Effect of Sucrose Esters on the Crystallization Behavior of Bulk Oil Systems

Sir:

Sucrose esters (SE) of FA can be used in foods as emulsifiers because they are nontoxic, tasteless, odorless, and are digested to sucrose and FA in the stomach. They can also be used in pharmaceuticals and cosmetics and in other products where a nonionic, nontoxic, biodegradable emulsifier is required. In addition to their major function of producing and stabilizing emulsions, SE have numerous other functional roles as texturizers, film formers, and modifiers of bulk-phase crystallization behavior (with bulk phase meaning a homogeneous oil phase). A few reports have dealt with the effect of SE on the crystallization behavior of fats and oils in bulk systems; however, some of these results vary and may be contradictory. It is of great interest to study the effects of SE on bulk fat systems, particularly with regard to their use in products such as chocolate and confections.

Yuki *et al.* (1) studied the crystallization behavior of a fat mixture formulated with 60 wt% hydrogenated soybean oil, 30 wt% palm oil, and 10 wt% rapeseed oil by recording the cooling curve and measuring the latent heat released when crystallization occurred. The process was also followed by DSC. They reported that the addition of 0.5 wt% of palmitic SE, waxy form (P-195), and stearic SE, waxy form (S-195), accelerated the crystallization process, whereas lauric SE, waxy form (L-195), retarded nucleation. Oleic SE, liquid form (O-190), however, had no effect on crystallization behavior. Nasir (2) described the isothermal crystallization behavior of a hydrogenated blend of 90% soybean and 10% cottonseed oils crystallized at 17°C by reporting the DSC melting curves. They showed that the addition of 0.5 wt% of palmitic SE, powder form (P-170), reduced the crystallization rate, whereas the addition of stearic SE, powder form (S-170), at the same concentration yielded a higher amount of solid crystals. Herrera and Marquez Rocha (3) studied the nucleation process of hydrogenated sunflower oil (SFO) with laser-polarized turbidimetry (LPT). When P-170 was added to the hydrogenated oil at different concentrations, an elongation of the induction times of nucleation and a hindering of $\beta' \rightarrow \beta$ polymorphic transformation were observed. The effect was explained as a co-crystallization mechanism between the fat and P-170. Hodate *et al.* (4) studied the crystallization behavior of palm oil with and without the addition of P-170 and S-170 by ultrasonic velocity measurements. These authors reported that the addition of S-170 and P-170 at 0.5 wt% retarded the crystallization of palm oil compared with pure palm oil in the bulk system. Martini and Herrera (5) studied the effect of SE with different HLB values on the nucleation behavior of high-melting milk fat fractions (HMF)–SFO blends. By measuring the induction times by LPT, they found a slight elongation of the induction times of crystallization for SE with high affinity for the hydrophilic phase (high HLB). P-170 and S-170 (HLB = 1), however, significantly delayed the crystallization process, especially when added at 0.5 wt%.

It is necessary to take a clear look when interpreting the effect of SE on the nucleation rate (J), based on the results obtained from polarized light microscopy (PLM). Variations in the definition of nucleation rate and different applications of concepts such as nuclei and induction time can lead to contradictory interpretations of the phenomenon, i.e., acceleration instead of inhibition (6). Such occurrences may be contributing to the variations in findings about the effect of SE in bulk oil systems.

The reciprocal of J, the induction time for nucleation, is the time statistically required to obtain one nucleus per unit volume (6,7). Any treatment that elongates this time inhibits nucleation. Once nuclei have been formed, they grow and develop into crystals. The nucleation process is strongly dependent on supercooling. Growth rate, however, depends on thermodynamic (supersaturation) and kinetic factors (solvent, impurities, agitation rate, viscosity). Avrami (8) stated that an overwhelming amount of evidence points to the conclusion that a phase is nucleated by tiny germ nuclei. The number of germ nuclei per unit region at time t decreases from the initial number because some of them are swallowed by the growing grains of the new phase. In fat systems, the crystal size distribution is related to processing conditions (9). When a fat system is crystallized at two different agitation rates, the induction time of nucleation and the size and number of nuclei are the same for the same supercooling. However, the number of crystals and the crystal size distribution with time are different for both agitation rates. Clearly, the number of crystals that form with time does not necessarily correlate with the number of nuclei. Thus, it is of great importance to discuss the information obtained from the different techniques that are usually used to study nucleation behavior. When we say "nuclei," we are referring to molecular aggregates of nano sizes. For the example shown in Figure 1, the average critical nucleus size determined by the combination of small-angle X-ray scattering and dynamic light-scattering techniques was 500 Å (see Ref. 10 for a discussion of the methods used). Therefore, very accurate techniques must be used to describe the nucleation process in order to disregard growth. Techniques of low sensitivity for solid contents lower

