Journal of Thermal Analysis, Vol. 47 (1996) 1787-1803

Review

APPLICATION OF DIFFERENTIAL SCANNING CALORIMETRY IN FOOD RESEARCH AND FOOD QUALITY ASSURANCE

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(Received December 18, 1995)

Abstract

Differential scanning calorimetry (DSC) is the most widely used thermal analytical technique in food research and it has a great utility in quality assurance of food. Proteins are the most studied food components by thermal analysis including studies on conformation changes of food proteins as affected by various environmental factors, thermal denaturation of tissue proteins, food enzymes and enzyme praparations for the food industry, as well as effects of various additives on their thermal properties. Freezing-induced denaturation of food proteins and the effect of cryoprotectants are also monitored by DSC. Polymer characterization based on DSC of polysaccharides, gelatinization behaviour of starches and interaction of starch with other food components can be determined, and phase transitions during baking processes can be studied by DSC. Studies on crystallization and melting behaviour of fats observed by DSC indicate changes in lipid composition or help characterizing products. Thermal oxidative decomposition of edible oils examined by DSC can be used for predicting oil stability. Using DSC in the freezing range has a great potential for measuring and modelling frozen food thermal properties, and to estimate the state of water in foods and food ingredients. Research in food microbiology utilizes DSC in better understanding thermoadaptive mechanisms or heat killing of food-borne microorganisms. Isothermic microcalorimetric techniques provide informative data regarding microbial growth and microbial metabolism.

Keywords: DSC, food components, food microbiology, food quality

Introduction

Cooking was a revolutionary innovation of early mankind, which improves food's palatability, digestibility and keeping quality. Cooking made available to

0368–4466/96/ $ 5.00

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man a much more efficient and variable menu than the raw, essentially vegetarian diet of most primates. Thermal treatment of food for various purposes is one of the most widely used operations also in the modern food processing. Understanding thermal and functional properties of food components and ingredients, or monitoring changes induced by thermal effects are, therefore, objectives of eminent importance to both food research and food quality assurance. Thermal analysis is no longer only a research tool for analysts, but it offers a real-time monitoring techniques in studying process-induced changes for the food technologists.

Since thermal analytical methods are so numerous, the material at our disposal is so diverse and it covers such a large area, it has been deemed necessary to concentrate in this review essentially on differential scanning calorimetry, which is perhaps the most widely used thermal analytical technique for studies of foods and food-related subjects. Even in this case, only a limited number of selected topics can be mentioned to illustrate application of DSC in food research and food quality assurance, partly by surveying the literature, partly from our own laboratory. Please note also that this review is attempted by a food technologist and a food microbiologist, not by specialist experts in thermal analysis, and as such, it reflects inevitably a subjectively biassed and superficial understanding of a complex field. The interest of specialists in the present subject is illustrated e.g. by a 1994 special issue of Thermochimica Acta which has been devoted to applications of calorimetry and thermal analysis to food systems and processes [1]. The advantage of scanning calorimetry is that it provides a direct estimate of the overall enthalpy change of transitions without requiring knowledge of the thermodynamic mechanism [2]. An additional advantage is that sample preparation required is minimal and, for instance, permits examination of intact muscle tissue or insoluble plant proteins. In terms of food processing, DSC can be used to simulate specific heat processing conditions encountered in a food system and to examine their effects on it [3–5]. At the same time, DSC may serve as a quality control technique to ensure that excessive processing conditions are not incurred.

The most important applications of DSC in examination of food components, foods, and food ingredients includes studies on protein stability and denaturation, phase transition of aqueous starch systems, thermal gelation of some other polysaccharides, phase behaviour of frozen carbohydrate systems, characterization of glass transition and cryostabilization of food, melting points and degree of crystallinity of lipids, and their testing for oxidative stability.

With appropriate constructional modifications, DSC seems to be a reliable, precise and relatively rapid technique for determining thermal conductivity of foods [6].

Protein thermal stability and denaturation

Proteins are perhaps the most studied food components and the use of calorimetry for measurements of protein thermal stability is of particular technol-

ogical value. Their study includes conformation changes as affected by various factors, thermal denaturation of tissue proteins, food enzymes and enzyme preparations for the food industry as well as effects of various additives on their thermal properties. In many areas of food technology, thermodynamic treatment of data may be quite irrelevant and concentrations that are much higher than that which allows aggregation are of interest [7].

