JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Relationship between Crystallization Behavior, Microstructure, and Macroscopic Properties in Trans Containing and Trans Free Coating Fats and Coatings

IMOGEN FOUBERT,*,†,‡ JEROEN VEREECKEN,† KEVIN W. SMITH,§ AND KOEN DEWETTINCK†

Laboratory of Food Technology and Engineering and BIOMATH, Faculty of Bioscience Engineering, Ghent University, Coupure links 653, B-9000 Gent, Belgium, and Unilever Research Colworth, Sharnbrook, Bedfordshire, MK44 1LQ, U.K.

The objective of this study is to gain further understanding into the relationship between crystallization behavior, microstructure, and macroscopic properties in coating fats. The isothermal crystallization behavior of two coating fats (one trans containing and one trans free) was examined, both as pure fats and in coatings, by DSC and microscopy. Furthermore, the hardness of the samples was examined after cooling in a water bath at two different temperatures and at three different storage times. Both fats seemed to show an α-mediated β' crystallization at lower temperatures and a direct β' crystallization at higher temperatures. The trans free coating fat clearly crystallized faster and in smaller crystals. The hardness was governed not only by the amount of solid fat present in the network but also by the structure of this network. The coating matrix components seem to have a pronounced influence on the microstructure and thus on the macroscopic properties.

KEYWORDS: Coating; crystallization; microstructure; hardness; fat

INTRODUCTION

Coatings can be used on confections, bakery products, and other snack foods. Of all the ingredients included in a coating, none has a greater influence on the characteristics of the coating than the fat phase. The function of the coating fat is to provide the continuous matrix that holds the other ingredients and contributes to flavor, aroma, and color. This fat matrix must be firm and dry to touch at ambient temperatures and not greasy or sticky. Upon consumption, the fat matrix should melt away quickly and completely at or near mouth temperature. Failure of the coating fat to melt rapidly will result in poor flavor release and, probably, a waxy aftertaste (*1*).

In recent years, trans fatty acids in foods have received considerable attention, both in the scientific literature and in the popular press. Reports in the scientific literature indicate that high levels of trans fatty acids in the diet, compared to high levels of cis fatty acids, result in unfavorable effects on both low-density lipoprotein and high-density lipoprotein cholesterol. In response to these reports, many organizations of health professionals have recommended reduced consumption of foods containing trans fatty acids (*2*). In the absence of partially hydrogenated oils—the major source of trans fatty acids—the manufacturers have to fall back to fats based on palm oil fractions and fats based on lauric fats.

The macroscopic properties of edible fats and thus also of coating fats are influenced by a series of factors, including the amount of solids, the polymorphism of the solid state, and the microstructure of the network of crystalline particles. Furthermore, the particular processing conditions utilized during crystallization can influence all these structure levels (*3*). Few studies have however involved all these structure levels. Brunello et al. (*4*) and Campos et al. (*5*) examined the relationship between these structure levels in pure fats, respectively cocoa butter and milk fat and lard. Braipson-Danthine and Deroanne (*6*), Humphrey and Narine (*7*), Narine and Humphrey (*8*), and deMan et al. (*9*) on the other hand have studied the relationships in fat blends involved in the preparation of industrial shortenings and in commercial shortenings.

The objective of this study is to gain understanding into the relationship between crystallization behavior (including polymorphism), microstructure, and macroscopic properties in fat blends used for coatings, as these have not been studied before. In the framework of the above-described trans issue it is important to understand differences in this relationship between different fats. Therefore, a trans containing and a trans free, lauric coating fat are compared. Not only the coating fats but also the coatings themselves are the subject of this research.

* Corresponding author. Tel: +32 9 264 61 68. Fax: +32 9 264 62 18. E-mail: imogen.foubert@UGent.be.
† Laboratory of Food Technology and Engineering, Faculty of Bioscience Engineering, Ghent University.
‡ BIOMATH, Faculty of Bioscience Engineering, Ghent University.
§ Unilever Research Colworth.

10.1021/jf060225e CCC: $33.50
Published on Web 08/19/2006

Table 1. Composition of Dark Coating

ingredient	weight percentage (%)
cocoa powder (10–12% fat)	16
coating fat	32
skimmed milk powder	3
sugar	49
lecithin	0.4
vanilla aroma	0.03

MATERIALS AND METHODS

Samples. The trans containing coating fat (TCF) based on partially hydrogenated palm oil as well as the trans free alternative (TFCF) based on palm kernel oil were supplied by Loders Croklaan (Wormerveer, Netherlands). With these coating fats a dark coating (TC and TFC) was produced by Loders Croklaan (Wormerveer, Netherlands). The composition of the dark coating is given in **Table 1**.

Fatty Acid Composition. Fatty acid methyl esters (FAME) were produced by reacting 1 drop (10−20 mg) of sample with 2 mL of isooctane and 50 μL of 2 N KOH reagent. The mixture was shaken for 2 min at room temperature and then allowed to settle. The isooctane layer was carefully removed and diluted ×2. High-resolution FAME GC was carried out on a Thermo Finningan trace GC fitted with a CP Select (CPSil88 bonded) CB 50 m × 0.25 mm i.d. 0.25 μm film. The helium carrier gas had an inlet pressure of 125 kPa. Sample solution (2.0 μL) was injected via a PTV split/splitless injector (right inlet, 125 kPa; mode, CT split; split ratio, 20:1). The oven temperature was programmed from 160 °C for 1 min, 160−200 °C at 1 °C/min, and 200−230 °C at 2 °C/min. Detection was via FID set to 260 °C.

