APPLICATION NOTE

Differential Scanning Calorimetry

**Authors**

**Patricia Heussen**

**Unilever**
**Research & Development**
**Vlaardingen, The Netherlands**

**Peng Ye, Kevin Menard, Patrick Courtney**

**PerkinElmer, Inc.**
**Shelton, CT 06484 USA**

# Practical Food Applications of Differential Scanning Calorimetry (DSC)

## Abstract

This note describes a number of important food applications utilising the PerkinElmer DSC demonstrating the versatility of the technique as a tool in the food industry.

## Introduction

Food is often a complex system including various compositions and structures. The characterization of food can therefore be challenging. Many analytical methods have been used to study food, including differential scanning calorimetry (DSC).[1] DSC is a thermal analysis technique to measure the temperature and heat flows associated with phase transitions in materials, as a function of time and temperature. Such measurements can provide both quantitative and qualitative information concerning physical and chemical changes that involve endothermic (energy consuming) and exothermic (energy producing) processes, or changes in heat capacity.

DSC is particularly suitable for analysis of food systems because they are often subject to heating or cooling during processing. The calorimetric information from DSC can be directly used to understand the thermal transitions that the food system may undergo during processing or storage. DSC is easy to operate and in most cases no special sample preparation is required. With a wide range of DSC sample pans available, both liquid and solid food samples can be studied. Typical food samples and the type of information that can be obtained by DSC are listed in Table 1. These tests can be used for both QC and R&D purposes. DSC applications are used from troubleshooting up to new product developments.

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*Table 1.* **Typical food samples and their application by DSC.**

| Type of Samples | Type of Information |
|---|---|
| Oils, fats and spreads | Onset temp of melt/crystallisation /polymorphic behaviour/oxidation stability |
| Flour and rice starch | Retrogradation/gelatinization/glass transition Tg |
| Vegetable powders | Glass transition Tg |
| Pastes and gels containing polysaccharides or gums | Specific heat Cp, onset temp of melt and crystallisation |
| Protein | Denaturation/aggregation |

In this note, several samples of food material systems are given to illustrate the versatility of DSC.

## DSC of oils and fats

Using a heat-cool-heat DSC program, the onset temperature, the heat of fusion (ΔH), the identification of polymorphic behaviour and crystallisation of oils and fats can be determined. An isothermal method or scanning method with an oxygen atmosphere can also be used to determine the oxidation induction time (OIT), in which case a heat-cool-heat method is applied to hydrogenated vegetable oils. Sometimes additional information about the sample is necessary for data interpretation, as for example in combination with XRD analysis which provides information on the specific polymorphic transitions. Most triglycerides[2] exist at least in three crystalline forms, α (alpha), β′ (beta-prime), and β (beta) that can be identified according to their X-ray diffraction patterns.[3]

In Figure 1 it can be observed that a α-modification is formed after a heat-cool treatment. This will be transformed into a β′-modification and after a certain time at room temperature partially to the β-modification. In Figure 2 the influence of storage time at room temperature is shown. The first heating of day 8 shows a better resolved peaks due to the transition of the less stable β′ to a more stable polymorphic fraction, as it was also confirmed by XRD.

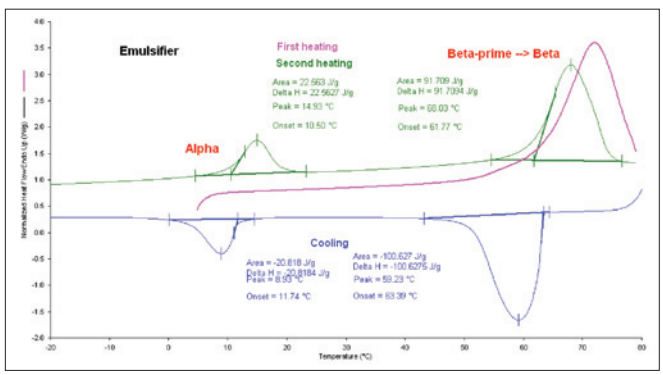


*Figure 1.* Heat influence on emulsifier.

