Determining Percent Solid in an Edible Fat

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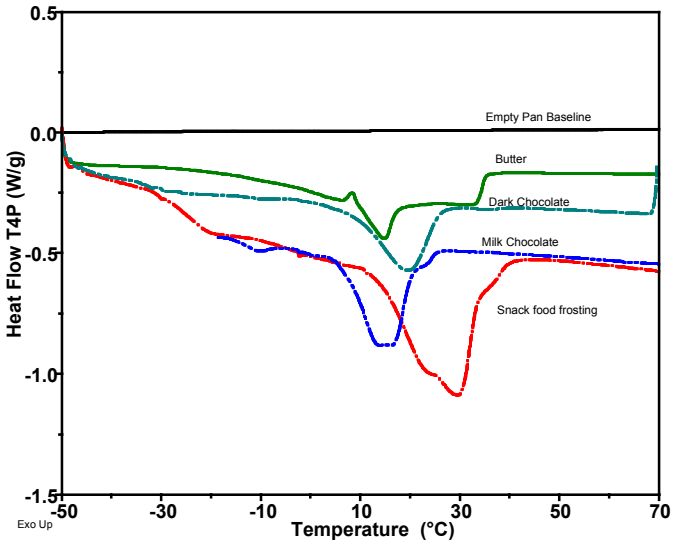
ABSTRACT

Improved performance from the new Q Series™ DSCs provides rapid and reliable analysis of fats and oils. Advanced Tzero™ Technology results in straighter baselines compensating for errors caused by thermal lag. Because of the special encapsulation requirements of edible fats, these errors can be significant when a conventional DSC treatment is used.

INTRODUCTION

Edible fats and oils play an important role in manufactured food products. Besides providing caloric energy themselves, they provide the non-polar phase that dissolves vitamins and flavor that make food healthy and palatable. With our increased consumption of snack foods and ready-to-eat meals, research continues into the role of edible fat constituents that control texture, taste, appearance and shelf life. Chocolate, margarine, butter and hydrogenated vegetable oils, to name a few, derive their texture and melting behavior from the mix of fat components in their formulations. One of the complexities of this science is that the melting behavior and texture characteristics are affected not only by the mix of constituents, but also by the thermal history which determines the polymorphism, crystallite size and phase distribution in the system.

Figure 1 - DSC Melting Curves for Four Edible Fats



DSC has long been a useful tool to characterize the melting behavior of edible fats and oils. DSC is able both to impose a thermal history and to measure the rate of melting as a function of temperature. Additionally, the DSC curve shows a displacement from the zero-signal baseline due to the heat capacity of the sample specimen. When the sample is encapsulated in a sealed pan, peaks in this curve indicate crystalline melting.

Figure 1 shows the DSC melting curves of four edible fats after cooling to -50 • C from the melt at 5 ºC/min. The melting region extends from below –30 ºC to above +40 ºC. The area of the peak indicates the total fat content. Moreover, the area below 22

ºC represents fractions that would be melted at room temperature, and those above 22 ºC, represents fractions that would be crystalline solid.

The integral over all the melting peaks is an indication of the fraction melted as a function of temperature. And taking the inverse of this integral and converting to percent, yields the percent solid. Figure 2 shows an example of this type of analysis for a snack food frosting. The DSC curve shows a broad melting region between –40 and +50 ºC with multiple peaks. The break between the two large peaks is made deeper by annealing. As the confectionary coating sits at shelf temperature the material naturally anneals, resulting in the solidification of the higher melting components and the melting of the lower melting components. Thus, from the area under the two peaks, the amount of melt and the amount of solid may be determined. The percent solid curve in Figure 2 is the integral over the melting peak, providing an indication of the fraction melted versus temperature.

