

Solvent fractionation of palm oil

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Introduction

Food manufacturers on both sides of the Atlantic are under increasing pressure to remove trans fatty acids and hydrogenated fats from their products. While there are a number of alternatives potentially available to them there is, nevertheless, usually a need for those alternatives to be able to provide structure and stability to the end product. That generally means having some solid fat present. If this solid fat cannot be produced by hydrogenation because the consumer has been 'taught' by the popular media to equate this on a label to the presence of trans fats then oils naturally rich in solid triglycerides must be used. The most readily available of these oils is palm oil.

Palm oil is probably the most flexible of vegetable oils in terms of its triglyceride composition and hence its functionality. It contains triglycerides that are liquid at room temperature, triglycerides that melt sharply at about body temperature and triglycerides that are even higher melting. In order to make the best use of each of these groups of triglycerides it is necessary to fractionate palm oil. While dry fractionation can and, indeed, often is used for this process a better, 'cleaner' separation is achieved by solvent fractionation.

A number of solvents have historically been used for this process but the most common ones are acetone and hexane. The fractions obtained from these two solvents do differ however, mainly in the distribution of partial glycerides across the fractions. Because, as indicated, there are three broad groups of triglycerides in palm oil it is possible to separate the oil into three fractions - a liquid fraction (oleine), a solid fraction (stearine or 'top'-fraction) and a middle-melting fraction ('mid'-fraction). This means that a two-stage fractionation process is needed.

Clearly this can be carried out in two ways. Either the oleine fraction can be removed in the first stage and then the mid and top fractions separated in the second stage, or the top fraction separated in the first stage and then the oleine and mid fractions separated in the second stage. There are good reasons for operating in the first way rather than the second. This is because then the presence of high-melting triglycerides helps nucleation in both fractionation stages, whereas, in the second way, these are removed prior to the second stage of fractionation.

The main 'solid' triglycerides in palm oil are POP (Palmitate-Oleate-Palmitate - representative of the middle-melting triglycerides) and PPP (Palmitate-Palmitate-Palmitate - representative of the high-melting triglycerides). Although the actual amounts are subject to natural variations typical levels were reported as long ago as the early 1980s to be 30.5% POP and 4.6% PPP.

To understand better the solvent fractionation of palm oil, model systems of both pure POP and PPP as well as mixtures/blends of the two triglycerides have been evaluated. Such studies are considered to be useful in determining the crystallization behavior of the components of palm oil. Acetone was used as the fractionation solvent.

One of the most critical phases in fractionation is nucleation and it is considered that the width of the metastable zone is of great importance in its influence on this process. This topic was extensively reviewed by J.W. Mullin of University College London, United Kingdom in his classic text "Crystallisation" that was published in 2001 as a fourth edition.

Metastable Zone

What exactly is the metastable zone? We have given more detailed examination elsewhere, but essentially it is the degree of undercooling (ΔT_{max}). This is best explained with reference to Figure 1. This diagram shows the changes in temperature of a pure triglyceride (e.g. POP) in acetone as it is first cooled to allow it to crystallize and then re-heated to allow it to re-dissolve. In a pure triglyceride such as POP the degree of undercooling is the difference between the cloud point, T_c , (where the first signs of nucleation are observed), and the clear point, T_{cp} . These two points can be determined in a model system by measuring the turbidity of the system or its degree of transmittance. When the triglyceride is cooled down the cloud point is first detected at the temperature at which the transmittance is reduced. Conversely, the clear point is the temperature at which the transmittance returns to its initial value when the system is reheated. The difference between these two temperatures is the degree of undercooling or the 'metastable zone'.

The growth temperature, T_g , is the temperature at which the crystal growth exotherm commences. In a pure system such as POP the cloud point and the growth temperature are coincident (as is shown in Figure 1); in a mixed system such as POP-PPP, the growth temperature will be lower than the cloud point. If the triglyceride /solvent system is then re-heated after crystallization has occurred, the crystals will begin to re-dissolve. The temperature at which they have completely dissolved is the clear point, T_{cp} . The difference between T_c and T_{cp} is called the 'metastable zone'.

