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USING THERMAL ANALYSIS AND COMBINED TECHNIQUES FOR FOOD CHARACTERIZATION
Report on panel presentation

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Introduction

Water and other naturally occurring compounds found in foodstuffs (meat, milk, eggs, vegetables, cereals) are heat sensitive. They undergo heat-induced structural changes with consequences on their physical, microbiological and sensory characteristics [1], and monitoring desired or detrimental effects of time-temperature parameters is used to maximize food-processing steps. Control of heating and cooling procedures used in food preparation and storage steps constitutes a way to maintain physical stability or long-term safety such as retardation of lipid oxidation in butter, hindering of starch staling in bread or fat blooming in chocolate, or phase separation in sauces [2, 3]. Food industry seeks also to promote structure destabilization, which is identified in dispersed systems (butter, whipped-creams or ice-creams) as essential to perceived quality [4]. Foods are multi-components and multi-phase systems, and researchers and technologists are usually dealing with complicated situations due to overlapping heat-induced transformations occurring in the same temperature range [5], non-equilibrium reactions or ill-defined molecular interactions from thermodynamic and chemical points of view. Application of differential scanning calorimetry (DSC) allows a rapid determination of characteristic temperatures of physical state transitions or phase transformations in food components. Examples include state transitions in water and fat, heat-induced denaturation and/or aggregation in protein solutions, sol–gel transitions in polysaccharide solutions, gelatinisation in starch-rich samples. Using DSC in combination with other analytical techniques can help for monitoring thermodynamic and kinetic reactions in parallel with identification of structural changes in food components. We will find below examples of physical parameters determined from DSC measurements in combination with thermomicroscopy or with nuclear magnetic resonance (NMR), which lead to discussion on water mobility in foodstuff. The other examples are concerned with DSC measurements performed simultaneously with other methods of thermal analysis such as thermogravimetry (TG), dynamic mechanical analysis (DMA). In these examples, the great advantage comes from investigation of the same sample under identical experimental conditions.

Examples of characterization

On freezing of 'bulk' and 'dispersed water'

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The behaviour of vegetable (green beans) submitted to regular cooling from 20 to –60°C and re-heating was determined by DSC (2 K min^{-1}) and optical microscopy. The results obtained compared to those obtained on bulk and disperse water within emulsions [6] point out (Figs 1a and b):

- A sharp release of energy at around –8°C showing freezing of extra cellular water follows by a scattering of the freezing of the cells.
- No heat exothermic peaks in the thermograms were observed at around –40°C. All is frozen at –15°C; this indicates the absence of any disperse water freezing.

The melting has been found to begin at –8°C showing the presence of solutes that decreases the melting temperature.

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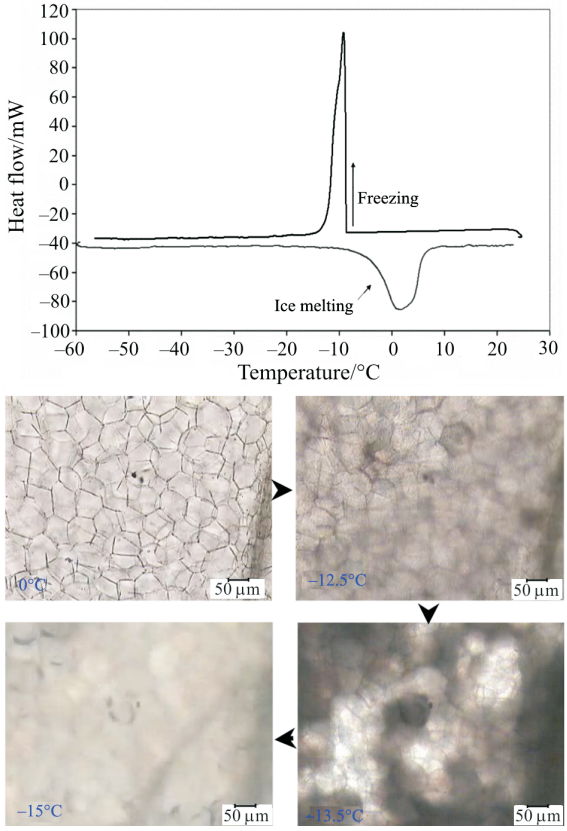

