On the Multiple Melting Transitions of Starch/Monoglyceride Systems

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ABSTRACT

Thermal analysis of rice starch/1-monoglyceride mixtures at intermediate water content (50%) was carried out using Differential Scanning Calorimetry (DSC) and Thermo-Mechanical Analysis (TMA). The DSC thermal profiles revealed multiple melting characteristics for the amylose–monoglyceride complexes. A mechanism based on partial melting followed by recrystallization (exothermic effect) and remelting is invoked to explain such behavior. Crystallization of amylose–lipid complexes occurs during starch gelatinization with a rate that is determined by the molecular nucleation step. The latter is strongly dependent on the nature of the complexing ligand molecule. Monoglycerides of good amylose complexing ability rapidly induce metastable (small size and/or less perfected) crystallites in the melted polysaccharide matrix which are inclined to reorganization/ annealing on subsequent heating in the DSC. The overall thermal behavior of these systems is best rationalized by considering the interactions between solvent and polymer, the morphology of the semicrystalline structure, as well as the kinetic effects inherent with the dynamic character of the thermoanalytical techniques employed. Due to the irreversible/non-equilibrium melting of amylose-lipid complexes, complications can arise in attempting to analyze melting data by the polymer-diluent method (Flory–Huggins equation). The general features of the TMA volume expansion curves suggested that lipids can retard granule swelling at low temperatures.

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INTRODUCTION

Because of their ability to monitor heat-induced thermal events in polymeric materials, such as phase transitions and conformational or compositional changes, thermal analysis techniques have gained remarkable popularity in studying similar phenomena in foods and their constituents (Biliaderis, 1983; Wright, 1984). Among the various thermoanalytical techniques available, Differential Scanning Calorimetry (DSC) has attracted most interest in food-related research since it can provide both qualitative (transition temperatures, co-operativity of first order transitions) and quantitative (heat of transition, kinetic parameters) information.

Following the pioneering work of Stevens & Elton (1971), DSC has been frequently used to study the phase transitions which aqueous suspensions of starch undergo on heating. In this respect, by analogy with synthetic polymers, gelatinization has been viewed as a melting process of starch crystallites. A good deal has been learned about the effects of water content (Donovan, 1979; Biliaderis *et al.*, 1980; Eliasson, 1980; Burt & Russell, 1983), heat–moisture treatments (Donovan *et al.*, 1983; Maurice *et al.*, 1985) and the presence of various solutes or other constituents (Donovan, 1977; Wootton & Bamunuarachchi, 1979; Hoover & Hadziyev, 1981; Allen *et al.*, 1982; Ghiasi *et al.*, 1982; Eliasson, 1983*a,b*) on the thermal properties of starches. Of particular interest to most researchers have been the observations that starch gelatinization temperatures increase and that multiple melting transitions arise at intermediate to low (<50%) water levels. A few studies have given emphasis to the elevation of the melting temperatures due to the decreasing amounts of water by using fundamental relationships, such as the Flory–Huggins equation (Flory, 1953) that describe polymer–diluent interactions (Donovan, 1979; Biliaderis *et al.*, 1980; Burt & Russell, 1983). However, little effort (Stute & Konieczny-Janda, 1983) has been devoted to understanding the nature of the multiple transitions of heated starch–water systems.

In a previous series of papers it was demonstrated that the thermal behavior of granular starch (Biliaderis *et al.*, 1986), as well as crystalline amylose–lipid complexes (Biliaderis *et al.*, 1985) should be viewed in dynamic, rather than in purely static, terms. As such, the physical properties of these systems depend on the nature of the crystalline and amorphous domains and their response to environments (temperature, solvent, etc.) to which they are exposed. At any given temperature and solvent concentration, the structural elements are in a state of dynamic equilibrium, with the extent of molecular mobility being determined by the chain stiffness and the intermolecular forces (mainly hydrogen bonding) which stabilize the chain segments within the crystallites. As temperature is

increased, however, more thermal energy is added to the system and chain mobility increases. This may allow certain transformations (structural rearrangements) to take place, even within the time frame of the DSC experiment, until a temperature is reached where the overall structure is disrupted (melting). Thus, the temperature dependence of the semicrystal-line structure and properties of starch systems must always be taken into account if non-isothermal methods are employed for their characterization. In the present study we focus attention on the thermal behavior of aqueous starch–monoglyceride mixtures using DSC and Thermomechanical Analy-sis (TMA, dilatometry mode) under dynamic conditions. In this context, we provide evidence that non-equilibrium melting (i.e. melting with reorganization) of metastable crystallites can account for the multiple melting transitions observed with these systems at intermediate water levels.

