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Effects of initial heating temperature on the crystallization rate of *trans*-free palm oil

Bing Fang · Lu Jiang · Fa Zheng Ren

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Abstract Because of the health problems associated with *trans* fatty acids (TFAs) in hydrogenated oil, the objective of this research was to accelerate crystallization of the *trans*-free unhydrogenated palm oil (UPO) as a hydrogenated palm oil (HPO) substitute. Crystallization thermograms of UPO blended with icing sugar (1:1.5 mass ratio) from different initial heating temperatures were measured by differential scanning calorimetry (DSC), to study its effects on crystallization rate. DSC thermograms of UPO and HPO cooled from two melt states (the complete melting state 80 °C and the incomplete state 40 °C) were also compared. Crystallization rates from temperatures above the melting point (m.p.) were faster than those below the top limit of the m.p. The reason may be that a higher initial heating temperature induced a completely melted state and thus a larger driving force toward the solid phase. Raising the processing temperature to 80 °C, UPO may have a crystallization rate the same as, if not faster than, HPO. This study provides a new way to accelerate the crystallization of the *trans*-free UPO, making HPO a realistic substitute in the food industry.

Keywords Unhydrogenated palm oil · *Trans* fatty acid · Initial heating temperature · Crystallization rate · Differential scanning calorimetry

Introduction

Palm oil is widely used as a fat additive in the food industry. The crystallization behavior is the most important character that influences fatty food processing. Hydrogenation was introduced to increase the crystallization rate to meet the demands of food processing [1]. Although it imparts fast crystallization rates and desirable flavors, hydrogenation also leads to the production of *trans* fatty acids (TFAs), which are widely accepted as having negative influences on human health [1–5]. Public health agencies have already encouraged food manufacturers to reduce or even eliminate TFAs in food products [4] and therefore *trans*-free unhydrogenated palm oil (UPO) was recommended as a substitute for hydrogenated palm oil (HPO). However, UPO crystallizes much more slowly than HPO, making it unsuitable for most food production processes. As a result, increasing the crystallization rate of the *trans*-free UPO by means other than hydrogenation has become necessary.

Various strategies have been used to increase the crystallization rate of UPO. First, lipid composition, utilizing different melting point (m.p.) triacylglycerols (TAGs), can significantly affect crystallization rates. Thus, chemical and enzymatic interesterification, fractionation, and a mixture of two oils are suitable options that have been applied in food industries [6–8]. Second, additives such as sucrose esters (SE) can influence the induction time of crystallization and the development of polymorphic forms [9, 10]. A number of investigations have been carried out into the effects of emulsifiers and surfactants on crystallization rate. Cerdeira et al. [11] found that in low-*trans* oil, the addition of sucrose esters P-170 and S-170 favored crystallization in β' form and delayed the appearance of the β form. Bazmi and Relkin [12] found addition of Credoman SE30 to

B. Fang · L. Jiang · F. Z. Ren (✉)
College of Food Science & Nutritional Engineering, China Agricultural University, P.O. Box 287, No. 17 Qinghua East Road, 100083 Haidian, Beijing, China
e-mail: renfazheng@263.net

B. Fang · L. Jiang · F. Z. Ren
Key Laboratory of Functional Dairy, Ministry of Education, 100083 Beijing, China

anhydrous milk fat and its low melting fraction samples led to higher initial crystallization temperatures (T_{on}). A higher T_{on} indicates a higher initial temperature at which crystals begin to form [13]. Furthermore, crystallization conditions such as crystallization temperature (T_c) and cooling rate will influence the type of polymorph and microstructure of the fat crystals. Martini et al. found the lower the T_c was, higher was the driving force for crystallization and consequently the higher the crystallization rate [13]. These results demonstrate that studying the initial heating temperature may help to find a new way to improve the crystallization rate. However, no study into the effects of the initial heating temperature on crystallization rate has been carried out. In the food industry, oil is always crystallized from a temperature below complete melting (approximately 30 °C), while nearly all the published papers deal with crystallization from a completely melted temperature (above the top limit of the m.p.). Meanwhile, it was found in our experiments that when heated to 80 °C, UPO and HPO displayed quite different crystallization rates compared with simulating the production process (30 °C). Therefore, studying crystallization from various initial heating temperatures is essential and this may lay the foundation for substitution of *trans* HPO.