Crystallization of the pure triglycerides and blends

A range of concentrations of POP, PPP and their blends in dry acetone were prepared and held, with stirring, at 40°C for 20 minutes prior to crystallization. The solutions were cooled at rates of between 12°C/h and 180°C/h using a temperature programmer and values for T_c and T_g were measured by means of turbidimetry of the solution. The systems were then re-heated at 30°C/h to measure the clear point (T_{cp}). Additionally some systems were studied by 'crash cooling' with a cooling rate of about 1000°C/h.

The solubility of both POP and PPP were measured by determining the clear point of each concentration. The solubility lines shown in Figures 2a (POP) and 2b (PPP) are calculated from these data using the equation noted by Timms. Also shown in these

Figures are the supersaturation curves (at cooling rates of 12 °C/h, 18 °C/h and 180 °C/h) of POP (Fig. 2a) and PPP (Fig. 2b).

Using the measurements of cloud point and clear point we can calculate the width of the metastable zone for a range of cooling rates and triglyceride concentrations. Examples of these are shown on Figure 3a (for POP) and Figure 3b (for PPP).

In the case of POP, the width of the metastable zone (ΔT_{max}) varied from about 13 °C to about 17 °C as the cooling rate increased and is relatively insensitive to cooling rate. With PPP, however, the width of the metastable zone varied from about 13 °C to about 19 °C at lower PPP concentrations but from about 9 °C to about 12 °C at higher PPP concentrations and shows a greater dependence on cooling rates. The greater dependency of PPP on concentration can also be seen from the supersaturation curves in Figure 2b which are not as parallel to the solubility curve as they are for POP.

Some difference between POP and PPP were seen in terms of the appearance of an exotherm after the cloud point had been reached. POP showed such an exotherm (as seen in Figure 1) whereas PPP did not. This is undoubtedly due to the differences in crystallizable material in both cases (this being higher for POP than for PPP).

The growth exotherm of the blends commences when the bulk of the POP crystallizes; growth and nucleation are effectively coincidental with pure POP, i.e. $T_c \approx T_g$. The presence of PPP, however, delays the growth exotherm by about 5 °C. The information obtained suggests that the nucleation process is not particularly sensitive to cooling rate and that for the cooling rates used very high concentration supersaturations are necessary before there is any appreciable nucleation. Lower cooling rates, however, should be used to prevent POP and PPP from co-crystallizing, particularly at higher levels of PPP.

Crystal Size and Crystal Habit

The size and habit of crystals produced during solvent fractionation are of importance in terms of ease of 'washing' of the crystals on a filter belt. The easier crystals are to wash the easier it is to remove entrained oleine. Electron microscopy of the POP and PPP crystals helps to give some indication of the shape and size of the crystals and hence of how easy (or not) it will be to wash out entrained material.

The POP crystals were essentially spherulitic (β -3) - Figure 4. Programmed cooling gave a slightly more open texture than did crash cooling which might help to improve the ease of washing. At a concentration of 3.8g/100g solution the spherulites were about 50 to 75 μ m in diameter. Reducing the concentration to 0.5g/100g also reduced the crystal diameter to 25 to 50 μ m.

In contrast, PPP gave flat, plate-like crystals (β -2) - Figure 5. At a cooling rate of 12 °C/h crystals of about 30 x 6 μ m were produced whereas at a cooling rate of 18 °C/h the crystals were close to 15 x 10 μ m. Crash cooling tended to produce amorphous clusters of up to about 50 μ m in diameter (Figure 5). Both polymorphs are produced with β -3 predominating when PPP is added to POP, but more β -2 crystals are present after programmed cooling than after crash cooling suggesting that the slower the cooling rate the greater the likelihood of a PPP-like phase being produced.

