

The Influence of Temperature on Interactions and Structures in Semisolid Fats

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ABSTRACT: The strength of fat crystal networks in oil increases at elevated temperatures due to increased adhesion between partially melted crystal surfaces. This strong adhesion, in combination with low oil viscosity (weak hydrodynamic force), is the reason for extensive fat crystal flocculation at elevated temperatures. The crystal flocs likely sinter, dramatically increasing the thickness of semisolid fats. Crystal growth also occurs. The described temperature-induced crystal changes may be suppressed by a controlled sintering process at low temperature. Emulsifiers, such as sorbitan esters of tristearate, also suppress the temperature-induced changes. Fat crystals can be used as thickeners or gelling agents for triglyceride oils in various applications. It is possible to direct the thickening to a specific temperature, and to control the degree of thickening, by choice of fat phase composition, additives, tempering conditions, and crystallization technique.

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KEY WORDS: Bulk crystallization, dispersions, elevated temperature, emulsifiers, fat crystals, rheology, sedimentation, sintering, vegetable oils.

Natural semisolid fats are important components in oil-continuous foods such as chocolate, butter, margarines, low-fat spreads, and shortenings. The fat phase in these foods determines properties such as consistency, emulsion stability and stability against oiling-out (1–5). Semisolid fats also appear in water-continuous foods. For example, oil droplets in cream contain fat crystals, which are necessary to achieve whippability (2,6,7). The role of fat crystals in ice cream is similar; its function is to retain air bubbles in the product (2,7).

Fat crystals in these products form flocs and networks, the structure of which is very important to product properties. Structure depends mainly on three factors—fat crystal size, morphology, and mutual adhesion (2,8,9). Crystal size may, to some extent, be controlled through the tempering procedure during crystallization. Morphology has been found to depend highly on the type of fat phase. Furthermore, adhesion between fat crystals in oils has been extensively examined. Interactions such as van der Waals forces (2,9–12), water bridges (13), and solid bridges (14,15) exist. Additional

interactions appear due to adsorption of emulsifiers to the crystals (16,17). However, most of the interaction studies mentioned here were performed at room temperature.

All food products containing semisolid fat are subjected to tempering processes during production, storage and/or consumption. Tempering during production is usually well controlled and is designed to produce a desired fat crystal network. Temperature during storage and consumption varies, depending on temperatures in refrigerators, climate, and consumers' habits. A way to reduce tempering problems is to understand the relationship between composition, interactions, structures, and temperature in these systems; that is the goal of this study. Special emphasis has been placed on changes induced by prolonged storage of samples at elevated temperatures.

EXPERIMENTAL PROCEDURES

High-melting fat crystals. Two different types of high-melting fats were studied—pure tristearin from Fluka (Buchs, Switzerland) and totally hydrogenated palm oil (palm stearin) from Karlshamns AB (Karlshamn, Sweden). Tristearin was of high purity (>99%). It has a density of 1.0577 g/mL, a mole mass of 892 g/mol, and a low iodine value (totally saturated fat). Tristearin is stable in polymorphic form β , with a melting point of 72°C. The α form, with a melting point of 53°C (18), appears in rapidly cooled fat.

Palm stearin has a mole mass of 756 g/mol and an iodine value of 2.6. Its purity and density are not specified. It is stable in the polymorphic form β' , which has a melting point of 57–59°C. The β' form is very stable and occurs even in palm stearin that is crystallized from organic solvents, such as acetone. Hence, we expect that the β' form converts only sparingly to the β form. The α -form occurs in the rapidly cooled palm stearin and has a melting point of 46°C. The palm stearin has the following composition of fatty acids: 53% C_{16:0}, 42% C_{18:0}, 2% C_{18:1}, 3% others. The composition of the triglycerides and their properties (melting temperature, heats of fusion, and oil solubility of β' form) were reported previously (14).

Intermediate-melting fats. Two intermediate-melting fats were studied—totally hydrogenated palm kernel oil (palm kernel fat) and partially hydrogenated rapeseed oil (Lobra

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34). Both fats were supplied and characterized [differential scanning calorimetry (DSC), X-ray, and HPLC] by Karlshamns AB. The triglyceride composition and their properties (melting temperature, heat of fusion, and oil solubility of β' form) were reported previously (14).

Palm kernel fat is stable in the the β' form, the melting point of which is 36°C (peak value). It crystallizes in α form at 13°C (peak temperature; crystallization starts at 22°C). The α form is unstable and converts, in less than 20 min, into the β' form at 0°C. The conversion is faster at higher temperatures. The β' form is stable for at least days (stability experiments have not been performed for longer periods). Palm kernel has a mole mass of roughly 680 g/mol. Lobra 34 is stable in β -form. It crystallizes in α form and converts to β form *via* β' form. This transformation can take hours or days depending on temperature. The mole mass of Lobra 34 is ~880 g/mol. Solubilities of palm kernel and Lobra 34 have been determined both experimentally and theoretically (14). The results indicate that at 10°C no precipitation occurs for fat concentrations less than 1% (w/w), where a slight opaqueness is observed. Concentrations of 2% or more gave clear precipitation.

Oils. Refined soybean oil from Karlshamns AB was used as the primary liquid oil phase. Interfacial tension between this oil and distilled water was slightly above 30 mN/m, indicating high purity with respect to surface-active components. The oil was not purified further prior to use. Density of the oil was determined as 0.92 g/mL at room temperature and 0.91 g/mL at 35°C. Further analytical data are available in a previous work (14).

Some experiments were performed, by means of HPLC, in a specially purified CPL soybean oil from Karlshamns Lipid Teknik (Stockholm, Sweden). This oil contained only triglycerides, while the level of other components (mono- and diglycerides, free fatty acids, lecithins, sterols, etc.) was below the detection limit of HPLC. Further characteristics of this oil are similar to that for refined soybean oil.

