Melting and recrystallisation of fat crystals in food

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Fats in food products are dynamic ingredients in the sense that they are continually undergoing melting and recrystallisation as the temperature of the product fluctuates. While, in many cases, these temperature fluctuations are small enough not to cause significant changes to occur in the food there are numerous examples of where changes can take place that are noticeable.

Take, for example, a confectionery coating. If this is made from 'real' chocolate, i.e. is based on cocoa butter, this melting-recrystallisation process can have a drastic effect on the product. This is because when the melted cocoa butter recrystallises it often does so in a different crystal form from the original and so manifests itself as a surface layer of fat bloom (see Figure 1). Even in compound coatings, which do not undergo such changes to the crystal form, there can be effects on the surface gloss as a result of melting and recrystallisation.

Margarines and spreads that have undergone similar melting-recrystallisation cycles, albeit at lower temperatures, often become 'grainy' as a result of these changes.

It is important to understand how these changes affect the surface of the fat at near-molecular levels so that we can, at least, have some idea about how to control them and, perhaps, modify their effects.

Fundamental research funded by IOI Loders Croklaan at YKI (Institute of Surface Chemistry in Stockholm[1] has given some useful clues as to what may be happening on the surface of fat crystals during melting-recrystallisation or solution-dissolution.

Nuclear Magnetic Resonance (NMR) spectrometry is often used to determine the ratio of solid:liquid in fats. It achieves this by energising the protons (hydrogen atoms) in the fat and measuring how quickly they lose this energy. Protons in the solid state lose this energy more quickly than protons in the liquid state thus allowing the calculation of solid fat content to be made.

The study referred to above uses much more complex NMR measurements and, instead of looking at conventional hydrogen atoms, it uses deuterium atoms - deuterium being an isotope of hydrogen with double the atomic weight.

One of the highest melting components in palm oil is a triglyceride known as tripalmitin (PPP). This has a finite, but limited solubility in other oils. In the YKI study the deuterated form of PPP was used. This is the form in which all the hydrogen atoms have been replaced by deuterium. The deuterated-PPP was added to an oil known as an MCT oil (or medium chain triglyceride oil). This is an oil almost totally composed of fatty acids with 8 and 10 carbon atoms. Enough PPP was added to the MCT oil to give a saturated solution at 28°C.

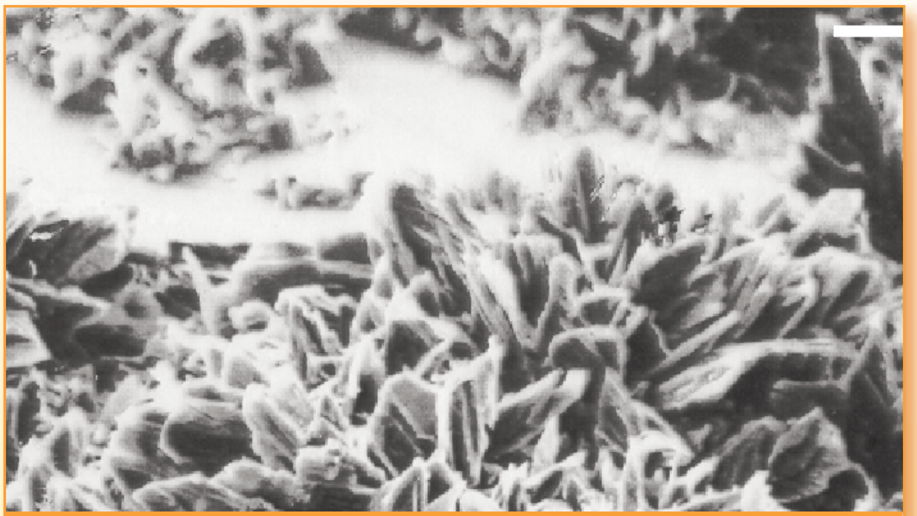

Figure 1: Scanning Electron Microscope photograph of fat bloom on chocolate (white bar = 10 microns)

When the temperature of this mix was raised to 33°C some of the PPP crystals dissolved. When the temperature was reduced back down to 28°C then the dissolved PPP came back out of solution and recrystallised. The rate at which recrystallisation occured could be monitored by the NMR measurements.