MATERIALS AND METHODS

Monocaprylin (1-C8), monocaprin (1-C10), monolaurin (1-C12), mono-myristin (1-C14), monopalmitin (1-C16), monostearin (1-C18), monoolein (1-C18:1), monolinolein (1-C18:2), monolinolenin (1-C18:3) were obtained from Sigma Chem. Corp. (St. Louis, Mo.). Rice starch (21% amylose content) was a commercial product. To remove internal lipids, dry rice starch was defatted by extraction with 85% aqueous methanol (48 h) in a Soxhlet extractor. An amylose fraction was prepared from purified (<0·5% protein) faba bean starch by hot aqueous leaching (98°C for 15 min, twice) and precipitation as amylose–butanol complex (Montgomery & Senti, 1964). The intrinsic viscosity of this fraction in 1N KOH (25°C) was 188 ml/g, corresponding to a degree of polymerization (DP) of 1400, according to Cowie & Greenwood (1957).

Preparation of faba bean amylose–monostearin complex was carried out according to Biliaderis *et al.* (1985). Crystallization of the complex took place isothermally at 85°C. All starch–monoglyceride mixtures were prepared by mixing defatted starch granules with an aqueous dispersion of the monoglyceride that had been previously heated at a temperature above its melting point. The final concentration of lipid was 1% on a dry starch basis. These samples were subsequently adjusted to 50% moisture content for both DSC and TMA analysis.

The DSC studies were carried out using a DuPont 1090 Thermal Analysis system equipped with a DuPont 910 cell base and a pressure DSC cell (1400 kPa with N_2). Ottawa sand was used as an inert reference material.

Details for the calibration and operation of this unit have been reported elsewhere (Biliaderis *et al.*, 1985). The reproducibility of peak transition temperatures for repeated analyses of the same sample was generally ±0·3°C. After each DSC scan, the samples were cooled and rescanned to examine the reversibility of the transitions. Transition enthalpies were expressed as Joules/g of heated dry material (starch or complex). Samples of 250 mg (50% water content) were firmly packed into quartz dilatometer vials for TMA analysis using a 3·14 mm puncture tester (Magness-Taylor type; applied force ca. 200 g). A DuPont 943 Thermo-mechanical analyzer equipped with a volume dilatometer probe was used to examine the thermally induced volume expansion of the starch specimens (Biliaderis *et al.*, 1986). The recorded linear dimensional changes were converted into volume expansion (%) using the expression:

$$\text{Volume expansion}\,(\%) = \frac{(A) \times (\text{Dimensional change})}{\text{Volume of starch sample}\,(M/D)} \times 100$$

where A is the cross-sectional area of the vial, M is mass and D is density of the starch (1·5 g/cm).

Data for both DSC and TMA were recorded at 0·4 s time intervals and stored on 8 in floppy disks. Data analyses were performed using the DuPont software analysis programs. Heating rates for DSC and TMA experiments were 10°C/min and 2°C/min, respectively.