Protein networks provide structural integrity to manyfold products. The nature of the network formed with a given protein depends on the balance between protein–protein and protein–solvent interactions. Protein network formation involves protein unfolding, i.e. protein denaturation, followed by soluble aggregate formation, then interaction of the aggregates into networks [8]. The use of heat to denature proteins is a common technique for forming networks with food proteins. In this regard, DSC is a powerful technique for protein stability study allowing both dilute and concentrated systems to be studied [7]. Thermal stability of several proteins of interest to the food industry were investigated indeed by DSC as affected by various environmental factors. Studies on egg proteins such as ovalbumin [8, 9], conalbumin [10] and lyzozyme [11], milk proteins such as beta-lactoglobulin [12–14], α-lactalbumin [15, 16] and casein, as well as muscle proteins such as myosin and actin [17, 18] and plant proteins such as vicilin from faba beans [8] and rapeseed storage protein [19], and globulins isolated from various cereal grains [20] can be mentioned.

The most important factors influencing protein denaturation in aqueous systems such as foods are *pH* effects, salt effects, sugars, metal ions with specific binding properties, anionic detergents, charge modification agents, and the moisture content.

The effect of *pH* on thermal properties of food proteins have been well documented. Maximum stability is observed generally between *pH* 5 and 8 while extremes of *pH*, in either the acid or alkaline region resulted in decreased denaturation temperatures and apparently smaller endotherms [21, 22]. The thermal stability of myosin filaments showed remarkable sensitivities to changes of *pH* and ionic strength [23, 24]. Under specific conditions of protein extraction, the apparent enthalpy (ΔH) can be used to estimate the proportion of protein in an isolate that is not denatured. However, it must be kept in mind that for proteins the observed ΔH value combines both an endothermic and an exothermic contribution. With wheat vital gluten, for instance, extremely small or no denaturation peaks were obtained with DSC analysis between 30 and 130°C, which may be due to a balance in the endothermic and exothermic events or a lack of cooperativity in the unfolding process [25, 26].

The importance of *pH* effects is particularly relevant in the production of protein concentrates and isolates. Here DSC provides a valuable tool for quality control purposes, and problems associated with poor *pH* control can be readily detected.

Barone and co-workers developed recently a thermodynamic model for thermal unfolding of small globular proteins that is able to characterize the dependence of the excess heat capacity function observable by DSC measurements from both the temperature and *pH* [27].

Effects of salts used in food products on thermal stability and functionality of proteins may be considerable. Major meat proteins as myosin and actin are sensitive to small changes in salt concentration, although for actin conflicting results have been reported [28, 29]. The significance of this salt dependency, particularly for actin, becomes apparent when preparing processed meat products such as sausages [30]. The effect of salt in reducing Td values is important to proper coagulation in cooked sausages. Since the use of salt has the opposite effect on milk or plant proteins [31, 32], when substituting muscle protein with plant protein, the required cooking temperature (i.e. the Td values as determined with DSC) should be checked carefully if these proteins are to make any contribution to the texture of the processed meat product.

Other food components which can affect protein thermal properties and thus the function of the protein during processing are the sugars. DSC data for both purified globular proteins as well as the mixed system of egg white showed an increase in Td values in presence of glucose or sucrose [33, 34]. The extent of stabilization varies both with the different sugars and proteins. The technological significance of this increased thermal stability depends on the desired use of the protein [3].

DSC studies have shown that protein-metal ion interactions, particularly the iron and aluminium complexes, markedly increase the thermal stability of conalbumin, the most heat sensitive protein of egg white [33]. Therefore, aluminium salt addition has been recognized to be beneficial in heat pasteurization of liquid egg, where heat sensitivity of conalbumin is a problem.

The introduction of DSC improved greatly also the understanding of protein-detergent interactions, using an anionic detergent such as sodium dodecyl sulfate [3, 10] and helped to clarify the utility of naturally occurring substances such as fatty acids to either stabilize or denature a protein.

The heat denaturation temperatures of proteins in solution are usually below 100°C. However, proteins become stable toward heat when the water content is low. The presence of water is of key importance to the denaturing effects. There is a moisture level below which an inverse relationship exists between denaturation temperature and moisture content [35, 36]. This critical moisture content varies with the protein. The denaturation temperatures increase when the moisture available includes only that which is associated with the proteins' hydration [35]. This increased stability and the general resistance to denaturation at low moisture content have significant implications in food processing, for instance, in drying [3].

