Chlorinated and Heat-Treated Flours: Studies of the Dynamics of Starch Gelatinization by Small-Angle Light Scattering

Z. H. BHUIYAN and J. M. V. BLANSHARD, Food Science Laboratories, Department of Applied Biochemistry and Nutrition, Nottingham University, Sutton Bonington, Loughborough, Leics, LE12 5RD, U.K.

Cereal Chem. 57(4):262-266

ABSTRACT

Chlorinated and heat-treated flours and their controls were dispersed in water at a concentration of 15% (w/w) and subjected to temperature jumps of ~ 2 and ~ 4°C. Their reactions were examined by the technique of small-angle light scattering. The time response of the birefringence loss was interpreted as a two-component exponential, and the variation with progressive gelatinization of both the fractional amplitude of the slow component (B/[A+B]) and the response time of the slow component τ_B was studied in detail. The numerically summed response curves of the slow components of the treated flours were significantly different from those of the control flours. The reproducibility of the technique appeared satisfactory. When the results were normalized and those of the respective controls were subtracted from those of the treated flours, a distinct difference in time response was observed. With ~ 2°C jumps, the maximum difference was at about 500 sec for both treated flours, whereas with ~ 4°C jumps, the maximum difference was at 150 sec for the heat-treated and 100 sec for the chlorinated flours. A summed response time index, $\sum_i B_i \tau_{Bi}$, clearly distinguished the treated and control flours. The differences were interpreted in terms of the semicooperative hypothesis of gelatinization, which gave evidence that the treated flours swell to a greater extent.

Although chlorine treatment of flour to improve the quality of high ratio cakes has been known for almost 50 years (Montzheimer 1931), considerable interest has recently been focused upon the nature of the changes induced by chlorination. The primary effect is upon the starch granules (Sollars 1958), despite their being responsible for only a minor uptake of chlorine (one-fifth to one-seventh) of the normal treatment. A recent review of this problem (Gough et al 1978) shows that much uncertainty surrounds the molecular mechanisms responsible for the effect.

The problem has been extended in scope by the patenting of thermal processes (Cauvain et al 1976a, 1976b; Doe et al 1968, 1969, 1970; Nicholas et al 1978) aimed at simulating the effect of chlorination, one using a heat treatment of cake flour, the other heating either the whole grain or the semolina before final milling. In both cases the advantages claimed for chlorine treatment are claimed for heat treatment.

Greenwood (1976) concurs with the conclusions of several investigators that very little difference exists in the pasting and gelatinization behavior of starches submitted to different levels of chlorination. Similarly, only minor differences occur in the gelatinization temperature (even in the presence of sucrose), the volume of the granule, the rate and pattern of amylase attack, and the appearance by scanning electron microscopy and differential scanning calorimetry. In contrast, chlorination unquestionably prevents a decrease in the volume of cakes after baking, strengthens and closes the structure, evens the texture, and produces a more uniform product. Frazier et al (1974) have, however, been able to distinguish rheologically between chlorinated and nonchlorinated flours and between heated and unheated cake flours during the latter stages of the baking process.

Such results suggest that the differences observed technologically arise from the distinctive dynamic response of the treated flours and starch granules in contrast to that of the untreated and that appropriate techniques are required to elucidate the characteristics of these modified flour starches. If this is so, then techniques that assess the properties of the flour and starch granules under equilibrium conditions will yield little useful information. This paper explores the use of a small-angle light-scattering photometer to study the dynamics of chlorinated and heat-treated flours dispersed in water rather than in sucrose solution.

Investigations already described (Marchant and Blanshard 1978) have examined various aspects of the dynamics of gelatinization of starch granules. They suggest that gelatinization involves three processes: a diffusion of water into the granules, a hydration-facilitated "melting," and a consequential swelling process. The latter two processes were investigated by the application to separated starches of fast (< 5 sec) temperature jumps of varying sizes. The results showed a time-dependent loss of birefringence over the gelatinization range which, particularly with jumps of 6°C and below, can be evaluated in terms of a two-component exponential. Marchant and Blanshard (1978) examined in some detail a possible explanation for the fast and slow components; the basic thesis argued in that publication will be assumed in this one. The starch granule is conceived of as an organized polymer system with crystallites and amorphous regions and with mutually interdependent energy relationships governing these regions. Further, the process of gelatinization is conceived of as a semicooperative process; the fast process reflects the melting of a proportion of the crystallites in a population of starch granules, and the slow process represents a disentagling and rearrangement of polymer chains. This latter process results in a further modification of the energy relationships of some adjacent crystallites which, if they fall below an energy threshold represented by the ambient temperature, also melt. In these studies native, chlorinated, and annealed wheat starches were examined. The authors merely noted that the response time of the chlorinated and annealed starches were strikingly disparate from those of native starch. These results, however, offered hope that the technique might prove valuable in exploring chlorinated and heat-treated flours.

