Influence of Rice Crystallinity on Cross-Linking

M. N. ISLAM, J. E. RUTLEDGE, and W. H. JAMES, Department of Food Science, Louisiana State University, Baton Rouge 70803

ABSTRACT

The failure to cross-link starch in white rice by phosphorus oxychloride and sodium trimetaphosphate has been related to the inherent degree of crystallinity in the ungelatinized kernel. Parboiled rice, because of its larger amorphous domain as evidenced by X-ray diffraction, gave satisfactory response to phosphorus oxychloride and sodium trimetaphosphate. Comparison of the molecular weight, size, and shape of epichlorohydrin, phosphorus oxychloride, and sodium trimetaphosphate, considering the compact crystal lattice of white rice, indicates that epichlorohydrin would have the easiest access into the grain. Instability of phosphorus oxychloride in alkaline solution, and the stronger ether linkage formed by epichlorohydrin, may also contribute to the discrepancy in cross-linking of white rice.

Recently we have reported (1,2) the process of cross-linking starch hydroxyl groups in the intact rice kernel for improving its canning stability. The cross-linked rice, because of its excellent heat-moisture stability and superior organoleptic properties, has a high potential for commercial incorporation in heat-processed formulations. Three cross-linking agents, namely epichlorohydrin, sodium trimetaphosphate, and phosphorus oxychloride, have so far been used by us to modify starch in the intact rice grain. We found that parboiled rice reacted well with these reagents, but raw white milled rice could be cross-linked to the desired extent only by epichlorohydrin. Neither sodium trimetaphosphate nor phosphorus oxychloride could be satisfactorily used to improve the canning stability of white rice, although there are reports (3–6) concerning successful use of both of these reagents for cross-linking ungelatinized powdered starch from sources other than white rice. The purpose of our present investigation was to seek the causes of this differential behavior of white rice toward the three cross-linking agents.

The first approach was made through X-ray diffraction of white and parboiled rice starch for possible correlation between the extent of cross-linking and the

degree of inherent crystallinity. This was then followed by consideration of other factors such as molecular weight, size, shape, and stability of the cross-linking agents.

MATERIALS AND METHODS

White rice of the Bluebelle and Bluebonnet 50 varieties was obtained from Dore Rice Mill, Inc.; Crowley, La.; canners' quality parboiled Bluebelle was obtained from Uncle Ben's, Inc., Houston, Tex. Bluebonnet 50 was parboiled in our laboratory according to the method described by Rao and Juliano (7).

The four rice samples (two white and their parboiled counter parts) were ground into a flour using a Wiley Mill with a 40-mesh screen. The rice flour was shaken repeatedly with 0.2% sodium hydroxide and centrifuged until the washings were negative to biuret reagent. The flour was then washed with distilled water until the washings were neutral to phenolphthalein. The starch preparation was then air-dried and the top and bottom crusts discarded. The method of sample preparation was similar to that described by Lugay and Juliano (8).

