallization temperature (\( T_c \)) of \( n \)-HD decreased with increasing concentrations of THL-17 from 15.9\( ^\circ \)C (in the pure form) to 14.0\( ^\circ \)C (in the solution containing 1.0 wt.\% THL-17). In contrast, 10G10S did not affect the \( T_c \) value, even at a concentration of 1.0 wt.\%. The results of this study suggest that the inhibition of \( n \)-HD crystal formation in the presence of THL-17 results from effects on both crystal nucleation and post-nucleation crystal growth processes.

Key words: polyglycerol fatty acid ester, \( n \)-hexadecane, DSC, impurity effect, nucleation

1 Introduction

Polyglycerol fatty acid esters (PGFEs), synthesized from polyglycerols and fatty acids, are bio-gradable surfactants that are used in many foods, cosmetics, toiletries and pharmaceuticals (1,2). One of the most important characteristics of PGFEs is the easy modification of their hydrophobicity and hydrophilicity, by changing the degree of polymerization of the glycerol and the degree of esterification with fatty acid moieties whose chemical structures can also be modified to reveal diversified functionalities. In addition, PGFEs are safe and can therefore be used as food emulsifiers, offering several functional properties such as acid resistance, salt resistance, thermal stability, and savoriness (3,4). Furthermore, hydrophobic PGFEs have been employed as crystallization controllers and crystal structure modifiers, causing the retardation of crystal growth and modifying of polymorphic transformations (5-7).

In 1967, Nash et al. reported that a polyglycerol fatty acid ester consisting of stearic, oleic and coconut fatty acid was effective as a cold inhibitor when added to vegetable oil (3). Matsushita et al. (8) investigated the inhibiting properties of a decaglycerol mixed-fatty acid ester (known commercially as THL-3) on the crystallization of edible oil, and its effect was further studied by Idris et al. (9). Petruccelli and Anon showed that a polyglycerol mixed fatty acid ester prepared by the esterification of six types of fatty acids and polyglyc-
erol inhibited the crystallization of waxes in sunflower seed oil (10). More recently, we developed PGFEs containing different fatty acids moietyes, which are effective in prohibiting the crystallization of the high-melting fractions in vegetable oils at chilled states (0 to 5°C), and 20°C (11-14).

In these studies, however, the fundamental mechanisms of the prohibiting effects of fat crystallization by the PGFEs are not understood. Thus, the purpose of this study was to investigate the effects of adding THL-17 (commercial name), a PGFE composed of decaglycerol and three different saturated fatty acids, on the crystallization kinetics of a model fat material, n-hexadecane (n-HD), using optical microscopy and DSC. For comparison, we used the hydrophobic polyglycerol stearic acid ester 10G10S: polyglycerol-10 decastearate. Previous studies showed that 10G10S retarded the rate of crystal growth of bulk n-HD (15), whereas it accelerated the nucleation of n-HD and the palm mid fraction (PMF) in oil-in-water (O/W) emulsion droplets, while retarding the crystal growth rate (16,17). Therefore, a comparative study of the two PGFEs was considered to be highly interesting.

2 Materials and Methods

N-HD (99 ± %, melting point 18°C) was purchased from Sigma-Aldrich Inc. (St. Louis, MO). THL-17 and 10G10S were produced by Sakamoto Yakuhin Kogyo Co. Ltd. (Osaka, Japan). THL-17 is a fully -esterified polyglycerol (polyglycerol-10) with three different types of saturated fatty acid moieties having carbon atoms between 8 and 18. 10G10S consists of polyglycerol (polyglycerol-10) with an average degree of esterification with stearic acid of 10. The iodine values of these two PGFEs were found to be less than 2.

To investigate the effect of THL-17 on the growth of n-HD crystals, THL-17 was added to the n-HD solution at concentrations ranging from 0.3 to 1.0 wt.% (relative to n-HD). To allow for close observation of the crystallization process, the n-HD was added to a test tube (10 × 90 mm), and placed in a water bath at 17°C for 2 hours. The n-HD seed crystals were then added to the supercooled n-HD liquid. Microscopic observation of crystal growth was carried out using an Olympus BX-50 microscope equipped with an Olympus PM-20 camera. During the crystal growth experiment, temperature was controlled using a Mettler FP84HT hot stage equipped with an FP900 controller. The sample (2 mg) was put on the stage whose temperature was kept at 17°C, prior to addition of the n-HD seed crystal.