Triglyceride Composition. High-resolution separation for triglycerides was achieved using an Agilent 6890+ GC system fitted with an automated on column injection onto a Quadrex 15 m 0.25 mm 0.1 μm film 65% phenyl-methyl silicone GC column. The samples were dissolved in isooctane at approximately 0.3 mg/mL. The injection volume was 0.1 μL. The helium carrier gas was set at constant flow of 1 mL/min. The oven program with injector in oven track mode was 80 °C for 0.5 min, ramping up to 330 °C at 50 °C/min, with triglyceride separation being achieved from 330 °C to 350 °C ramping at 1 °C/min. Detection was via FID.

SFC. SFC was measured by pulsed NMR (pNMR) with a Bruker Minispec pc 20 (Bruker, Karlsruhe, Germany). Melted fat was placed in NMR tubes (3 replicates) and submitted to the tempering treatments of the IUPAC 2.150 serial tempered method. The SFC was determined in the range of 0−45 °C at 5 °C intervals following 60 min incubations at each temperature.

Isothermal Crystallization Curves via Stop-and-Return Technique (DSC). The isothermal crystallization curves were obtained with a TA Q1000 DSC (TA Instruments, New Castle, DE) with a refrigerated cooling system. The DSC was calibrated with indium (TA Instruments, New Castle, DE), azobenzene (Sigma-Aldrich, Bornem, Belgium), and undecane (Acros Organics, Geel, Belgium) before analyses. Nitrogen was used to purge the system. Coating or fat (5−15 mg) was sealed in hermetic aluminum pans using sample preparation procedure B as described by Foubert et al. (*10*), and an empty pan was used as a reference. The applied time−temperature program was as follows: holding at 70 °C for 10 min to ensure a completely liquid state, cooling at 5 °C/min to the isothermal crystallization temperature (±0.05 °C), holding for the required crystallization time, and then heating at 20 °C/min to 70 °C (crystallization times were set at 1−60 min, depending on the stage of the crystallization). Thus different crystallization times were allowed to occur before remelting. The melting curves were integrated using a linear baseline with the end point determined by the calculation algorithm as described by Foubert et al. (*10*) and the starting point at the same *y*-value as the end point. Three repetitions were performed for each combination of temperature and time. The area of the melting peak (corresponding to the melting enthalpy) thus increased with increasing time at the isothermal crystallization temperature as the degree of previous crystallization increased. Hence, the degree of crystallization as a function of time at the crystallization temperature could be determined, despite the fact that some crystallization has occurred before the isothermal temperature was reached.

Table 2. Fatty Acid Composition of Coating Fats[a]

	composition (wt %)			composition (wt %)	
fatty acid	TCF	TFCF	fatty acid	TCF	TFCF
8:0		2.3	18:0	10.5	11.5
10:0		2.9	18:1 cis	18.9	0.5
12:0	0.4	54.1	18:1 trans	36.1	0.4
14:0	0.9	19.5	18:2	2.1	0.1
16:0	30.1	8.6	others	1.0	0.1

[a] Single measurements were made on each sample.

Table 3. Triglyceride Composition of Coating Fats TFCF and TCF[a]

triglyceride	composition (wt %)	triglyceride	composition (wt %)
A. Triglyceride Composition of TFCF			
CCLa	3.8	MMM	9.0
CLaLa	6.7	MMP	5.1
LaLaLa	25.2	MPP	3.7
LaLaM	22.4	PPP	3.2
LaMM	13.8	PPS	1.3
B. Triglyceride Composition of TCF			
MOP	1.7	PLO/PLE	1.0
POP/PEP	19.4	SOS/SES	2.4
PLP	3.7	SOO/SEE + SLS	18.0
POS/PES	5.0	OOO/EEE	7.0
POO/PEE	38.2	AOO/AEE	1.5

[a] Positional isomers have not been separated. Single measurements were made on each sample.

Determination of Melting Curve after Penetration Test (DSC). These melting curves were obtained with a 2010 CE DSC (TA Instruments, New Castle, DE) with a refrigerated cooling system. Calibration was the same as for the TA Q1000 DSC described above. A small sample (5−15 mg) of the crystallized coating or fat was sealed in a hermetic aluminum pan and immediately placed in the DSC at the temperature of performance of the penetration test. The sample was then heated at a rate of 20 °C/min to 70 °C. The melting curves were integrated as described above.

Microscopic Analyses. Microscopic analyses were conducted by the use of a Leitz Diaplan microscope (Leitz Diaplan, Leica, Germany) equipped with a Linkam PE 94 temperature control system (Linkam, Surrey, U.K.). Samples were imaged with a Nikon Coolpix 4500 (Nikon, Melville, NY).

Hardness (Penetration Test). The hardness of the crystallized (20 mL in plastic beaker crystallized in a temperature controlled water bath for 30 min at a specific temperature) and stored samples was determined with a penetration test on a texture analyzer TA 500 (Lloyd Instruments, Hampshire, U.K.) with a cylindrical probe with a diameter of 4.51 mm (CNS Farnell, Hertfordshire, U.K.). The probe penetrated the product at a constant speed of 10 mm/min to a distance of 10 mm. To ensure measurement of the hardness at the specified temperature, the texture analyzer is placed in a temperature controlled cabinet (±0.5 °C) (Lovibond, Dortmund, Germany). Hardness was defined as the maximum penetration force (*N*).

