Microstructural Evaluation of Model Starch Systems Containing Different Types of Oils[1]

E. A. DAVIS, J. GRIDER, and J. GORDON[2]

ABSTRACT

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Starch phase transitions, birefringence, and swelling were measured in mixtures of oil, starch, and water containing oils of differing saturation, fatty-acid chain length, and conformation. Onset temperatures of the first phase transition seen by differential scanning calorimetry were similar for all samples, but enthalpies for samples containing saturated oils or intermediate amounts of mono- and polyunsaturated oils were lower than those containing highly unsaturated oils. Samples dispersed in added oil were examined microscopically. Some birefringence was present at the end of the first phase transition (68° C), after heating to 97° C, and after three days of storage at 4° C. Samples dispersed in additional water instead of oil lost birefringence. Starch from samples that had lower enthalpies was less swollen and retained more birefringence.

Many studies of starch-lipid interactions have focused on interactions of starch with free fatty acids, monoglycerides, or other surfactant molecules rather than triglycerides, even though triglycerides are an essential component of many formulated food systems. Interactions of triglycerides in starch systems might differ from those of monoglycerides or free fatty acids because of differences in amphiphilic character, dispersion states, and steric considerations. Characteristics of triglycerides, however, reflect their fatty acid composition and distribution.

Studies of starch-lipid interactions parallel studies of the sequence of transitions accompanying the group of changes collectively known as gelatinization. Of particular interest are the events that occur either just before, during, or immediately after the phase transitions measured by differential scanning calorimetry (DSC). Loss of birefringence as a measurement of structural changes is generally associated with low-temperature phase transitions in the presence of excess water, but few studies have reported interrupting the process immediately after the initial phase transition in order to separate it from subsequent granule swelling.

Both the DSC phase transition and loss of birefringence are usually considered to be dependent on the availability of enough water to facilitate the transformation, and an additional role in limiting water availability has been attributed to lipids. The amount of water necessary is approximately two parts water to one part starch. Starch retrogradation is influenced by the extent and manner to which starch granules swell and undergo phase transitions with different amounts of water and formulation change. Thus, the manner by which starch granules undergo initial transformation with subsequent reorganization will influence the extent and type of staling seen in cereal-based products.

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[2]Department of Food Science and Nutrition, University of Minnesota, St. Paul, MN 55108.

Accordingly, the objectives of this study were to examine the onset temperature for the first phase transition of wheat starch-water model systems by DSC in the presence of oils of different degrees of unsaturation, fatty acid lengths, and conformation and to examine loss of birefringence and swelling immediately after the initial phase transition (56–68° C) and after heating to 97° C. In addition, previously heated samples were examined after storage for three days at 4° C.

MATERIALS AND METHODS

Corn oil (ICN Biochemicals), soybean oil (Sigma Chemical Co.), safflower oil, cottonseed oil, coconut oil, and hydrogenated coconut oil (ICN Nutritional Biochemicals) were used. Wheat starch (Aytex P) was obtained from Henkel. The ratio of starch to water to oil was 1:2:0.66 by weight.

DSC Measurements

Oil, starch, and water were sequentially added to calorimeter pans for all oils except coconut; because coconut oils were more solid than liquid, the coconut oils and starch were premixed. Total sample weight was 8–9 mg. Indium and water were used to standardize and calibrate the calorimeter (Perkin Elmer model DSC-2). DSC operating conditions were: 5° C/min, 0.5 mcal/sec, temperature ranges 10–68° C or 10–97° C. The reference cell was either an empty aluminum pan or, in the samples containing the coconut oils, a pan with an extra piece of aluminum was used. Enthalpies in calories per gram of starch are reported as the average of a minimum of six replications. Additional measurements were made using a Mettler calorimeter (model DSC-30).

Microscopy

Samples were examined and photographed within 15 min of heating after completion of the DSC scans, either at the end of the endotherm at 68° C, or at the end of the scan at 97° C. Additional samples from DSC scans at both temperatures were stored at 4° C for three days in the calorimeter pans. The samples were dispersed in either oil or water on the microscope slide and examined by ordinary and polarized light microscopy.

RESULTS

DSC Transitions

Onset temperatures and enthalpies for the mixtures of oil, starch, and water are shown in Table I. Onset temperature for the control without oil averaged 56.40° C. The range in temperatures for the oil-containing samples was from 56.65° C for corn oil samples to 57.30° C for coconut oil samples.

The enthalpies ranged from 1.73 cal/g of starch for the control to 1.57 cal/g starch for samples containing soybean or corn oil. The enthalpies appear to form three groups: control and safflower oil samples with enthalpies of 1.73; hydrogenated coconut and coconut oils, 1.65–1.66; and cottonseed, soybean, and corn oils, 1.57–1.58.