Figure 2 - Melting and Percent Solid Data For a Snack Food Frosting

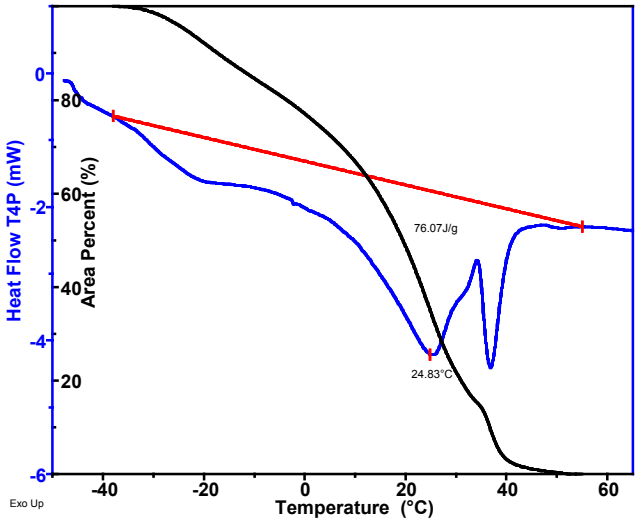
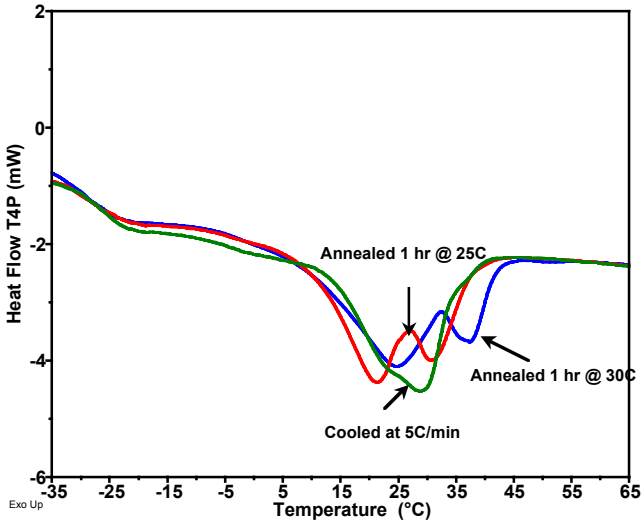


Figure 3 shows the same material scanned by DSC using identical analysis conditions, but with the sample having been treated by different thermal histories showing that the solid fraction is a function of thermal history, that is, how long the material has annealed at a given temperature. The DSC enables the examination of this behavior by imposing a thermal history, then measuring the melting profile. The DSC is ideally suited to investigate how a particular formulation is affected by annealing as the finished product sits on the shelf.

Figure 3 - Snack Food Frosting after Three Thermal Treatments



EXPERIMENTAL

While the DSC technique is straightforward for determining the fraction solid, there are a number of considerations for obtaining good data.

Sampling and Encapsulation. Since the samples are partially melted at room temperature, care must be taken to obtain representative samples. A small sample size is preferable to minimize temperature gradients (as discussed below) and to avoid sample spillover. The materials must be encapsulated in a hermetically sealed pan since small amounts of dehydration (highly endothermic) can appear to be melting and hence compromise the results. The hermetic sample pans from TA Instruments are especially effective in this use since there is a double surface for sealing and the upper surface is immune from contamination from the oils that otherwise often prevent a good seal on many hermetic pans. Sample pan leakage is an especially serious problem when a power compensation-type DSC is used since small amounts of moisture released from the sample can dramatically shift the power compensation DSC baseline. Heat flux-DSC's are much less prone to contamination and are essentially self-cleaning as materials that evaporate from the sample are purged only past hot surfaces, do not condense out and do not cause baseline shift.

Baselines. Having a straight baseline is especially important for edible fat melting peaks as they typically extend over tens of Celsius degrees. Here's why. When the partial area is calculated to obtain the percent solid, a baseline for the peak must be assumed. If the underlying instrument baseline is not straight then the same curvature that appears in the instrument baseline must be used under the peak.

Temperature Control and Thermal Lag. Because thermal sample conditioning is an important part of the solid fat analysis it is important to have accurate and reproducible temperature control. In many DSC systems, it is difficult to know whether the sample temperature is well controlled since the sample temperature read-out sensor is better coupled to the furnace than it is to the sample (*1*). Thermal lag constitutes a considerable source of error in the determination of solid fat content unless it is properly provided for either in the hardware or software (*2*).

The Q Series DSC

The data presented here are obtained using the Q1000 DSC, with its Advanced Tzero™ Technology. This technology offers unique opportunities to improve solid fat determination. The improvements are in three areas: straight baselines, better temperature control and reduction of thermal lag related errors.

Straight baselines. The Tzero thermocouple, used in the Q series DSCs, enables the DSC cell to be calibrated in a unique way (*3*). The automated calibration not only defines the calorimetry of the DSC but also defines the steady state and transient temperature gradients in the cell. This allows the DSC sensor system to be characterized in terms of its heat flow characteristics. The resultant measured heat flow is a better indication of the heat flowing to the sample, without the usual distortion and baseline character that normally are superimposed. The most obvious result is a baseline that has roughly an order of magnitude less in curvature than conventional DSCs (*4*).

Figure 1 shows the straight baseline achieved with an empty pan. For this type of broad peak analysis the curvature observed in most DSC's would result in an error of several percent in the determination of percent solid.