RESULTS AND DISCUSSION

Characterization of the Fat Samples. Table 2 shows the fatty acid composition of the two coating fats. The TCF indeed contains more than 35% elaidic acid (C18:1 trans), while the TFCF contains less than 1% of this trans fatty acid. It is also apparent that the TFCF contains a high amount of lauric and myristic acid, which can be explained by the fact that the fat blend is based on palm kernel oil. **Table 3** shows the triglyceride composition of the two coating fats. The weight percentages of

Table 4. Solid Fat Content (SFC) of the Coating Fats

temp (°C)	SFC (%) TCF	SFC (%) TFCF	temp (°C)	SFC (%) TCF	SFC (%) TFCF
0	94.71 ± 0.10	99.18 ± 0.28	25	62.67 ± 0.19	86.43 ± 0.12
5	94.08 ± 0.16	99.12 ± 0.06	30	48.65 ± 1.04	46.45 ± 0.86
10	90.38 ± 0.32	98.85 ± 0.12	35	10.55 ± 0.91	5.88 ± 0.28
15	83.12 ± 0.41	97.42 ± 0.02	40	0.25 ± 0.12	0.93 ± 0.22
20	72.30 ± 0.27	93.90 ± 0.07	45	0.09 ± 0.05	0.25 ± 0.05

the 10 most abundant triglycerides are each time represented. **Table 4** shows the SFC curves of both coating fats. The difference between the two fats is especially apparent at temperatures below 30 °C. At 25 °C the SFC of TCF has already dropped to 63% while TFCF maintains a high SFC value up to 25 °C.

Isothermal Crystallization Behavior of Coating Fats. Using DSC, the crystallization in a cooling tunnel was simulated. The fats were completely melted and then cooled to a certain temperature, where the samples were kept isothermally for a certain period of time. In some experiments the fats began to crystallize during cooling to the isothermal temperature (which also happens in reality in a cooling tunnel) making it impossible to integrate the isothermal crystallization curves. This was solved by heating the fat after certain isothermal periods and integrating the melting curve to obtain the melting enthalpy which is related to the amount of fat that had crystallized at the moment the heating was started. This way of obtaining crystallization curves is called the "stop-and-return" technique (as described above).

Figure 1 shows the melting enthalpy (as a measure of the crystallinity) as a function of the isothermal time for TCF and TFCF. Since for coatings it is important that the product has almost completely crystallized and is thus "dry" as it leaves the cooling tunnel, the temperature range studied is for each fat around the temperature at which the fat is almost completely crystallized within a period of 30 min. For TCF this temperature is around 19 °C. From this temperature onward no significant differences were found between the melting enthalpy at 30 min and the melting enthalpy at longer isothermal times. For TFCF this temperature is 30 °C. It is thus clear that the crystallization of TFCF is much faster compared to TCF. A very quick crystallization is indeed typical for lauric fats such as TFCF (*11*).

Figure 1a shows that the crystallization of TCF slows down as the temperature increases and the melting enthalpy at equilibrium also decreases as the temperature increases. Furthermore, **Figure 1a** shows a clear difference in crystallization kinetics between a temperature of 23 °C and lower temperatures. The difference in crystallization rate between 21.5 °C and 23 °C is indeed much more pronounced compared to the difference between 20 °C and 21.5 °C. To try to explain this, the crystallization behavior was investigated by studying the peak maxima of the melting profiles as a function of time for each of the temperatures. For temperatures of 21.5 °C and below two peaks were visible at an isothermal time of 0 min. At longer crystallization times (1 min at crystallization temperatures below 20 °C, 5 min at a crystallization temperature of 20 °C and higher) the low melting peak disappeared and only one peak was visible in the melting profile. This is illustrated in **Figure 2** for a crystallization temperature of 17 °C. At 23 °C only one peak was visible, irrespective of the crystallization time. The peak maximum of this peak coincides more or less with that of the higher melting peak at the lower crystallization

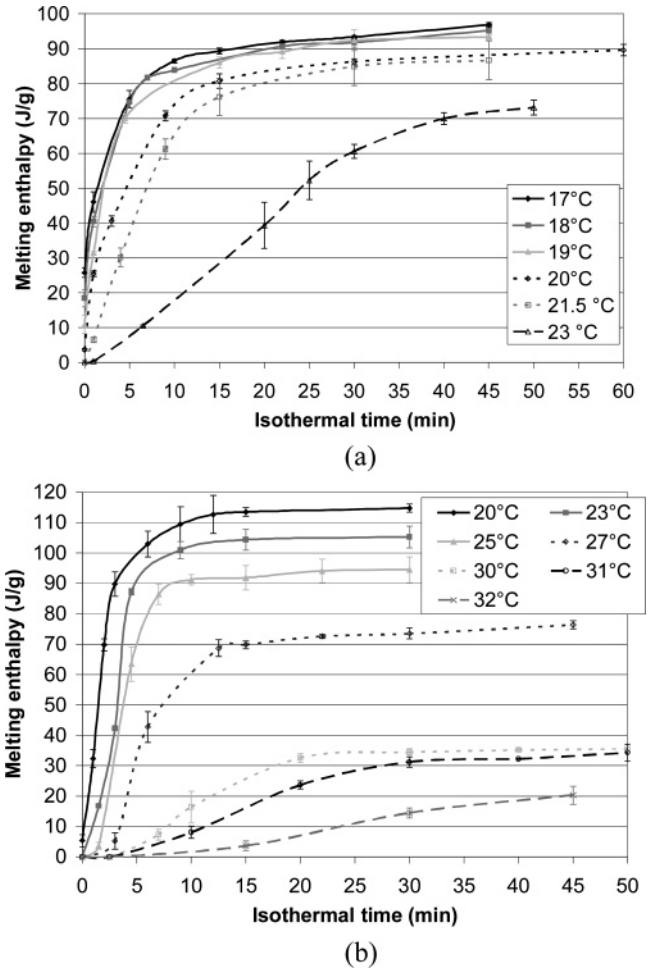

Figure 1. Melting enthalpy of (a) TCF and (b) TFCF as a function of isothermal time at different crystallization temperatures.