Refined rapeseed oil (Lobra oil) was supplied by Karlshamns AB. The iodine value of this oil is 117, and the cloud point -16°C. Its density is 0.912 g/mL, and the content of erucic acid is low. The composition of fatty acids is: 4.6% C₁₆, 1.5% C₁₈, 59.1% C_{18:1}, 21.1% C_{18:2}, 10.5% C_{18:3}, 0.5% C₂₀, 1.3% C_{20:1}, 0.3% C₂₂, 0.2% C_{22:1}, and 0.7% others. The composition of triglycerides is: 0.7% POP, 0.3% PLeP, 0.6% POSt, 7.5% POO, 6.2% POLe, 3.7% PLeLe, 0.4% StOSt, 1.8% StOO, 32.1% OOO, 24.5% OOLe, 15.2% OLeLe, 4.4% LeLeLe, 0.9% OOA, 1.0% OLeA, and 0.9% LeLeA (where P stands for C₁₆, St for C₁₈, A for C₂₀, O for C_{18:1} and Le for C_{18:2}).

Some experiments were performed in medium-chain triglyceride (MCT) oil, Captex 355 from Karlshamns AB. This oil contained mainly caprylic/capric triglycerides. Its density is 0.94 g/mL, the iodine value is less than 0.5, and the melting point is below 0°C. Its refractive index is 1.4486, the viscosity at 25°C and 28 mPas, and the surface tension 30 mN/m. Composition of the fatty acids is: 0.5% C₆, 60.7% C₈,

38.2% C₁₀, 0.4% C₁₂, and 0.2% others. The composition of triglycerides is: 0.6% CoCyCy, 23.8% CyCyCy, 42.9% CyCyCi, 26.3% CyCiCi, 5.6% CiCiCi, and 0.2% CiCiCa (where Co stands for C₆, Cy for C₈, Ci for C₁₀, and Ca for C₁₂). Some triglycerides had melting points close to room temperature (for example CiCiCi ~ 18°C, and CiCiCa ~ 26°C). Small amounts of these triglycerides may crystallize/melt when the experimental temperature is changed between 10, 22, and 35°C.

Lastly, nontriglyceride oil (dodecane) was used as an oil phase in some experiments. Dodecane was of analytical grade and supplied by Merck (Darmstadt, Germany).

Emulsifiers. The influence of the following nonionic emulsifiers on the temperature-induced processes was studied: pure monoolein, sorbitan tristearate (Famodan TS), and sorbitan monostearate (Famodan MS) from Grindsted A/S (Brabrand, Denmark); ethoxylated emulsifiers: polyoxyethylene (12) castor oil [Bredol 691; ethoxylated (12) castor oil] and polyoxyethylene (20) castor oil [Bredol 697; ethoxylated (20) castor oil] from Akzo Nobel (Stenungsund, Sweden). We also have examined a technical lecithin (zwitterionic emulsifier)—Metarin P from Lucas Meyer (Hamburg, Germany). The first three nonionic emulsifiers and the lecithin were of food quality, while ethoxylated castor oils are for feed products. All emulsifiers were dissolved in the oil phase prior to use. The emulsifiers have been further described in our previous work (11,13,14,16,17).

Other chemicals. Acetone for recrystallization of solid-fat crystals (palm stearin and tristearin) was of analytical grade and was supplied by Merck.

Sedimentation experiments. Simple sedimentation experiments provide a powerful qualitative method for comparison of particle interactions in dispersions. As the adhesion between particles increases, they can stick to each other and form large flocks and bulky sediments. Increased repulsion has the opposite effect—particles do not stick to each other, pass each other more easily when settling, and form denser, more compact sediments. This relation is often cited in the literature (8,19). Sedimentation experiments, where the force involved (gravity) is weak, are suitable to study weak interactions, whereas methods such as rheology fail due to the strong shear forces in conventional rheometers.

Rheology. A Bohlin CS (controlled stress) rheometer from Bohlin Rheology (Lund, Sweden) was used in the rheological studies. The samples were located in a gap between lower plate and upper plate with cone. The upper plate exerts a specified stress (torque) on a sample, and the bottom plate is stationary. The angular deflection rate of the upper plate is read optically and calculated to shear rates. In our studies, the Bingham yield stress of samples was determined. Bingham yield stress is the stress necessary to achieve uniform flow throughout the entire sample and corresponds to breaking of both weak and strong bonds. For some samples, the storage (elastic) modulus in the linear region was also determined in the oscillation mode. Because our samples were dispersions of particles in an oil phase, wall-slip may occur. At wall-slip

conditions, the particles in a dispersion lose contact with the wall of the measuring system, and measurements are carried out on an oil film (of an order of magnitude of particle diameter) close to the wall (20,21). Wall-slip occurs differently when the geometry is changed. Therefore, measurements with a cone/plate and a plate/plate geometry give indication of wall-slip, if results differ. In these experiments, no such difference was found, indicating that there were no wall-slip conditions.

The cone/plate geometry normally requires particles that are not larger than 1/10 of the gap (15 μm in this case). The largest particles in these samples did exceed this limit. However, the lack of difference between the results from the cone/plate and the plate/plate experiments shows that these large particles did not influence the results because of their relatively low concentration in the samples.

Microscopy. Light microscopy was applied to detect any extensive differences in the crystal network image due to addition of intermediate fats and/or emulsifiers, or due to storage at different temperatures. The microscope used was a Zeiss Axioplan (Zeiss, Germany); the objective was Plan Neofluar with a differential interference contrast prism. Magnification degrees on photographs were 240 \times and 1200 \times . Samples were observed at room temperature.

Other techniques. HPLC, DSC, and X-ray diffraction at Karlshamns AB were used to determine the composition of fatty acids and triglycerides of fats and oils (HPLC), the melting range of palm stearin and palm kernel fat (DSC), and the stability of their different polymorphic forms (X-ray diffraction). BET adsorption analyses with nitrogen gas were performed at Chalmers University (Gothenburg, Sweden) to determine the specific surface area of palm stearin and tristearin recrystallized in acetone.