In our study, the effects of initial heating temperature on UPO's crystallization were studied. We also compared the crystallization rates of HPO and UPO from initial heating temperatures above and below the top limit of the m.p. This study could enable a new way to accelerate the crystallization of UPO and thereby extend the application of UPO as an HPO substitute in food products.

Experimental

Materials

UPO- and HPO-based (including approximately 20% unhydrogenated soybean oil) shortenings and icing sugar were obtained from Kraft Foods (Suzhou, China). The top limit of the m.p. for both the two palm oils is 42 °C. Fatty acid methyl ester (FAME) standards were purchased from Sigma. All the other reagents were of analytical grade and were from Beijing chemical industry (Beijing, China).

UPO and HPO samples were mixed with icing sugar at room temperature until uniformly distributed.

Methods

Fatty acid composition

The fatty acid (FA) composition was analyzed using gas chromatography (GC) after conversion into the corresponding methyl esters by a base-catalyzed protocol [14]. The FAMEs were analyzed on a Schimadzu Model 14B GC instrument (Shimadzu, Japan) equipped with a flame-ionization detector (FID). A DB-23 capillary column (60.0 m length, 250 μm internal diameter, and 0.25 μm film thickness, Agilent J & W, Santa Clara, CA, USA) was used. The injection volume was 1 μl. The injector and detector temperatures were kept at 240 °C. The initial column temperature was held at 65 °C for 3 min, then the temperature was programed to increase to 195 °C at 10 °C min^{-1}, then to 205 °C at 1 °C min^{-1}, to 230 °C at 5 °C min^{-1}, and held for 2 min.

Differential scanning calorimetry measurements

Samples (approximately 10 mg) were sealed in aluminum pans. The crystallization thermograms were then measured using differential scanning calorimetry (DSC) (TA Instruments, Crawley, UK).

The effects of initial heating temperature

UPO sample was cooled from different initial heating temperatures to -10 °C with a rate of 2 °C min^{-1}. The initial temperatures were 80, 70, 60, 50, and 45 °C (temperatures at which samples were completely melted), 42 °C (the top limit of the m.p.), 35 and 30 °C (temperatures at which samples were not completely melted).

Comparison of UPO and HPO from different initial heating temperatures

The crystallization behaviors of UPO and HPO samples were compared, by both being crystallized to 10 °C at 2 °C min^{-1}. We chose two initial heating temperatures—above and below the top limit of the m.p. (80 and 40 °C, respectively).

Results and discussion

Composition analysis

FA compositions of UPO and HPO are listed in Table 1. The palm acid content was 48.0% in UPO and 42.6% in HPO. The oleic acid content was 39.2% in UPO and 38.5% in HPO. These results are similar to the values reported in the literature [15]. No TFA existed in UPO, while the TFA content in HPO was up to 8.3% in our study.

Oils are mainly mixtures of various TAGs, which are esters of three fatty acids with one glycerol. Unsaturated FAs such as oleic acid preferentially take up the sn-2 position and there is usually a symmetrical configuration [16]. Therefore, it can be concluded from Table 1 that the

Table 1 Fatty acid (FA) compositions of UPO and HPO

FA composition/%	UPO	HPO
Palm acid (16:0)	48.0	42.6
Stearic acid (18:0)	3.8	5.7
Oleic acid (18:1)		
cis	39.2	30.2
trans	0	8.3
Linoleic acid (18:2)	8.6	10.1

