Gelatinization of Wheat Starch. III. Comparison by Differential Scanning Calorimetry and Light Microscopy[1]

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ABSTRACT

A single endotherm was obtained at a high water-to-starch ratio (2:1). As the ratio was decreased to 1:1, the endotherm decreased and developed a trailing shoulder. Light photomicrographs of starches removed from the differential scanning calorimeter pans show that, at high water-to-starch ratios, birefringence is lost over a narrow temperature range of about 7°C. That range increases to about 30°C at a low water-to-starch ratio (1:2). No difference was found between endotherms of large and small granule wheat starches.

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When starch granules are heated in excess water, a phase transition from order to disorder called gelatinization occurs (Donovan 1979). Several changes occur simultaneously during gelatinization, including uptake of heat by the starch granules (Stevens and Elton 1971), loss of crystallinity as measured by the loss of birefringence and X-ray diffraction patterns (Priestly 1975), hydration of starch followed by granule swelling and increased suspension viscosity (Leach et al 1959), and decreased relaxation time of water molecules as measured by pulsed nuclear magnetic resonance (Lelièvre and Mitchell 1975).

In systems having limited water, relatively small losses in crystallinity may occur upon heating. No gelatinization was reported when water content was less than 30% (Collison and Chilton 1974, Hellman et al 1954) or when fewer than four water molecules per anhydro glucose unit were present (Donovan 1979).

Phase transitions, which starches undergo upon heating in the presence of water, were studied recently, using differential scanning calorimetry (DSC) (Biliaderis et al 1980; Donovan 1979; Donovan and Mapes 1980; Eliasson 1980; Stevens and Elton 1971; Von Eberstein et al 1980; Wootton and Bamunarachchi 1979a, 1979b). Although work on starch gelatinization has been extensive, applying DSC has greatly expanded our understanding of this important phenomenon. The calorimeter uses small samples, which minimize thermal lag within the system, and hermetically sealed pans, which prevent loss of water. It also allows one to determine the temperature range over which gelatinization occurs and the enthalpy involved in the transition.

The birefrigence of potato starch heated in a differential thermal analysis apparatus at a high water-to-starch ratio was reported (Wada et al 1979).

This article reports the effects of water-to-starch ratios on thermograms of wheat starch and correlates loss of birefringence with the DSC thermograms.

MATERIALS AND METHODS

Differential Scanning Calorimetry

A Perkin-Elmer DSC-2 with an Intracooler-II system was used. The starch was weighed in aluminum pans and water added with a syringe. The pan was sealed and reweighed to determine the amount of water added. When small amounts of water were added, the pans were allowed to stand at least 1 hr before heating in the calorimeter. Samples were then heated in the DSC at 10°C/min, a sensitivity of 0.5 or 1.0 mcal/sec, and a chart speed of 10 or 20 mm/min. An empty pan was used as the reference. A subsequent thermogram showed excellent repeatability.

Polarization Microscopy

Pictures were taken using a Reichert light microscope operating in brightfield and polarization modes. Photomicrographs were taken with Kodak high-contrast copy film.

Isolation of Small and Large Starch Granules

Hard wheat flour (cv. Cloud) was milled on a Buhler experimental mill and fractionated into gluten, prime starch, and tailings (Wolf 1964). The tailings fraction was slurried with water in a blender for 1 min and centrifuged (1,000 × *g*) for 10 min. The upper gel layer resuspended in the blender. This process was repeated until no starch was obtained during centrifugation. The combined starch from the tailings fraction was resuspended in water, centrifuged, and the top gel layer removed with a spatula. This procedure was repeated two or three times until a clean fraction of small starch granules was obtained (Yamazaki 1955).

The prime starch fraction was suspended in water, centrifuged (1,000 × *g*) for 10 min, and the top 20% removed with a spatula and discarded. When this process was repeated three times, a fraction was obtained that consisted mainly of large starch granules. The