Onset temperatures for DSC transitions were not greatly different from those reported by others for wheat starch. Enthalpies for both control and samples containing oil are in the low range of enthalpies reported at this wheat starch-to-water ratio (Allen et al 1982). To verify that the low values were not caused by instrumentation, determinations were also made using a Mettler calorimeter and another Perkin-Elmer DSC-2 instrument in independent laboratories, and similar values were found.

TABLE I
Differential Scanning Calorimetry Enthalpies and Onset Temperatures of Endotherms of Mixtures of Oil, Starch, and Water[a]

Type of Oil	Endotherm Onset Temperature (°C)	Enthalpy (cal/g of starch)
Control (no lipid)	56.40 ± 0.68	1.73 ± 0.09
Safflower	57.07 ± 0.11	1.73 ± 0.04
Hydrogenated coconut	56.85 ± 1.07	1.66 ± 0.13
Coconut	57.30 ± 0.29	1.65 ± 0.14
Cottonseed	57.02 ± 1.65	1.58 ± 0.17
Soybean	56.92 ± 0.14	1.57 ± 0.15
Corn	56.65 ± 1.13	1.57 ± 0.20
Overall average	56.74 ± 0.49	1.64 ± 0.07

[a] Means of at least six replications.

Microscopy

Typical micrographs of samples heated to 68° C and dispersed in oil before viewing in the microscope are shown in Figure 1. Examples are given for the three groupings of oils based on enthalpies. Extensive swelling occurred similarly in the control (Fig. 1A) and safflower oil samples. This degree of swelling was accompanied by loss of birefringence in most but not all of the granules. Coconut oils showed intermediate amounts of swelling (Fig. 1B) and loss of birefringence. Limited swelling coupled with retention of birefringence is shown in Figure 1C and D for soybean oil samples; similar results were found for corn and cottonseed oils. After storage for three days at 4° C, the samples that had been heated to 68° C were only slightly more swollen and slightly less birefringent than those examined immediately after heating.

Control and samples containing safflower oil heated to 97° C and subsequently redispersed in oil were also more swollen and less birefringent than the samples containing the five other types of oil. Starch granules from hydrogenated coconut samples were less swollen than those from coconut oil and resembled cottonseed and soybean oil samples in degree of swelling and retention of birefringence. Starch granules from corn oil samples were the least swollen and most birefringent of all the samples examined after heating to 97° C. Some birefringence persisted in samples