To measure the growth rate of the n-HD crystals at a constant temperature (isothermal crystallization), microscopic images of the crystal shape front of n-HD with the THL-17 additive were taken, using an optical microscope (OLYMPUS BH-2) in combination with a CCD camera and a videotape recorder. The rates of crystal growth were measured over the temperature range from 16 to 18°C.

DSC experiments were carried out using a FP-900 Thermosystem (Mettler-Toled). The sample was held in a glass crucible and Al2O3 was used as a reference material. The sample was cooled from 60 to −10°C, held for 1 min at −10°C, and then heated to 60°C. The heating and cooling treatments were carried out at a fixed rate of 2°C/min.

3 Results

Figure 1 shows the retardation effect on the crystal growth of n-HD produced by adding THL-17 at 17°C as seen in the test tubes. The crystal growth behavior of pure n-HD is also shown for comparison. For the pure sample, crystal growth commenced immediately after the addition of the seed crystal, and the needle crystals occupied the test tube after 5 minutes. The whole crystallization event in the test tube was achieved after a period of 60 minutes (Figs. 1(A)). Adding 0.3 wt.% THL-17 inhibited the crystal growth rate such that half of the whole test tube was occupied by the n-HD crystals after 5 minutes, although the whole crystallization event was completed after 60 minutes (Figs. 1(B)). When THL-17 of 1.0 wt.% was added, crystal growth did not occur at all even 60 minutes after crystal seeding (Figs. 1(C)).

Figure 2 presents optical micrographs taken during the crystal growth processes of the seed crystal with and without 0.8 to 1.0 wt.% THL-17 additive at 17°C. In the sample containing 0.8 wt.% , crystal growth from the seed crystal occurred rapidly during the isothermal condition for 3 hours (Fig. 2(A)). The addition of 0.9 wt.% THL-17 retarded crystal growth to a large extent, since no continuing growth from the seed crystals was observed and several new branches of crystal edges developed after 3 hours (Fig. 2(B)). Adding 1.0 wt.% completely inhibited growth of the seed crystal, as
showed in Fig. 2(C). Table 1 summarizes crystal growth features of the seed crystals at different Tcs with the addition of 1.0 wt.% of THL-17. No crystal growth was observed over a 3 hour period at a temperature of 16.6°C, whereas crystal growth was extended as the Tc decreased and the crystallization time increased.

The linear growth rates of n-HD crystals with the addition of THL-17 were measured with varying concentrations of THL-17 using an optical microscope. For this purpose, the rate of displacement of the growing lateral surface of the plate-like crystals of n-HD was monitored in situ at 16.7 and 17.1°C as shown in Fig. 3. The basal surfaces were not observed because the lateral surfaces grew at a much faster rate. Figure 3 clearly shows that increasing concentrations of THL-17 caused a decrease in the growth rate of the n-HD crystals, and that the decrease was more evident in the crystallization at 17.1°C than at 16.7°C. This result was in good agreement with the results of adding 10G10S investigated under the same crystallization conditions (15-17).

Figure 4 illustrates the DSC cooling thermopeaks of n-HD with and without the addition of THL-17 and 10G10S (0.1 to 1.0 wt.%). A single exothermic peak always appeared and the Tc of the pure sample was found to be 15.9°C. The addition of THL-17 lead to a decrease in the Tc value, from 15.4°C (0.1 wt.%) to 14.0°C (1.0 wt.%). In contrast, adding 10G10S lead to a decrease in the Tc value to 15.4°C with 1.0 wt.% additive, but the extent of the decrease in Tc was less remarkable than THL-17 (Fig. 4(B)), as summarized in Fig. 5.

Table 1 Effects of Adding THL-17(1.0 wt.%) on the Crystallization Behavior of n-hexadecane at Different Crystallization Temperatures after Crystal Seeding.