Sample preparation. Palm stearin and tristearin were recrystallized in acetone to obtain well-defined fat crystals. For that purpose, each fat was dissolved in acetone and rapidly cooled in a freezer (-18°C) to produce small crystals. The samples were shaken by hand during the crystallization process. After filtration, the samples were placed in a fume hood for one day to evaporate the acetone. The remaining acetone was then evaporated in a vacuum dryer. The crystals were examined with respect to melting point, polymorphic form, morphology, and specific area by the methods mentioned in the last paragraph. Four different batches of palm stearin were crystallized, and their specific surfaces were 7.44, 9.7, 10.5, and 9.6 m^2/g . The specific surface of tristearin was 3.6 m^2/g .

To prepare dispersions, the oil was first warmed to 40°C together with additives (intermediate fats and emulsifiers) to obtain a uniform solution. The solutions were then cooled to room temperature (no precipitation of additives was observed), and a desired amount of crystals was mixed into the oil. After dispersing in a vibro-mixer, the samples were placed in a vacuum dryer to evaporate traces of water and to evacuate air. The samples were then placed in a water bath at a specified temperature. The temperature and cooling in the

water bath were controlled by a computer. The samples were allowed to sediment in the water bath, and sediment volumes were monitored during a period of weeks. Identical samples were sedimented at different temperatures, starting at low temperatures and ending at high ones. Calibrated test tubes (with steps of 0.1 mL) with tight locks were used. The accuracy of sediment volume determinations was ± 0.05 mL, less than 1% of the total sample volume (~ 6 mL). Rheological samples were tempered for 24 h at each temperature, starting at low temperatures and ending at high ones. A rheological test was performed after each tempering step.

RESULTS AND DISCUSSION

The influence of temperature on network strength of palm stearin β' . Palm stearin β' crystals (specific surface ~ 7.44 m^2/g) were mixed at 25% level into refined soybean oil. The dispersion was tempered first at 10°C for 24 h. The dispersion was then tempered at 20 and 35°C for 24 h with subsequent rheological measurements at each temperature. The results (Bingham yield stress and storage modulus) are presented as a function of temperature in Figure 1. Because the viscosity of oil diminishes, and the amount of solid-fat crystals decreases due to their partial melting, one would expect a continuous decrease in the dispersion firmness with increasing temperature. This decrease was observed only at low temperatures ($\leq 20^\circ\text{C}$), and a strong increase was observed at elevated temperatures ($>20^\circ$) for both storage modulus and Bingham yield value. Both parameters were higher at 35 than at 10°C .

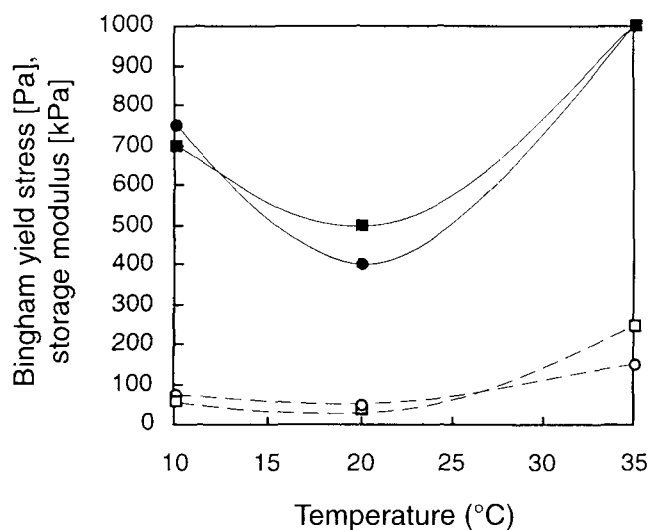


FIG. 1. Bingham yield stress (closed symbols) in [Pa] and storage modulus (open symbols) in kPa for a 25% palm stearin β' dispersion (specific surface ≈ 7.44 m^2/g) in soybean oil (■, □) and in chromatographically purified soybean oil, CPL soybean oil (●, ○). The dispersion was tempered 24 h prior to measurements, starting at low temperatures and ending at high.

In the next experiment, a dispersion containing 3% palm stearin β' crystals in soybean oil was prepared, and the experimental technique was altered from rheology to sedimentation. Both methods mirror the same parameters of dispersions—viscosity of oil, amount of solid particles, and interaction strength. The dispersion was allowed to settle in a water bath for three weeks at each temperature, starting at a low temperature and ending at a high one. The sediment volume for three identical samples is presented in Figure 2 as a function of storage temperature. Again, a decrease in sediment volume was observed at low temperatures ($\leq 20^\circ\text{C}$) and an increase occurred at elevated temperatures ($20\text{--}40^\circ\text{C}$). The crystals melted at 45°C . A maximum in sediment volume appeared at 35°C . Good reproducibility between three identical samples was observed. There was good agreement between trends induced by temperature as observed in rheology for highly concentrated β' crystal dispersions (25%) and the trends observed in sedimentation for less concentrated β' dispersions (3%).

Tristearin β . Tristearin β crystals were investigated in subsequent experiments. Sedimentation results for 3% tristearin in refined soybean oil are presented in Figure 2. The results show that, despite the sediment volume of tristearin being lower than for palm stearin, the observed trend is the same: the sediment volume has a minimum close to room temperature and a maximum at elevated temperature. The maximum is observed at a temperature higher than for palm stearin (40°C compared to 35°C), and the crystals dissolve at 55°C (45°C for palm stearin). These differences can be directly related to melting point of both crystals ($57\text{--}59^\circ\text{C}$ for palm stearin β' and 72°C for tristearin β). Consequently, the polymorphic forms of fat crystals, their morphology and melting

points, do not influence the temperature-induced changes in fat crystal networks.

