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Flour starch thermal characteristics

Modulated scanning calorimetric study

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Abstract Thermal characteristics of refined wheat flour blend made with 90% Ohio soft red winter wheat and 10% Canadian Hard Red Winter Wheat are explored using a series of modulated differential scanning calorimeter conditions. Influences of pan type, period, amplitude of the thermal modulation, and underlying thermal heating rate on flour starch thermal transitions are presented. Wheat flour was blend 1:1 with water, and then heated at various heating rates while the amplitude and period of the instantaneous heating rate was modulated between ±0.5 and ±1.0 °C amplitude and 60 s to 80 s period. Study shows faster heating rates favor increased total heat flow and results in proportional increases in both reversing and non-reversing thermokinetic events of recrystallization. Slower overall heating rates (e.g., 2.5 °C min^{-1}) produced better resolution of thermal events related to preexisting structural phases, but allowed more time for creation of new events such as recrystallization, annealing.

Keywords Flour · Starch · Modulated · Calorimetry · Thermal transition · Reversing · Nonreversing

Introduction

Water is an efficient plasticizer of the amorphous regions of starch. This behavior causes changes in the functional properties of food materials during processing and affects final product attributes [1]. The main source of starch in biscuit product is flour. Soft wheat flour is comprised of 74% starch, 9% protein, 2.5% fat, 0.5% ash, and 14% moisture.

The heat capacity of a starch–water system above the glass transition does not reach the expected value derived from glucose at similar moisture which suggests that there are, yet unidentified, molecular motions responsible [2]. The crystalline regions may be metastable because of internal defects. Amorphous regions in native starch may have strain induced by the organization of the crystallites. The various processes of change (annealing, reorganization, retrogradation) are driven by the higher energy metastable state seeking lower energy equilibrium state.

Previous studies have found the least interactive effects of phase changes and period and scan rates by the combination of [40 s period] and overall heating rate of 4–8 °C min^{-1}. Increase periods from 40 s to 80 s, no change in H_{total}, incr H_{rev} and decr H_{nrev}. The longer the time of modulation, the greater the portion of reversing heat flow within total heat flow [3–5].

MDSC has been used effectively to measure annealing of amylose to enzyme resistant thermostable crystals and the effects of sugars on gelatinization [6, 7]. However, there are parameters which must be considered when using MDSC. The frequency of modulation can increase to a point where the bulk sample temperature either lags or cannot follow the temperature cycle which affects the measurement of the kinetic processes and leads to potential artifacts which are caused by inappropriate deconvolution of the data.

Sufficient modulation cycles are required, and slow average heating rates may be necessary in order to obtain a minimum of 4 to 5 modulation cycles over the critical region of a transition. The lower average heating rate

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increases the time of an MDSC® experiment by a factor of 5 to 10 over traditional DSC [8, 9]. Ideally, the temperature modulation could be fast, on the order of 5 to 10 s, which would permit a heating rate of about 20 °C min^{-1} for a transition that is 10 °C wide. The problem is that most samples cannot follow such a fast modulation due to a number of thermal resistances within the sample, pan and sensor.

A practical way of determining the effect of these resistances on the measurement is to perform an MDSC® experiment at room temperature on the sample to be analyzed.

Modulated DSC-Tzero

Heat capacity = Amplitude of modulated heat flow/amplitude of modulated heating rate

$$Q_s = T_s - T_{ps}/R_p$$

$$T_{ps} = T_s - Q_s \times R_p$$

where Q_s is the sample heat flow, T_s is the sample sensor temperature, T_{ps} is the sample pan temperature, and R_p is the contact resistance between sample pan and sensor. Contact resistance between the pan and sensor incorporates factors for heat conduction through the sensor and pan where they contact one another and conduction through the gas layer between the pan and sensor. Component thermal resistances depend on pan material and a "geometric factor" [8, 9].