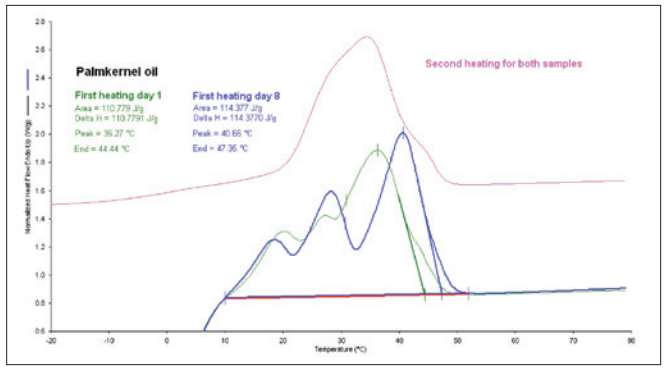


*Figure 2.* Time influence on palmkernel oil melting behaviour.

DSC is used to study fat phase transitions and melting range. It is one technique to explain the physical and textural properties of fats in bulk and final products. The combination of DSC and XRD is often used to identify the stable β-form, which can result in grainy mouth feel in final products.

DSC is used to compare batches of a product to study the melting behaviour indicating differences in crystallinity of the fat or composition of the end product. Different scanning rates are used to investigate the cooling effect on the crystallisation of a specific fat. The solid fat content (SFC) of a fat system can be determined over a given melting range. The solid fat content values are calculated through the partial areas of DSC heating curves usually between 5-60 °C and compared to NMR (Minispec) data.[4,5]

To study the aging of a fat or end product the sample is kept at an isothermal temperature to mimic e.g. refrigerator conditions. Comparing the DSC thermograms of a fresh sample and after a known storage time gives information on phase transitions during these storage conditions.

Other studies[6] involve tempering to investigate the influence on the final product after temperature abuse or due to transport at ambient. Tempering consisted of warming the systems up to a temperature between 15 and 30 °C and cooling down to 5 °C. These results can be correlated with the storage modulus (G′).

DSC melting and crystallisation behaviour of different types of oils and fats are studied when replacing them in a product. In a factory and also at lab scale, different ingredients are added at different stages of the production process. Adding an ingredient which is not at the correct temperature can cause encapsulation of other ingredients or may stay present in the product as a particle. The filling temperature of a product is important for example to obtain the desired firmness of a product and to prevent graininess.

An AOCS[7] method can be carried out for quality control of fats to analyse these raw materials used in food products. This is a "fingerprint" method whereby the sample is melted, subsequently cooled down with a predefined scanning rate to a low temperature. After crystallisation for a specific time, a heating curve is obtained also with a predefined scanning rate.

### DSC of starch samples

Starch[8,9], a major structure-forming food hydrocolloid[10], is a polymeric mixture of essentially linear (amylose) and branched (amylopectin) molecules. Small amounts of non-carbohydrate constituents (lipids, phosphorus, and proteins) present in native starch also contribute to its functionality. Starch is used as thickening agent in e.g. dry sauce bases, instant soups, mayonnaise, spreads. Starch pastes can be used as stabilizers for oil emulsions in for instance dressings.

Native starch or modified starch used in these types of food products can show different endothermic peaks in the DSC thermograms respectively, retrogradation (recrystallized amylopectin), gelatinization (50 < T < 80 °C depending on the type of starch), amylose-lipid complex (T > 100 °C) or recrystallized amylose (T > 140 °C) can be observed.

Retrogradation is only possible in processed (cooked or modified starch) materials which have been stored at lower temperatures. Retrogradation can expel water from a polymer network also known as syneresis but it can also cause dough to harden.

The hydrogen bond arrangement of amylopectin and amylose makes it difficult for water to penetrate into intact starch granules. When the water is heated the granules swell and gelatinization is observed. DSC measures the temperature at which irreversible changes occur in the granule. This process can also be observed by polarised light microscopy during heating.

The starch powders can be analysed dry to obtain information about the pure sample. Additionally, after adding a known amount of water, information is obtained about the degree of gelatinization. The level of water used is of influence on the gelatinization degree and peak shapes. Starch with low and intermediate water content can show more melting endotherms. The gelatinization information can be used to determine the temperature and time necessary for e.g. rice which is used in instant soups. If the rice has a too high amount of gelatinization left in the product, this will result in hard uncooked rice in the instant soup.

Most starches and rice products contain a lipid (fat) which can form an amylose-lipid complex. This complex can be formed during gelatinization.[1] It is also a thermo reversible complex and should show an exothermic peak on cooling. Sometimes the modification of the amylose with a lipid is performed to control the texture of the final starch.

The composition of plain rice[11] is starch (76.5%), water (12%), protein (7.5%), fat (1.9%) and minors (2.1%). An example of a native rice (Figure 3) and rice slurry (Figure 4) show the presence of retrogradation and amylose-lipid complex endotherms.