temperatures. On the basis of these results the following crystallization mechanism can be proposed. At lower temperatures (lower than 23 °C) the fat first crystallizes in the α polymorph and later on transforms into a β' polymorph. This transition occurs later at higher crystallization temperatures. At a crystallization temperature of 23 °C the fat crystallizes from the melt immediately in the β' polymorph. Taking into account the complexity of the triglyceride mixture of TCF also involving geometric and positional isomers, no β polymorph was expected (*12*). Chen et al. (*13*) have already proven that palm oil shows an α-mediated β' crystallization at isothermal temperatures lower than 22 °C and a direct β' crystallization at higher temperatures, which corresponds completely to the hypothesis mentioned above.

Figure 1b shows that the crystallization of TFCF also slows down as the temperature increases. The melting enthalpy at equilibrium also decreases as the temperature increases. To get more insight in the crystallization mechanism the peak maxima of the melting profiles were investigated as a function of time for each of the temperatures. At a crystallization temperature of 20 °C and an isothermal time of 0 min two peaks were visible in the melting profile. At longer isothermal times the low melting peak disappeared. At temperatures above 20 °C only one peak was visible at all isothermal times. On the basis of these results the following crystallization mechanism can be proposed. At 20 °C the fat first crystallizes in the α polymorph, which very quickly transforms into a β' polymorph. At higher temperatures the β' polymorph is formed directly from the melt. No β

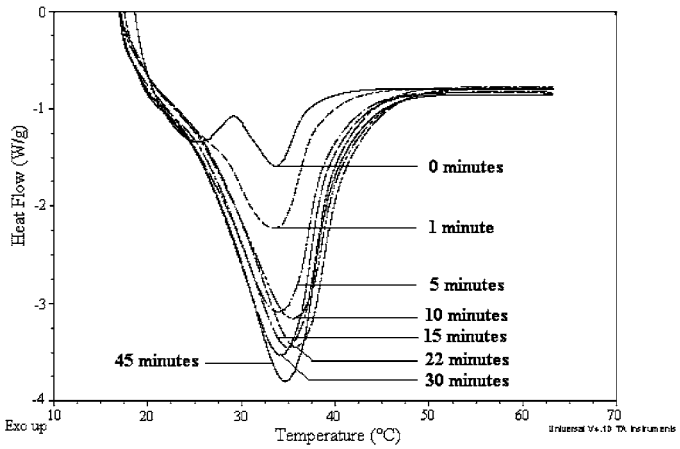

Figure 2. Melting curves of TCF as a function of isothermal time at a crystallization temperature of 17 °C.

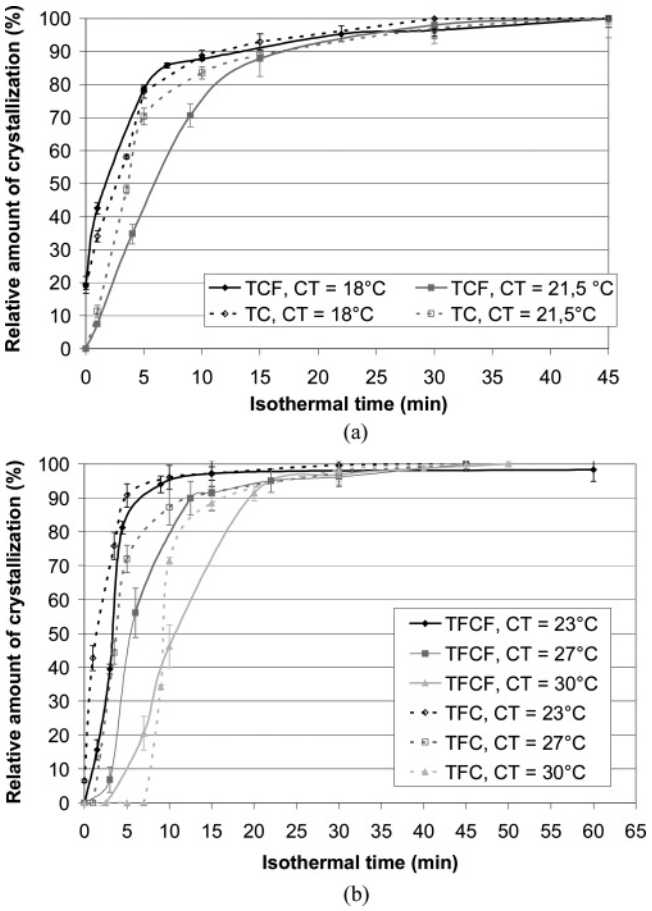

Figure 3. Relative amount of crystallization as a function of time for (a) TCF/TC and (b) TFCF/TFC at two different crystallization temperatures (CT).

polymorph was expected as palm kernel oil (on which TFCF is based) is very stable in the β' polymorph and a β polymorph only occurs after months of storage (*14*, *15*). It can also be seen from **Figure 1b** that between 25 °C and 30 °C the equilibrium amount of crystallinity dramatically decreases, which coincides with the sharp decrease in the SFC profile between these temperatures (**Table 4**). These observations may be explained by the fact that about 35% of the triglycerides in TFCF are medium chain triglycerides (incorporating C and La) and thus have a melting point between 25 and 35 °C (*16*). Thus, these triglycerides will not be able to crystallize at the highest temperatures but will crystallize at the lower temperatures.