Summary

In our current low-trans or even trans-free world the use of palm fractions is becoming increasingly important. In order to be able to optimally fractionate palm oil a knowledge of the crystallization behavior of the main solid components is critical. In general terms these can be equated to POP and PPP as being representative of these solid components. A study of each of these individually gives us important fundamental information about how these triglycerides crystallize. Information of this kind is of great relevance in whichever order the fractionation is carried out. It is probably most common to remove the oleine fraction first and then, in a second stage, to separate the POP-rich fraction from the PPP-rich fraction. For such systems information on the crystallization characteristics of a mixed POP-PPP system is important, especially for the first stage of crystallization in which a POP-rich phase crystallizes in the presence on PPP.

Reference

Smith K.W., Cain F.W., Talbot G - 'Crystallisation of 1,3-dipalmitoyl-2-oleoylglycerol and tripalmitoylglycerol and their mixtures from acetone' - Eur. J. Lipid Sci. Technol. 107 (2005) 583-593

Timms R.E. - 'Choice of solvent for fractional crystallization of palm oil' in *Palm oil technology for the eighties*. Eds. Pushparajah, E. and Rajasurai, M. Incorporated Society of Planters, Kuala Lumpur, Malaysia, 1983, pp 277-290

Figure 1 The metastable zone

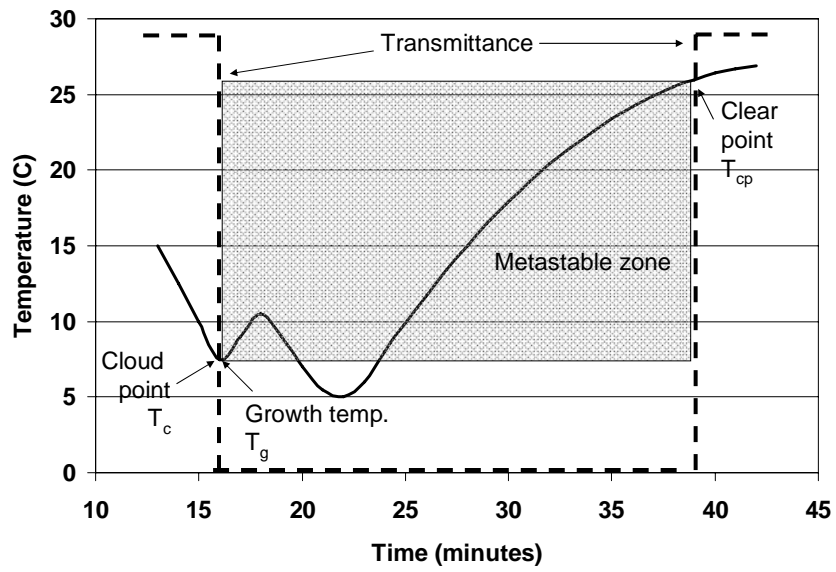


Figure 2 Solubility and supersaturation curves for (a) POP and (b) PPP in acetone. Figure reproduced from reference 3 with permission (copyright 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