Material and sample preparation

Wheat flour (blend of HRW and SRW), was obtained from Toledo Flour Mill. Starch pastes (50% w/w) were prepared by mixing 1 g of starch or flour with 1 g of pure water.

A 25–35 mg sample of starch paste was transferred to a pre-weighed Perkin Elmer stainless steel O-ring pan and weighed accurately. At 50% (w/w) starch solids, starch forms a uniform paste that readily flattens, with gentle pressure, into the DSC pan, maximizing thermal contact. Sample mass of 25–35 mg were needed to observe the small amylopectin crystalline transition for wheat starch in flour. "As is" mass of flour (13.5% moisture) was used to calculate peak areas. An empty pan of matching mass was used as a reference.

MDSC method

Thermal glass transition and crystalline melting of amylopectin and amylolipid complex were measured using TA Instrument Q1000 Modulated Differential Scanning Calorimeter (software V4.3A) equipped with MCA (mechanical cooling accessory) refrigeration unit.

Melting point and enthalpy for indium (m.p. 156.6 °C, $\Delta H = 28.55$ J g^{-1}) were used for temperature and cell constant (1.56) calibration. Instrument was separately calibrated for each pan type. MDSC cell was purged with N2 gas at 50 ml/min and refrigeration unit was purged with nitrogen gas at 50 ml/min. Overall heating rates from 2.5 to 10 °C min^{-1} were used.

Superimposed on the linear heating rate was a 40, 60, or 80 s oscillating, sinusoidal heating amplitude, which in the heat-only method varied from ±0.3 °C to ±0.5 °C. Instrument calibration was checked for heat capacity with a 40.19 mg sapphire disc.

Results

Total and reversing heat capacity for a sapphire disc, no pan, was measured using either a 40, 60, or 80 s period for overall heating rate of 5 °C min^{-1} and 10 °C min^{-1}. The total range in heat capacity values measured under these condition varied by ~1% for the total C_p and 5% for the reversing C_p signals. Apparent heat capacity is not very dependent on period change or heating rate in the absence of other resistances (i.e., pan). Results are shown in Fig. 1.

Sapphire sample is placed in either an aluminum pan or a stainless steel (SS) O-ring pan and heat capacity is measured at either 40 or 80 s period at an overall heating rate of 5 °C min^{-1}. The influence of pan type on the measured heat capacity of sapphire is shown in Fig. 2 and results are tabulated in Table 1. Table 1 shows the measured heat capacity, total and reversing, for sapphire disc alone or contained in either an aluminum pan or a SS O-ring pan. Results for total heat capacity of sapphire in an SS O-ring pan ranged from 0.7491 to 0.7724 J g^{-1} $°C^{-1}$ depending upon the modulation period. The reversing heat capacity demonstrated an even wider range of values, 0.8609 and 0.5022 J g^{-1} $°C^{-1}$, for 80 and 40 s modulation, respectively. The results for heat capacity of sapphire obtained with the aluminum pan were very similar to the sapphire disc, no pan.

Introduction of resistances due to pan and pan type, especially samples undergoing fast modulation, may have difficulty following the temperature cycle due to a number of thermal resistances within the sample, pan and sensor. Resistance of SS O-ring pan compared to aluminum make a difference especially at the shorter modulation periods.

Flour is mixed with water to plasticize the amorphous regions of the flour starch. A great deal of steam pressure is generated when sample is heated. The hermetically sealed aluminum pans were prone to leaks, as shown in Fig. 3,