Both coating fats thus show a comparable crystallization behavior: formation of the β' polymorph via the α polymorph at low crystallization temperatures and direct formation of the β' polymorph at higher temperatures. The crystallized β' polymorph of the two fats also has a comparable melting point. The big difference between the two fats is the difference in crystallization rate, which is much higher for TFCF compared to TCF. This will result in different temperatures to be used in a cooling tunnel.

Isothermal Crystallization Behavior of Coatings. A coating consists of a matrix of different components (sugar, milk powder, cocoa powder) in a continuous coating fat phase. To get an insight into the effect of these matrix components, the same isothermal DSC experiments at selected temperatures were applied to the coatings. To be able to compare better the crystallization of coating fats and coatings, the amount of crystallization is expressed relative to the equilibrium amount of crystallization (melting enthalpy at the longest crystallization time). After all, the melting enthalpy of the coatings was only one-third of the melting enthalpy of the coating fats since only 34% fat is present in the coatings. The results are shown in **Figure 3a** and **Figure 3b** for TCF/TC and TFCF/TFC, respectively.

At a crystallization temperature of 18 °C no significant differences in crystallization kinetics between TCF and TC could be observed, while at a crystallization temperature of 21.5 °C the crystallization of TC was markedly faster compared to TCF. This can be explained by the fact that the matrix adds extra heterogeneous nuclei to the system. The lower the degree of supercooling (higher crystallization temperature), the more pronounced the effect of these extra nuclei, thus explaining the difference in effect of the matrix at 18 °C compared to 21.5 °C.

When comparing TFCF with TFC, the crystallization of the coating is also faster than that of the coating fat at each of the crystallization temperatures studied. However, at short times, a different phenomenon appears to occur at an isothermal crystallization temperature of 30 °C. This may be due to the fact that it is very difficult to measure the small melting enthalpies that result from low degrees of crystallization (i.e., the determination is imprecise for the initial low levels of crystallization).

Microscopic Analysis of Coating Fats. The microstructure of the coating fats was studied in the same temperature range as the isothermal crystallization behavior. For coating fat TCF, less fat crystallized in a less dense network (at equilibrium) as the crystallization temperature increased. This difference was most apparent from 23 °C onward (**Figure 4**). This coincides with the clear decrease in the equilibrium amount of crystallinity as can be deduced from **Figure 1a** but also with the change in crystallization mechanism as discussed above. However, this change does not seem to influence the morphology of the final crystals. In addition, during the isothermal crystallization at temperatures where DSC showed an α-mediated β' crystallization, no change in crystal morphology could be observed.

The microstructure of TFCF at equilibrium initially remained the same when the crystallization temperature increased, but changed clearly above 30 °C. Above this temperature less fat crystallized and bigger crystals were formed (**Figure 4**). From 30 °C onward less triglycerides are able to crystallize (see also discussion in section on isothermal crystallization behavior), resulting in fewer nucleating sites which, consequently, gives rise to bigger crystals. This change in morphology thus does

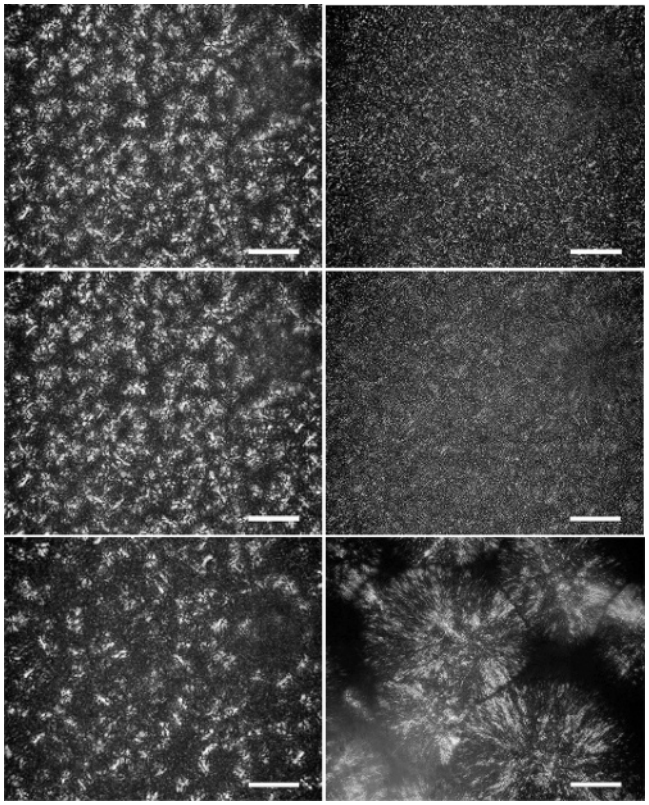

Figure 4. Microscopic images (500× magnification) of TCF (left column) and TFCF (right column) crystallized for 30 min at different temperatures (from top to bottom: 18, 20, and 23 °C for TCF and 20, 27, and 32 °C for TFCF). The white bars represent 500 μm.