Heat treatment of food proteins at temperatures higher than 100°C and at low water content occurs in processes such as roasting, frying, and extrusion cook-

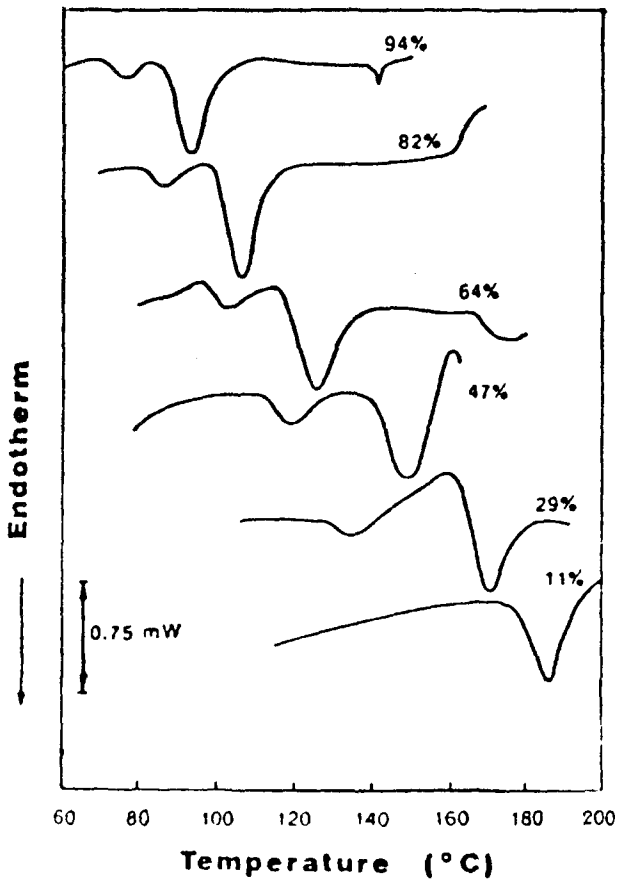

Fig. 1 DSC curves of a soy-protein isolate at various water contents [37]

ing. For example, extrusion cooking of soy-bean protein is used to produce 'textured vegetable protein', which gives a meat-like texture after it is rehydrated. To produce such textured vegetable protein, soybean protein containing 15–40% water is cooked at high temperature for a short time in an extruder. The heating temperature is about 140 to 150°C. Figure 1 shows DSC curves obtained by Japanese authors [37] for a soy-protein isolate at various water content. Their results showed that the temperature needed for texturization in an extruder was that of the denaturation of soybean protein, which depended on the water content.

One of the major advantages of DSC is the ability to follow the thermal denaturation of the complex protein mixtures in food systems. DSC curves are helpful in optimization of thermal processing conditions because processing and environmental effects can be measured and meaningfully interpreted. For both egg proteins [33] and meat proteins [23], the thermal behaviour of these mix-

tures represents a combination of the isolated proteins. Even a combination of proteins from different sources, such as addition of egg white or whey protein to minced fish gives a thermal behaviour resembling that of a composite of the individual protein sources [38]. This fact raised attention also to the use of DSC to estimate proportion of various meats in a specific meat product.

In other cases specific protein–protein associations can alter significantly the thermal behaviour of proteins, elicitating a stabilizing or destabilizing influence [3].

DSC of e.g. meats or egg white show multi-peak transitions as can be illustrated by the DSC curves taken by a SETARAM microDSC equipment in our laboratory (Fig. 2). In the DSC curve of minced pork meat, the melting of lipids under 40°C separates well from the denaturation endotherms of major meat proteins found between 50 and 80°C. It is known from the literature [39] that the first zone of transition around 55°C is due to denaturation of myosin subunits which is overlapped by several not well separated transition processes mainly related to denaturation of sarcoplasmic proteins, and connective tissue, particularly collagen. The endotherm with a peak temperature of about 76°C is largely due to denaturation of various forms of actin. Related studies [40, 41] revealed that tenderness and juiciness of cooked meat correlate with differences of the DSC protein denaturation pattern and explained, why normal meat should be cooked at approx. 65°C (not greater than 70°C) whereas the so-called DFD (dark-firm-dry) meat, in relation to its higher *pH*, should be cooked at 80–85°C.

Considering the concentrated and complex nature of these proteinaceous foods, one should bear in mind that DSC only measures net changes between