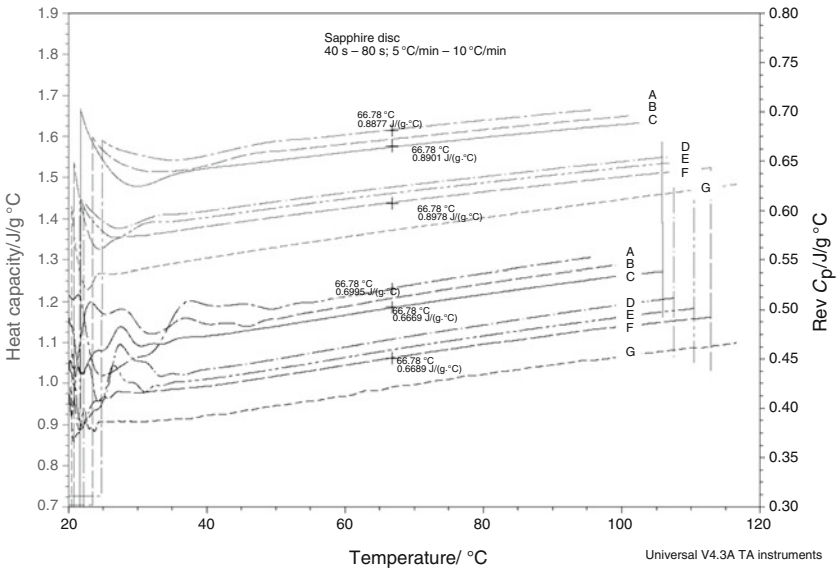

Fig. 1 Heat capacity measurement: sapphire discs total heat capacity of sapphire disc—*gray*; reversing heat capacity—*black*: *A* 80 s period, 10 °C/min; *B* 60 s period, 10 °C/min; *C* 40 s period, 10 °C/min; *D* 80 s period, 5 °C/min; *E* 60 s period, 5 °C/min; *F* 40 s period, 5 °C/min; *G* 80 s period, 2.5 °C/min

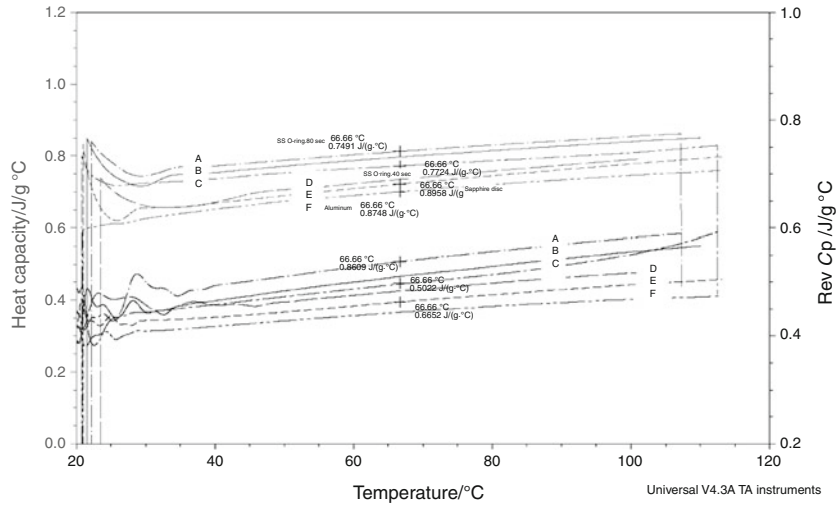

Fig. 2 Heat capacity of sapphire: aluminum pan versus SS O-ring pan total heat capacity—*gray*; reversing heat capacity—*black*: *A* 80 s period, 5 °C/min, SS O-ring pan; *B* 60 s period, 5 °C/min, SS O-ring pan; *C* 40 s period, 5 °C/min, SS O-ring pan; *D* 80 s period, 5 °C/min, aluminum pan; *E* 40 s period, 5 °C/min, aluminum pan; *F* 40 s period, 5 °C/min, sapphire disc