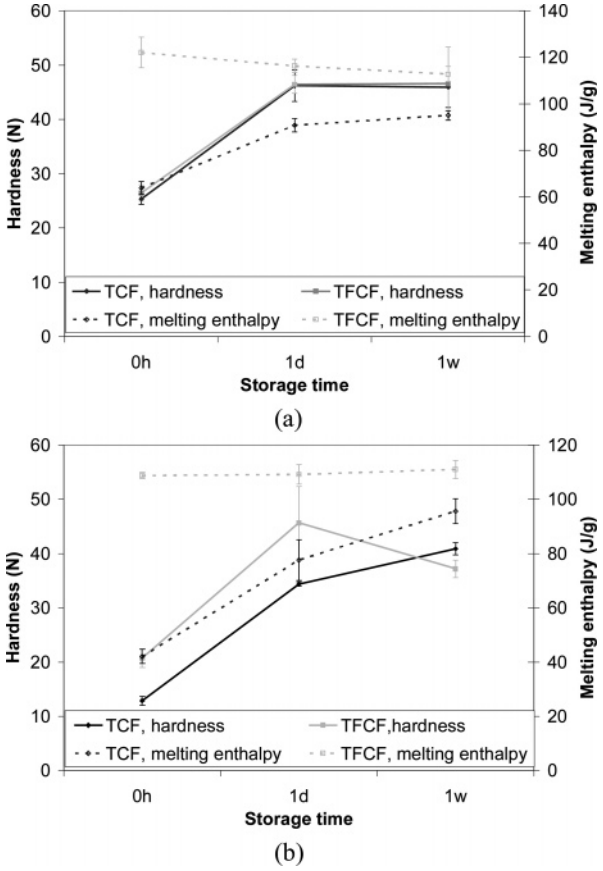

Figure 5. Hardness and melting enthalpy of the coating fats as a function of storage time after a crystallization at (a) 10 °C and (b) 15 °C .

not coincide with a change in crystallization behavior since this occurs at lower temperatures (20 °C).

When comparing the microstructure of the two coating fats (**Figure 4**), it is very clear that TFCF forms smaller crystals. This could also be observed when the two fats were crystallized at the same temperature (detailed results not shown). The explanation for this phenomenon is probably the faster crystallization with instantaneous formation of a large number of nuclei. This fast crystallization is accompanied by a rapid increase in viscosity, thus limiting molecular diffusion and crystal growth (*17*).

Hardness of Coating Fats as a Function of Crystallization Temperature and Storage Combined with Melting Profile/Microscopy. The hardness of the coating fats was examined after cooling in a thermostated water bath at 10 °C and 15 °C for 30 min. These crystallization temperatures are lower than those studied in the isothermal crystallization behavior due to differences in the volume of the samples. Thus the exact crystallization temperatures cannot be compared with the isothermal crystallization behavior. Trends as a function of temperature, however, are assumed to remain valid for the different crystallization volumes. The hardness was examined immediately after the cooling process and also after 1 day and 1 week of storage at room temperature (19−21 °C). To be able to explain better certain phenomena, the hardness tests were coupled with measurements of the melting profile and with microscopical analyses under the same conditions. The hardness as well as the melting profile experiments were performed in triplicate.

Figure 5 shows the hardness as well as the melting enthalpy of both coating fats as a function of storage time after a crystallization at 10 °C and 15 °C. After cooling at 10 °C, the hardness of TCF increases significantly during the first day of storage, which is also the case for the melting enthalpy. Due to the rather slow crystallization of TCF (see above) the crystallization is not complete after the cooling process, and thus the sample crystallizes further during storage, leading to a higher melting enthalpy and a higher hardness. Indeed, different studies (*5*, *6*, *18*, *19*) have already demonstrated that higher amounts of crystallinity lead to harder networks. After 1 day of storage, the sample has reached equilibrium as there are no significant differences between 1 day and 1 week of storage, neither for the melting enthalpy nor for the hardness, nor for the microscopical analyses. When the crystallization temperature is increased to 15 °C, it takes even longer before the equilibrium amount of crystallinity is reached, which can be seen from the fact that the melting enthalpy continues to rise between 1 day and 1 week of storage. This is also reflected in a continued increase in hardness between 1 day and 1 week of storage.

After a cooling at 10 °C, the hardness of TFCF also increases significantly during the first day of storage. The melting enthalpy however remains constant, meaning that the fat is already completely crystallized after the cooling. The latter is explained by the faster crystallization of TFCF compared to TCF. Thus the increase in the hardness during storage cannot be explained by an increase in solid fat. Narine and Marangoni (*20*) and Braipson-Danthine (*21*) have already proven that SFC is insufficient to explain the differences in hardness. Also, polymorphism cannot be an explanation, as the peak maximum of the melting curve does not change during storage. In addition, no clear difference could be detected in the microscopical analyses performed, but it should be stressed that the crystallization volume is very much different (one drop versus 20 mL) and a 2D crystallization is compared with a 3D crystallization.

This could cause crystallization mechanisms or crystallization kinetics with the formation of different crystallization structure with varying macroscopic properties. Another very plausible explanation for the change in hardness is sintering of the crystals (*12*). After 1 day of storage, also TFCF has reached equilibrium as there are no significant differences in hardness between 1 day and 1 week of storage.