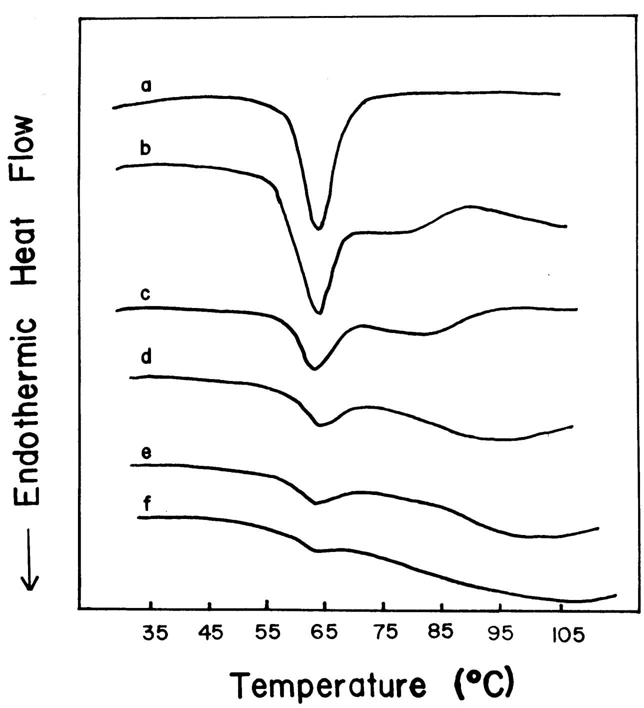

Fig. 1. Differential scanning calorimeter thermograms of wheat starch heated with different water-to-starch ratios: a, 2.0: b, 1.0; c, 0.75; d, 0.5; e, 0.44; f, 0.35. Sensitivity was 1 mcal, and chart speed was 20 mm/min.

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starch fractions were dried with methanol, sprinkled onto double-stick tape, coated with gold palladium, and viewed in an ETEC U-1 scanning electron microscope operated at 10 kV. The small granules generally were less than 8 μm in diameter and the large granules larger than 20 μm.

RESULTS AND DISCUSSION

When wheat starch was heated with various amounts of water, thermograms like those shown in Fig. 1 were obtained. At high water-to-starch levels (2:1), only a single endotherm was observed (Fig. 1a); the onset temperature was 57°C and the peak temperature 64°C. Figure 1 shows the single endotherm characterized by Stevens and Elton (1971) during gelatinization transition. As the water-to-starch ratio was decreased to 1:1, the size of the endotherm decreased and developed a trailing shoulder (Fig. 1b). At lower water-to-starch ratios, the second endotherm shifted progressively to higher temperatures (Fig. 1c and e). Our results were similar to those reported by Donovan (1979), who suggested that phase transitions of starch in a system having excess water resulted from disordering of individual starch chains that are stripped from ordered regions of the granules. Donovan suggested that, in the presence of less water, the transition is characterized as a solvent-aided melting of crystallites in the starch granules. The melting is responsible for the appearance of the second peak.

Polarization Microscopy

After samples at various water-to-starch ratios were heated (10°C/min) to desired temperatures in the DSC, the pans were opened and the starch dispersed in water. The DSC controls the