Correct Peak Shape. The distortion of peak shapes by restricted heat flow across the thermal gap between the DSC cell and the encapsulated sample is well known (*5*). Earlier papers on Tzero have explained how a third thermocouple junction on the Q Series‰ DSC sensor is used to provide an additional compensation for temperature gradients that occur in the sensor as a result of heat flow to the sample (*3*). Having this extra Tzero signal provides a more complete, four-term, heat flow equation to be derived and evaluated for the DSC cell (*4*). With Advanced Tzero‰ Technology the recorded heat flow data does not include the adverse effects of heat flow across the thermal resistance to the DSC cell and pan. Moreover, with Advanced Tzero the X-axis recorded temperature is a much better indication of the actual sample temperature since thermal lag from the analyzer and pan has been removed (*1*). This enables the instrumental distortion to the peak shape and the thermal lag to be addressed for in the output signals. The result is a much more accurate determination of the fraction melted versus temperature (*2*).

Figure 4 - Fat Additive Using Advanced Tzero™ Technology

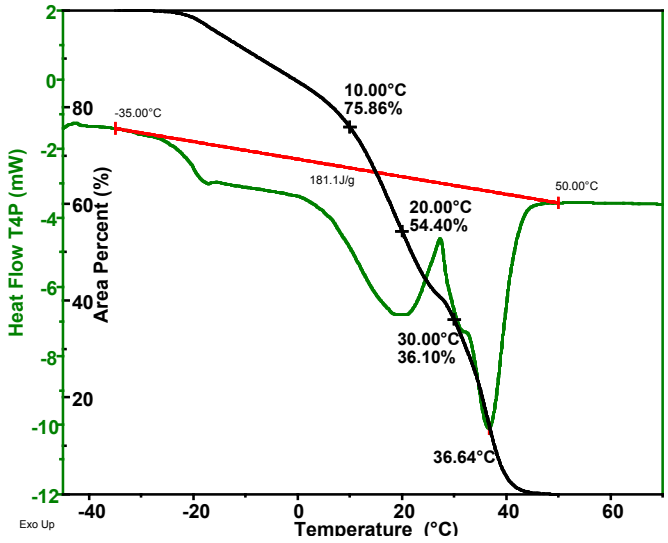
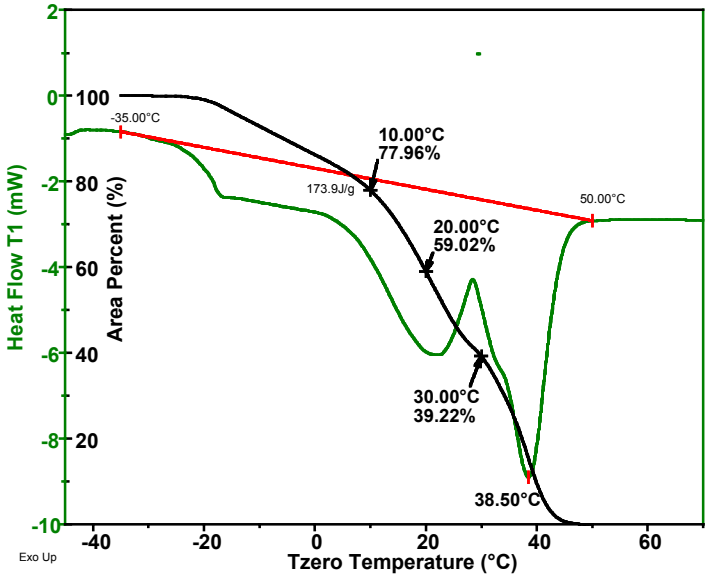


Figure 5 - Chocolate Fat Additive Using a Conventional DSC Approach



RESULTS

Conventional DSC performance may be compared with that of Tzero Technology. Figures 4 and 5 compare these two treatments. Qualitatively the curves look the same. But the Percent Solid versus temperature results are significantly different. Comparing the Percent Solid results at 10, 20, and 30 Celsius degrees shows that errors are two to four percent for conventional DSC. The temperature of the peak maximum is also in error in the conventional DSC by about two Celsius degrees. These errors are more serious when using large samples, fast heating rates and/or massive, or poorly coupled, sample pans. However, even in the above example when a sample size of 3.5 mg was used, the errors using a conventional DSC were significant.

CONCLUSION

The Q Series DSC offer significant improvements in the investigation of the solid fat content in edible fats. Through a new DSC design and with a new Tzero sensor technology these units are able to make more reliable and accurate measurements. Through straighter baselines and compensation for thermal lag errors, the Q1000 with Advanced Tzero™ Technology is a valuable tool in the design of food products.

REFERENCES

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KEYWORDS

differential scanning calorimetry, foods, melting