Purified soybean oil and hydrocarbon oil. In the next experiment, chromatographically purified soybean oil (CPL soybean oil, contains only triglycerides) was used as a dispersion medium for palm stearin β' crystals, and a rheological experiment was performed. The results are presented in Figure 1, where the same trend as previously was observed: a rheological minimum at room temperature and a maximum at elevated temperature (35°C). Thus, nontriglyceride components of vegetable oil, such as mono- and diglycerides, free fatty acids, or tocopherols, do not play a major role in network changes induced by elevated temperature.

An experiment in the hydrocarbon oil dodecane was performed to determine whether changes induced by elevated temperature depend on interaction between triglyceride oil and fat crystals. In this experiment, 3% tristearin β crystals sedimented in dodecane (palm stearin β' crystals were not suitable for that experiment due to high solubility in hydrocarbon oil) (Fig. 2). The sediment volume of tristearin is twice as high in dodecane as in soybean oil due to a stronger adhesion between tristearin crystals. Furthermore, the solubility of tristearin is higher in dodecane than in soybean oil, and melting occurs at a lower temperature (40°C as compared to 55°C). The trend induced by storage at elevated temperature is the same as in all other mixtures examined, with a sediment volume minimum and maximum. Thus, this trend must be related to strong adhesion between fat crystals at elevated temperature, and not to interactions between oil and crystals.

Bulk crystallization and storage time of model dispersion. Rheological measurements (Bingham yield values) were performed on dispersions of 10% palm stearin β' in soybean and rapeseed oil. Three dispersions were prepared by different techniques: (i) mixing dry crystals into oil with no further treatment; (ii) mixing, melting at 60°C , and subsequent crystallization at 10°C ; and (iii) mixing, melting, and crystallization, as in (ii), with subsequent homogenization to break up a part of the network. The results for soybean and rapeseed oil are presented in Figure 3. The structure formed by particles crystallized directly in oil is stronger than the structures formed by crystals mixed into oil. Homogenization breaks some strong bonds (solid bridges) in soybean oil, but these bonds reform during storage at elevated temperatures. The trend of a maximum in rheological parameters for samples stored at elevated temperatures existed for all fat crystal dispersions, independent of sample mixing, crystallization, and homogenization.

All dispersions studied were stored for a long period (24 h) at each temperature prior to measurement. To investigate the influence of storing time on the trends induced by elevated temperature, Bingham yield stress was determined for 10% palm stearin β' dispersion stored for a short period (10 min) in soybean oil. The results are presented in Figure 3 and are compared with the results for an identical sample with long storage time in oil. Long storage times produce a Bingham yield value one order of magnitude higher at low tempera-

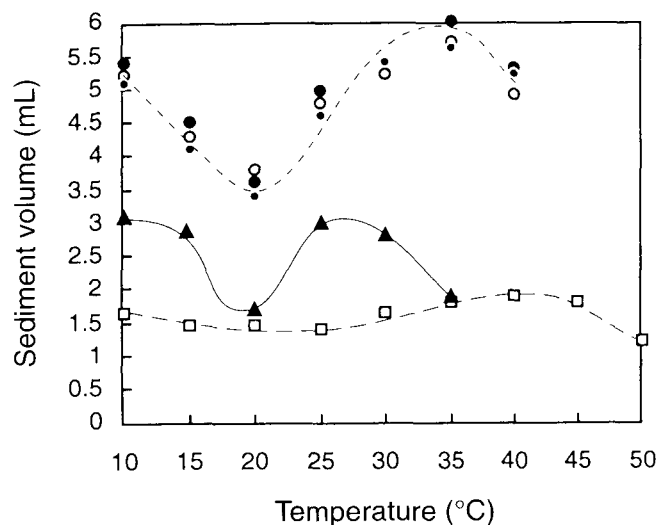


FIG. 2. Sediment volumes for three identical samples of 3% palm stearin β' dispersion (specific surface $\approx 9.7 \text{ m}^2/\text{g}$) in soybean oil (●, ○), and of 3% tristearin β (specific surface $\approx 3.6 \text{ m}^2/\text{g}$) in soybean oil (■, □) and dodecane (▲). The dispersions were allowed to settle at each temperature for a week, starting at low temperatures and ending at high ones.

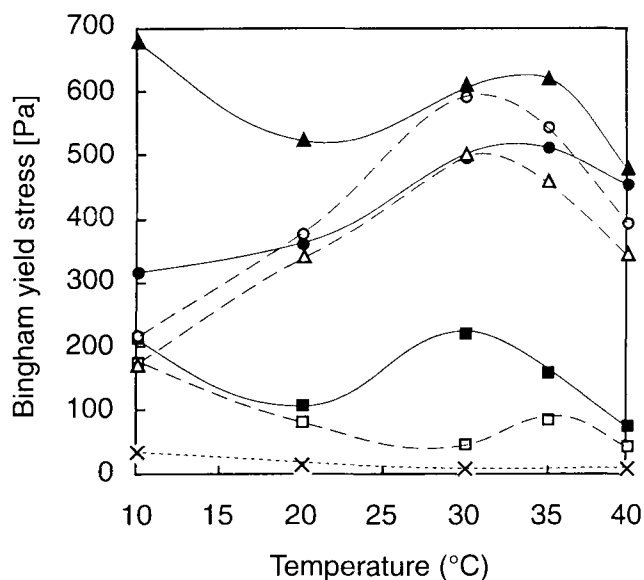


FIG. 3. Bingham yield stress for 10% palm stearin β' dispersion in soybean oil (closed symbols) and rapeseed oil (open symbols). Three dispersions were prepared by mixing dry crystals (specific surface $9.6 \text{ m}^2/\text{g}$) into the oil ($\blacksquare, \blacksquare$); by melting palm stearin at 60°C and crystallizing at 10°C ($\blacktriangle, \blacktriangle$); and by crystallizing with a subsequent homogenization in a mixer (\bullet, \bullet). The dispersions were tempered at each temperature for 24 h prior to measurement, starting at low temperatures and ending at high. X denotes the results for a mixed dispersion tempered for 10 min at each temperature prior to measurement.

tures, and two orders of magnitude higher at elevated temperature, than those of short storage time. Furthermore, no rheological maximum appears at elevated temperature for short storage time. Thus, high network strength of semisolid fat at elevated temperature is not only due to a strong adhesion between fat crystals but also to slow structural changes accompanying this strong adhesion.