MATERIALS AND METHODS

Samples of chlorinated flour, of flour heat-treated according to the Lyons patent (Doe 1968), and of their untreated counterparts were supplied by N. W. R. Daniels and P. J. Frazier (Spillers Ltd.). The chlorinated flour and its control both contained 7.8% protein

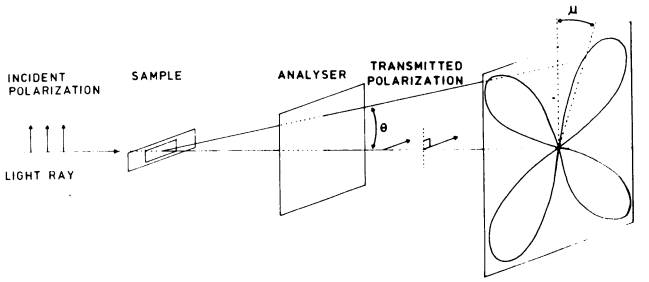

Fig. 1. Schematic diagram of small-angle light-scattering apparatus showing typical H_v scattering pattern and scattering angles Θ and μ.

0009-0352/80/04026205/$03.00/0

and had pH values of 4.9 and 6.2, respectively. The heat-treated flour and its control contained 6.6% protein.

The flour samples were dispersed in water at a concentration of 15% w/w. Each dispersion of starch granules was mounted on a No. 3 (22 × 50 mm) glass coverslip and covered by a No. 0 (18 × 18 mm) coverslip glued in position with a fast-hardening epoxy resin to exclude air bubbles from the sample and to ensure an airtight seal

The small-angle light-scattering photometer has been previously described (Marchant et al 1977). Its essential principle is illustrated in Fig. 1. In brief, the photometer consists of a polarized helium-neon 5-mW gas laser (632.8 nm), a 632.8-nm interference filter, an air-flow temperature-controlled hot-stage, a polaroid analyzer, and a solid-state photodetector. The changes in birefringence with temperature were studied in both the equilibrium and dynamic modes as follows.

Equilibrium Mode. The characteristic intensity profile of the light scattered by the starch granules was recorded by scanning through the H_v scattering pattern in the $\mu = 45°$ radial direction under constant temperature conditions. The area subtended by each curve is related to the birefringence; hence progressive gelatinization is evidenced by a fall in the area (and also by a shift in the peak maximum towards the origin, reflecting swelling of the granules). This permits the gelatinization process to be recorded in a fashion similar to that of hot-stage microscopy (Marchant et al 1977). The photodetector in this type of measurement may be used masked or unmasked; we chose to use it unmasked to avoid modifying it for the dynamic mode.

Dynamic Mode. The photometer was unmasked and centered on the brightest region of one of the cross lobes (thereby directly integrating the scattered light intensity over the sensitive area of the detector). It recorded the change when the starch/water dispersion was subjected to sudden temperature jumps of approximately 2 or 4° C. The output from the detector, which is directly proportional to the light intensity, and the sample temperature were recorded on a two-pen (y-t) chart recorder having a variable range. The output from the detector was typically either a single, fast exponential process or a double (fast and slow) exponential. The intensity profile was recorded before the first temperature jump. After each jump, the temperature was held constant until no further loss of birefringence occurred. The intensity profile was then recorded before the initiation of a further ~ 2 or ~ 4° C jump. This intensity scan recorded the progress of gelatinization between successive jumps and also permitted adjustment of the photometer to changes in the shape of the scattered light profile before the temperature was raised.

The procedure was to start temperature jumps at 30° C and proceed through the whole gelatinization range using small (~ 2 or ~ 4° C) jumps. The jumps were dialed up on a decade switch, but the actual temperature change was also recorded. Successive runs therefore approximated each other but were not absolutely identical in their progression of temperature.

To assess the reproducibility of the technique, three separate runs were performed on the same heat-treated flour, using ~ 2° C jumps, and comparable runs were performed on the chlorinated flour and the control flours for both treated samples.