RESULTS AND DISCUSSION

Before we analyze the melting behavior of defatted rice starch–monoglyceride mixtures, it is important to examine the typical thermal profile of the native rice starch. In accord with previous calorimetric findings on cereal non-waxy starches (Donovan & Mapes, 1980; Burt & Russell, 1983; Colonna & Mercier, 1985; Biliaderis *et al.*, 1986), rice starch heated at 50% water content exhibited several transitions, as shown in Fig. 1. Although there is some diversity of opinion regarding the origin of M1 and M2 endotherms (Donovan, 1979; Evans & Haisman, 1982; Biliaderis *et al.*, 1986), the general consensus is that both transitions reflect heat–moisture induced disorganization phenomena of starch crystallites. The M2 transition is only present at intermediate to low water levels and shows the characteristic melting temperature dependence on the amount of diluent (water) present (Flory, 1953). On the other hand, the two high temperature (100–140°C) peaks must be attributed to the amylose–lipid complexes. Supporting evidence for this interpretation is found in the thermal curve of the defatted rice starch (Fig. 1). Upon removal of the complexing agent (lipid), no transitions were observed in this temperature region.
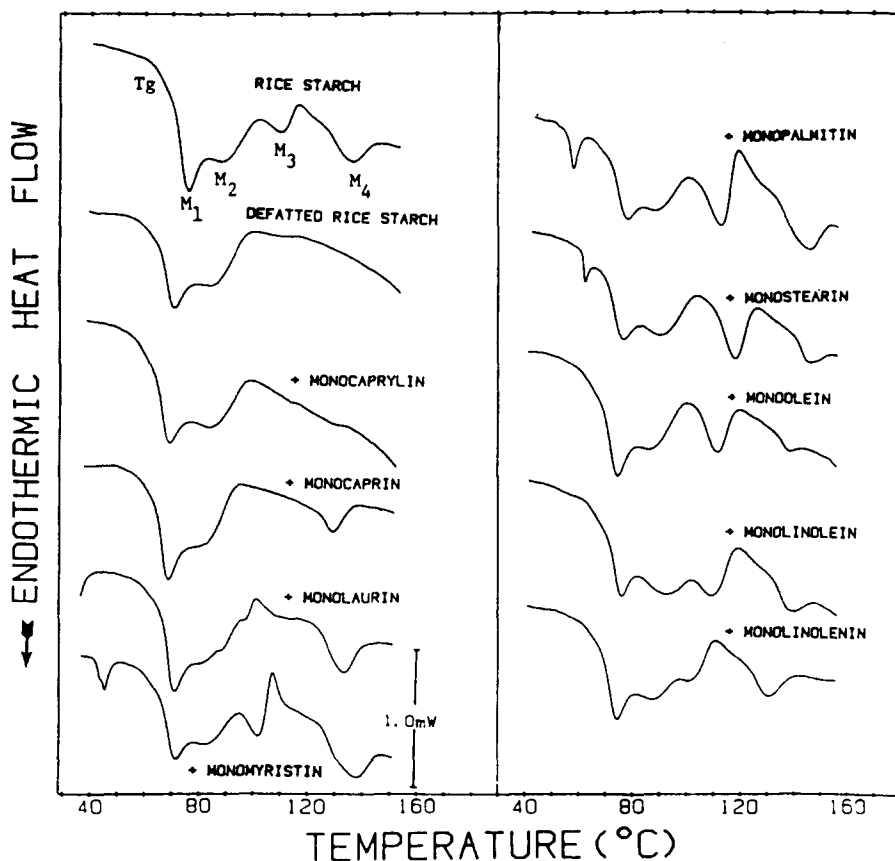
Fig. 1. DSC thermal curves of native, defatted and defatted rice starch–1–monoglyceride mixtures; heating rate, 10°C/min; water content, 50% (w/w). Weight of starch from top to bottom (mg): left, 5·80, 4·80, 6·04, 5·38, 5·39, 5·65; right, 5·05, 5·94, 5·41, 6·29,\5·79.

Although the multiple melting behaviour of amylose–lipid complexes has been shown by several investigators (Wirakartakusumah, 1981; Bulpin *et al.*, 1982; Donovan *et al.*, 1983), its nature, in terms of temperature/solvent dependence of the complex structure, has not been widely recognized. Stute & Konieczny-Janda (1983) have first reported on the metastable character of amylose complexes with fatty acids. Furthermore, in recent studies on isolated complexes it was demonstrated that double melting peaks do arise from reorganization during the DSC scan (Biliaderis *et al.*, 1985). Using the same insights, the exotherm between the M3 and M4 transitions of the rice starch (Fig. 1) suggests that similar phenomena may also occur at the starch granule level. This implies that the M4 peak is due to melting of reorganized material.

In addition to the above first-order melting transitions, there is evidence

for the existence of a second-order transition (glass transition, T_g) associated with the amorphous regions of the starch granule (Maurice *et al.*, 1985; Biliaderis *et al.*, 1986). This transition is more difficult to detect calorimetrically because of the nature of the amorphous phase. Most of the granular non-crystalline material is located between the crystallites (e.g. regions of dense branching in the amylopectin molecules) and therefore it does not possess the typical properties of a bulk amorphous phase. As such, the intercrystalline amorphous phase does not exhibit, upon heating, the heat capacity changes (ΔC_p) one would anticipate with a second-order transition. Furthermore, by analogy with other semicrystalline polymers (Wissler & Crist, 1980; Kirkpatrick & Wunderlich, 1985), it is very likely that the glass transition of granular starch extends over a broad range of temperatures (20–30°C) and thus becomes less conspicuous. Nevertheless, thermal activation/softening of the amorphous granular regions does occur prior to crystallite melting at T_g. It is noteworthy, also, to point out here that, besides the well known solvent-induced depression of the melting point, a diluent/solvent acts as a plasticizer in the amorphous phase of a semicrystalline polymer, thereby lowering its T_g. Water, for example, has been shown to be an effective plasticizer for starch (Maurice *et al.*, 1985; Biliaderis *et al.*, 1986) and other natural biopolymers (Salmen & Back, 1977; Marshall & Petrie 1980; Irvine, 1984). This phenomenon is, however, a free-volume effect (Sears & Darby, 1982) and, as such, it does not depend on the interaction between polymer and diluent.