Sintering in MCT Oil. Sedimentation of a dispersion of 5% palm stearin β' in MCT oil was investigated. The dispersion had a final sediment volume of 4 mL (total sample volume was 6 mL) at 10°C . The sample volume increased to 5.2 mL in the presence of 0.5% β' stable intermediate fat (palm kernel fat), and to 4.5 mL in the presence of β stable intermediate fat (Lobra 34). This increase in sediment volume is likely due to sintering processes, achieved through a controlled post-crystallization of the intermediate fats. At 22°C (room temperature), the sediment volume of 5% palm stearin lowers from 4 to 2.9 mL, and the sediment volumes of the sample with 0.5% palm kernel fat was only slightly lower (5.5 to 5.1 mL). Thus, sintering by palm kernel fat seems to be irreversible with a moderate increase in temperature.

The origin of temperature-induced changes in fat structure. Fat crystal solubility in oil increases with temperature and is the origin of an increase in adhesion between fat crystals, increased network strength, flocculation, sintering, and crystal growth. Thus, the higher oil solubility of palm stearin compared to tristearin is one reason for the more extensive changes observed in the former case. Increased solubility

likely leads to formation of a diffuse low-density layer of triglyceride molecules on the fat crystal surface, due to higher mobility of chains and more rapid exchange of molecules between the oil and the surface (3). The nature of adhesion in the low-density triglyceride layer may be similar to adhesion observed in polymer-covered surfaces where the solubility of polymer chains in the polymer is higher than in solvent.

The fat crystal (palm stearin β') flocculation due to warm storage in soybean oil is clearly observed in Figure 4. Floccs have a star-like character. Similar changes occur for palm stearin stored in MCT oil at room temperature, where the crystals have higher solubility than in soybean oil. The floccs in MCT oil have a brush-like character. This anisotropic brush-like character indicates a relatively large contact area between crystals in floccs, and the isotropic, star-like floccs in soybean oil indicate a smaller contact area between crystals

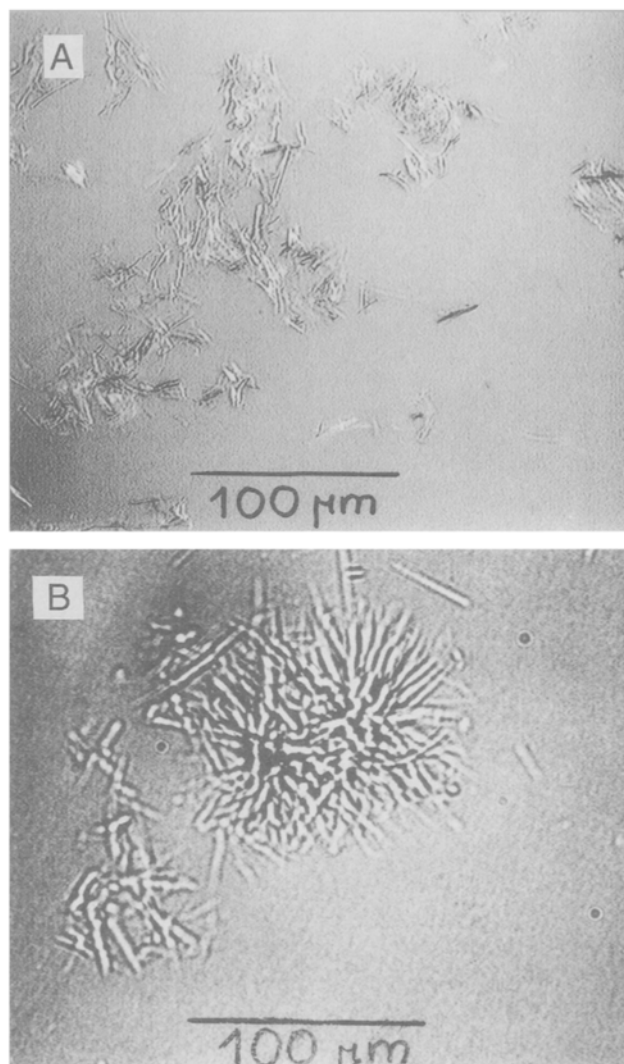


FIG. 4. Light micrographs of 5% palm stearin β' dispersion in soybean oil at room temperature. A) Sample stored only at low temperatures (room temperature or lower); B) sample stored at 35°C for 24 h, with subsequent storage at low temperatures (room temperature or lower).

in flocs. The flocculation process, leading to an increase in sample firmness, is slow. This is indicated in Figure 3, where the Bingham yield stress maximum at elevated temperature does not occur for short tempering times prior to measurement. Furthermore, slow flocculation also seems to occur at low temperature (storage of sample of 10% palm stearin in soybean oil at 10°C for about 24 h increases the yield stress from 35 to 200 Pa). In flocculated systems (Figs. 4B and 5A), crystal surfaces may come close together, and molecular contact occurs. Bridges of liquid, semi-solid, or solid triglycerides most likely exist in the vicinity between crystals at elevated temperature and contribute to the sample firmness.

Crystal growth occurred during the storage of samples at elevated temperature (Figs. 4 and 5). Because small crystals have higher solubility than larger crystals, they will dissolve preferentially and the dissolved material is transported to the larger crystals (Ostwald ripening) (8,20,22). However, crystal growth alone should lead to an increase in network strength

because networks formed by large crystals are looser than networks formed by small crystals (9). Thus, crystal growth may not lead to increased sample firmness at elevated temperatures. Further, warm storage of β' fat may lead to polymorphic transition to β form. Again, this transition alone cannot be the reason for increased sample firmness. The magnitude of polymorphic transition has not been determined in our studies, but is assumed to have no significant influence on the observed effects.

