X-Ray Diffraction and Crystal Size

Sir:

X-ray diffraction technique is one of the best methods to study polymorphism of fats systems. The only information authors usually report is the interplanar distances calculated from the angles at which diffraction lines appear; these clearly determine the polymorphic form. However, in many other fields using crystallography, X-ray patterns are also used to determine crystal size from the broadening of the diffraction line at half the line of maximum intensity. To investigate the meaning of the diffraction line width in fat systems and the relationship with other techniques widely used to determine crystal size, we crystallized a blend of 30–70% high-melting in low-melting milk fat fractions at two different cooling rates. The crystallization process was followed by polarized-light microscopy. Crystal size distribution was determined by analyzing 200 crystals.

In 1918, Bragg developed an equation to calculate crystal size from the broadening of a diffraction line at half the line maximum intensity by employing only ordinary principles of optical diffraction and starting from the following equation, usually called Bragg's equation (1,2):

$$n\lambda = 2d \sin \theta \quad [1]$$

The use of the equation developed by Bragg, which is considered a simplified version of Scherrer's equation, is nowadays a well-established method widely employed in inorganic chemistry to calculate particle size from X-ray patterns (3). The equation is as follows:

$$\beta_{hkl} = 0.89\ \lambda/L_{hkl} \cos \theta \quad [2]$$

where β_{hkl} is the broadening of the diffraction line measured at half the line maximum intensity, λ is the X-ray wavelength, L_{hkl} is the crystal size, and θ is the diffraction angle. The broadening of a peak is related to the crystal size and to the wavelength λ provided by the equipment used. Usually, the peak is not a line but an interval. The Bragg β_{hkl} can be written as

$$\beta_{hkl} = (B_{hkl} - b) \quad [3]$$

where B_{hkl} is the broadening measured on the X-ray pattern, and b is the unavoidable broadening error of the equipment, which is typical of each instrument. It is determined with a standard of known particle size, usually LaB_6. Bragg's equation interprets the crystallizing system as one with a uniform particle size.

Figure 1 shows video images of the crystals obtained for a 30:70 blend of high-melting and low-melting milk fat fractions crystallized at 25°C using two different cooling rates (0.2 and 5.5°C min) and an agitation rate of 50 rpm. The Mettler dropping point of the blend was 38.0°C. Both images were taken immediately after the release of latent heat (4). As was previously reported (4), images showed clearly that the system did not form single crystals. Instead, small crystals accumulated. Slow cooling promoted crystallization, and, as a result, crystals were denser. This was evidenced by their darkness (4). Figure 2 shows the crystal size distribution found when the areas of 200 crystals were measured for both samples. The diameters of circles having areas equivalent to the measured areas were reported. Distributions showed that there is not a uniform crystal size. The slowly crystallized sample had a broader distribution of crystal size.

Figure 3 shows the X-ray diffraction patterns obtained for the samples shown in Figure 1 after dry filtering under vacuum. The patterns corresponding to both slow and fast rates showed two strong signals at 3.8 and 4.3 Å, which are characteristic of the β′-form. The diffraction line broadening at half-maximum intensity measured on the X-ray pattern for the strongest line (3.8 Å) had no significant differences between the cooling rates used ($P < 0.01$). In both cases, β was 2.9 ± 0.1 mm, and therefore L_{hkl} was 482.3 Å. Diffraction lines are produced by units smaller than the smallest crystal size that can be observed in a polarized light microscope (2000 Å). That is why diffraction patterns of fat systems seem to have no relation to the actual crystal sizes obtained when they are crystallized at different cooling or agitation rates or to different temperatures. For different crystal size distributions with different means, patterns do not show differences in the diffraction line broadening measured at half-maximum intensity.

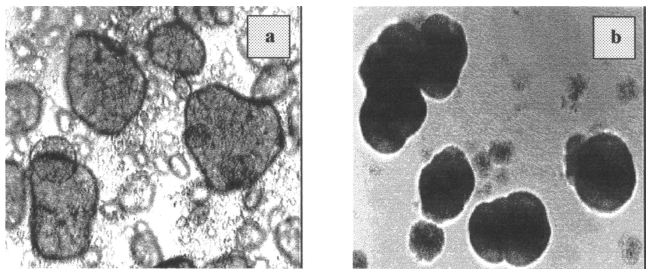

FIG. 1. Video images of a 30:70 blend of high-melting and low-melting milk fat fractions, crystallized to 25°C at 50 rpm: (a) slow cooling rate (0.2°C/min); (b) fast cooling rate (5.5°C/min).