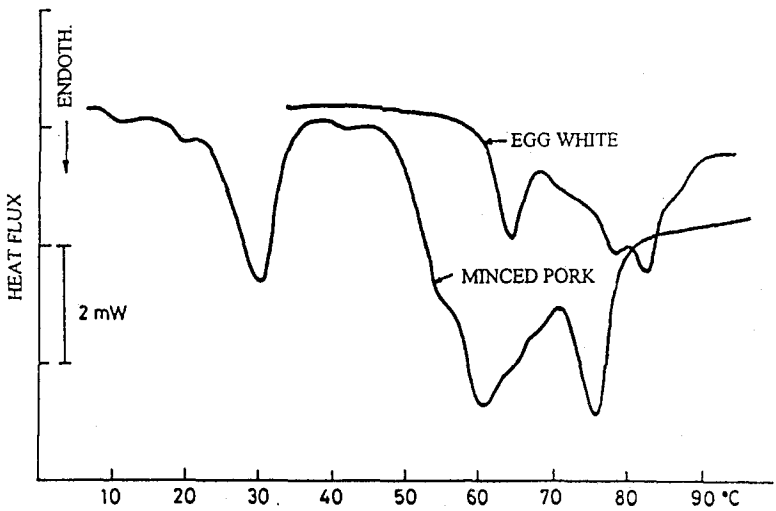

Fig. 2 Microcalorimetric curves of minced pork meat and egg white

endotherms caused by denaturation and the exothermic process of aggregation and more than one change are progressing simultaneously. Re-scanning of these curves showed no transitions in the range of protein-changes, demonstrating that their denaturation was irreversible. In the DSC curve of egg white the 63°C peak is due to conalbumin, the approx. 82°C peak is mainly the transition of ovalbumin, while the overlapped transitions in the intermediate temperature range may be related to transitions of e.g. lyzozyme, and the ovomucoid [33, 39].

Using DSC, Donovan and Mapes have reported already in 1976 [42] that upon storage at 22°C or higher the ovalbumin slowly changed to an even more thermostable form, called 'S-ovalbumin'. On this basis, Canadian authors developed recently a sensitive DSC-method to detect the presence of incubator reject eggs in egg white products (Fig. 3) [43].

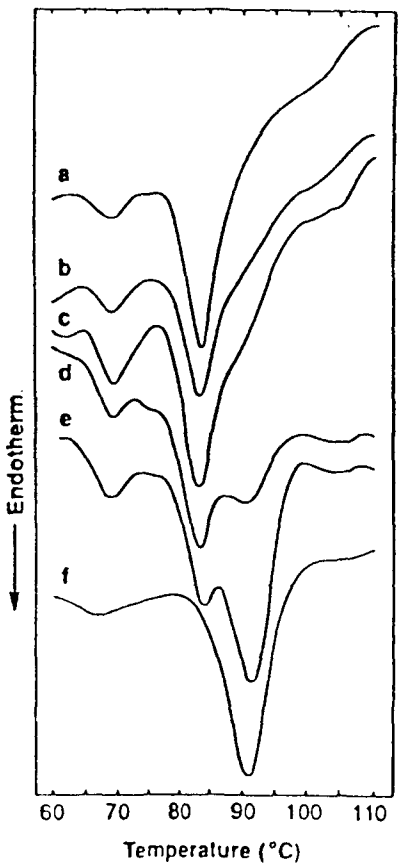

Fig. 3 DSC curves of mixtures of egg white (EW) from fresh and incubator reject (IR) eggs. a. 100% fresh EW; b. 93% fresh+7% fertile dead IR; c. 88% fresh+12% infertile IR; d. 75% fresh+25% infertile IR; e. 50% fresh+50% infertile IR; f. 100% infertile IR [43]

Figure 4 illustrates our investigations with chicken breast and thigh meat. The thigh muscle shows similar protein transition temperatures as the pork meat, while the breast muscle resulted in a broader temperature range of transitions. The characteristic differences between the thermograms of breast and thigh muscles [44–46] may be due to differences in their *pH* and contraction state [47], as well as to different ratio of red to white muscle fibres within the muscle.

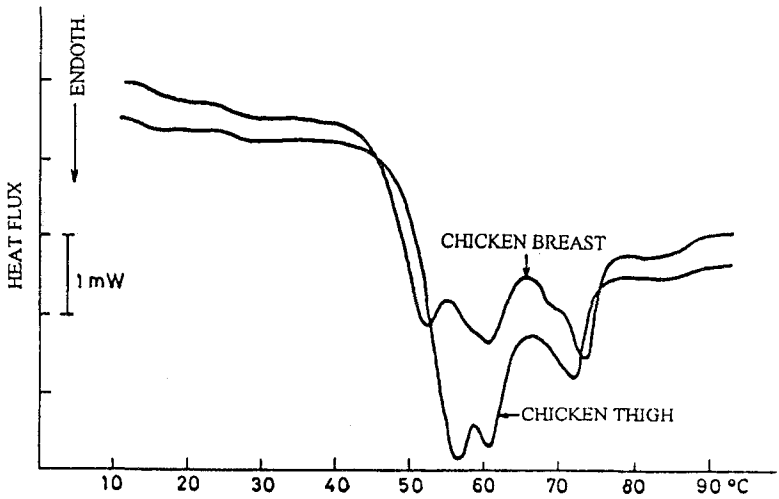

Fig. 4 Microcalorimetric curves of chicken breast and thigh meats

It should be mentioned also that thermal properties of proteins may be different, if they are studied in isolation than those which are measured *in situ* [39].