Addition of intermediate-melting fats. In further experiments, the melting behavior of the fat by addition of an intermediate-melting fat was changed to imitate natural fat blends that contain triglycerides with a broad melting range. We added 4% β' stable palm kernel fat or 5% β stable Lobra 34 to samples that contained 3% palm stearin β' in soybean oil or 3% tristearin β . The dispersion medium was soybean oil and dodecane, respectively. The sediment volumes of these samples are presented in Figures 6 and 7, together with the sediment volumes for corresponding reference samples (without intermediate fat). Results for palm stearin β' in soybean oil (Fig. 6) indicate that the temperature-induced trend is not changed by the presence of intermediate fats in oil—the maximum in sediment volume at elevated temperature is slightly less pronounced, but appears at the same temperature as in pure oil. The trend also remains the same for tristearin β in soybean oil (Fig. 6), and the maximum is more pronounced after addition of intermediate fats. The behavior is opposite for tristearin β in dodecane (Fig. 7)—intermediate fats lower the network strength at all temperatures, and the maximum is

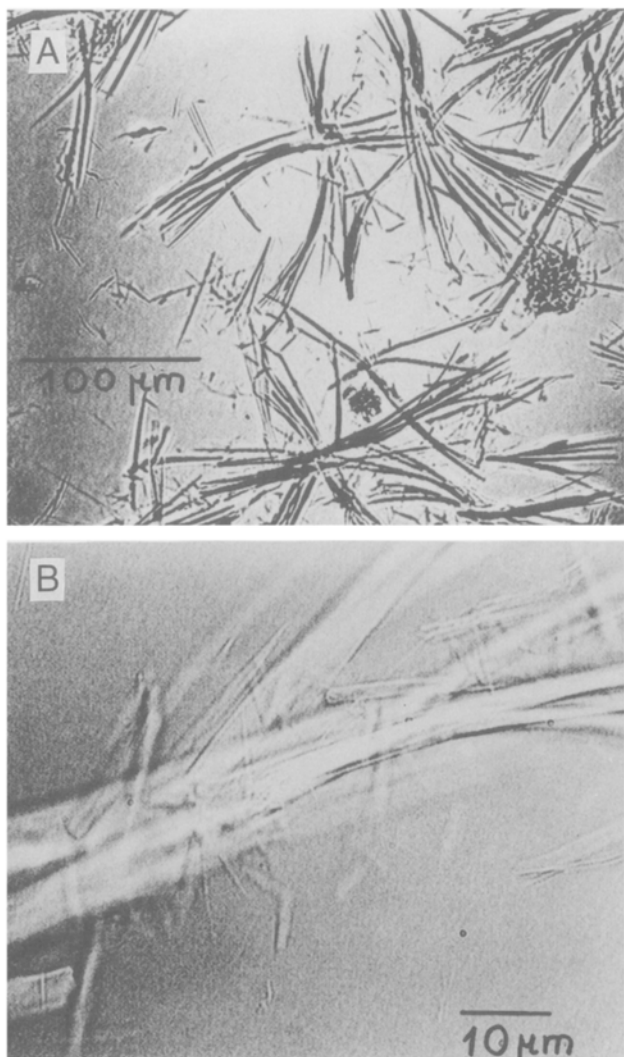


FIG. 5. Light micrographs of 5% palm stearin β' dispersion in medium-chainlength triglycerides oil at room temperature. A) No additive to oil; B) 0.5% palm kernel fat in oil.

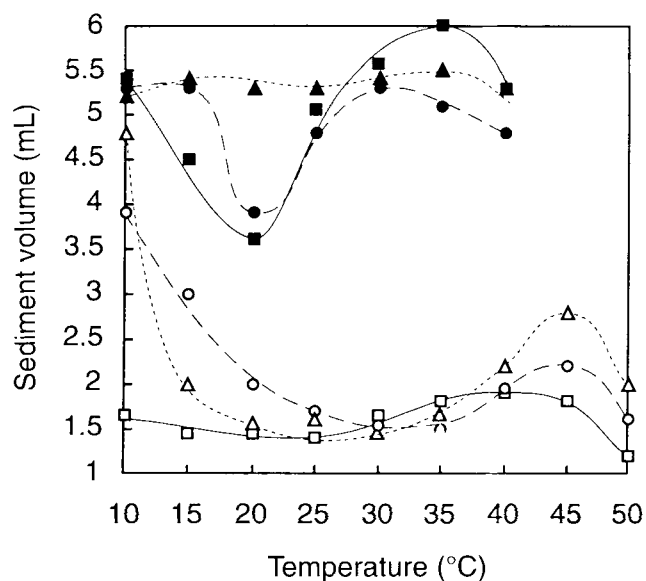


FIG. 6. Sediment volumes of 3% fat crystals in soybean oil (■, □); in soybean oil containing 5% Lobra 34 (Karlshkamns AB, Karlshamn, Sweden) (●, ○); and in soybean oil containing 4% palm kernel fat (▲, △). The dispersions were allowed to settle at each temperature for a week, starting at low temperatures and ending at high ones. Closed circles, palm stearin β' crystals (specific surface 9.7 m²/g); open circles, tristearin β (specific surface 3.6 m²/g).