UPO Unhydrogenated palm oil, *HPO* hydrogenated palm oil

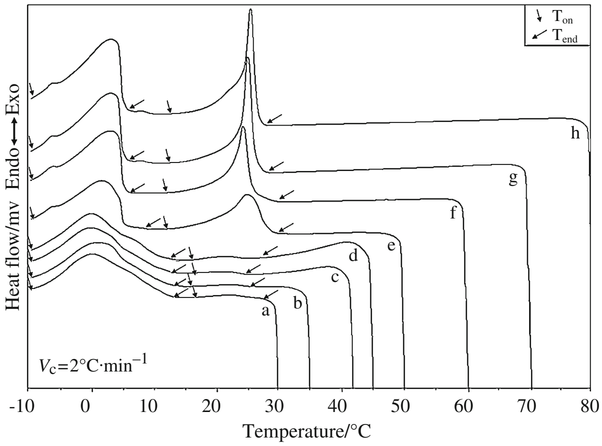


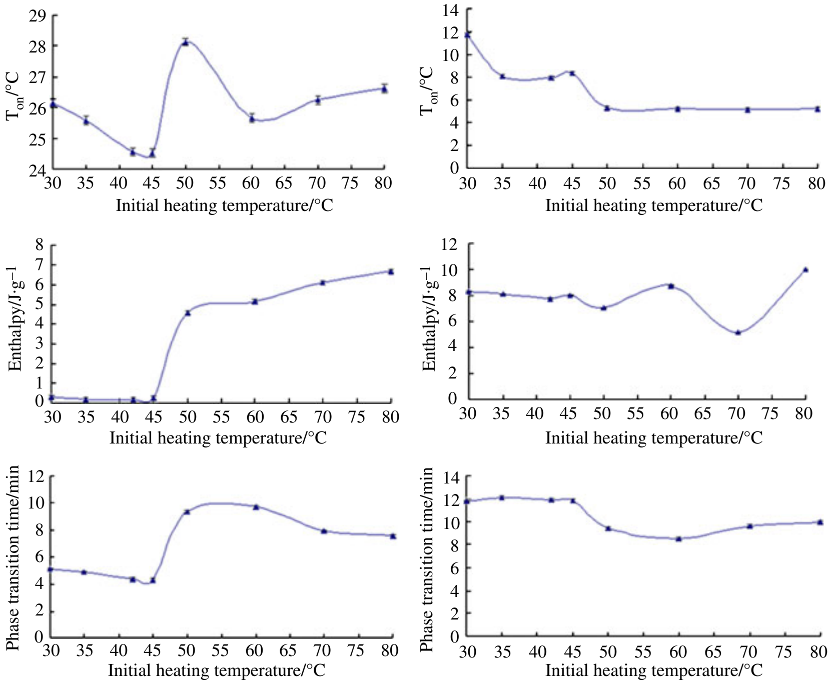
Fig. 1 DSC crystallization curves (2 °C min^{-1}) obtained in bulk UPO blends with icing sugar (UPO: sugar 1:1.5 mass ratio) (*a*) 30 °C, (*b*) 35 °C, (*c*) 42 °C, (*d*) 45 °C, (*e*) 50 °C, (*f*) 60 °C, (*g*) 70 °C, (*h*) 80 °C. Each of the measurements described above was carried out using at least three freshly prepared samples

main TAGs in UPO were POP (sn-1, 3-dipalmitoyl-2-oleoylglycerol), OPO (sn-1, 3-dioleoyl-2-palmitoylglycerol), and PPO (sn-1, 2-dipalmitoyl-3-oleoylglycerol), which are in agreement with the literature [17]. The melting point of TAG can influence the rates of nucleation and crystallization [12]. It is thought that the higher percentage of POP in UPO than in HPO would induce a long α lifetime and consequently a slow crystallization rate [17]. In the food industry, HPO was used more widely than UPO due to its faster crystallization rate. Therefore, the primary requirement for the replacement of *trans* HPO in the food industry is to accelerate the crystallization of UPO.

Effects of the initial heating temperature on the crystallization rates of UPO

Crystallization thermograms of UPO samples starting from different initial heating temperatures are shown in Fig. 1. In this experiment, we chose three different initial heating temperature ranges: above the m.p. (45, 50, 60, 70, and 80 °C), at the top limit of the m.p. (42 °C), and at temperatures where the oil was not completely melted (30 and 35 °C). It can be seen there were two peaks for all samples. The heat flow of both peaks decreased as the initial heating temperature decreased, especially for the first peak. The first peaks were difficult to discern when the initial heating temperatures were below 45 °C. In our research we mainly discussed the first exothermal peak beginning around 30 °C and the second recrystallization peak in the vicinity of 0 °C, because this crystallization process is not widely observed in the food industry.

Fig. 2 Crystallization parameters from different initial heating temperatures. **a** The Ton of the first peak, **b** the Ton of the second peak, **c** the phase transition enthalpy of the first peak, **d** the phase transition enthalpy of the second peak, **e** the phase transition peak time of the first peak, **f** the phase transition peak time of the second peak. Each of the measurements described above was carried out using at least three freshly prepared samples



Calorimetric parameters of different initial heating temperatures obtained from DSC curves are compared in Fig. 2. It can be seen that as the initial heating temperature increased, T_{on} varied irregularly but the phase transition enthalpy mainly increased, which indicates a large Gibbs free energy had to be overcome in the liquid phase. From these results, it was found that raising initial temperature above the m.p. can significantly accelerate the crystallization rat of UPO. This may be caused by the thorough melt phase imparting a large driving force toward solidification. However, crystallization is an exothermic process, so increasing the temperature may hinder the process. In accordance with the Gibbs–Helmholtz equation, the accelerating effect above the m.p. was in inverse proportion to the initial heating temperature. The influence of temperature on crystallization rate was apparently a combination of these two effects.