The DSC thermal curves for the defatted rice starch heated in the presence of 1-monoglycerides are also presented in Fig. 1. After the first heating, the samples were slowly cooled (3°C/min) and rescanned (Fig. 2). Neither the defatted starch nor the sample heated with 1-C8 showed any evidence for amylose–lipid complex formation (Figs 1 and 2). The former suggests that no significant amounts of residual lipid are left after solvent extraction, while the latter implies that 1-C8 does not readily form complexes with the linear starch fraction. On the other hand, samples containing 1-C14, 1-C16 and 1-C18 (saturated and unsaturated mono-glycerides) exhibited two high temperature (100–140°C) endotherms often separated by an exothermic transition. In this respect, it is of interest to note that Stute & Konieczny-Janda (1983) also reported similar thermal response for the amylose–stearic acid complex. Such behaviour can be interpreted as partial melting, followed by recrystallization and final melting.

In Fig. 3, the apparent transition enthalpies of the complexes, taken from the rescan curves, are presented as a function of the fatty acid chain length of the saturated monoglycerides. Similar plots for the amylose-complexing ability of the monoglycerides are also included. The data for
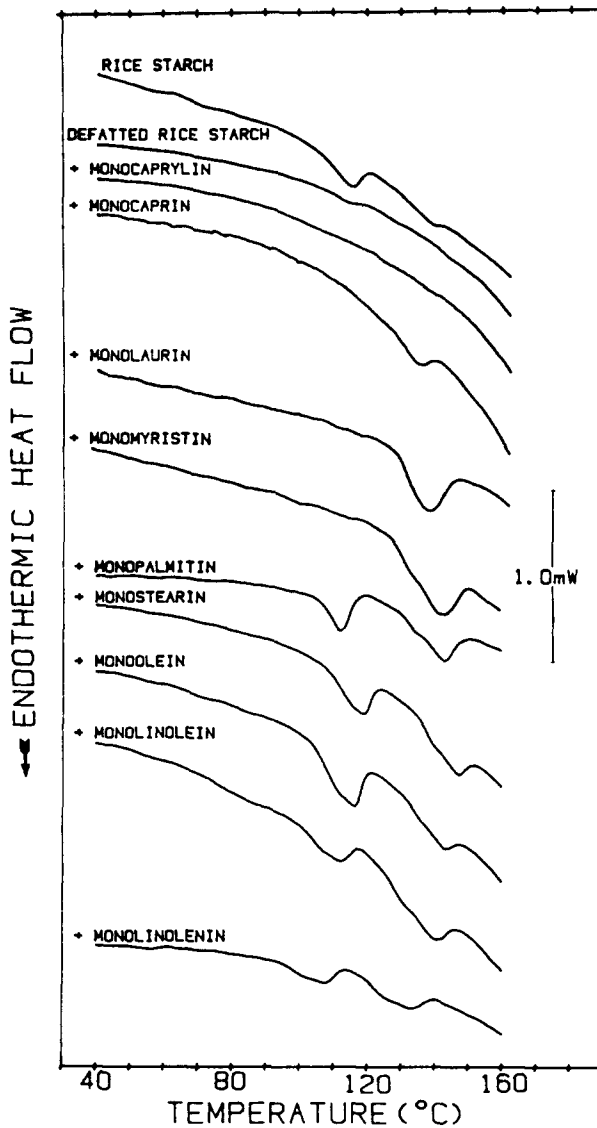
Fig. 2. DSC thermal curves of the samples presented in Fig. 1 after cooling and reheating; heating rate, 10°C/min.