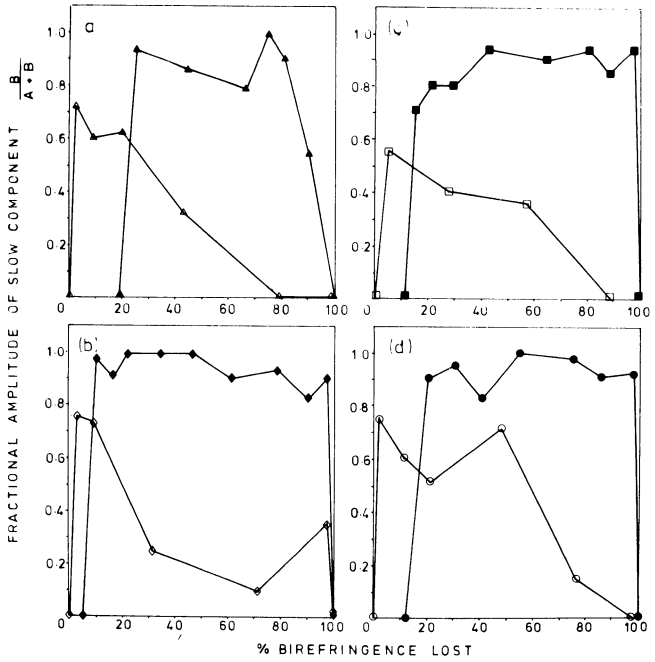

Fig. 2. Change in the fractional amplitude of the slow component (B/[A + B]) during the gelatinization process as monitored by change in birefringence in response to ~ 2 and ~ 4° C temperatures for **a**, untreated control (▲ and △); **b**, chlorinated flours (◆ and ◇); **c**, untreated control (■ and □); **d**, heat treated flours (• and o). The solid symbols are for ~ 2° C jumps, the outlined symbols for ~ 4° C jumps.

RESULTS

In response to temperature jumps of ~ 2 and ~ 4° C in less that 5 sec, the time-dependent change in birefringence usually consisted of a two-component exponential process (although the first or second component might be missing in any one jump). The fast component had a time constant (the response time) less than that of the temperature jump and the slow component a time constant of greater length. The time response was analyzed in accordance with the equation:

$$\Delta I_{Hv} = A \exp(-t/\tau_A) + B \exp(-t/\tau_B)$$

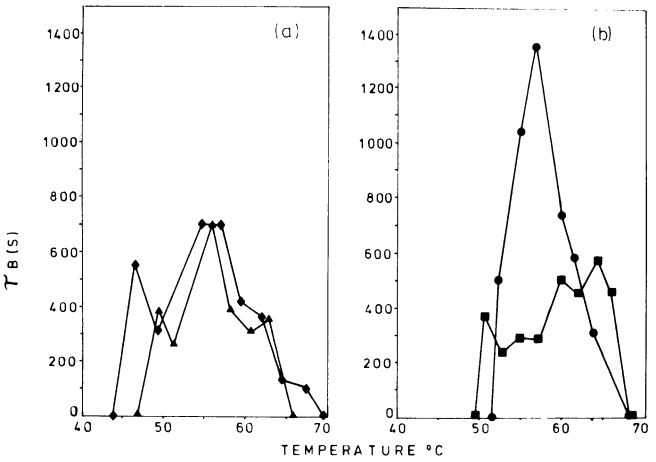

Fig. 3. Variation in the response times, τ_B, with temperature, in response to ~ 2° C jumps for **a**, untreated control (▲) and chlorinated (◆) flours and **b**, untreated control (■) and heat-treated (•) flours.

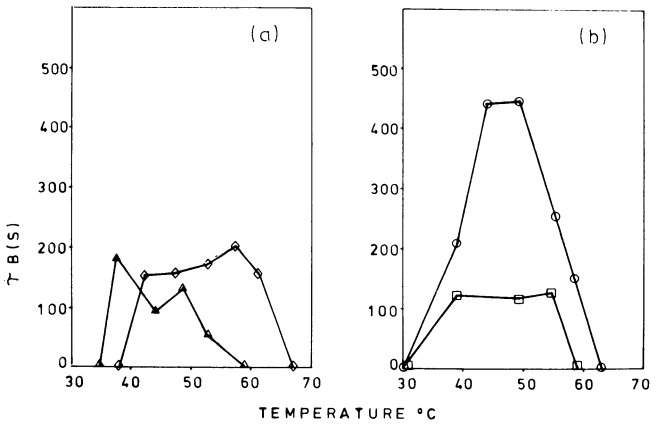

Fig. 4. Variation in the response times, τ_B, with temperature, in response to ~ 4° C jumps for **a**, untreated control (△) and chlorinated (◇) flour, and **b**, untreated control (□) and heat-treated (o) flour.

where τ_A and τ_B refer to the response times (ie, the time in which the signal falls to 1/e of its initial value) for the fast and slow processes, respectively, and A and B are the amplitudes, representing the relative contributions of the fast and slow processes to the total effect (ΔI_{H_v}) at the time of observation, t. Because τ_A was too short to be conveniently determined by this method, interest was concentrated on τ_B, A, and B.