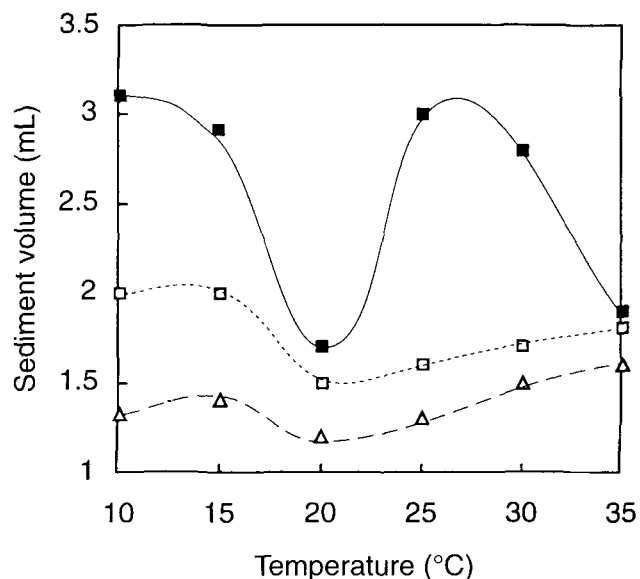


FIG. 7. Sediment volumes of 3% tristearin β dispersion (specific surface $3.6 \text{ m}^2/\text{g}$) in dodecane (■), in dodecane containing 5% Lobra 34 (□), and in dodecane containing 4% palm kernel fat (△). The dispersions were allowed to settle at each temperature for a week, starting at low temperatures and ending at high. Company location as in Figure 6.

much less pronounced. Thus, the results indicate that the intermediate fats adsorb to fat crystals and participate in interactions, which affects flocculation at elevated temperatures. For palm stearin β' in soybean oil (Fig. 8), small amounts of intermediate fats seem to suppress the flocculation, but this effect is rather weak. The same effect, although stronger, also

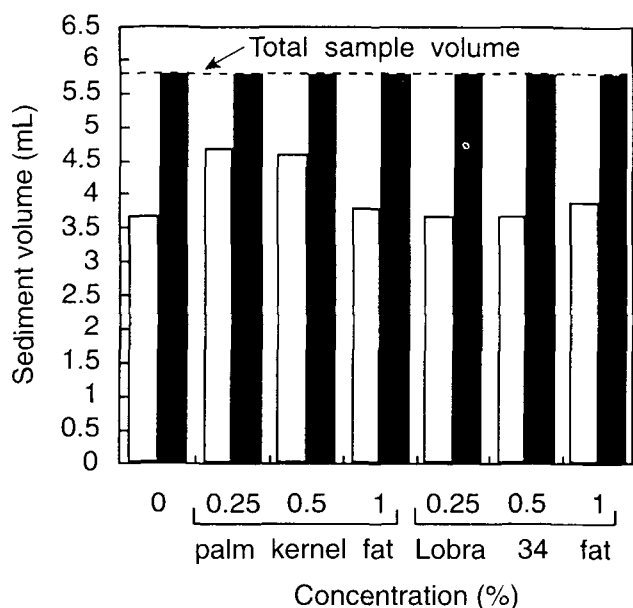


FIG. 8. Sediment volumes of 5% palm stearin β' dispersions (specific surface $\approx 11.5 \text{ m}^2/\text{g}$) in soybean oil, as a function of intermediate fats (Lobra 34 and palm kernel fat) concentration in the sample. The dispersion was allowed to settle at 10°C for weeks. The temperature was lowered from 20 to 10°C during 24 h (□). Samples were then stored at 35°C for 24 h, and the temperature was lowered again to 10°C (gradient time 24 h) where sedimentation during a period of weeks was performed (■).

appears for tristearin in dodecane (Fig. 9), and the opposite effect occurs for tristearin in soybean oil (Fig. 10), where a small amount of intermediate fats increases the flocculation and firmness during storage at elevated temperature.

From a technical point of view, it is interesting to know what happens with the high firmness of fat produced at elevated temperature, after subsequent cooling. Some experiments and their results are presented below. Thus, sediment volume of 5% palm stearin β' in soybean oil at 10°C is presented in Figure 8, where a comparison is made between dispersions stored and settled at only 10°C (white bars) and dispersions stored at 35°C for 24 h prior to settling at 10°C (grey bars). A comparison is also made between dispersions without any additives to oil and dispersions containing small amounts (up to 1%) of intermediate fats in oil. The results show that the volumes of all dispersions rose to a maximum volume of 5.8 mL after storage at 35°C . This result means a dramatic increase in the network strength during warm storage, due to processes as flocculation and sintering. No differences due to the presence of intermediate fats were detected.

Emulsifiers. Some emulsifiers were able to suppress the processes leading to increased firmness of fat stored at elevated temperatures (flocculation and sintering). One such emulsifier was sorbitan tristearate, which was able to suppress