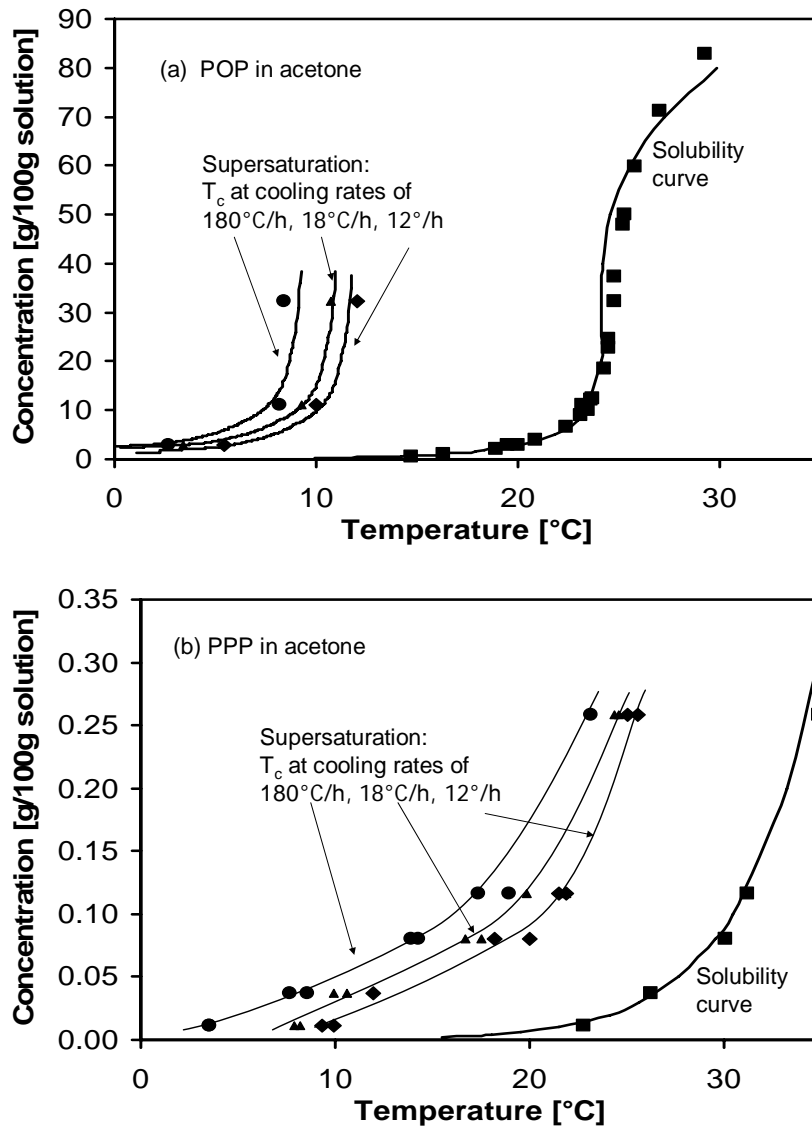


Figure 3 Influence of cooling rate on clear point and metastable zone width (deltaTmax) for (a) POP and (b) PPP

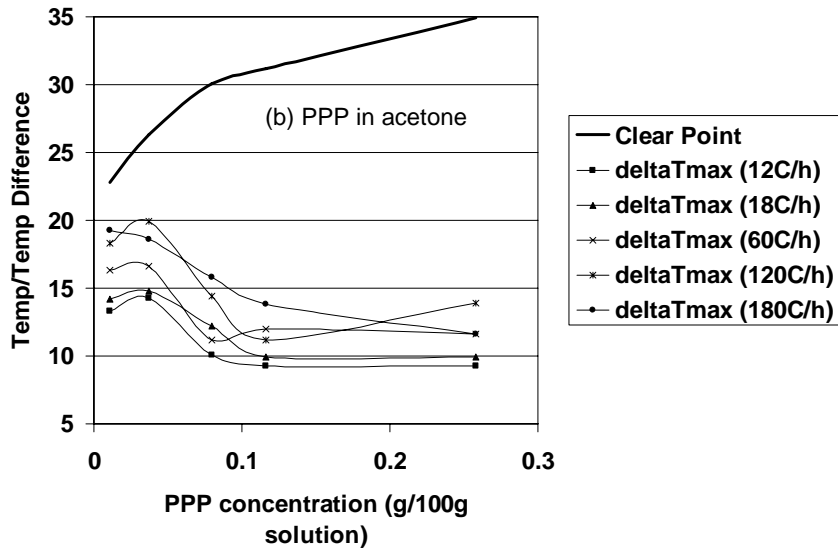
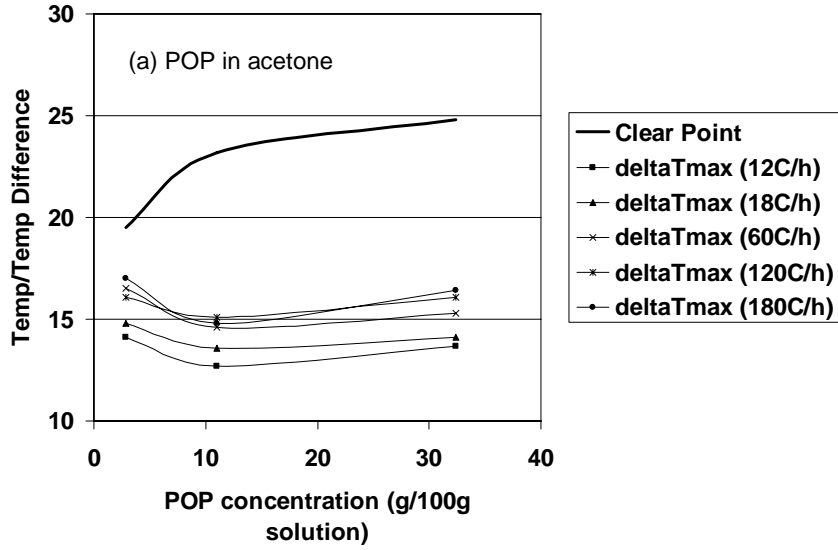