Regarding effect of additives on the so-called water-binding capacity and thermal properties of pork muscle tissue, the effects of addition of curing salt and sodium pyrophosphate on a meat paste from lean leg of pork have been investigated in an other study in our Department [48]. Figure 5 shows that addition of 2% curing salt (i.e. increasing the ionic strength) reduced both the heat denaturation temperatures of the muscle proteins and the enthalpy of the transitions. The 0.3% pyrophosphate added increased somewhat the heat stability, particularly that of the most heat-sensitive component, also in samples with increased ionic strength. Similar effects of chlorides and phosphates were reported by several authors for other meats [30, 45, 46].

In relation to the utilization of pork rind in meat products, the effect of various skin processing techniques has been compared by microcalorimetry in our laboratory [49] by assessing among others the denaturation of its collagen.

Freezing, although it is a quality-friendly food preservation technology, may alter protein conformation and thermal properties. Using DSC, it has been shown for egg white that after freezing the enthalpy of heat denaturation was re-

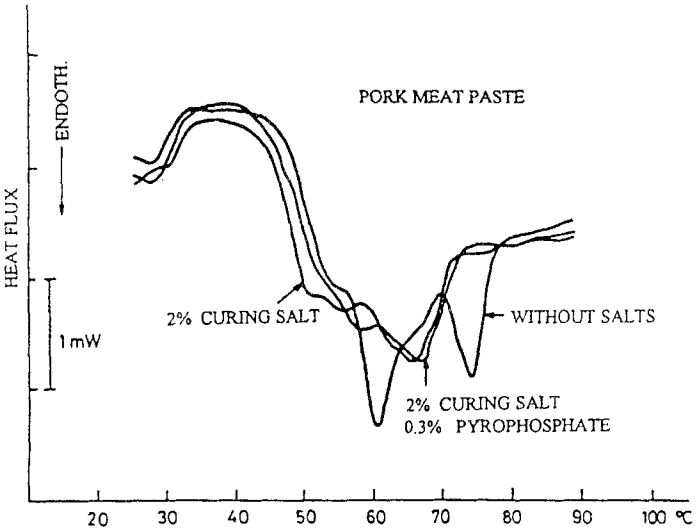

Fig. 5 Effect of addition of 2% curing salt and/or 0.3% sodium-pyrophosphate on microcalorimetric thermal stability of pork muscle tissue [48]

duced, however, no changes in the denaturation temperatures were observed [50]. The susceptibility to freeze denaturation, which may impact technological properties, is a function of the protein [3]. Thus, investigation of thermal properties of food products by DSC may provide a technique for monitoring conformational changes that can occur even during storage, particularly, if environmental factors are not carefully controlled.

Microcalorimetric DSC technique was also used in our laboratory to investigate the effect of frozen storage or the thermal stability of pork muscle tissue [51, 52]. Figure 6 illustrates that 6 months of frozen storage at –20°C reduced the enthalpy of thermal transitions, i.e. some denaturation took place [51, 52]. It appears that the heat sensitive protein components are somewhat more sensitive also to frozen storage than the actin [53–55]. Cryoprotectants such as a sucrose:sorbitol mixture – due to a protein-carbohydrate/polyol interaction – retarded the denaturation process during the frozen storage and probably increased somewhat the denaturation temperature during heating, as has been reported also for egg white proteins [39].

Thermal behaviour of carbohydrates, phase transitions of polysaccharides

Regarding DSC of food carbohydrates, calorimetric methods have frequently applied e.g. to characterize the thermal behaviour of different sugars when heated or cooled, and to the study of phase transitions which aqueous suspensions of granular starch and some other polysaccharides undergo on heating in