these plots, adapted from Krog (1971), are based on iodine affinity measurements in dilute polysaccharide solutions. Although such methods for evaluating amylose complexing efficiency of the ligand molecule are not related to the DSC technique, interestingly, all plots exhibited similar trends. This suggests that DSC may prove a rapid method to assess the amylose complexing ability of a surfactant in a starch-containing product on the basis of the magnitude of the amylose–ligand melting transition(s).
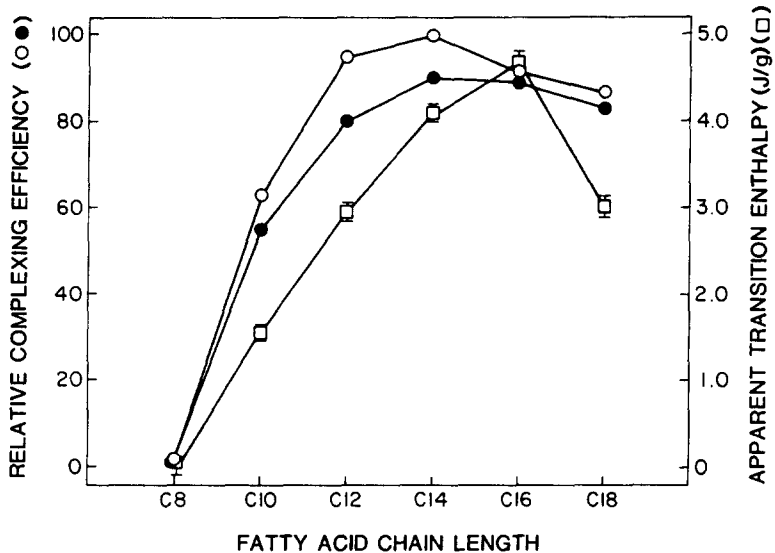
Fig. 3. Dependence of the melting enthalpy of the amylose–lipid complex (Joules g of complex) and amylose complexing efficiency on the chain length of the saturated 1-monoglycerides. Amylose complexing efficiency (data adapted from Krog, 1971) is based on the determination of remaining amylose in solution after separation of the complex (○), or determination of the reduction in iodine affinity of amylose in the presence of added monoglycerides (●).

However, in the presence of uncomplexed lipid the calculations and thus interpretation of the enthalpies for the complex, become uncertain (Eliasson & Krog, 1985). Nevertheless, using DSC one can probe these phenomena under conditions commonly encountered in processing of starch-based materials; i.e. intermediate/low moisture contents, dynamic heating–cooling cycles, formation of the complex in the presence of amylopectin and other non-starch ingredients, etc. Although it is generally accepted that monoacyl lipids do exist *in situ* within starches of cereal origin, it is not clear whether they occur as inclusion complexes inside helical segments of amylose or they are simply entrapped between starch molecules (Morrison, 1981). Furthermore, the exact conformational state of amylose in the granule is still a matter of speculation. However, it is known that the V-type of X-ray diffraction pattern develops only after gelatinization of cereal starches (Banks & Greenwood, 1975). This suggests that ordering of amylose–lipid helices into crystalline arrays occurs under gelatinizing conditions. As such, one would expect the crystallization exotherm of these complexes to be superimposed on the melting endothermic transitions of starch crystallites and thus the apparent enthalpy of the latter process to be reduced. This postulate is indeed consistent with the experimental results

of this study. The gelatinization enthalpies of rice and defatted rice starches were 13.2 ± 0.2 J/g ($n = 4$) and 14.5 ± 0.3 J/g ($n = 4$), respectively, the smaller enthalpy being that of the native sample due to amylose–lipid complex formation. It is also interesting to note that the difference between these two values (1.3 J/g) corresponds well to the melting enthalpy of the complex (1.4 J/g, $n = 4$), estimated from the thermal curves of the native starch. Similarly, there was a substantial reduction in the gelatinization enthalpies of defatted rice starch heated with good complexing ligands; 1-C14 (10.8 J/g), 1-C16 (10.7 J/g) and 1-C18 (10.1 J/g). This observation further suggests that, upon gelatinization, amylose molecules become more accessible to interact with the monoglycerides. In this respect, the ligand induces helicity in the amylose chains and thereby crystallization (exothermic effect).