Table 1 Heat capacity of sapphire

Pan type	Period (s)	Heating rate/°C min^{-1}	Tot C_p/J g^{-1} $°C^{-1}$	Rev C_p/J g^{-1} $°C^{-1}$
None	40	10	0.8877	0.6975
None	80	10	0.8901	0.6669
None	80	5	0.8978	0.6689
SS O-ring	80	5	0.7491	0.8609
SS O-ring	40	5	0.7724	0.5022
Aluminum	40	5	0.8748	0.6652

when used with food samples containing significant moisture due to volatilization of moisture and pressure build up in the pan. However, with pans that can be reliably sealed, modulated differential scanning calorimetry provides a powerful resolution enhancement to standard DSC, however, optimal MDSC conditions for the sample must be chosen. The study of crystalline phase transitions in a partially crystalline food polymer such as starch is difficult due to numerous small transitions representing the various components (e.g.. amorphous, crystalline regions of amylopectin; crystalline amylolipid complex). Figure 4 shows three discrete transitions, 63, 80, and 107 °C corresponding to amorphous glass transition, amylopectin and amylolipid crystalline melt.

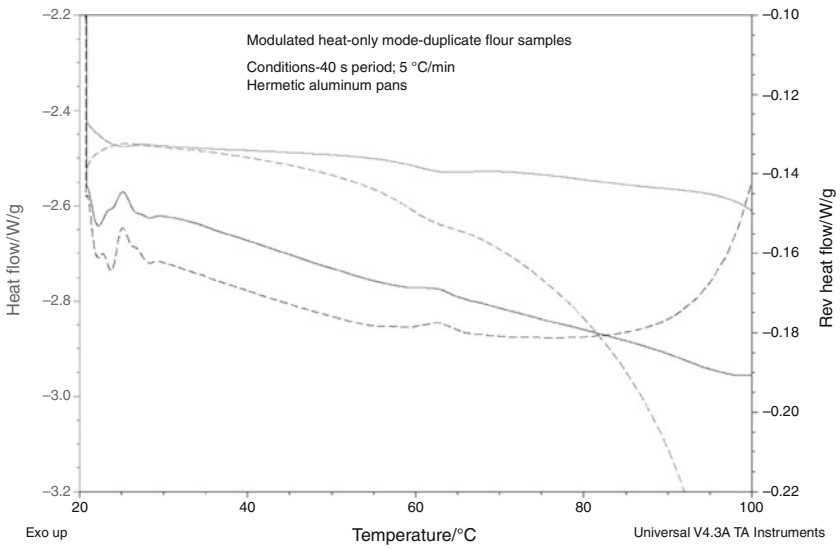

Fig. 3 Flour is mixed with water to plasticize the amorphous regions of the flour starch

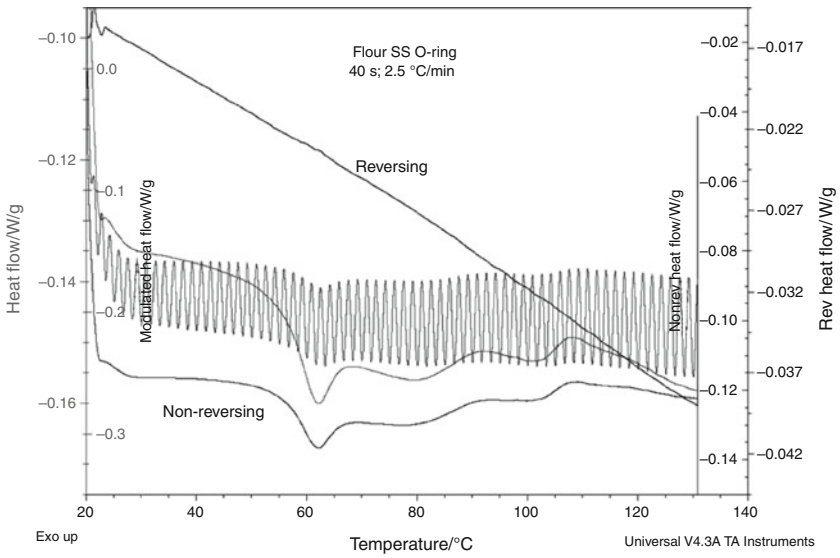

Fig. 4 Thermal transition of flour starch plasticized with excess water. MDSC conditions: 40 s modulation, heat-only, 2.5 °C/min overall heating rate