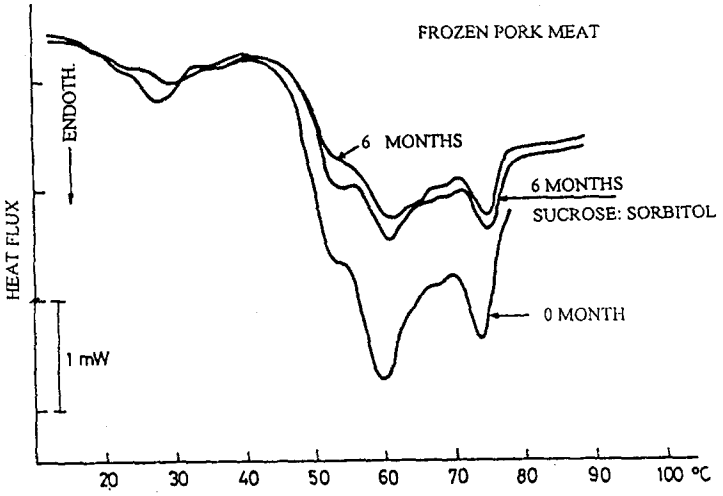

Fig. 6 Microcalorimetric curves (scanning rate 1.0°C per min) of frozen pork meat (pH=5.95) as affected by a 6-month storage at −20°C in presence or absence of 5% of sucrose:sorbitol (1:1) mixture during storage [51]

both pure and complex food systems [56, 57]. Figure 7 shows typical gelation thermograms of a few starches studied by us. Starch gelatinization behaviour in flours after hydration was found to be related to starch damage and flour protein content [58]. Also the proportion of starch/water greatly influences the temperature characteristics and the peak multiplicity [59] of the thermogram. With added solutes such as sucrose and sodium chloride, the increase of starch gelat-

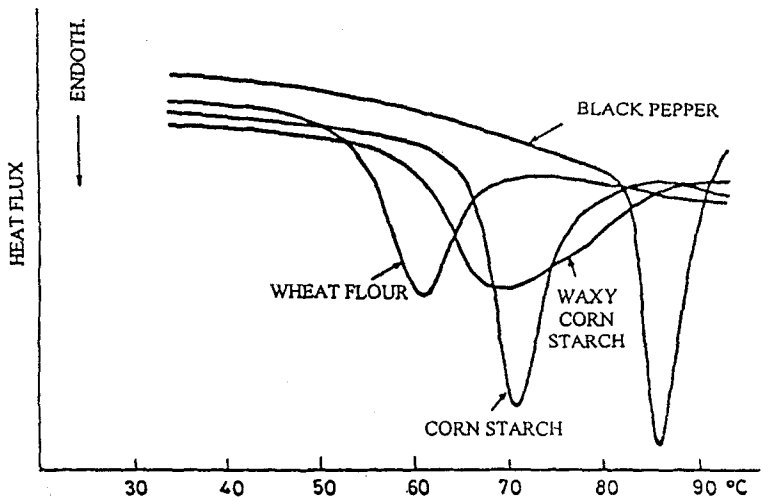

Fig. 7 Heat gelatinization curves of aqueous suspensions of various starches and starchy flours

inization temperature correlates with the decrease of water mobility [60]. High pressure DSC studies indicated that enthalpy levels much higher than those in high-moisture gelation are needed to attain proper gelatinization and plastification of starch at low water contents [61]. DSC of starch gelatinization revealed also that the so-called 'hard-to-cook' textural defect of legume seeds developing during storage at high temperature and humidity is related to starch alterations [62].

Calorimetric studies have been applied to investigate e.g. recrystallization of starch [63] as a part of the retrogradation on aging of starch gels [64], which is important to the texture of some foods, for example in staling of bread [65], as well as to characterize starch-lipid interactions [66, 67]. Evidence summarized by a recent review [68] demonstrates that glass- and melting transitions (of evident importance in baking processes) [69], take place when aqueous starch systems are heated and that water influences the temperature of these events. None of these topics – although important for many food technologies – nor a deeper discussion of starch gelatinization in a perspective of polymer science can be dealt with in this brief and superficial presentation.

Thermal properties of frozen foods

Low temperature DSC, involving also derivative thermograms, is well suited to study systems representing frozen food products [70] and insights gained by appreciation of the similarities between synthetic amorphous polymers and glass-forming aqueous systems, here with regard to low temperature thermal properties [71]. This technique and other thermoanalytical techniques provide invaluable tools for evaluating food ingredients for cryostabilization technology, with the glass transition as a key process [72–75] and for optimizing product formulations and technologies from points of view of chemical and textural stability of frozen food systems.