The results were displayed in two ways. The first was the change in amplitude B with progressive gelatinization. The change of birefringence for any one jump was found by dividing the change in intensity for this jump by that observed over the whole process, but because the changes in birefringence for some jumps were large, the change of amplitude with progressive gelatinization was found by using the mid-point of the change in birefringence between the extremes registered for each jump. In practice, the change in the value of B was expressed as a fractional amplitude B/(A + B). Figure 2 represents the results for the two treated flours and their controls for both ~ 2 and ~ 4°C jumps. The second display showed the change in response time τ_B as a function of temperature, the temperature being the mid-point between the two extremes of the jump. The results for ~ 2 and ~ 4°C jumps for the four flours are illustrated in Figs. 3 and 4, respectively.

DISCUSSION

A cursory examination of the results in Figs. 3 and 4 suggests that the response times for the treated flours tend to be longer than those for the untreated flours for ~ 2 and ~ 4°C jumps. In contrast, the samples show little difference in the variation of the fractional amplitude B/(A + B) with increasing loss of birefringence, except that the ~ 2 and ~ 4°C jumps follow a similar pattern. The basis for these differences must be examined more carefully.

Even though at this stage we do not know the exact mechanism whereby heating and chlorination have their effect, in terms of Marchant and Blanshard's model the result is a modification of the melting and swelling processes. To assess the contribution of the time-dependent process to the overall behavior of the starch granules over the gelatinization range, however, both the amplitude and response time of each time-dependent process are needed. In other words, having analyzed the decay into an amplitude, B, and a response time, τ_B, we need to recombine them, to sum the response for each temperature jump over the total number of jumps for the whole gelatinization range, and to examine the possible technological significance of differences. We can thereby assess the extent of differences in the flours' dynamic responses over the whole gelatinization range.

The method of calculation is illustrated in Fig. 5. The example is for the chlorinated and control flours subjected to ~ 2°C jumps, and the resultant curve is Fig. 6. The solid zones of Fig. 5, which represent the time-dependent decays arising from τ_B are summed. This is done by the numerical summation of each Be^{-t}/τ_B component of the total response for all individual (i) decays that have slow components, yielding $\sum_i B_i e^{-t}/\tau_{B\,i}$.

We were particularly interested, however, in assessing any difference in the summed time dependency between the controls and the treated flours. Such a difference might be expected if the dynamics of gelatinization, particularly the swelling of treated flours, are different from those that have not been so treated.

Three approaches were taken. The first relied on the fact that the cross-hatched region under the curve can be shown analytically to have the remarkably simple form $B\tau_B$ because on integration between the limits t = 0 and t = ∞,

$$\int_0^\infty Be^{-t}/\tau_B = B\tau_B$$

This result for each ~ 2°C jump may be plotted as a histogram as in Fig. 7, the steps on the horizontal axis representing ~ 2°C jumps, or be summed over the whole gelatinization process and expressed as a summed response time index, $\sum_i B_i\tau_{Bi}$. The index values for the different flours are also shown in Fig. 7. This integrated index clearly distinguishes between treated and untreated flours. The results also show that the technique is sensitive to differences in the untreated control flours and hence, possibly, will provide a method for examining aspects of flour quality. This point is being pursued further.

In the second method, time dependency is examined at the expense of neglecting the absolute values of the amplitudes. If the summed time dependences for the four flours are normalized to 100 at t = 0, the results may be displayed as in Fig. 8. If, subsequently, the control value is subtracted from the treated value in each case, the difference may be plotted against time (on a log scale for convenience), as is shown in Figs. 9 and 10 for ~ 2 and ~ 4°C jumps, respectively. The coincidence of the maxima for the ~ 2°C jumps and the similarity of the ~ 4°C jumps is most noticeable. The value of the maxima shifted from about 500 sec for ~ 2°C jumps to about 100–150 sec for ~ 4°C jumps. Although the value on the ordinate of the maxima appears greater for the ~ 4°C jumps than for the ~ 2°C jumps, no great significance should be attached to this because it is almost certainly a consequence of the normalization procedure.