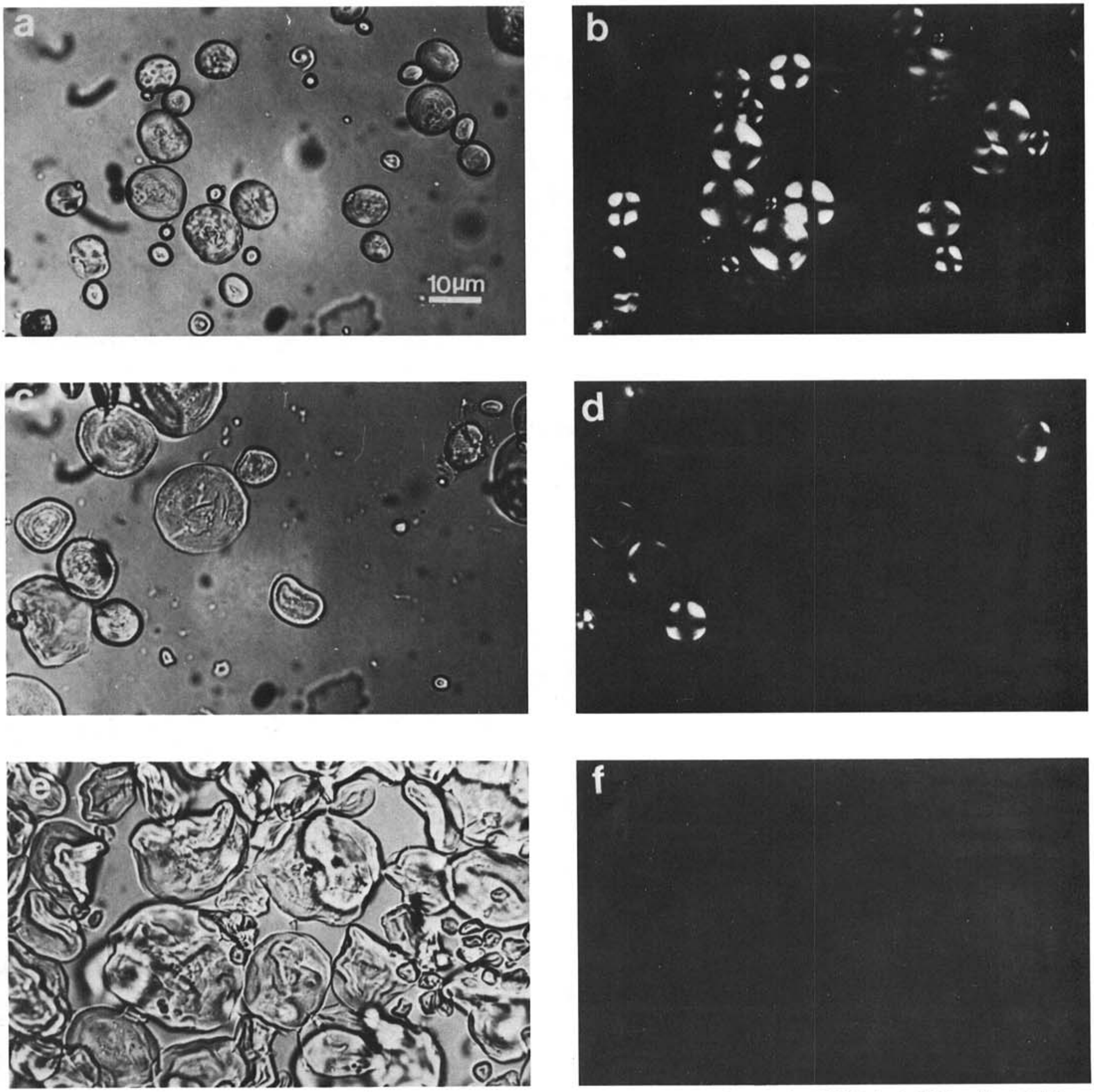

Fig. 2. Brightfield and polarizing micrographs of wheat starch heated in the differential scanning calorimeter to (**a, b**) 57°C, (**c, d**) 64°C, and (**e, f**) 67°C at a water-to-starch ratio of 2.0.