To further test the above tentative mechanism for the melting behavior of amylose–lipid complexes (i.e. partial melting → recrystallization → remelting) the thermal properties of a purified amylose–monostearin (1-C18) complex were examined at various water contents (Fig. 4) and under different heating rates (Fig. 5). This sample was crystallized isothermally at 85°C to resemble the temperature conditions under which amylose–lipid complex formation takes place on starch gelatinization. The small peaks at 60°C (Figs 4 and 5) correspond to the melting transitions of the uncomplexed monoglyceride (Eliasson & Krog, 1985). There were several observations made in this study which provide valuable insights into the thermal behavior and crystallization habit of these materials. First, melting of the complex was highly cooperative, yielding a single transition at high water concentrations (10–30% complex in water). Similarly, single melting characteristics were also exhibited by the starch–monoglyceride mixtures at 20% solids (data not shown). As the water content was lowered, however, multiple melting transitions were observed in the thermal profiles (Fig. 4). Again, an exothermic effect was evident between the two melting peaks. This implies that, after partial melting, secondary crystallization/ annealing processes occur during the DSC heating experiment. It also indicates that reorganization of the complex to a crystalline structure of more perfected and/or larger crystallites (both would exhibit higher melting temperatures) is strongly influenced by the amount of water present in the system; i.e. it is more pronounced at low water contents. Secondly, if recrystallization does occur upon heating, its extent—and therefore its manifestation in the thermal curve—will be dependent on the heating rate. Figure 5 illustrates how the thermal profile of the complex varies with the heating rate. At slow heating rates, the original metastable crystallites are given sufficient time to reorganize and thus the thermal profiles contain a relatively large contribution from recrystallization of the complex. With
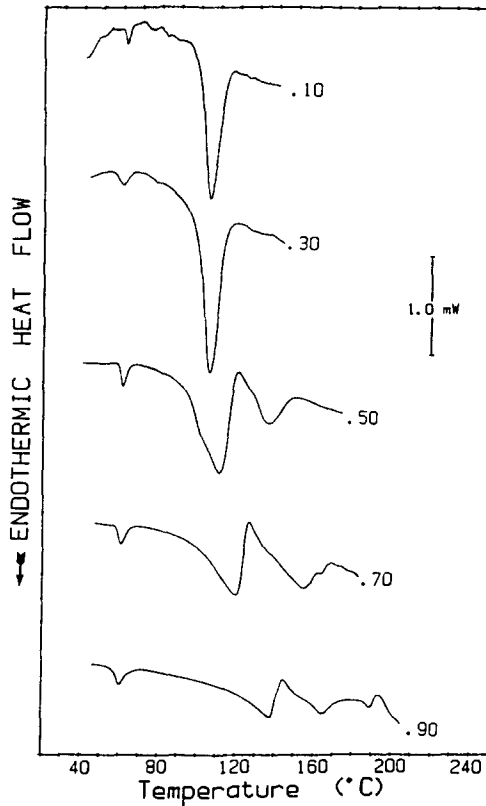
Fig. 4. DSC thermal curves of amylose–monostearin complex at different water contents; numbers designate the weight fraction of the solid material. Weight of complex from top to bottom (mg): 1·22, 2·93, 4·77, 7·01 and 8·05. Heating rate, 10°C/min. All data files were normalized to a constant sample weight of 5·00 mg.

increasing heating rate, however, the magnitude of the low temperature endotherm increases relative to the high temperature peak. From these findings, it is apparent that the melting phenomena of amylose–lipid complexes are largely dependent on secondary processes occurring during thermal analysis. Thirdly, examining again the results in Fig. 4, there is clear evidence for the depression of the melting temperature of the complex by increasing amounts of diluent (water). This behaviour, which arises from thermodynamic effects due to polymer–diluent interactions, is described by the Flory–Huggins equation (Flory, 1953) under equilibrium conditions. However, as shown in the thermal curves of Figs 1 and 4, equilibrium, or at least zero-entropy production melting (i.e. melting of a metastable material without reorganization), conditions are not met for these systems, particularly under limited moisture content/moderate heating rate regimes. As such, quantitative analysis of melting data using the diluent method
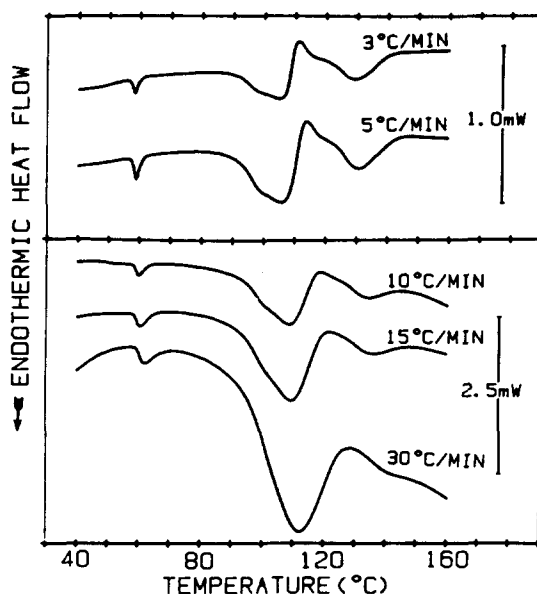
Fig. 5. DSC thermal curves of amylose–monostearin complex (50% in water) at different heating rates. Weight of complex from top to bottom (mg): 4·08, 4·01, 4·07, 4·04 and 4·08. The corresponding enthalpies (J/g) of the overall melting process (including both endotherms and the exothermic effect) were 22·7, 24·7, 21·5, 23·4 and 22.9.

(Flory-Huggins expression) to determine equilibrium melting points (T_m°) or enthalpies of fusion per repeating unit (ΔH_u), is not applicable.