The third method evaluates the contribution of the slow component as a percentage of the total. This is determined by calculating the value of $\sum_i B_i e^{-t}/\tau_{B\,i}$ for each flour at t = 0. This represents $\sum_i B_i$ ie, the summed amplitudes of the individual slow

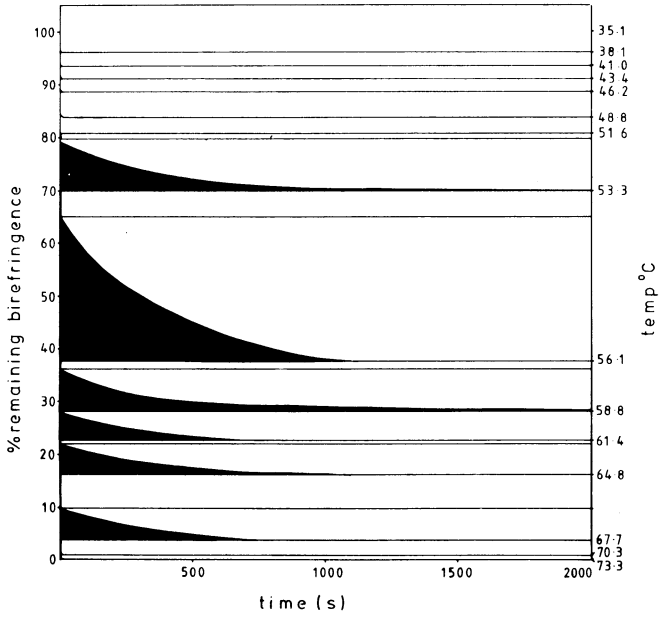

Fig. 5. Birefringence time response curves recorded consecutively for the control to the chlorinated flour. The left hand ordinate records on a linear scale the changes in birefringence in response to the temperature jumps indicated on the right hand ordinate. The solid zones represent the slow second component, B exp (−t/τ_B), of each jump.

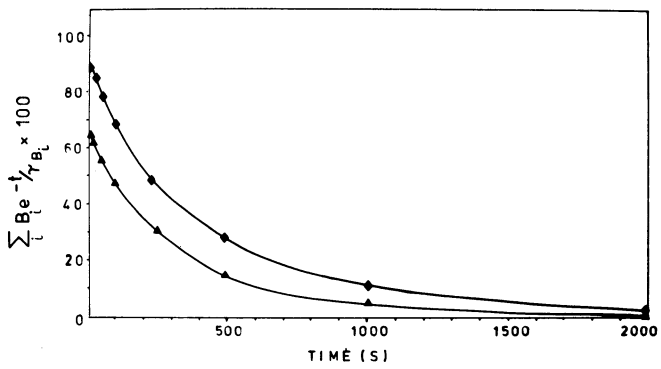

Fig. 6. The numerically summed birefringence-time response curves of the slow components for the chlorine-treated flour (♦) and also for the control flour (▲) shown in Fig. 5, $\sum_i B_i(\exp^{-t}/\tau_{Bi})$ in response to ~ 2°C jumps.

components for the overall gelatinization process. Usually the summed amplitudes of the slow components are greater for the treated than for the untreated flours (Table I).

The reproducibility of results has been questioned The results for three separate runs conducted on different days for the same sample of heated wheat flour have been worked through, and the error bars on Figs. 8 and 9 indicate that in the appropriately calculated form remarkably little scatter exists in their time response. Furthermore, when their summed response time indices are calculated, the values are 54,069, 54,574, and 53,668. These are remarkably close when one notes that the control flour has a value of 30,806.

The outstanding point that emerges from an examination of these results is that both chlorinated and heat-treated flours submitted to this dynamic method exhibit similar physicochemical responses, that is, loss of birefringence in comparison with the control flours. The treated flours possess a more substantial slow component over the total gelatinization range. The component can be expresses in terms of both amplitude and response time. If we consider rheological or nuclear magnetic relaxation as analogies, then the shorter the relaxation time, the more rigid the molecular organization. Extending these ideas to the starch granule, we can consider the untreated starch granules to be more rigid than the untreated.