Fig. 1 Water in green bean a – DSC curves during freezing/thawing; b – cryomicroscopy images during freezing

On 'molecular' and 'structural' mobility

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'Mobility' has been addressed as a food stability indicator [7]. Particular care must be used to specify what is meant with the term 'mobility'. Mobility is defined by the analytical parameters measured according to the time frames or the frequencies of the methods used. For example, NMR, can detect molecular motions in the picosecond–millisecond range, while DSC and DMA detect relaxations over a millisecond–second range.

A correlation between macromolecular (glass transition, by DSC) and molecular mobility (as detected by electron spin resonance) has been reported for the case of sugars [9]. In more complex, heterogeneous food systems, however, a vast discrepancy between molecular and structural mobility can be expected. For example, cellulose equilibrated in the water activity range from 0.1–0.9 (moisture content <18%) did not show any evidence of glassy to rubbery transition by DSC analysis (–80 to 200°C range) and freezable water was detectable only at moisture contents >19% [10]. A significant ^{1}H and ^{2}H NMR molecular mobility was detected in these samples as shown in Fig. 2.

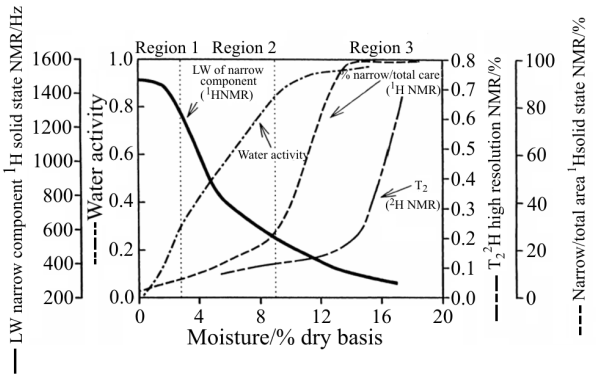

Fig. 2 Summarized chart for cellulose changes in water activity, high resolution ^{2}H NMR T_2 relaxation times, LW of ^{1}H solid-state NMR narrow component and ^{1}H solid-state NMR relative ratio of the narrow/wide component. Dotted lines indicate the three sorption regions. Reprinted, with permission, from [8]

Combined techniques can shed light on thermal effects

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The DSC records from many food samples show a number of 'humps' and 'bumps' that have to be interpreted. They mainly depend on the fact that foods are multi-phase and multi-component systems, which undergo a number of transitions and/or chemical reactions that can occur in the same temperature range and can produce a partial compensation between endo- and exothermal effects. The same interpretation problems arise with traditional thermal analyses, TG and DMA. Improved sensitivity and a more reliable interpretation can be attained through a suitable combination with another instrument, like mass spectrometer, gas chromatographer, IR spectrophotometer, etc., which acts as a 'sensor' that is kept at room temperature. DSC and DTG coupling allows the simultaneous evaluation of different physico-chemical and structural properties of dough, which are both affected by the temperature scan, as seen from curves in Fig. 3.

These examples indicate that thermal behaviour of wheat flour dough is explained by two different properties of starch granules (Fig. 3), by molecular interactions between proteins and polysaccharides in buckwheat flour and also by technological processing such as dehulling of buckwheat (Fig. 3). In particular DSC technique was used to assess starch and protein transitions and TG to study the water partition between the phases of the dough. The information collected provides a rationale for explaining the results of baking trials. Chemical and biochemical investigations confirmed the results [11]. By replacing the standard TG cell with Knudsen cells, it is possible to suck moisture out of the sample at a constant rate in isothermal conditions.