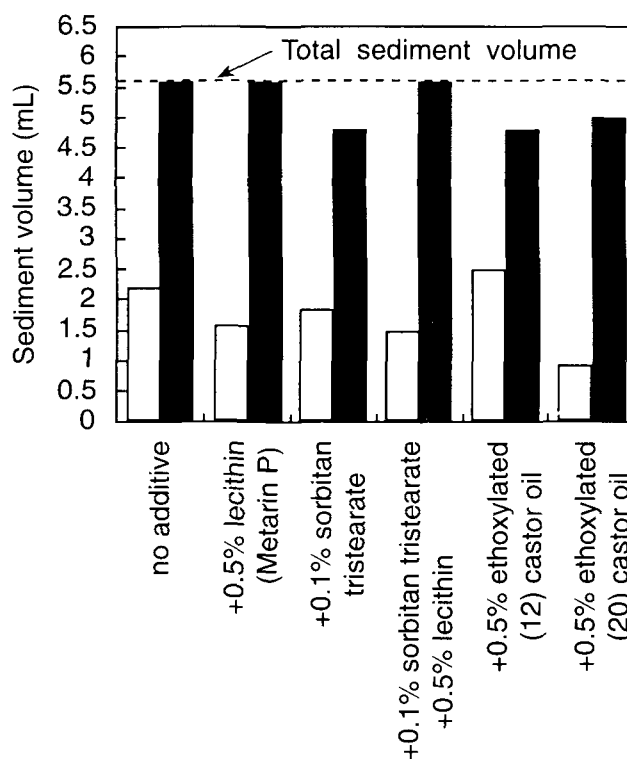


FIG. 9. Sediment volume of 5% palm stearin β' dispersion (specific surface $\approx 11.5 \text{ m}^2/\text{g}$) in soybean oil without any additives, and with 0.5% of various emulsifiers. The dispersions were allowed to settle at 10°C for some weeks. The temperature was lowered from 20 to 10°C during gradient time 24 h (□). Samples were then stored at 35°C for 24 h; the temperature was lowered again to 10°C (gradient time 8 min) for sedimentation during a period of weeks (■). Metarin P, Lucas Meyer (Hamburg, Germany); ethoxylated (12) castor oil and ethoxylated (20) castor oil, Grindstedt A/S (Brabrand, Denmark).

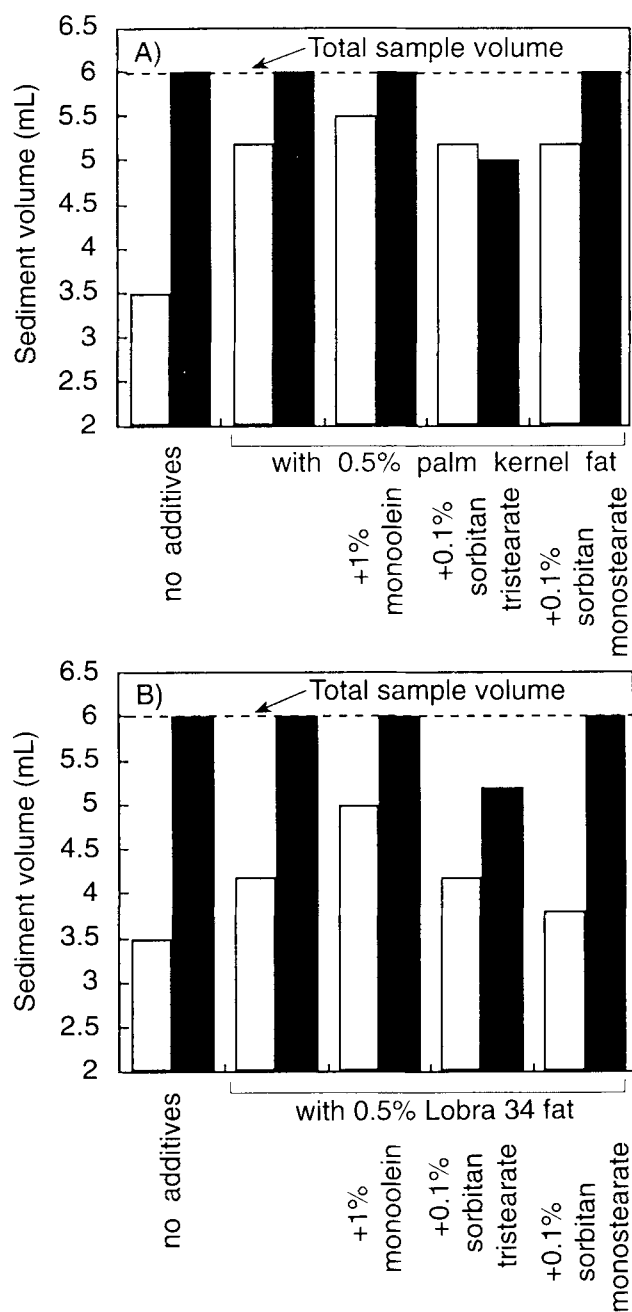


FIG. 10. Sediment volumes of 5% palm stearin β' dispersion (specific surface $\approx 11.5 \text{ m}^2/\text{g}$) in soybean oil without any additives, with 0.5% intermediate fat, and with a combination of 0.5% low-melting fat and various emulsifiers. The dispersions were allowed to settle at 10°C for weeks. The temperature was lowered from 20 to 10°C during 24 h (\square). Samples were then stored at 35°C for 24 h, and the temperature was lowered to 10°C (gradient time 24 h) for sedimentation during a period of weeks (\blacksquare). A) The intermediate fat additive is palm kernel fat; B) The intermediate fat additive is Lobra 34. Company location as in Figure 6.

the increase in firmness of 5% palm stearin β' dispersion in soybean oil that contained 0.5% palm kernel fat (Fig. 10A), 5% palm stearin β' crystal dispersion in soybean oil that contained 0.5% Lobra 34 (Fig. 10B), and 5% palm stearin β' crystals in soybean oil in the absence of any intermediate fats (Fig. 9). Ethoxylated castor oil had a similar effect on 5%

palm stearin β' in soybean oil in the absence of intermediate fats (Fig. 9). No effects were found with emulsifiers such as monoglyceride, lecithin, sorbitan monostearate, and a mixture of sorbitan tristearate and lecithin. The emulsifiers' effect must be due to adsorption onto fat crystals, which has been studied previously. A lack of this effect with lecithin was surprising, as lecithin is known to adsorb strongly to fat crystals in oils (16) and to weaken adhesion. The reason may be a desorption of lecithin at elevated temperatures, or distortions due to aggregation of lecithins on the surface and/or in their vicinity.

Technical applications. Triglyceride oils are widely used in foods, feeds, pharmaceuticals, and technical applications. Their applicability is sometimes limited due to lack of control of rheological properties, such as viscosity, gelling, or yielding. In water-continuous systems, this control is secured by a large number of well-studied gelling polysaccharides and proteins. However, no food-approved gelling polymers are soluble in triglyceride oils. Thickening of triglyceride oils by fat crystals is known within traditional semisolid fat products. This study has shown that different fat fractions can be used as thickening additives to oils. One can direct the thickening action to high temperatures, or to low temperatures depending on the fat type, amount, concentration, and preparation technique.

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