Reports in the literature, however, suggest that little difference exists in the gelatinization temperature of chlorinated and heat-treated flours as monitored, for example, by differential scanning calorimetry (Jacobsberg and Daniels 1974). Such results would eliminate the possibility of a substantial modification of the internal

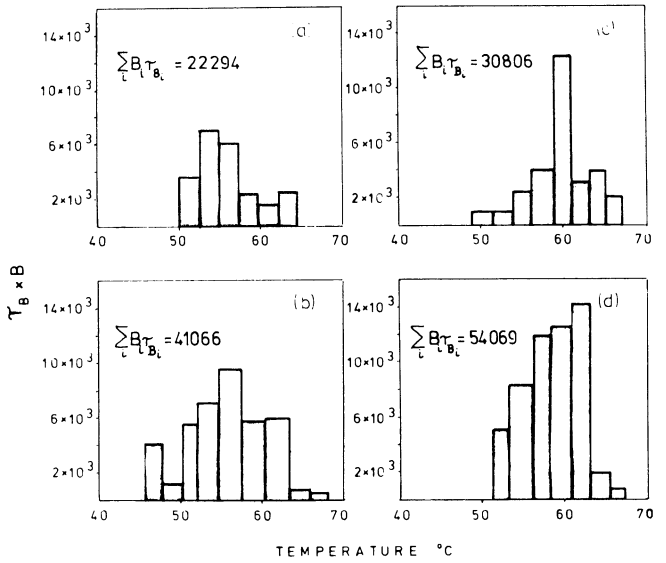

Fig. 7. Histograms of the index ($\tau_B \times B$) for successive ~ 2° C jumps and the summed index ($\sum_i B_i \tau_{Bi}$) for each flour for **a,** the control for **b,** the chlorinated flour and **c,** the control for **d,** the heat-treated flour, in response to ~ 2° C jumps.

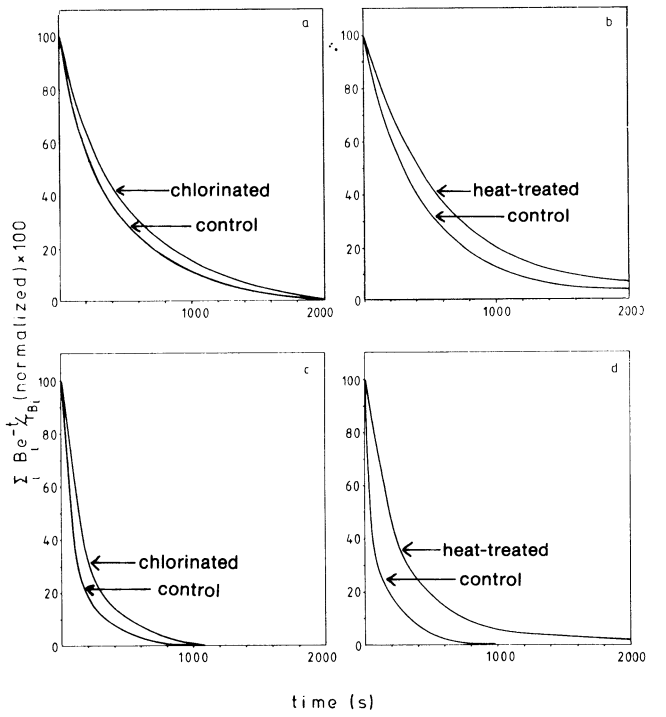

Fig. 8. The numerically summed, normalized × 100, birefringence-time response curves of the slow components for the **a,** chlorinated and control flours and **b,** heat-treated and control flours in response to ~ 2° C jumps, and **c,** chlorinated and control flours and **d,** heat-treated and control flours in response to ~ 4° C jumps.

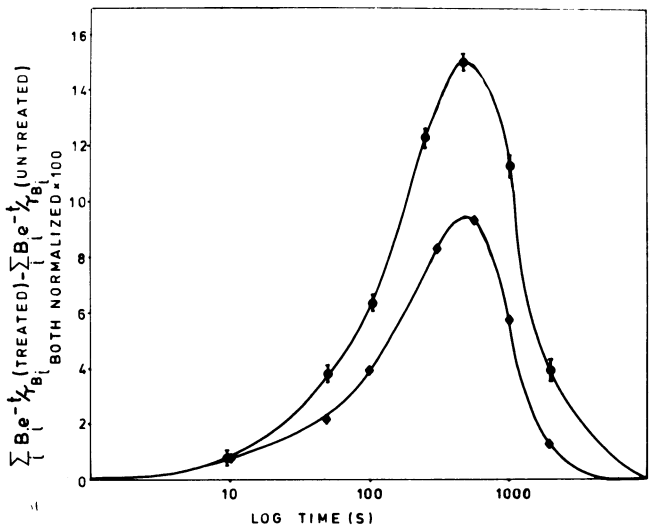

Fig. 9. The difference between the numerically summed, normalized × 100, birefringence-time response curves of the slow components of the chlorinated (♦) and heat-treated (•) flours and their respective controls to ~ 2° C jumps, showing the times of maximum difference.