In view of the experimental findings of this study, as well as the general principles governing the crystallization and melting of synthetic polymers, it would be interesting to consider the interactions between starch and monoglycerides from a polymeric perspective. The mechanical and thermal properties of semicrystalline polymers are directly linked to the morphology and organization of their crystallites (Mandelkern *et al.*, 1981; Wunderlich, 1981). In addition, their thermal behavior must be viewed in terms of temperature-dependence of metastable states. Since most of the processes involved are under kinetic control, their manifestation in a thermal curve will depend on the dynamic parameters governing non-equilibrium phase changes. These include heating rate, nucleation and (re)crystallization rates, as well as melting kinetics. Accordingly, if one considers amylose–lipid interactions within the conceptual framework of polymer crystallization, several stages can be distinguished, as illustrated in the simplistic scheme of Fig. 6. Two kinetic levels arise from this model. First is the association of amylose chains with the ligand lipid molecule. This provides the additional conformation order (helicity) required for molecular nucleation to commence. The second stage is the organization (crystal growth)
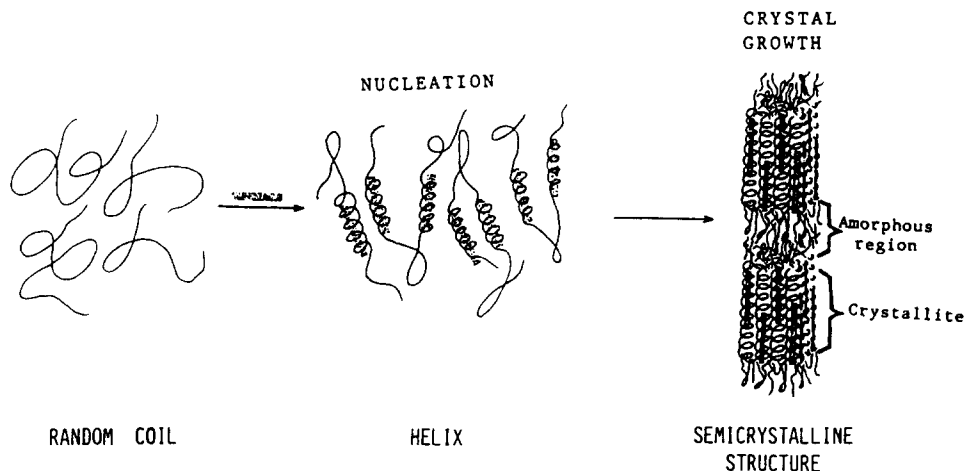
Fig. 6. Schematic representation of the monoglyceride-induced conformational changes and organization of amylose chains into a supermolecular structure.

of amylose–lipid helices into a semicrystalline structure. In the context of this model, the thermal profiles of Fig. 1 suggest that the time frame of the overall process is mainly determined by the molecular nucleation step; i.e. crystallization is very fast compared to nucleation. Moreover, of interest to the present discussion is the observation that crystallization of amylose–lipid complexes primarily occurs during starch gelatinization. One can rationalize this behavior as follows. At temperatures below the T_g, the molecular mobility of the amorphous granular regions (including amylose) is substantially reduced to allow for extensive interaction between amylose and monoglycerides. As the temperature exceeds the T_g, however, the mobility of the system is increased and thus the ligand can induce crystallization of the amylose chains. For the latter, it is also possible to envisage a situation where partial disentanglement and segregation of amylose and amylopectin molecules occur during gelatinization. Due to the differences in structure between these macromolecules, as well as the inability of amylopectin to effectively interact with lipids, one would expect enhanced crystal growth rates from such molecular segregation. In this respect, during gelatinization, good amylose complexing ligands are expected to induce, rapidly, many nucleation sites in the partially melted polysaccharide matrix. Such a highly nucleated system would result in many small and defective crystallites which would be prone to reorganization upon further heating. The thermal profiles of starch–1-C14 and starch–1-C16 mixtures (Fig. 1) were indeed in accord with this view. After partial melting of the initially grown metastable crystallites (M3 transition), perfection and/or thickening occurs, presumably via increased motion of
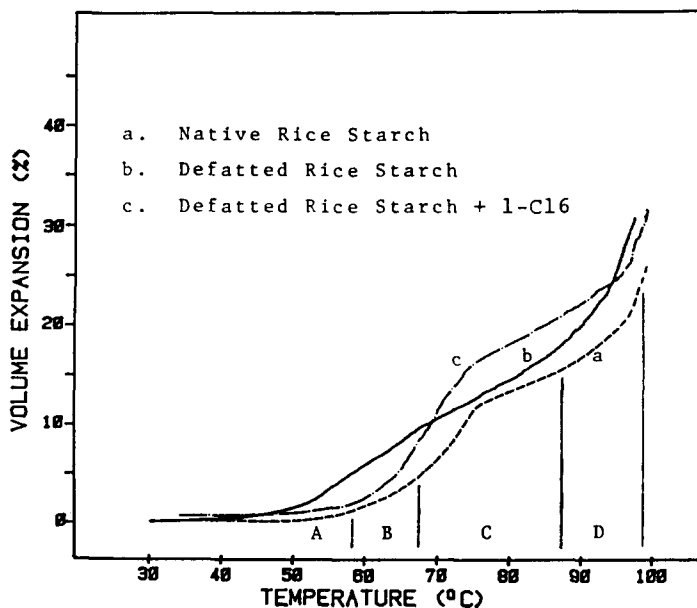
Fig. 7. Typical TMA curves of native, defatted and defatted rice starch–monostearin mixture. Sample weights (mg): a. 251, b. 249, c. 248. Starch concentration 50% w/w in water; heating rate, 2°C/min. Regions on the TMA curve designated as A, B, C and D are specified in the text.