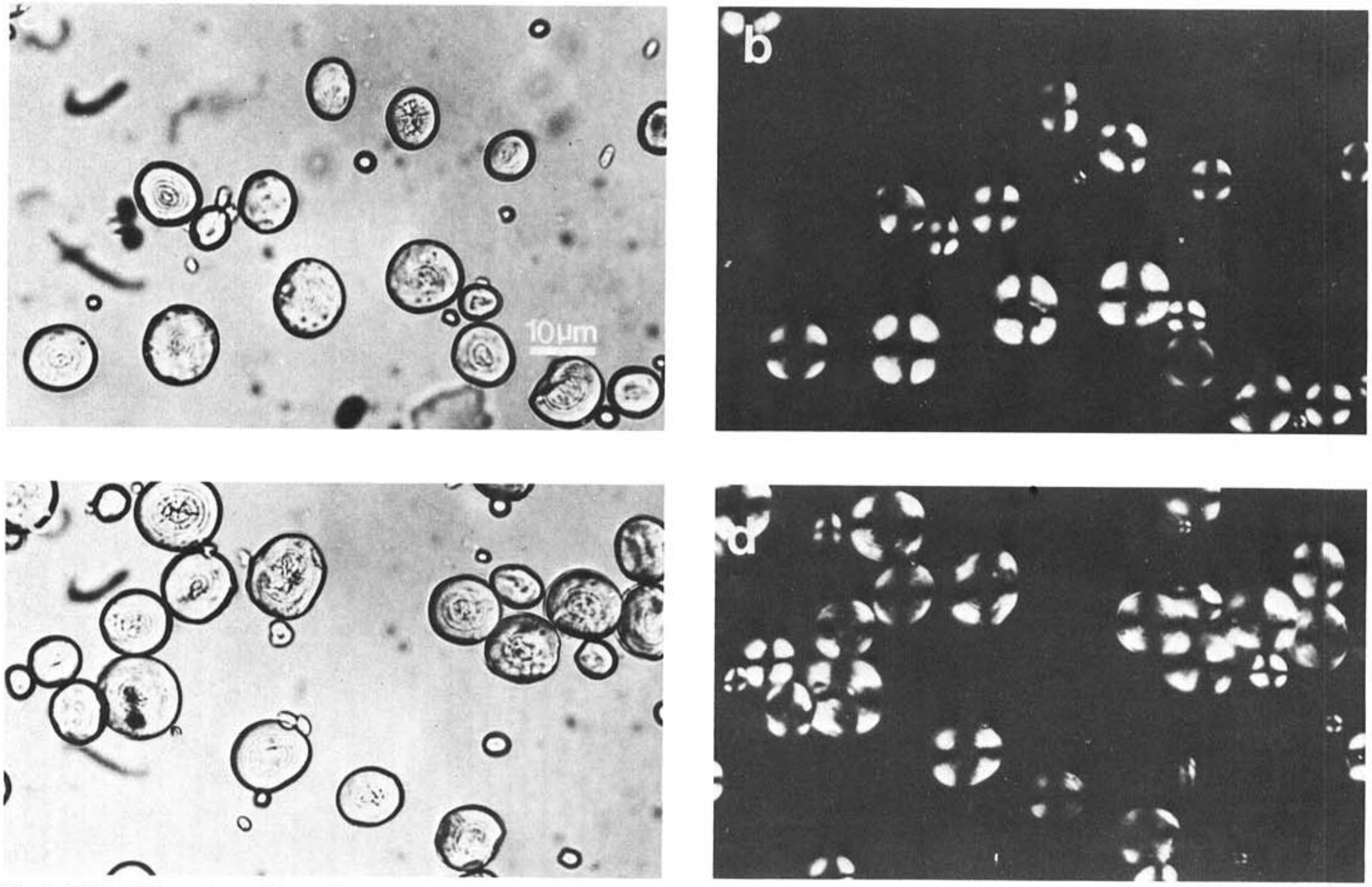

Fig. 3. Brightfield and polarizing micrographs of wheat starch heated in the differential scanning calorimeter to (**a, b**) 57° C and (**c, d**) 64° C at a water-to-starch ratio of 0.5.