In the food industry, a stable crystal can be formed through crystallization from approximately 30 °C in a cooling environment of 10 °C. Therefore, in our experiments, it was thought an entire crystallization peak was completed and no recrystallization process began above 10 °C, corresponding to a stable state and a fast crystallization. The end temperature of the first peak (Fig. 3a) and the beginning temperature of the second peak (Fig. 3b) were compared. The time at which the first crystallization process was completed (Fig. 2e) was chosen to evaluate the crystallization rate. Meanwhile, in view of the temperature range between the two peaks (Fig. 3c), crystallization from 50 °C may have the fastest crystallization rate. Crystallization from temperatures below 50 °C would not be stable for a long time at temperatures below 10 °C, because a phase transition occurs there, beginning from a temperature above 10 °C.

Crystallization rates of HPO and UPO from different initial heating temperatures

The crystallization curves for HPO and UPO samples mixed with icing sugar, when cooled from 80 to 10 °C at 2 °C min^{-1}, are shown in Fig. 4a, b, respectively. Crystallization curves for the same samples from 40 to 10 °C at 1 °C min^{-1} are shown in Fig. 4c, d. It can be seen that there was only one exothermic peak for both samples when crystallized from 80 °C, whereas when they were crystallized from a lower initial temperature (40 °C) the samples experienced a polymorph transition. No polymorph transition peak occurred when starting from a higher initial temperature (80 °C) (Table 2).

It was reported that the DSC exothermic peak observed at about 22–26 °C during the cooling process was caused by crystallization of the α polymorph, and the exothermic peak at 16 °C was caused by the crystallization of the β' form [1, 14]. Therefore, it can be thought that HPO crystallized to the stable β' form through the transformation of the α form, while UPO did not experience this when starting from the initial temperature of 80 °C. Meanwhile, when the temperature reached a final temperature of 10 °C, HPO had not yet completed the formation of stable crystals. It can be seen UPO began to crystallize and attained the stable state earlier than HPO. That is, UPO had a faster crystallization rate. When crystallization started from 40 °C, there were two exothermic peaks, indicative of the crystallization of high-melting and low-melting TAGs [18]. Although UPO still had a higher initial crystallization temperature for both peaks, it also had a much longer phase transition temperature range than HPO. As a result, UPO had a slower crystallization rate than HPO under the crystallization conditions used in the food industry, which limited its application.

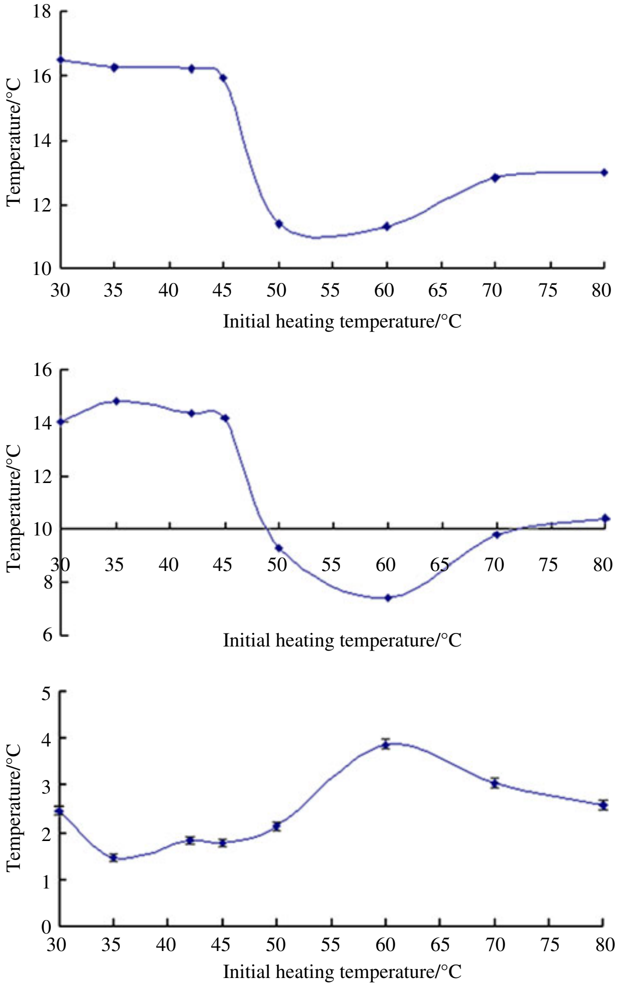


Fig. 3 Temperature parameters of the two peaks. **a** Temperature corresponded to the end of the first heat flow peak; **b** temperature corresponded to the beginning of the second heat flow peak; **c** the temperature range between the two peaks