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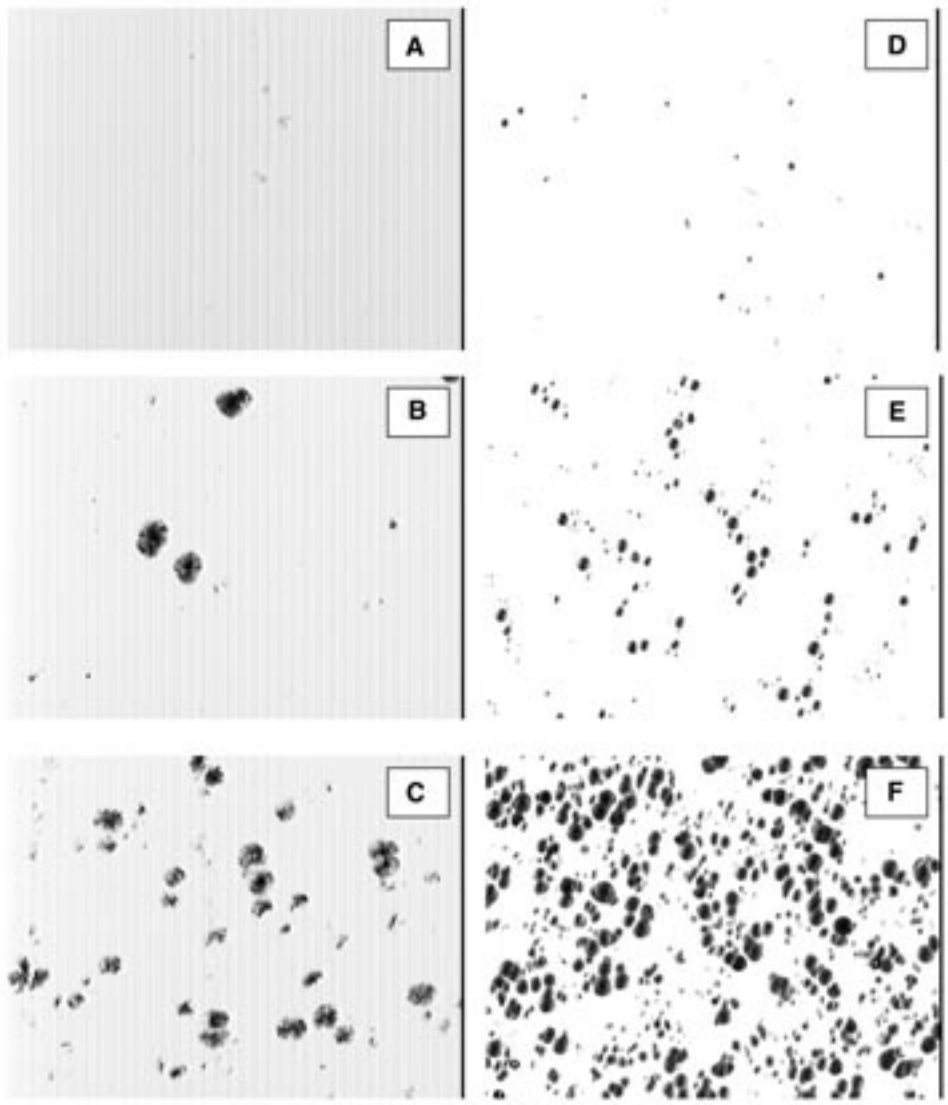

FIG. 1. Images of crystals corresponding to a 60–40% high-melting milk fat fraction–sunflower oil blend crystallized at 38°C with a cooling rate of 0.2°C/min and an agitation rate of 100 rpm. Zero time was the moment when the crystallization temperature was reached. Left column: the blend without emulsifiers at (A) 13, (B) 14, and (C) 28 min; right column: the blend with the addition of stearic sucrose esters in powder form (S-170) at 0.1 wt% at (D) 45, (E) 60, and (F) 90 min.

than 0.5%, such as DSC, NMR, and rheological measurements, must not be used to evaluate nucleation effects. Studies have shown when working with the pulsed NMR (pNMR) method, at times small amounts of crystals are visible in the melt before any solids are detected. Clearly, at this stage, well beyond the induction time for nucleation, the pNMR signal is measuring crystal growth (11). Although the PLM technique is sensitive enough for these kinds of studies, an understanding of important basic concepts is essential. When evaluating the effect of SE on nucleation behavior based on PLM results, growth crystals, that is, crystals larger than the resolution of the method, do not have to be considered nuclei, especially when these crystals are actually clusters and not single crystals. The result of considering the clusters obtained with time as nuclei may lead to conclusions about the effect of SE that could contradict reality. If more time is needed for a process to start and the whole process takes more time, this is obviously a delay. No matter how we define a concept, it cannot contradict facts. Figures 1A–C show representative images with time of a blend of 60% HMF with 40% SFO crystallized at 0.2°C/min to 38°C, and Figures 1D–F show the same fat blend with the addition of S-170 at 0.1 wt% (HLB = 1; Mettler dropping point, 59.5°C; monoester content, 1%; di-, tri-, and polyester content, 99%; Mitsubishi-Kasei Food Corporation, Tokyo, Japan). For the sample without S-170, the induction time for crystallization was 11 ± 1 min, whereas when the SE was added, it was 40 ± 3 min. In comparing Figures 1A and 1D, S-170 obviously delayed nucleation, since more