<table>
<thead>
<tr>
<th>Period (h)</th>
<th>crystallization temperatures</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>16.2°C</td>
</tr>
<tr>
<td>0 ~ 1</td>
<td>+</td>
</tr>
<tr>
<td>1 ~ 2</td>
<td>+</td>
</tr>
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<td>2 ~ 3</td>
<td>+</td>
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− : no growth  
± : slow growth  
+ : rapid growth
The present experimental results demonstrated that the additives of THL-17 and 10G10S both retarded the crystal growth rate of n-HD in the bulk state. However, the difference in the retardation effects between the two additives appeared in the DSC cooling experiments, in which Tc decreased with the THL-17 additive more remarkably than with the 10G10S additive, as shown in Figs. 4 and 5. This indicates that there may be differences in the molecular interactions between n-HD and the two PGFE additives. To investigate this property, we observed the binary mixing behavior of the n-HD/THL-17 and n-HD/10G10S solutions.

Figures 6 (A) and (B) show the DSC heating thermopeaks of the binary mixtures of n-HD/THL-17 and n-HD/10G10S. A single endothermic peak was observed in the n-HD/THL-17 mixture after the addition of THL-17 up to 20 wt.%, and a small endothermic peak started to appear just above the melting point of the n-HD with the addition of 30 wt.%. Further increases in the concentration of THL-17 caused the separation of the endothermic peaks of n-HD and THL-17 which melted at 30°C in a pure state. The separation of the melting peaks of n-HD and 10G10S in the n-HD/10G10S mixture was detectable from the mixture containing 5 wt.% 10G10S, which melted at 50°C in a pure state.

Phase diagrams of the two binary mixture systems were constructed based on the DSC results, as shown in Fig. 7. Clearly separation of the two components occurred in n-HD/10G10S mixture. In contrast, the binary mixture of n-HD/THL-17 indicated that partial
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dissolution of THL-17 into n-HD crystals occurred up to the concentration of 20 wt.% THL-17. This may show the important role of THL-17 during the nucleation and crystal growth processes of n-HD as discussed below.

4 Discussion

The two experimental results of growth rate of the seed crystals (Fig. 3) and the DSC cooling thermopeaks to obtain Tc (Figs. 4 and 5) differ in such a way that the nucleation process is not involved in the former case, whereas nucleation and the crystal growth processes are involved in the DSC experiments. The crystal growth rate revealed in Figs. 1 to 3 is determined by the rate of incorporation of n-HD molecules into crystal lattice positions at the interface of the seed crystals and the supercooled liquid. The retardation effect of the crystal growth rate caused by the additive can be ascribed to the prohibition of adsorption and incorporation of the n-HD molecules at the crystal-liquid interface (18). The fact that two PGFEs retarded the crystal growth rate in the same manner means that every additive molecule prohibits the adsorption and incorporation of the n-HD molecules at a molecular level without forming any clusters.

The crystal nucleation process involves the formation of molecular clusters of n-HD prior to the formation of crystal nuclei (19). In this process, the presence of THL-17 may disturb the formation of n-HD clusters by the partial incorporation of THL-17 molecules into the n-HD crystals, retarding the nucleation rate of the n-HD crystals. This effect may be ascribed to the shape of the THL-17 molecule, in which three fatty acid chains with different chain lengths are esterified to a polymerized glycerol group. In contrast, 10G10S may not be effective in disturbing the formation of clusters because of its bulky shape that is composed of a polymerized glycerol group and a stearic acid moiety.

The result of using the THL-17 additive for this investigation indicates its functionality for enhancing the retardation of crystallization, for both crystal nucleation and crystal growth. These properties may provide the key to applying the retardation effects of THL-17 to the crystallization of edible fats and oils under chilled conditions.

5 Conclusion

The effects of using the polyglycerol mixed fatty acid
ester THL-17 as an additive in the crystallization process of \( n \)-HD were examined using optical microscopy and DSC. The results were compared with those obtained using 10G10S. We clarified that THL-17 inhibited the growth of \( n \)-HD crystals in a manner similar to 10G10S. However, only THL-17 was found to inhibit the nucleation of \( n \)-HD.

References