Figure 4 Electron micrographs of POP crystals after (a) cooling at 12 °C/h and (b) crash cooling Figure reproduced from reference 3 with permission (copyright 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

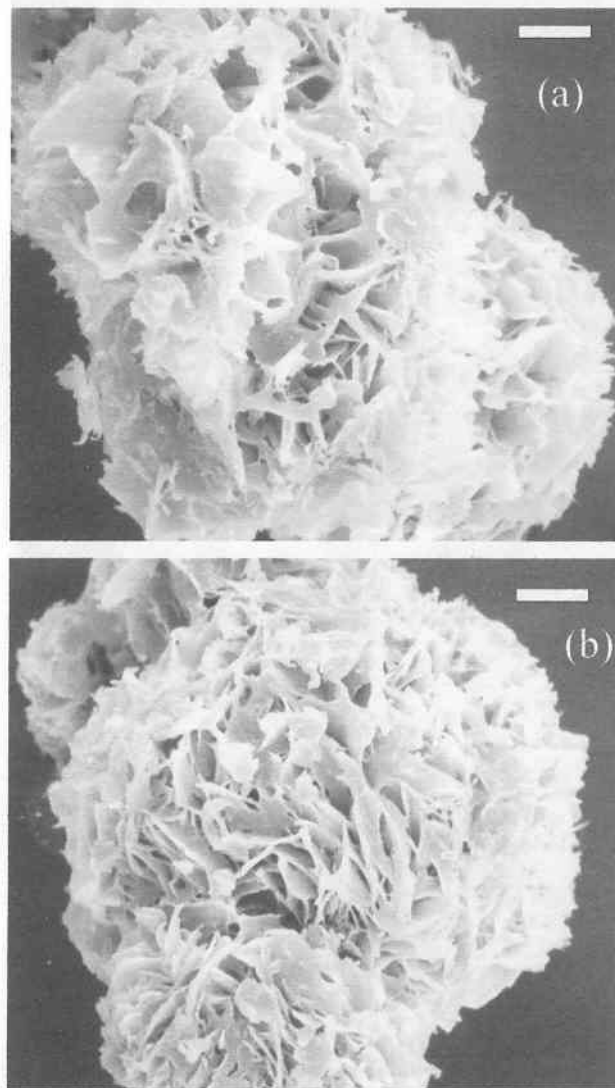


Figure 5 Electron micrographs of PPP crystals after (a) cooling at 12 °C/h and (b) crash cooling. Figure reproduced from reference 3 with permission (copyright 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