The effect of heating rate on flour starch is shown in Fig. 4. A 40 s modulation period was chosen so that at the maximum overall heating rate of 10 °C min^{-1} a sufficient number of modulations are obtained. Amplitude was automatically selected by the software for heat-only conditions for each heating rate. Both the reversing and the non-reversing signal increase as the overall heating rate increases from 2.5 to 10 °C min^{-1}. For both signals, one major endotherm is observed at ~70 °C and at least one smaller endotherm at 75 to 85 °C is observed.

The effect of shorter modulation periods at 2.5, 5, and 10 °C min^{-1} heating rates are shown in Fig. 5. Modulation periods used provided for sufficient number of oscillations over the thermal transition event. The results are shown in Fig. 5. Conditions of slow heating (2.5 °C min^{-1}) and long periods (80 s) had smaller signals, making it hard to detect transitions. However, there appeared to be less "noise". Modulations of 15 to 20 s at either 5 or 10 °C min^{-1} heating rate seemed to produce numerous endo and exotherms (Fig. 6).

Discussion

Thermal transitions of flour starch

Polymer "change" processes have been defined as annealing (heating to temperatures below the melting point), reorganization (crystal improvement at crystallization temperature), and recrystallization (melting and recrystallization) [10]. Softening and swelling of the amorphous regions of starch is a necessary thermophysical change, allowing subsequent phase changes (e.g., crystalline melting).

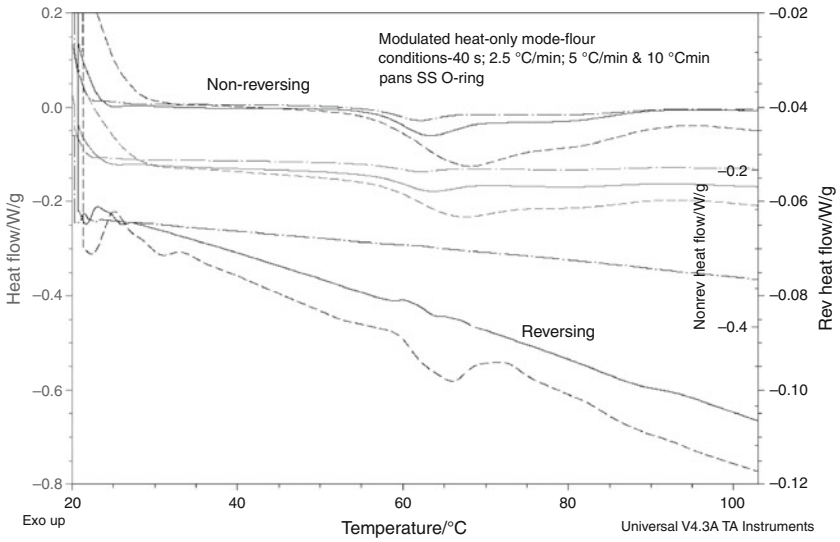

Fig. 5 Flour starch: effect of heating rate—40 s modulation period, heat-only. *Dash-dot lines* 2.5 °C/min, *solid lines* 5 °C/min, *dashed lines* 10 °C/min