Having made the measurements it was possible to fit mathematical equations to them in order to define how the recrystallisation was occurring. One of the more common crystallisation models or equations is known as the Avrami equation. Without going into the complex mathematics of this, it is enough to say that it is possible, from some of the terms in the equation, to predict what the likely shape is of the crystals being formed, for example, whether they are rod-like or more circular.

The results clearly showed (Figure 2) that the recrystallisation when the temperature was reduced back down from 33°C to 28°C, took place in two stages. The first stage was very

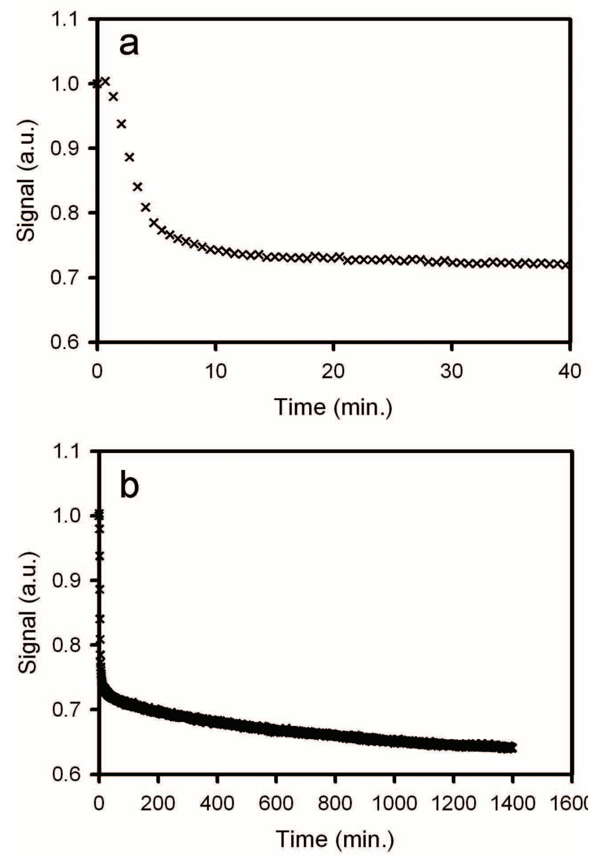

Figure 2: Recrystallisation of deuterated PPP from MCT (defined by NMR signal fro the liquid phase)

rapid - of the order of 10 minutes (Figure 2a) - while the second stage took much longer - several hours at least (Figure 2b). In fact, looking at the shorter time-scale (Figure 2a), it appears as if all crystallization has finished after only 15-20 minutes; looking at the longer time-scale (Figure 2b) shows that crystallization continues for a much longer period. The Avrami equation for the second stage suggested the formation of rod-like crystals. The Avrami equation for the first is less clearly interpretable and could result from either rod-like or disc-like crystals.

So, what can we interpret from these results? Indeed, firstly, why should the recrystallisation occur in two stages? Let's go through what might be happening from the point when we heat the system up from 28°C to 32°C. Obviously, some partial dissolution of the PPP crystals will take place. In other systems it has been reported by Mullin[2] that pits are etched on the surface of crystals as they dissolve. It is possible then that molecules of PPP are removed from the crystal surface by a combination of pit etching and general stripping of crystal layers. Mullin[2] also says that, during crystallisation, rough surfaces give higher crystal growth rates than do smooth faces. Thus, from the observations, it is possible that the first, rapid stage of crystallisation is where the pits formed during dissolution are filled in to give a smooth surface. The slower second stage could be due to rebuilding crystal layers on this smooth surface, a much slower process.

It may also be the case that this slower crystallisation takes place on some crystal faces in preference to others. Dissolution could take place from all crystal faces and, thus, will also probably give rise to pitting on all faces. When the fat recrystallises, it will initially fill the 'pits' on all faces (a rapid process) but then, as the surface becomes smoother, it may be that crystallisation occurs preferentially on certain faces.

Clearly, there are a number of uncertainties associated with the interpretation of the results which means that further work is needed - and is ongoing - to validate these theories but the fundamental information which this work provides will be of immense importance in understanding the melting-recystallisation processes which take place in a wide range of foods.

References

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