chain defects and ingestion of tie-chain segments. As such, the net free energy of the crystallites decreases and thus their melting point is increased (M4 transition). Amylose–fatty acid inclusion complexes formed at temperatures above 110°C have been reported to exhibit birefringence (Davies *et al.*, 1980; Stute & Konieczny-Janda, 1983). In this respect, when the recrystallized amylose–monostearin complex (i.e. it showed only the M4 endotherm) was examined under polarized light it was found only partially birefringent.

The starch–monoglyceride mixtures (50% in water) were further examined by thermomechanical analysis. Figure 7 shows representative TMA curves for native, defatted and defatted rice starch–1-C16 mixture. The volume expansion thermal profile of rice starch can be divided into four regions, as indicated in Fig. 7.

A. This region shows little changes in thermal expansion, indicative of a polymeric material being below its T_g.

B. A region of increased swelling, due to enhanced segmental motion of the polymer chains undergoing a glass transition.

C. An intermediate region of partial melting/annealing of starch crystallites as well as crystallization of amylose–lipid complexes.

D. A region of abrupt swelling that is attributed mainly to the melting of starch crystallites; it coincides with the temperature region of the M2 transition.

In contrast to the native sample, the defatted starch started to swell at lower temperatures and expanded steadily with increasing temperature. In addition to the differences in the onset of expansion phenomena, there were also differences in the shape of the TMA curves. Thus, the native starch showed a more pronounced plateau in the region of 75–85°C. This swelling behavior can be rationalized on the basis of at least two processes: (a) crystallization of amylose–lipid helices, which, in itself, leads to volume decreases, and (b) stabilization of the swollen granular structure by the amylose–lipid crystallites that act as physical cross-links in the polysaccharide matrix (Flory, 1974). A similar volume expansion pattern was observed with monoglycerides of good complexing efficiency (e.g. 1-C16, Fig. 7). The latter further substantiates the stabilizing role of amylose–lipid complexes in the starch gel structure. It is interesting, finally, to note that these monoglycerides also inhibited the onset of the swelling phenomena to almost the same degree of the native rice starch sample.

CONCLUSIONS

Heated aqueous rice starch–1-monoglyceride mixtures were characterized by various transitions. At intermediate water contents (50%) and moderate heating rates (10°C/min), starch granules heated with good amylose-complexing agents exhibited non-equilibrium melting for the amylose–lipid complexes. Thus, two melting transitions separated by an exothermic peak were observed. Evidence was provided that the DSC thermal profiles represent the composite effect of two opposing processes; melting of rapidly grown metastable crystallites and annealing/reorganization upon subsequent heating. On the basis of the thermal analysis studies presented herein, it was concluded that the overall thermal behavior of amylose–lipid complexes, when examined by dynamic methods (DSC, TMA), can

Thermal Behaviour of Starch/Monoglyceride Systems

(I)   Solvent–polymer interactions (thermodynamic and free volume effects manifested by changes in T_g and T_m)
(II)   Morphological effects (crystallite size and organization)
(III) Kinetic effects (rate of crystal growth/annealing vs. melting kinetics)

Fig. 8. Representation of the various parameters involved in phase transitions of starch–monoglyceride systems.

be explained by considering several parameters operating simultaneously (Fig. 8). In this respect, it is important to recognize the dynamic character of the system in terms of specific interactions between solvent and polymer in the solid state. Some of these effects are of thermodynamic origin, while others are kinetic in nature.

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