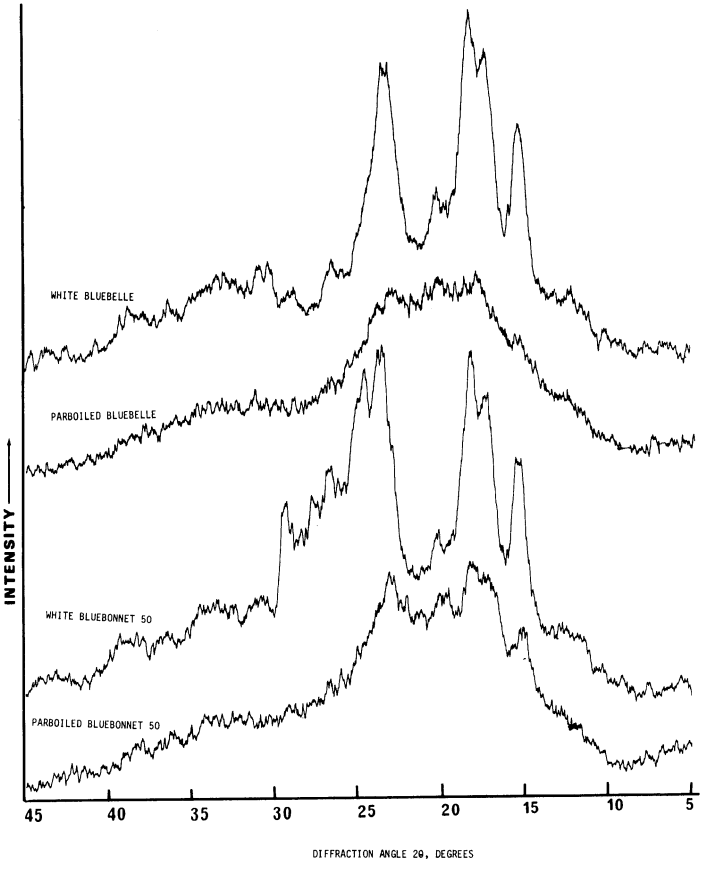

Fig. 1. X-ray diffractograms of rice starch from Bluebelle and Bluebonnet 50.

TABLE I. X-RAY DIFFRACTION INTENSITY (COUNTS PER SEC.) OF BLUEBELLE AND BLUEBONNET 50 RICE STARCHES

Source of Starch	2θ = 15.2°C.	17.2°C.	18.1°C.	23.4°C.	Source of Starch	2θ = 15.2°C.	17.1°C.	18.1°C.	23.5°C.	24.5°C.
White Bluebelle	135.5	193.0	222.5	184.0	White Bluebonnet 50	132.0	179.5	210.5	209.5	190.0
Parboiled Bluebelle	49.5	99.0	97.0	91.0	Parboiled Bluebonnet 50	71.0	110.5	119.0	110.0	81.0

The powdered starch materials were analyzed with a Norelco X-ray diffraction unit. The rice starch was scanned from 5° to 45°C. at 2° 2θ per min. The diffraction conditions were as follows: CuKα radiation with Ni filter; high-tension voltage, 40 kv.; current, 15 ma. Intensities were calculated by drawing base lines according to the method described by Moore (9).

RESULTS AND DISCUSSION

X-ray diffractograms of white Bluebelle and Bluebonnet 50 along with their parboiled counterparts are presented in Fig. 1. All four diffractograms show similar major peaks. The principal indexes for Bluebelle were at 2θ = 15.2°, 17.2°, 18.1°, 23.4°C., and for Bluebonnet 50, 15.2°, 17.1°, 18.1°, 23.5°C., and an additional one at 24.5°C. These peaks correspond to interplanar distances of 5.83, 5.16, 4.90, 3.80, and 5.83, 5.19, 4.90, 3.79, 3.63 Å, respectively.

Diffraction intensities at various 2θ angles for both varieties are given in Table I. The diffraction intensities for white Bluebelle rice ranged from 135.5 to 222.5 counts per sec., whereas those for parboiled Bluebelle ranged from 49.5 to 99.0 counts per sec. Similarly, for white Bluebonnet 50 the values ranged from 132.0 to 210.5, and those for parboiled Bluebonnet 50 ranged from 71.0 to 119.0. Since the magnitude of the diffraction intensity indicates the relative extent of the crystalline domain, it is evident that the parboiling process markedly reduced the extent of the crystalline domain naturally present in white rice.

White rice starch, with a larger crystalline domain and a more compact crystal lattice than those of parboiled rice starch, would present in rice kernels a smaller specific surface area than would parboiled rice starch, which is mostly amorphous in form. Consequently, parboiled rice, because of its larger specific surface area, would react more rapidly and efficiently with cross-linking reagents than would white rice. This explains, at least in part, why parboiled rice gave satisfactory responses to each of the three reagents, namely, epichlorohydrin, sodium trimetaphosphate, and phosphorus oxychloride.

White rice was not reactive to phosphorus oxychloride or sodium trimetaphosphate, although it gave a satisfactory response with epichlorohydrin. Ungelatinized crystalline starches other than white rice have been reported in the literature (3–6) to cross-link successfully with phosphorus oxychloride and sodium trimetaphosphate. These findings suggest that two important factors influence the extent of cross-linking in starch: a) the type of chemical reagent, and b) the form in which starch is subjected to the action of the reagent.

Epichlorohydrin, which reacts with either parboiled or white rice, evidently possesses some advantageous characteristics that are missing in phosphorus oxychloride and sodium trimetaphosphate, both of which react with parboiled rice but neither of which reacts with white rice.