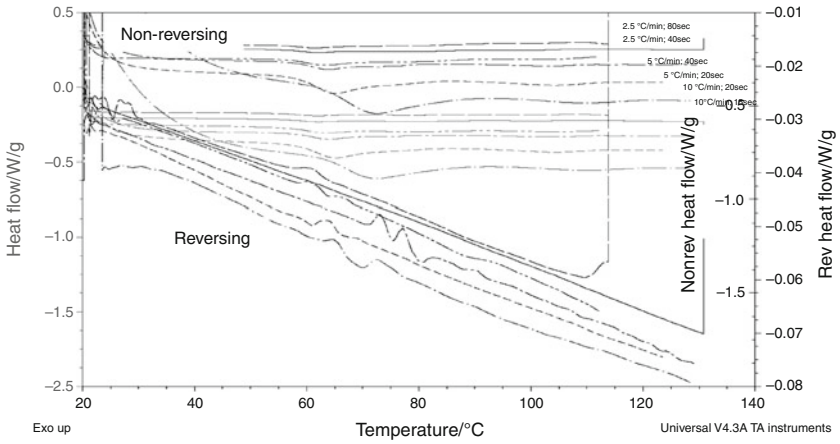

Fig. 6 Flour starch: effect of shorter periods: *long dashed line solid line* 40 s, 2.5 °C/min; *long and two short dashed line* 40 s, 5 °C/min; *long and one short dashed line* 20 s, 5 °C/min; *short dashed line* 20 s, 10 °C/min; *long dashed dotted line* 15 s, 10 °C/min

Constraints of the amorphous regions can prevent the melting of metastable crystals upon reaching the enthalpy of the supercooled melt. Crystals can act as cross-links to maintain strain. Then, upon partial melting the strain relaxes and melting accelerates. Without the release of strain, initial melting occurs at a higher temperature [10]. Crystallites which recrystallize upon cooling will have a lower melting temperature.

Flour starch: effect of heating rate

If annealing occurs during the temperature scan, slower heating rates will show higher melting temp. We see that higher heating rates lead to higher melting temperature as shown in Fig. 4. Faster heating rates, 10 °C min^{-1}, shift melting temp higher which implies a relaxation type transition during gelatinization. Faster heating rates do not allow as much time for the kinetic events such as chain folding (annealing) and amylolipid complex formation (crystallization).

Flour starch: effect of shorter periods

Shorter periods (15 and 20 s period at 5 and 10 °C min^{-1}) had more noise in reversing signal. Reversing exo and endotherms may result from the reversible glass transition, softening/swelling of amorphous regions (i.e., glass transition), and crystalline melt. Nonreversing exo and endotherms could be, respectively, linked to the formation of amylolipid starch complex or to enthalpic relaxation of molecular chains.

Conclusions

Modulated DSC is a powerful enhancement to regular DSC. Overall heating rate of 4 °C to 5 °C min^{-1} and 40 s period allowed sufficient resolution of the thermal glass transition of amorphous starch from the crystalline amylopectin melting peak of flour starch. In the case of wheat starch in flour, three thermal events could be resolved,

amorphous glass transition, crystalline amylopectin melt and crystalline amylolipid complex melt.

In order for the MDSC experiment to be effective, the entire sample must be capable of following the imposed temperature modulation. Using SS O-ring pans, the amplitude of ±0.3 °C per 40-s period at a heat rate of 5 °C min^{-1} resulted in a heat-only profile and appropriate number of oscillation. However, measurement of sapphire total C_p and C_{prev} provided values that were too high or too low compare to sapphire calibration standard and sapphire measured in aluminum pans.

Faster heating rates favor increased total heat flow and results in proportional increases in both reversing and non-reversing thermokinetic events of recrystallization. Faster heating rates do not allow time for the kinetic events such as chain folding and amylolipid complex formation, favoring a single reversing and non-reversing thermal events like crystalline melt and enthalpic relaxation.

A slower scan (e.g., 2.5 °C min^{-1}) produced better resolution of thermal events related to preexisting structural phases but allowed more time for creation of new events (recrystallization, annealing) that did not exist in the initial sample and would not typically occur during baking, especially for wheat starch at 50% w/w solids.

The oscillating, sinusoidal heating period for the selected overall linear heating rate, was maximized (e.g., 80 s per period) while still providing at least 4 to 6 oscillations per transition event. However, it was found that slowing the heating rate to increase the number of sinusoidal heating periods was undesirable because signal intensity decreased.

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