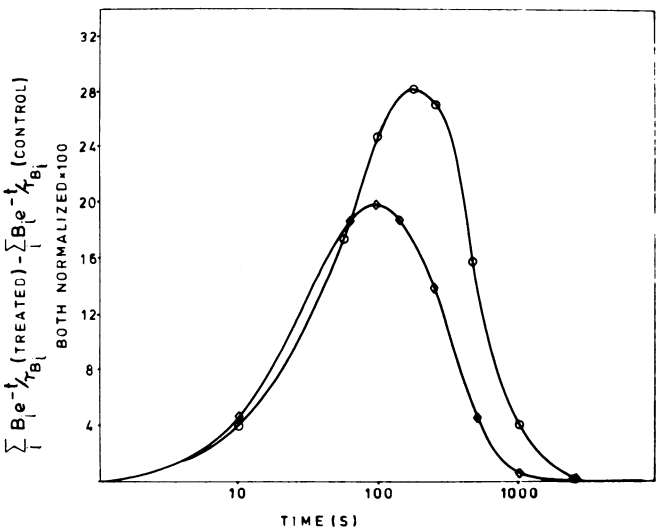

Fig. 10. The difference between the numerically summed, normalized × 100 birefringence-time response curves of the slow components of the chlorinated (◊) and heat-treated (o) flours and their respective controls in response to ~ 4° C jumps, showing the times of maximum difference.

crystallite structure, as is caused by annealing. If we accept this latter conclusion (and assume that it holds over the whole gelatinization range), then for any given temperature jump, the actual loss of birefringence is approximately the same. What differs must be the method by which it occurs and the consequences this has for the granule structure. The loss of birefringence in the untreated flours takes place somewhat faster than in the treated flours (affecting a greater proportion of the faster component and producing faster response times for the slow component). In contrast, the treated flours respond more slowly and, according to the semicooperative hypothesis of gelatinization, have more time for some reorganization, particularly in the later stages of gelatinization. On the bases of this model, raising the temperature over a given range should lead to more substantial swelling of the treated than of the untreated starch granules. The angle at which the scattering intensity is at a maximum (Θ_{max}) is related inversely to the spherulitic scattering radius, r (in this instance the starch granules), and also to the wavelength of the incident light, λ. This relationship is expressed by:

$$\Theta_{max} = 2 \sin^{-1} (\lambda / \pi r)$$

Therefore, any change in the radius of the granules should be reflected in the position of Θ_{max}. For any given increase in temperature, Θ_{max} should shift towards the center beam more substantially for the treated than for the untreated flours. A reexamination of the results from the equilibrium mode showed this to be true. It is evident in the plot of $\Theta_{max}(T°C)/\Theta_{max}(36°C)$ versus temperature for the heat-treated and control flours (Fig. 11).

With these assumptions and the results described in this article, the picture that emerges is that for a given temperature jump, the treated starch granules, both chlorinated and heated, do not lose more birefringence than the untreated ones do, but are able to swell more and possibly to do so with some reorganization of the polymer chains. Frazier et al (1974) found, after submitting flour/water slurries to different heating processes and observing the subsequent gel strength rheologically, that the heated and chlorinated flour samples had significantly higher gel strengths than did those from the control flours. Although their technique, using a bulk rheological measurement, was very different from that described in this paper, in both cases the results emphasize the importance of the relative rates of swelling of the treated and untreated starch granules.

The recent studies of Nicholas et al (1978) Cauvain et al (1977), and Kissell et al (1979) have pointed to surface phenomena being responsible for the distinctive behavior of chlorinated and heat-treated flours. Studies using the light-scattering technique continue to examine various possible chemical and physicochemical explanations of the effects of chlorination and heat. In addition, the developing interest in modifying starches physically by heat or even physiologically in the growing crop provides a wide field of study within which this technique may continue to provide penetrating insights into the changes in granule architecture and the relationship of such modifications to cereal technology.

Table I.
Values of $\sum_i B_i$ for the Variously Treated Flours and Their Controls for ~ 2 and ~ 4°C Temperature Jumps

	Size of Temperature Jump	
Flour Type	~ 2°C	~ 4°C
Chlorinated	88.5	25.9
Control	63.8	27.5
Heat-treated	86.3	42.9
Control	80.4	25.0