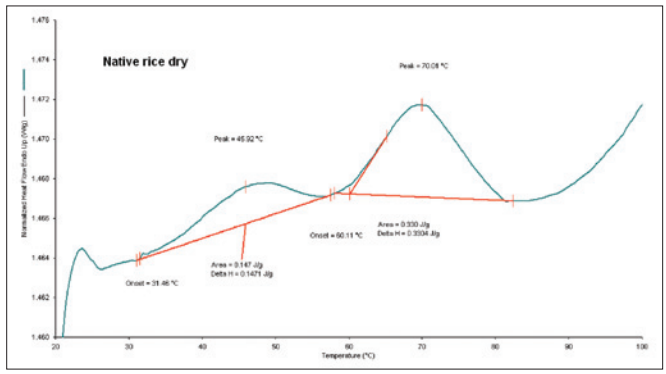


*Figure 3.* Native rice dry sample showing a retrogradation peak around 45 °C and a gelatinization peak around 70 °C.

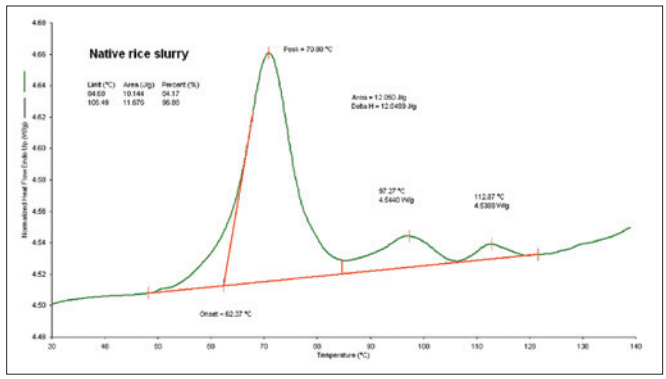


*Figure 4.* Native rice wet sample showing a gelatinization peak at around 70 °C and some amylose-lipid complex at 112 °C.

### DSC of vegetable powders

Since food products are complex mixtures of several compounds, it is often difficult to determine their glass transition (Tg) temperatures accurately. Understanding the glass transition[12] phenomenon provides an insight into the causes of the cohesiveness of many important powders and influencing the wetability or solubility of the powder, which is important for new product development. Food material often contains water which can be present as free or bound water. The free water is related to the wateractivity (Aw). The plasticization effect of water leads to depression of the glass transition temperature causing significant changes in the physicochemical and crystallization properties during storage. Loss of physical stability by the effect of moisture and temperature will reduce flowability and increase caking tendency and, to a smaller extent, affect other physical properties such as colour. A Tg is only observed for amorphous matter. Sugars in a powder can undergo a phase transition from amorphous to crystalline at a given relative humidity during storage and thus have an effect on the glass transition temperature.

DSC is widely used to study glass transition phenomena. The effect of water as a plasticizer on Tg was studied for vegetable powders stored at different Aw values (humidity). At a higher Aw value the samples take up more water. In Figure 5 it is shown that the Tg drops to lower temperatures as the amount of water in the sample increases. The knowledge of Tg in combination with the water activity is important in predicting the physical state of the powder at various conditions, from free flowable to stickiness or phase transitions to crystalline matter.

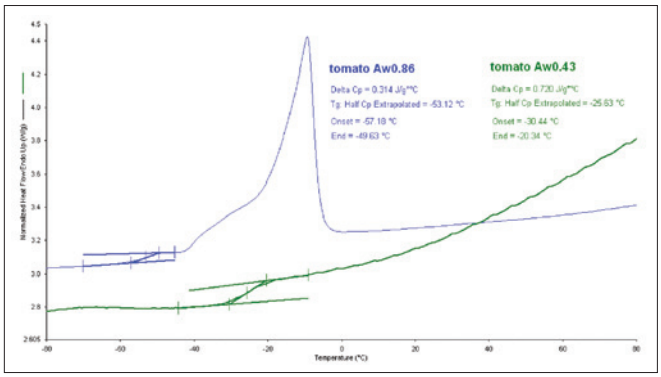


*Figure 5.* Water influence on Tg of tomato, the Aw 0.86 also shows an endothermic peak which is due to the melting of free water.

Proteins denaturation is also intensively studied by DSC. The influences of pH, salt and polysaccharides were investigated[13] for food proteins.

## Conclusion

DSC is an essential tool to reveal the underlying phase-compositional principles of food systems. For systems with a clearly established phase-composition-functionality relation, DSC can contribute to the development of novel food products.

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**PerkinElmer, Inc.**
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
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