DSC of lipids

DSC is a suitable technique for investigating the melting and crystallization of lipids [76–78], for qualitative determination of the glyceride composition of oils and fats [79], and for identification or detecting their adulteration [80]. Melting curves of sunflower, linseed, olive and grape oils are shown from a paper of Kaisersberger [81] (Fig. 8). Because of the overlapping melting ranges of the different components in natural fats, and because of their polymorphism, determination of single components of a fat mixture is not possible from DSC melting curves [81]. With an appropriate cooling accessory, DSC is a rapid method for evaluating water-in-oil emulsions based on showing the freezing point depression of water present. It provides information also about emulsion

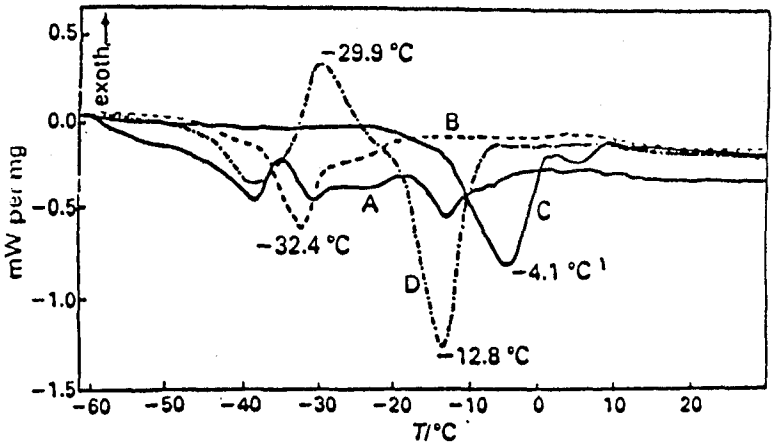

Fig. 8 DSC melting curves of sunflower (A), linseed (B), olive (C) and grape (D) oils [81]

stability, indicating the existence or absence of droplet size homogeneity through the pattern of the cooling curve.

DSC data were used to calculate the kinetic parameter and activation energy of the thermal oxidative decomposition of edible oils and fats [82]. The high sensitivity for oxidation of unsaturated fatty acids is reflected in the onset of oxidation exotherms of sunflower oil at a relatively low temperature as compared to that of hardened coconut fat (Fig. 9) [81].

DSC techniques in food microbiology

DSC techniques are increasingly used also in applied and basic research in relation to general and food microbiology.

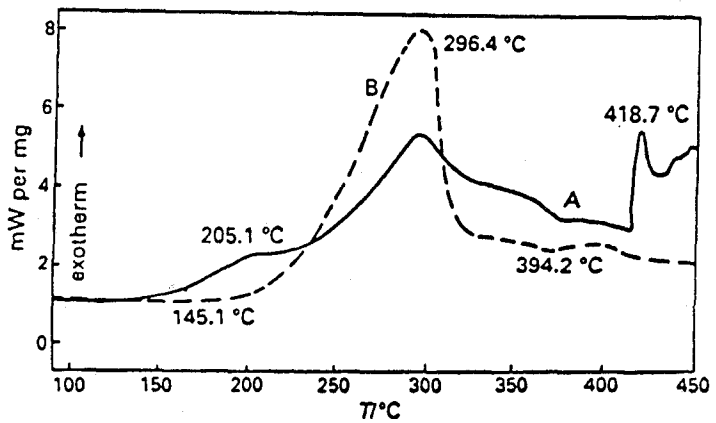

Fig. 9 Oxidation curves of sunflower oil (A) and hardened coconut fat (B) in a DSC test in a static air atmosphere [81]

Studying membrane fluidity by DSC of thermophilic bacteria in association with growth-temperature related changes in lipid composition and Ca^{2+} effects [3] helps to understand thermoadaptive mechanisms of these important micro-organisms.

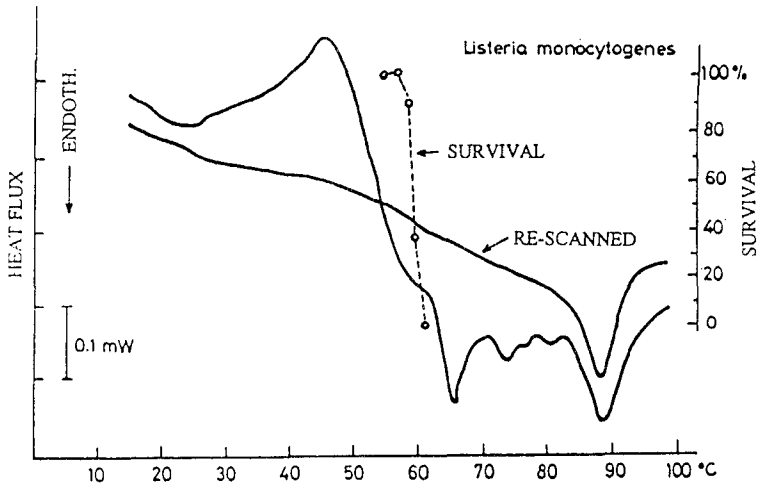

Fig. 10 Microcalorimetric DSC transitions of whole cells of *Listeria monocytogenes* suspended in a phosphate buffer, in comparison with the lowest temperature range of loss of viability during heating at the same heating rate (0.5°C min^{-1}) as in the DSC test