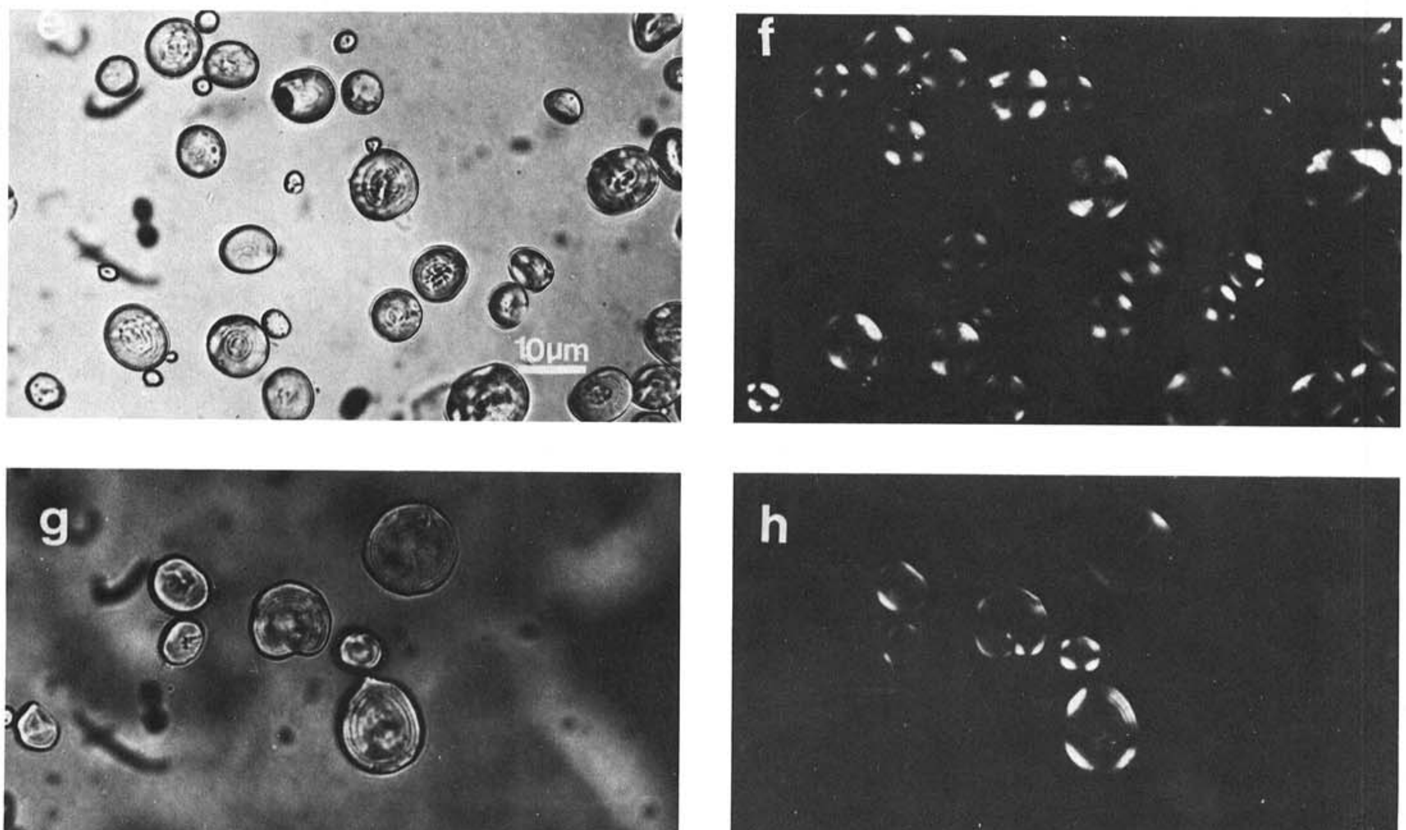

Fig. 4. Brightfield and polarizing micrographs of wheat starch heated in the differential scanning calorimeter to (**e, f**) 67° C and (**g, h**) 87° C at a water-to-starch ratio of 0.5.