time was needed to observe the first crystals in the microscope's video images. The images in Figures 1B,C,E, and F show growth crystals. They are not single crystals but clusters that grew by the accumulation of needles. A similar growth behavior was described for other fat systems (12). Therefore, no conclusion about the number of nuclei can be obtained from these images. Solid fat content measurements showed that more time was needed to achieve the equilibrium crystal mass at 38°C when S-170 was added to the blend (data not shown). The overall crystallization process also was slower. Figure 1 shows that, without taking into account that the images were taken at different times, wrong conclusions will be obtained when comparing the number of crystals in Figures 1C and F, simply because the crystallization rates were different. In addition, the accumulation mechanism depends on processing conditions, and the number of growth crystals does not correlate with the number of nuclei formed when crystallization started.

SE can be used for controlling crystallization at a level of addition suitable for practical uses. Thus, understanding the effect of SE on nucleation is of great importance, not only from the academic point of view but also for technological applications.

REFERENCES

1. Yuki, A., K. Matsuda, and A. Nishimura, Effect of Sucrose Polyesters on Crystallization Behavior of Vegetable Shortening and Margarine Fat, *J. Jpn. Oil Chem. Soc. 39*:24–32 (1990).
2. Nasir, M.I., Effect of Sucrose Polyesters and Sucrose Polyester–Lecithins on Crystallization Rate of Vegetable Ghee, in *Crystallization and Solidification Properties*, edited by N. Widlak, R.W. Hartel, and S. Narine, AOCS Press, Champaign, 2001, pp. 87–95.
3. Herrera, M.L., and F.J. Marquez Rocha, Effects of Sucrose Ester on the Kinetics of Polymorphic Transition in Hydrogenated Sunflower Oil, *J. Am. Oil Chem. Soc. 73*:321–326 (1996).
4. Hodate, Y., S. Ueno, J. Yano, T. Katsuragi, Y. Tezuka, T. Tagawa, N. Yoshimoto, and K. Sato, Ultrasonic Velocity Measurements of Crystallization Rates of Palm Oil in Oil–Water Emulsions, *Colloids Surf. A 128*:217–224 (1997).
5. Martini, S., and M.L. Herrera, Effect of Sucrose Esters on Nucleation Behavior of Milk Fat–Sunflower Oil Blends, 94th AOCS Annual Meeting and Expo, Kansas City, MO, May 4–7, 2003.
6. Martini, S., and M.L. Herrera, Practical Considerations in Nucleation Studies: The Light Polarized Microscopy Technique, *J. Am. Oil Chem. Soc. 79*:411–412 (2002).
7. Boistelle, R., Fundamentals of Nucleation and Crystal Growth, in *Crystallization and Polymorphism of Fats and Fatty Acids*, edited by N. Garti and K. Sato, Marcel Dekker, New York, 1988, pp. 189–226.
8. Avrami, M., Kinetics of Phase Change. II. Transformation-Time Relations for Random Distribution of Nuclei, *J. Chem. Phys. 8*:212–224 (1940).
9. Herrera, M.L., and R.W. Hartel, Effect of Processing Conditions on Crystallization Kinetics of a Milk Fat Model System, *J. Am. Oil Chem. Soc. 77*:1177–1187 (2000).
10. Watson, J.N., L.E. Iton, R.I. Keir, J.C. Thomas, T.L. Dowling, and J.W. White, TPA-Silicalite Crystallization from Homogeneous Solution: Kinetics and Mechanism of Nucleation and Growth, *J. Phys. Chem. B 101*:10094–10104 (1997).
11. Wright, A.J., S.S. Narine, and A.G. Marangoni, Comparison of Experimental Techniques Used in Lipid Crystallization Studies, *J. Am. Oil Chem. Soc. 77*:1239–1242 (2000).
12. Martini, S., M.L. Herrera, and R.W. Hartel, Effect of Processing Conditions on Microstructure of Milk Fat Fraction/Sunflower Oil Blends, *Ibid. 79*:1063–1068 (2002).

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