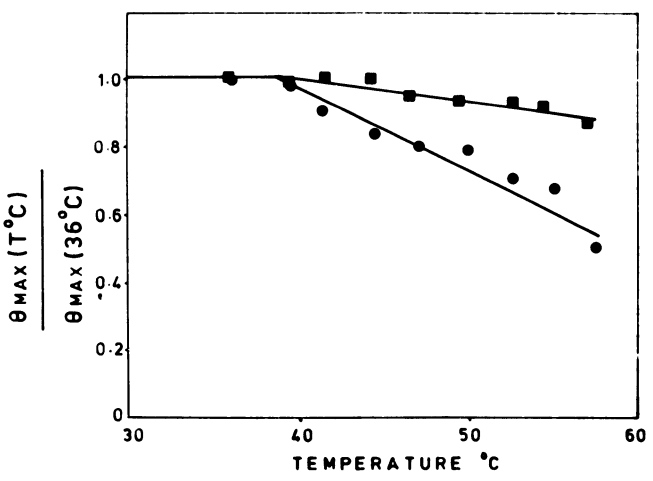

Fig. 11. Variation of the angle of maximum scattering intensity (Θ_{max}) at different temperatures, normalized to the value of Θ_{max} at 36°C, versus temperature, for heat-treated (•) and control (■) flours, to show the greater swelling behavior of the heat-treated flour in response to ~ 2°C jumps.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support for Z. H. Bhuiyan from United Biscuits and the supply of treated and untreated flour samples from N. W. R. Daniels and P. J. Frazier (Spillers Ltd). We are also grateful for the initial help of J. L. Marchant, the technical support of M. C. A. Chapman, and the continuing enthusiastic interest of R. A. Lawrie.

LITERATURE CITED

CAUVAIN, S. P., GOUGH, B. M., and WHITEHOUSE, M. E. 1977. The role of starch in baked goods. II. The influence of purification procedure on the surface properties of the granule. Staerke 29:91.

CAUVAIN, S. P., HODGE, D. G., MUIR, D. D., and DODDS, N. J. H., inventors; FLOUR MILLING AND BAKING RESEARCH ASSOCIATION, assignee. 1976a. Improvements in and relating to treatment of grain. British patent 1,444,173, July 28.

CAUVAIN, S. P., HODGE, D. G., MUIR, D. D., and DODDS, N. J. H., inventors; FLOUR MILLING AND BAKING RESEARCH ASSOCIATION, assignee. 1976b. Treatment of grain. U.S. patent 3,976,298, Aug. 10.

DOE, C. A. F., and RUSSO, J. V. B., inventors; J. LYONS AND CO., LTD., assignee. 1968. Flour treatment process. British patent 1,110,711, April 24.

DOE, C. A. F., and RUSSO, J. V. B., inventors; J. LYONS AND CO., LTD., assignee. 1969. Heat treatment of flour. Canadian patent 808,591, Mar. 18.

DOE, C. A. F., and RUSSO, J. V. B., inventors; J. LYONS AND CO., LTD., assignee. 1970. U. S. patent 3,490,917, Jan. 20.

FRAZIER, P. J., BRIMBLECOMBE, F. A., and DANIELS, N. W. R. 1974. Rheological testing of high-ratio cake flours. Chem Ind. London:1008.

GOUGH, B. M., GREENWOOD, C. T., and WHITEHOUSE, M. E. 1978. The role and function of chlorine in the preparation of high ratio cake flour. Crit. Rev. Food Sci. Nutr. 10:91.

GREENWOOD, C. T. 1976. Starch. Adv. Cereal Sci. Technol. 1:119.

JACOBSBERG, F. R., and DANIELS, N. W. R. 1974. Gelatinization properties of high-ratio cake flours. Chem. Ind. London:1007.

KISSELL, L. T., DONELSON, J. R., and CLEMENTS, R. L. 1979. Functionality in white layer cake of lipids from untreated and chlorinated patent flours. Cereal Chem. 56:11.

MARCHANT, J. L., and BLANSHARD, J. M. V. 1978. Studies of the dynamics of gelatinization of starch granules employing a small-angle light-scattering system. Staerke 30:257.

MARCHANT, J. L., CHAPMAN, M. C. A., and BLANSHARD, J. M. V. 1977. An investigation of equilibrium and dynamic aspects of starch gelatinization using a small-angle light-scattering photometer with a solid state photo-detector. J. Phys. E. 10:928.

NICHOLAS, E. M., BOYNTON, G. E., RUSSO, J. V. B., and TOTTY, R., Inventors; J. LYONS AND CO., LTD., assignee. 1978. Flour treatment process. British patent 1,499,986, Feb. 1.

MONTZHEIMER, J. N. 1931. A study of methods for testing cake flour. Cereal Chem. 8:510.

SOLLARS, W. F. 1958. Cake and cookie flour fractions affected by chlorine bleaching. Cereal Chem. 35:100.

[Received August 9, 1978. Accepted November 8, 1979]