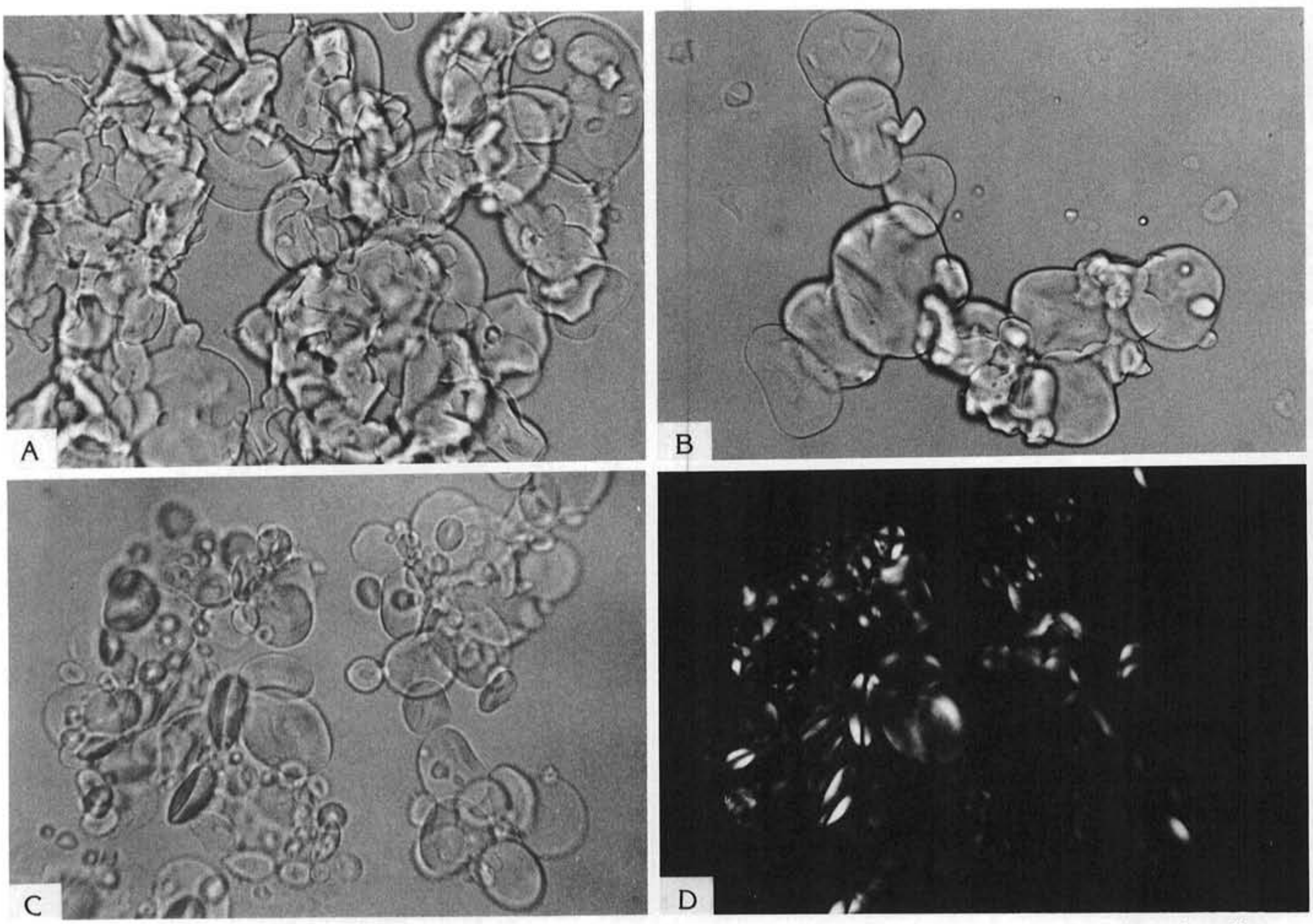

Fig. 1. Wheat starch, water, oil samples heated to 68° C in a differential scanning calorimeter and redispersed in oil for microscopy. **A,** Control, no oil present during heating; **B,** coconut oil; **C,** soybean oil; **D,** soybean oil, polarized light.

examined after three days of storage at 4° C.

Samples were also redispersed in water, instead of oil, before microscopy (Fig. 2). Control samples heated to 68° C (Fig. 2A) were more swollen than those redispersed in oil (Fig. 1A). The introduction of additional water into the heated samples after cooling to room temperature appeared to induce further loss of order. Control samples were more swollen and less birefringent than the oil-containing samples, but it was difficult to distinguish an order of swelling and birefringence for the various types of oils as was possible when the samples were examined in oil (Fig. 1).

Control samples heated to 97° C and redispersed in water are shown in Figure 2B. The more extensive swelling compared to the 68° C sample (Fig. 2A) was as expected. As was the case for water dispersed samples that had been heated to 68° C, the additional swelling caused by dispersion in water made it difficult to distinguish an order of swelling among the oil-starch combinations.

DISCUSSION

The crucial role of water in the first phase transition (measured by DSC) is well recognized. Cloke et al (1983) reported that no endotherm was found when wheat starch was heated in oil in the absence of water. Ghiasi et al (1983) reported that hydrated starch granules heated in mineral oil on the hot stage of a polarizing microscope lost birefringence over a 20 to 30 degree range. This behavior was in contrast to the loss of birefringence within a narrow temperature range (10° C) at water/starch ratios of 2:1 (Ghiasi et al 1982).

The observation that birefringence could be retained in granules that were heated through the first phase transition suggested that a certain amount of order was still present in the granules. The retained order was easily disrupted by introducing additional water at room temperature, and disruption was accompanied by loss of birefringence and additional swelling. Some order persisted even in some samples heated to 97° C, and the sensitivity of this order to additional water emphasized that the water continued to mediate structural change even in samples heated to high temperatures. A similar comparison of dispersion in water and oil was discussed by Evers and Stevens (1985).

Based on enthalpies, swelling behavior, and loss of birefringence, the oils studied here formed three groups that could also be related to fatty acid composition (Table II). Safflower oil, which has the highest enthalpy, most swelling, and least birefringence, also has the highest percentage of polyunsaturated fatty acids. Coconut oils, the most saturated oils, were intermediate in enthalpy and swelling. The soybean, corn, and cottonseed group contains relatively high levels of polyunsaturated fatty acids, but it also contains significant amounts of saturated and monounsaturated fatty acids. This group of oils was the most effective in limiting the first phase transition and swelling. Depending on the positional distribution of the fatty acids on the glyceride and the specific molecular configuration, the hydrophobic saturated moieties might be more available for interaction with amylose via complex formation and the mixed triglycerides more effective than simple glycerides, Pearce et al (*unpublished*) demonstrated by using free radical stearic acid probes and electron spin resonance measurements that binding of stearic acid occurs through the hydrophobic rather than the hydrophilic parts of fatty acids.

Physical considerations may also affect lipid-starch interactions. The existence of surface barriers to diffusion of water into the granule, or of water binding via formation of micellar states by lipids, have been suggested (Eliasson et al 1981, Eliasson and Krog 1985). Barriers to water diffusion seem more reasonable in the case of triglycerides, because mesophase formation usually is not associated with triglycerides.