When the crystallization temperature was increased to 15 °C, the crystallization was nevertheless complete after the cooling since the melting enthalpy was the same for all storage times. The peak maximum also did not change as a function of storage time. As for a crystallization temperature of 10 °C, the observed increase in hardness during the first day of storage consequently should be completely due to a change in microstructure. Similarly, as for a crystallization temperature of 10 °C, no change in crystal size, number, and morphology could be observed in the microscopical images. It was remarkable that the hardness decreased again between 1 day and 1 week of storage (after crystallization at 15 °C, but not after crystallization at 10 °C). Presumably the microstructure changed again, leading to the lower hardness value. Unfortunately, this could not be observed from the microscopical analyses.

Despite the fact that TCF was not yet completely crystallized immediately after the cooling, the hardness (for crystallization at 10 °C) was equal to that of the completely crystallized TFCF. It thus seems that TCF forms a stronger network than TFCF immediately during the primary crystallization. From the microscopical analyses, it was observed that the crystals formed by TFCF are smaller than those formed by TCF. As such, a lower value of the hardness was expected for TCF because, in a network composed of large particles, the attractive forces will be weaker (*5*). This is contradictory to what was observed. For crystallization at 15 °C, the amount of crystallization is even further from equilibrium immediately after cooling, meaning that the stronger network formed by TCF can no longer compensate for the lower amount of solid fat. Consequently, the hardness of TFCF is significantly higher than that of TCF. Since the network of TFCF becomes stronger during storage, the hardness of TFCF remains equal to or higher than (depending on the crystallization temperature) that of TCF even after 1 day of storage when the crystallization of TCF has completed/continued (depending on the crystallization temperature). After 1 week of storage the hardnesses are still equal after a crystallization at 10 °C, but after a crystallization at 15 °C the hardness of TCF has overtaken that of TFCF, partly due to the continued increase of the hardness of TCF due to further crystallization but also partly due to the decrease in hardness of TFCF due to another change in microstructure weakening the network.

Thus, it can be concluded that the hardness is governed not only by the amount of solid fat present in the crystal network but also by the structure of this network.

Hardness of Coatings as a Function of Crystallization Temperature and Storage Combined with Melting Profile. Figure 6 shows the hardness as well as the melting enthalpy of both coatings as a function of storage time after cooling at 10 °C and 15 °C.

After a cooling at 10 °C, the melting enthalpy of TC increases during the first day of storage (as was also the case for TCF) because the crystallization has not completed after the cooling. The increase was more pronounced in TCF compared to TC because, due to the faster crystallization of TC compared to TCF (see above), the crystallization will be closer to completion after the cooling. The melting enthalpy of TC then decreases

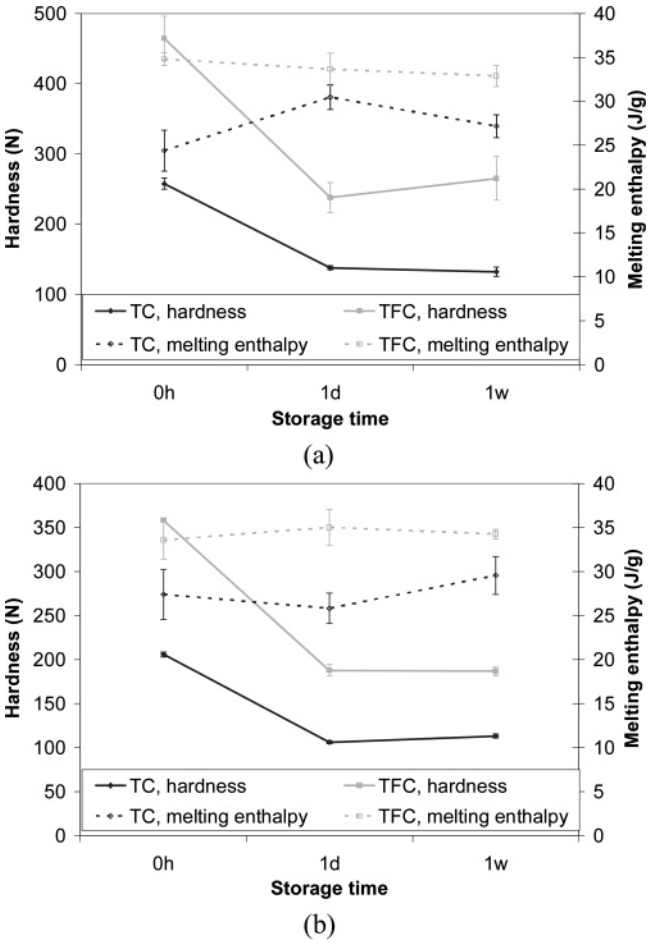

Figure 6. Hardness and melting enthalpy of the coatings as a function of storage time after a crystallization at (a) 10 °C and (b) 15 °C.

between 1 day and 1 week of storage to obtain a level which is not significantly different from the value immediately after the cooling. No explanation for the decrease during further storage could be found. After a cooling at 15 °C, the melting enthalpy of TC does not increase during the first day of storage, which is contrary to what would be expected, and also no decrease during further storage could be observed. The melting enthalpy of TFC does not change during storage, neither after a cooling at 10 °C nor after a cooling at 15 °C, as was also the case for the melting enthalpy of TFCF. Since TFCF was already crystallized completely at the end of the cooling, TFC will, taking into account the faster crystallization (see above), surely be crystallized completely.