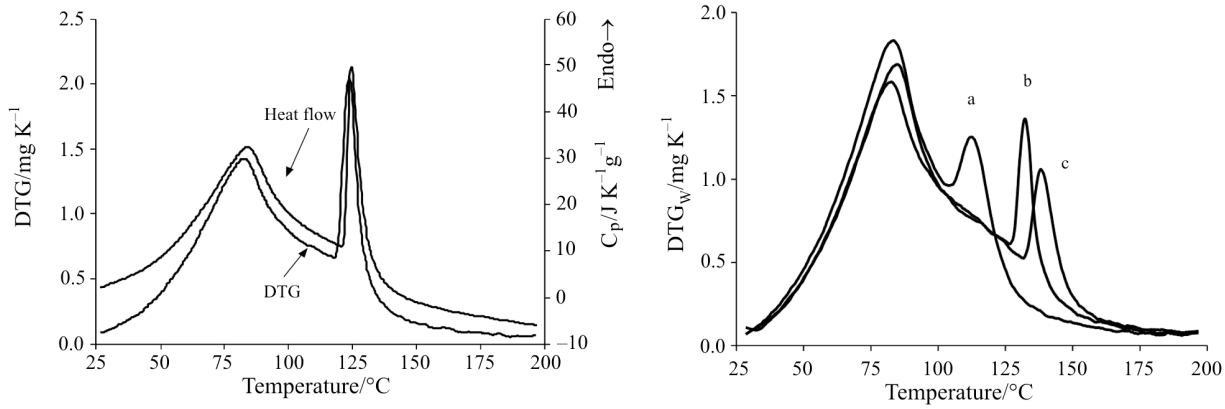

Fig. 3 Left – DTG-DSC traces of wheat flour dough at 2 °C min^{-1} heating rate [10], right – DTG traces of wheat flour /buckwheat flour mixed (50%, mass/mass) dough in the presence of polysaccharides from either whole (curve a) or dehulled buckwheat (curve b), wheat flour dough in similar experimental conditions (curve c)

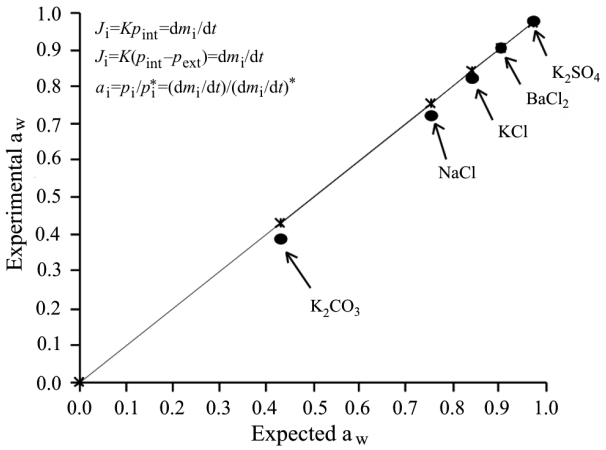

Fig. 4 Saturated salt solutions used to calibrate the Knudsen TG for determination of water activity

This matter flux is proportional to the pressure drop across the Knudsen orifice of the cell. Keeping the external pressure some order of magnitude below that within the cell, the matter flux may be referred to as a measure of the partial pressure of the volatile hosted in the cell. The ratio between the out-flux of water from a given food sample and that from a pure water sample (in a separate run performed with the same Knudsen cell at the same temperature), one can achieve a reliable estimation of the relative humidity, or (in the case of liquid samples) water activity of the sample hosted within the cell [10, 11] and define with a single experiment the whole isothermal desorption curve for a given sample (Fig. 4).

Conclusions

This panel presentation shows that heat-induced behaviour of water and other food components and identification of their contribution to DSC curves are more accurately studied using other combined or simultaneous techniques. First order state transitions associated with ice formation/melting in vegetables are similar to those observed for fat crystallisation in oil-in-water emulsions. In these dispersed systems calorimetric parameters are changed due to structural transitions associated with interfacial regions. Glass transition and molecular mobility are of great importance to structural stability and shelf life of foods. They reveal changes related to different time scales. Thermal behaviour of flour dough and its relation to water partition between starch gelatinisation and gluten reticulation is shown to be dependent on physicochemistry of dough components.

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