Triglycerides may control water transport throughout the sample as well as immediately at the surface of the granules. Using freeze-etching techniques, Hsieh et al (1981) demonstrated in batter systems with corn oil as the shortening agent that, after heating to 102° C, oil pools were closely associated with starch granules. When monoglycerides were added to the system, no structures indicating close starch-monoglycerides associations were observed. Fretzdorff et al (1982) also demonstrated by freeze-fracture techniques that lipid pools were present in model dough systems. Thermal, birefringence, and swelling data in the present study indicated water transport either into the granule or from one part of the sample to another may be slower in the soybean group and coconut oils than in the highly unsaturated safflower oil.

Formulation is thought to control recrystallization of starch molecules during storage, and water transport from one part of the sample to another may be involved also during the storage period. It has been suggested that control of these changes is related to amylose-lipid complexes and reorganization of amylopectin structures (Axford and Colwell 1967; Fearn and Russell 1982; Bulpin et al 1982; Russell 1983a,b; Biliarderis et al 1985; Eliasson and Krog 1985; Miles et al 1985). Under the conditions of the present study, stored samples were only slightly more swollen and less birefringent than fresh samples. Thus, if reorganization occurred during storage, it was at a different level of organization than that measured by birefringence and swelling.

TABLE II
Fatty Acid Composition of Oils[a]

Oil	Saturated	Monounsaturated	Polyunsaturated
Safflower	9	12	75
Coconut	87	6	2
Cottonseed	26	18	52
Soybean	14	23	60[b]
Corn	13	24	59

[a] Expressed as g/100 g, based on data in *Composition of Foods* (USDA 1979).
[b] 18:3, 6 g/100 g for soybeans; less than 1 for other oils.

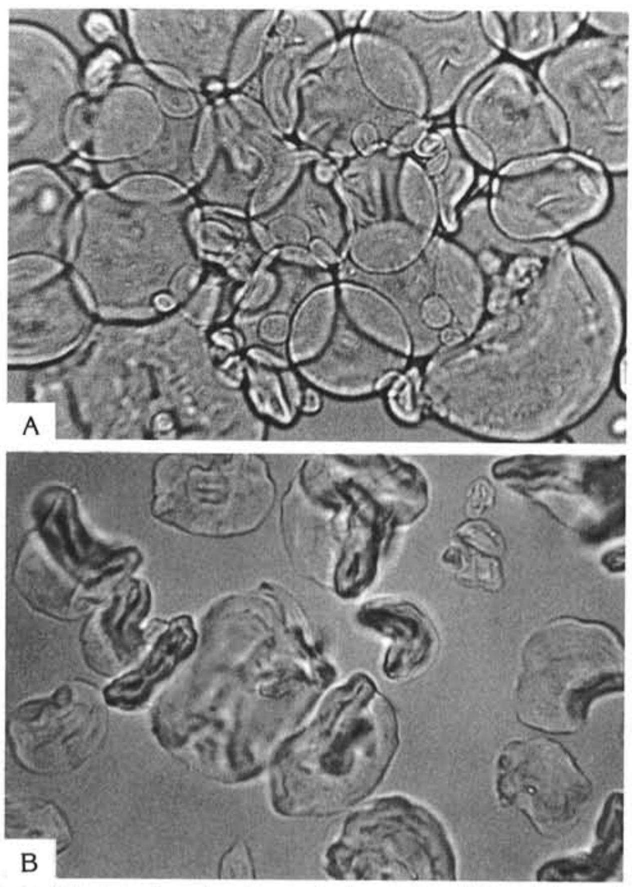

Fig. 2. Wheat starch and water samples heated in a differential scanning calorimeter and redispersed in water for microscopy. **A**, Control, no oil present during heating, heated to 68° C; **B**, control, heated to 97° C.

CONCLUSIONS

Oils could be grouped into three groups according to their effects in the oil, starch, and water systems. Adding safflower oil, the most highly unsaturated oil, produced results similar to those for the control sample without oil. Coconut oil and hydrogenated coconut oil were intermediate in their effects, followed by soybean, corn, and cottonseed oils. Enthalpies for the first phase transition (onset temperature, 58°C) were smaller for systems that contained oils with more highly saturated fatty acids and oils with substantial amounts of saturated and monounsaturated fatty acids in addition to polyunsaturated fatty acids. Low enthalpies were associated with less granule swelling and greater retention of birefringence. Birefringence persisted to 97°C if additional water was not added to the gel system. Storing the samples of oil, starch, and water systems for three days at 4°C resulted in small amounts of additional swelling and some loss of birefringence.

That the partially disrupted structural order of starch after the first phase transition was further disrupted after introducing additional water into the system indicated that lipids may interfere with the diffusion of water from one region of the sample to another in systems of oil, starch, and water. Water transport may be slower in the presence of highly saturated oils than in less saturated oils.

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