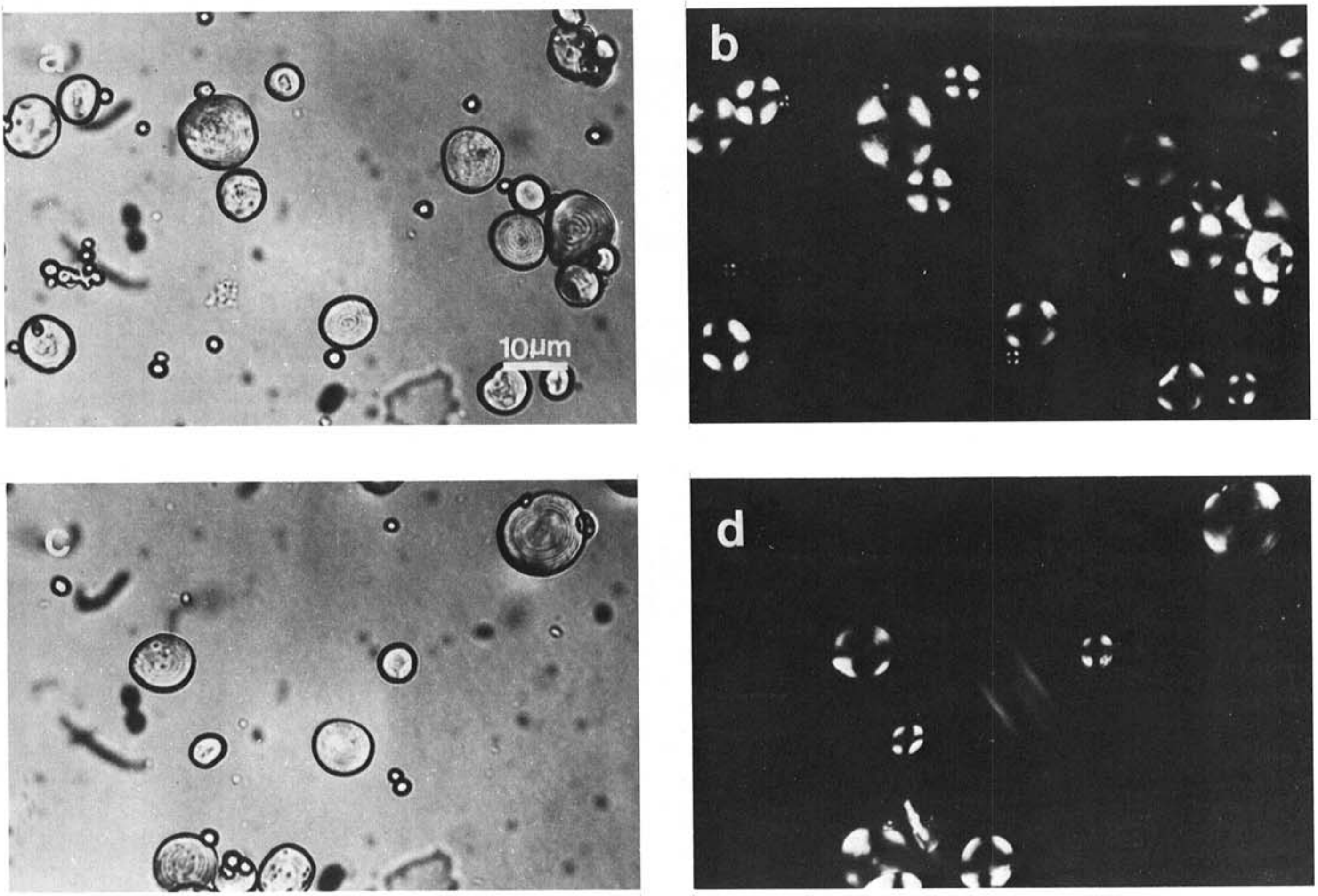

Fig. 5. Brightfield and polarizing micrographs of wheat starch heated in the differential scanning calorimeter to (**a, b**) 67°C and (**c, d**) 87°C at a water-to-starch ratio of 0.35.

sample temperature with good accuracy and can be programmed to stop heat at any temperature. After reaching the desired temperature, the sample was rapidly cooled (320° C/min) to room temperature. Light photomicrographs of those samples taken under normal and polarized light are presented in Figs. 2–5. Micrographs of wheat starch heated in the DSC to 57, 64, and 67° C at a water-to-starch ratio of 2.0 are shown in Fig. 2. At 64° C, most of the granules had lost birefringence. At 67° C, birefringence was completely lost, and the granules were extensively swollen and deformed.

Figures 3 and 4 show wheat starch heated to 57, 64, 67, and 87° C at a water-to-starch ratio of 0.5. Gelatinization of wheat starch at the two water levels was initiated at the same temperature (Fig. 1a and d). However, complete loss of birefringence was significantly delayed in the low-water system. Even at 87° C, some granules were partially birefringent (Fig. 4d), and the granules were not extensively swollen or deformed in any of the low-water samples. The delay in complete loss of birefringence was more pronounced in samples with water-to-starch ratios of 0.35 (w/w). As shown in Fig. 5, most of the granules retained partial birefringence even at 87° C. Thus, in systems having more water (2:1), birefringence is lost over a narrow temperature range of about 7° C, but the range increases to about 30° C at a water-to-starch ratio of 0.5. Low water contents also restrict swelling and deformation of granules.

An interesting question is why higher starch-to-water ratios cause the temperature range for birefringence loss to widen without delaying the temperature of initiation, as is often suggested in the literature (Hoseney et al 1977). Ungelatinized starch granules are often found in food systems heated to high temperatures (Varriano-Marston et al 1980); however, at a water-to-starch ratio of 0.5, as shown in Fig. 4, essentially all birefringence is lost when the sample is heated in the DSC to 87° C.

A major difference between the two treatments is that the DSC pan is sealed so that water is not lost from the system during heating and can therefore be recycled in the DSC pan; water used to gelatinize one starch granule by stripping is available to gelatinize a second granule by solvent-aided crystal melting. The delay in complete loss of birefringence probably stems either from the time required for the water to translocate or from the energy required to melt the crystals at the low water content. This is similar to the mechanisms suggested by Biliaderis et al (1980) and Donovan (1979).

To determine if the delay in complete loss of birefringence depended on time or temperature (energy), we heated samples with a water-to-starch ratio of 0.5 to various temperatures and held the temperature for 1 hr. No difference in loss of birefringence was observed after holding the samples 1 hr at a specific temperature, so we concluded that temperature must control the loss of birefringence in such low-water systems. This finding is in agreement with Donovan's (1979) work with the Flory equation.