Several studies demonstrate the applicability of DSC for resolving transitions in whole cells in relation to thermostability of cellular constituents. The observed tansitions represent lipid melting, protein unfolding and melting of nucleic acids. This type of works helps to identify the crucial target of heat killing of bacteria, and to understand the mechanism of the heat destruction of micro-organisms, which is eminently important for heat preservation of food [84–87]. Figure 10 illustrates from our studies DSC transitions of whole cells of *Listeria monocytogenes* suspended in a phosphate buffer solution, in comparison of the lowest temperature range of heat inactivation of the bacterium [88]. The exothermic heat flow observed from approx. 25°C onward is assumed to be related to oxidative metabolism of the cells in the vital temperature range. The series of endothermic transitions began to appear within the temperature range, where the loss of viability occurred. According to previous literature [89] the reversible transition near to 90°C was the 'melting' process of the intracellular DNA. There is some evidence that the first irreversible denaturation event and the loss of viability are associated with melting of one of the ribosomal subunits [85, 90].

DSC studies of Canadian authors [91] showed excellent correlation between the onset of protein denaturation and maximum growth temperature for various species of the *Bacillus* genus.

A correlation found between the melting temperature of intracellular DNA, determined by DSC of whole bacteria, and its guanine+cytosine content [92] might provide a simple means facilitating quicker bacterial classification and identification.

Applications of calorimetry in applied microbiology started perhaps with investigating heat production of microbial cultures in various substrates [93–95]. Microcalorimetry was suggested as a rapid method for estimation of bacterial levels in food [96] and for thermal detection of spoilage in canned foods [97]. The next Figure (Fig. 11) illustrates from our laboratory changes of heat flow recorded during isothermic incubation of *Streptococcus bovis* and *Bacillus cereus* cultures, respectively.

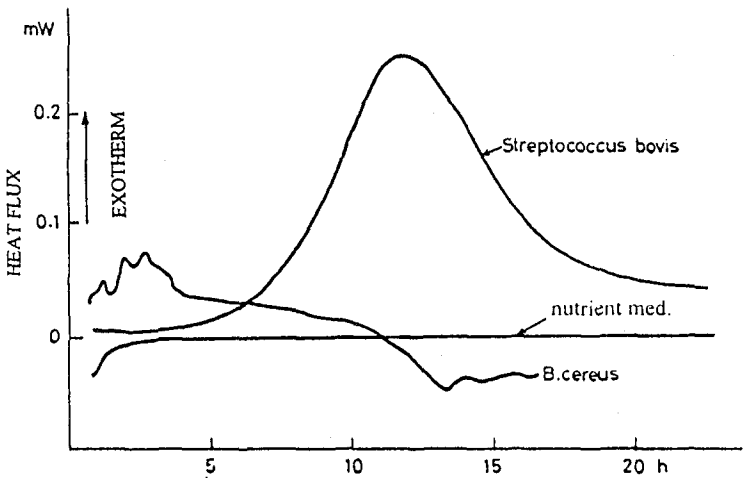

Fig. 11 Heat-flow changes in cultures of *Streptococcus bovis* and *Bacillus cereus* recorded by a SETARAM micro-DSC equipment during isothermic incubation at 35°C in batch vessels

Microcalorimetry of microbial growth in various media provides informative data regarding microbial metabolism and may assist identification or differentiation of taxonomic entities [98–100]. Thermograms obtained by modern thermal bioactivity monitors allows calculation of growth and activation energy parameters [101, 102]. Microbial, biotechnological, or in general: biological calorimetry is a vast area in itself which several conferences have been devoted already by the International Society of Biological Calorimetry.

Limitations and prospects

Finally, a few words on limitations. One factor of particular significance in studying heat treatments by DSC is the effect of heating rate on the apparent transition temperature values, whether it is related to thermal lag associated

with instrumentation, to the effect of heating rate on the resolution or to the kinetics of the transition [33, 103]. Therefore, it is important to use exact processing conditions for thermal analysis both in quality control and examining heat processing effects.

Interpretation of thermal response curves of foods or biomasses is quite difficult. However, it is hoped that the use of computerized deconvolution of thermograms may aid understanding the individual contribution of components. The use of 'stepwise' differential scanning calorimetry approach might enhance sensitivity or resolution in the thermal analysis of these items [104].

For many food systems the complexicity of processes and changes requires additional techniques and complementary physicochemical information to interpret the DSC data [105], or to increase the information value of the thermal analysis. Nevertheless, it is hoped that even this humble review confirmed, how valuable assistance is offered by DSC both for food research and food quality assurance.

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