The macroscopic behavior of the coatings is quite different compared to the behavior of the coating fats. For both coatings and both crystallization temperatures, the hardness decreases significantly during the first day of storage, which is opposite to the behavior of the coating fats. This decrease cannot be explained by a decrease in the amount of crystallization (melting enthalpy remains the same) nor by polymorphism (peak maximum remains the same). Thus, a change in the microstructure will be the cause of the decrease in hardness. No significant differences could be observed in the hardness between 1 day and 1 week of storage. While the hardness of TCF and TFCF was not significantly different, the hardness of TFC is almost double that of TC. It thus seems that the shorter chain triglycerides of TFCF interact in a different way with the other components in the matrix to obtain a firmer network with a higher hardness as a consequence. Alternatively, the crystals

of TFCF are able to form a stronger network around the matrix than can the TCF.

It can thus be concluded that the different matrix components not only have an effect on the crystallization but also have a very pronounced influence on the microstructure and thus on the macroscopic properties such as the hardness.

ABBREVIATIONS USED

TCF, trans containing coating fat; TFCF, trans free coating fat; TC, trans containing coating; TFC, trans free coating; FAME, fatty acid methyl ester.

ACKNOWLEDGMENT

I.F. is a Postdoctoral Fellow of the Research Foundation—Flanders (FWO—Vlaanderen). Loders Croklaan is acknowledged for providing the samples.

LITERATURE CITED

(1) Pease, J. J. Confectionery fats from palm oil and lauric oil. *J. Am. Oil Chem. Soc.* **1985**, *62*, 426−430.
(2) Hunter, J. Alternatives to trans fatty acids in foods. *Inform.* **2004**, *15*, 510−512.
(3) Marangoni, A. G.; Narine, S. S. Identifying key structural indicators of mechanical strength in networks of fat crystals. *Food Res. Int.* **2002**, *35*, 957−969.
(4) Brunello, N.; McGauley, S. E.; Marangoni, A. Mechanical properties of cocoa butter in relation to its crystallization behavior and microstructure. *Lebensm.-Wiss. -Technol.* **2003**, *36*, 525−532.
(5) Campos, R.; Narine, S. S.; Marangoni, A. G. Effect of cooling rate on the structure and mechanical properties of milk fat and lard. *Food Res. Int.* **2002**, *35*, 971−981.
(6) Braipson-Danthine, S.; Deroanne, C. Influence of SFC, microstructure and polymorphism on texture (hardness) of binary blends of fats involved in the preparation of industrial shortenings. *Food Res. Int.* **2004**, *37*, 941−948.
(7) Humphrey, K. L.; Narine, S. S. A comparison of lipid shortening functionality as a function of molecular ensemble and shear: Crystallization and melting. *Food Res. Int.* **2004**, *37*, 11−27.
(8) Narine, S. S.; Humphrey, K. L. A comparison of lipid shortening functionality as a function of molecular ensemble and shear: microstructure, polymorphism, solid fat content and texture. *Food Res. Int.* **2004**, *37*, 28−38.
(9) deMan, L.; deMan, J. M.; Blackman, B. Physical and textural characteristics of some North American shortenings. *J. Am. Oil Chem. Soc.* **1991**, *68*, 63−69.
(10) Foubert, I.; Vanrolleghem, P.; Dewettinck, K. A differential scanning calorimetry method to determine the isothermal crystallization kinetics of cocoa butter. *Thermochim. Acta* **2003**, *400*, 131−142.
(11) Timms, R. E. Processing of palm kernel oil. *Fette, Seifen, Anstrichm.* **1986**, *88*, 294−300.
(12) Walstra, P. *Physical chemistry of foods*; Marcel Dekker Inc.: New York, 2003.
(13) Chen, C. W.; Lai, O. M.; Ghazali, H. M.; Chong, C. L. Isothermal crystallization kinetics of refined palm oil. *J. Am. Oil Chem. Soc.* **2002**, *79*, 403−410.
(14) Riiner, Ü. Investigation of the polymorphism of fats and oils by temperature programmed X-ray diffraction. *Lebensm.-Wiss. -Technol.* **1970**, 3, 101−106.
(15) Rossell, J. B. Differential scanning calorimetry of palm kernel oil products. *J. Am. Oil Chem. Soc.* **1975**, *52*, 505−511.
(16) Hagemann, J. W. Thermal behaviour and polymorphism of acylglycerides. In *Crystallization and polymorphism of fats and fatty acids*; Garti, N., Sato, K., Eds.; Marcel Dekker: New York, 1988; pp 9−95.
(17) Dibildox-Alvarado, E.; Toro-Vazquez, J. F. Evaluation of tripalmitin crystallization in sesame oil through a modified Avrami equation. *J. Am. Oil Chem. Soc.* **1998**, *75*, 73−76.
(18) de Man, J. M. Effect of cooling procedures on consistency, crystal structure and solid fat content of milk fat. *Dairy Ind.* **1964**, *29*, 244−246.
(19) Haighton, A. J. Blending, chilling and tempering of margarines and shortenings. *J. Am. Oil Chem. Soc.* **1976**, *53*, 397−399.
(20) Narine, S. S.; Marangoni, A. G. The difference between cocoa butter and Salatrim lies in the microstructure of the fat crystal network. *J. Am. Oil Chem. Soc.*, **1999**, 7−13.
(21) Braipson-Danthine, S.; Deroanne, C. Influence of SFC, microstructure and polymorphism on texture (hardness) of binary blends of fats involved in the preparation of industrial shortenings. *Food Res. Int.* **2004**, 941−948.

Received for review January 25, 2006. Revised manuscript received June 30, 2006. Accepted July 20, 2006. Loders Croklaan is acknowledged for financial support.

JF060225E