Effect of Starch Granule Size

Wheat starch has relatively large lenticular and small spherical starch granules. Although both perform equally well in baking (Hoseney et al 1971), differences in chemical and physical properties have been reported (Kulp 1973). Stevens and Elton (1971) used the DSC to study the effect of granule size and reported that the endotherm peak temperature was 3° C higher for the small granule starch than for the large granules. We found similar results for large and small granules when using the endotherm peak. We did not, however, find a difference in the transition temperature of small and large starch granules when onset temperature was used to compare the samples rather than the peak temperature. The peak temperature is affected by experimental conditions, including sample size and heating rate (Jespersen 1978, Pope and Judp 1977).

LITERATURE CITED

BILIADERIS, C. G., MAURICE, T. J., and VOSE, J. R. 1980. Starch gelatinization phenomena studied by differential scanning calorimetry. J. Food Sci. 45:1669.

COLLISON, R., and CHILTON, W. G. 1974. Starch gelation as a function of water content. J. Food Technol. 9:309.

DONOVAN, J. W. 1979. Phase transitions of the starch-water system. Biopolymers 18:263.

DONOVAN, J. W., and MAPES, C. J. 1980. Multiple phase transitions of starches and Nägeli amylodextrins. Staerke 32:190.

ELIASSON, A. C. 1980. Effect of water content on the gelatinization of wheat starch. Staerke 32:270.

HELLMAN, N. N., FAIRCHILD, B., and SENTI, F. R. 1954. The bread staling problem. Molecular organization of starch upon aging of concentrated starch gels at various moisture level. Cereal Chem. 31:495.

HOSENEY, R. C., ATWELL, W. A., and LINEBACK, D. R. 1977. Scanning electron microscopy of starch isolated from baked products. Cereal Foods World 22:56.

HOSENEY, R. C., FINNEY, K. F., POMERANZ, Y., and SHOGRAN, M. D. 1971. Functional (breadmaking) and biochemical properties of wheat flour components. VIII. Starch. Cereal Chem. 48:191.

JESPERSEN, N. 1978. Thermal methods of analysis. Page 487 in: Instrumental Analysis. H. H. Bauer, G. D. Christian, and J. E. O'Reilley, eds. Allyn and Bean, Inc., Boston, MA.

KULP, K. 1973. Characteristics of small-granule starch of flour and wheat. Cereal Chem. 50:666.

LEACH, H. W., McGOWEN, L. D., and SCHOCH, T. J. 1959. Structure of the starch granule. I. Swelling and solubility patterns of various starches. Cereal Chem. 36:534.

LELIÈVRE, J., and MITCHELL, J. 1975. A pulsed NMR study of some aspects of starch gelatinization. Staerke 27:113.

POPE, M. I., and JUDD, M. D. 1977. Differential Thermal Analysis. A Guide to the Technique and Its Application. Heyden, London. Application. Heyden, London.

PRIESTLY, R. J. 1975. Moisture requirements for gelatinization of rice. Staerke 27:416.

STEVENS, D. J., and ELTON, G. A. 1971. Thermal properties of the starch/water system. I. Measurement of heat of gelatinization by differential scanning calorimetry. Staerke 23:8.

VARRIANO-MARSTON, E., KE, V., HUANG, G., and PONTE, J., Jr. 1980. Comparison of methods to determine starch gelatinization in bakery foods. Cereal Chem. 57:242.

VON EBERSTEIN, K., HÖPCKE, R., KONIECZNY-JANDA, G., and STUTE, R. 1980. DSC—Untersuchungen and Starken. Staerke 32:397.

WADA, K., TAKAHASHI, K. S., and KAWAMURA, A. 1979. Differential thermal analysis (DTA) applied to examining gelatinization of starches in foods. J. Food Sci. 44:1366.

WOLF, M. J. 1964. Wheat starch isolation. Methods Carbohydr. Chem. 4:6.

WOOTTON, M., and BAMUNARACHCHI, A. 1979a. Application of differential scanning calorimetry to starch gelatinization. I. Commercial native and modified starches. Staerke 31:201.

WOOTTON, M., and BAMUNUARACHCHI, A. 1979b. Application of differential scanning calorimetry to starch gelatinization. II. Effect of heating rate and moisture level. Staerke 31:262.

YAMAZAKI, W. T. 1955. The concentration of a factor in soft wheat flours affecting cookie quality. Cereal Chem. 32:26.

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