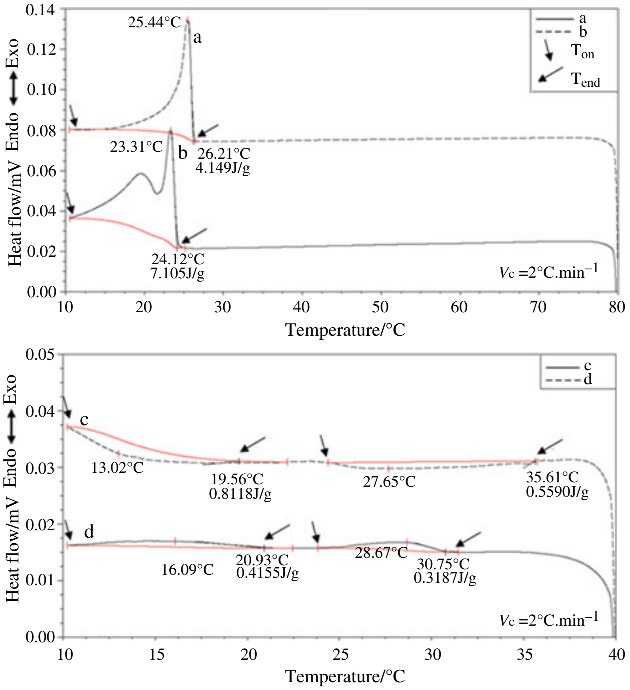


Fig. 4 Comparing the crystallization behaviors of UPO and HPO blended with the same icing sugar, (*a*) and (*c*) both were HPO, from 80 and 40 °C, respectively; (*b*) and (*d*) both were UPO, from 80 and 40 °C, respectively. Each of the measurements described above was carried out using at least three freshly prepared samples

Table 2 Crystallization parameters of UPO and HPO samples from different initial heating temperature

Initial heating temperature/°C	Parameters	UPO sample	HPO sample
80	T_{on}/°C	26.21 ± 0.23	24.11 ± 0.21
	Enthalpy/J/g	7.96 ± 0.06	4.42 ± 0.05
	Phase transition peak time/min	30.49 ± 0.29	29.39 ± 0.31
40			
The first peak	T_{on}/°C	30.65 ± 0.32	35.60 ± 0.38
	Enthalpy/J/g	0.28 ± 0.03	0.54 ± 0.06
	Phase transition peak time/min	13.46 ± 0.12	14.42 ± 0.12
The second peak	T_{on}/°C	20.74 ± 0.29	20.84 ± 0.21
	Enthalpy/J/g	0.40 ± 0.04	1.85 ± 0.02
	Phase transition peak time/min	27.39 ± 0.25	27.40 ± 0.21

It can be concluded from the results that the initial heating temperature in food production (approximately 30 °C) would induce a slow crystallization rate for *trans*-free UPO. From this point of view, if manufacturers increase the production temperature above the m.p. there would be a large driving force for crystallization and consequently a fast crystallization rate. Meanwhile, in combination with the results of the effects of initial heating temperature on the UPO crystallization rate, if food producers increase the process temperature to 50 °C before cooling, then substitution of UPO for HPO may become practical.

Conclusions

Crystallization from various initial heating temperatures revealed that there may be an optimal heating temperature that could give UPO the fastest crystallization rate. In our experiments, for example, the optimal initial heating temperature was 50 °C. When applied to *trans*-free UPO in the food industry, choosing a production temperature above the m.p., so that oil can melt completely, would accelerate its crystallization. When comparing the crystallization rates of UPO and HPO from temperatures above and below the top limit of the m.p., it was found that samples crystallized from a temperature above complete melting would directly form a stable crystal, without the polymorph transition process. Crystallization from an initial heating temperature above the m.p. endowed UPO with a crystallization rate as fast as, if not faster than, HPO. Therefore, we could increase the initial production heating temperature of UPO to accelerate its crystallization, making substitution of HPO much more viable.

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