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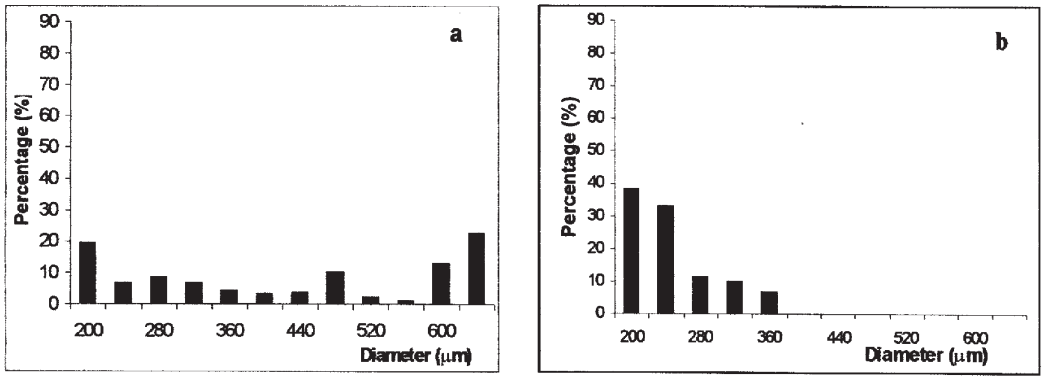

FIG. 2. Matching crystal size distributions of the blend corresponding to the video images shown in Figure 1: (a) slow cooling rate (0.2°C/min); (b) fast cooling rate (5.5°C/min).

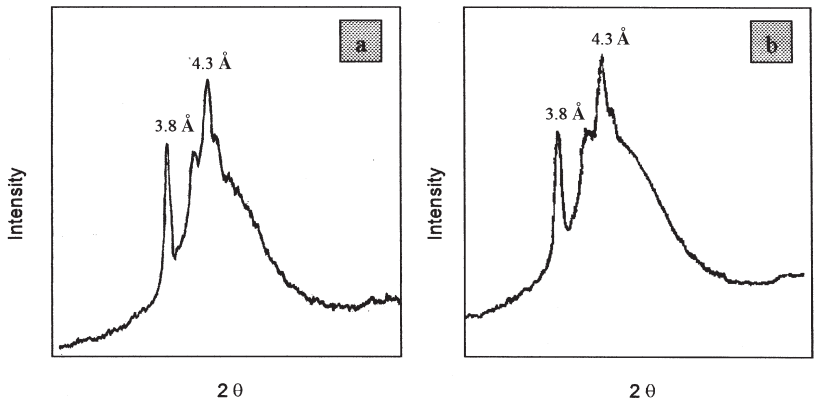

FIG. 3. Matching X-ray diffraction patterns of the samples corresponding to the video images shown in Figure 1: (a) slow cooling rate (0.2°C/min); (b) fast cooling rate (5.5°C/min).

These results are in agreement with previous crystallization studies by polarized-light microscopy. Kellens *et al.* (5) reported different morphologies for the same polymorphic form of pure tripalmitin isothermally crystallized to different temperatures. When hydrogenated sunflower oil was isothermally crystallized at 30°C and then stored for 48 h, the polymorphic transition $\beta' \rightarrow \beta$ occurred but β' and β forms showed very similar morphologies and it was not possible to identify polymorphism on the basis of microscopic appearance (6).

X-ray patterns show that the size of unit that produces the diffraction lines is smaller than crystal sizes observed by polarized-light microscopy. This is a proof that fat crystals are not single crystals but grow by accumulation. Therefore, polymorphism cannot be determined on the basis of microscopic appearance. Processing conditions determine the size of the agglomerates but not primarily crystal size. It is very important to take into account the agglomeration mechanism when designing a process.

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