A comparison of the molecular weights and structures of the three cross-linking reagents (Fig. 2) shows that epichlorohydrin has the lowest molecular weight and a fairly linear shape, which would be augmented by the instability of the epoxide ring in the presence of alkali. Phosphorus oxychloride has a higher molecular weight and a nearly tetrahedral shape. Since the starch granules in white rice are present in a highly compact arrangement which directly limits the depth of access of chemical reagents for cross-linking within the kernel, the smaller, more nearly linear molecules of epichlorohydrin would be more diffusible into the compact white rice

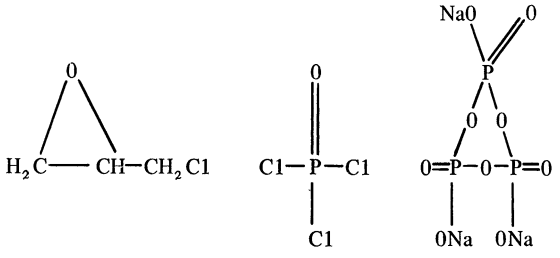

Fig. 2. Structures and molecular weights of three cross-linking reagents.

kernel than would the larger tetrahedral molecules of phosphorus oxychloride. Sodium trimetaphosphate, with its much higher molecular weight and complex structure, would have fewer opportunities for cross-linking than either epichlorohydrin or phosphorus oxychloride.

The stability of the reagent in the reaction mixture undoubtedly has some influence on the overall cross-linking efficiency. Phosphorus oxychloride is highly unstable in the presence of either water or sodium hydroxide solution, yet this reagent has been reported (3) to cross-link powdered starches. Compared to rice kernels, powdered starch would have a much larger specific surface area exposed to the reaction medium for cross-linking with phosphorus oxychloride before the latter was hydrolyzed to phosphoric acid and HCl.

Attempts in this laboratory to cross-link white Bluebelle rice with phosphorus oxychloride in pyridine, in which the reagent is stable, were unsuccessful. Moreover, sodium trimetaphosphate, which is fairly stable in alkaline medium, also failed to cross-link white rice as desired. These findings further emphasize the importance of a) molecular size and shape of the chemical reagent with respect to the efficiency of the cross-linking reaction, and b) the extent of specific surface area of starch exposed to the reaction medium.

The experiments with white rice indicate that the relative affinities of the three reagents in a descending order are epichlorohydrin, phosphorus oxychloride, and sodium trimetaphosphate. Furthermore, the type of cross-bond which results in these reactions, such as ether linkages from epichlorohydrin which are stronger than ester linkages from the phosphorus compounds, undoubtedly has a significant influence on the canning stability of cross-linked rice.

Acknowledgment

Appreciation is expressed to J. S. Hanor, Associate Professor of Geology, Louisiana State University, Baton Rouge, for providing the X-ray diffraction data.

Literature Cited

1. RUTLEDGE, J. E., ISLAM, M. N., and JAMES, W. H. Improved canning stability of rice by chemical modification. Cereal Chem. 49: 430 (1972).
2. RUTLEDGE, J. E., ISLAM, M. N., and JAMES, W. H. Improved canning stability of parboiled rice through cross-linking. Cereal Chem. 51: 46 (1974).
3. FELTON, G. E., and SCHOPMEYER, H. H. Thick-bodied starch and method of making. U.S. Patent 2,328,537; Chem. Abstr. 38: 889 (1944).
4. KERR, R. W., and CLEVELAND, F. C., Jr. Process for the preparation of distarch

phosphate and the resulting product. U.S. Patent 2,801,242 (1957); Chem. Abstr. 51: 18666 (1957).
5. KERR, R. W., and CLEVELAND, F. C., Jr. Surgical dusting powder and process therefor. U.S. Patent 2,938,901; Chem. Abstr. 54: 16886 (1960).
6. KERR, R. W., and CLEVELAND, F. C., Jr. Orthophosphate esters of starch. U.S. Patent 2,884,413; Chem. Abstr. 53: 16569 (1959).
7. RAO, S. N., and JULIANO, B. O., Effect of parboiling on some physicochemical properties of rice. J. Agr. Food Chem. 18: 289 (1970).
8. LUGAY, J. C., and JULIANO, B. O. Crystallinity of rice starch and its fractions in relation to gelatinization and pasting characteristics. J. Appl. Polym. Sci. 9: 3775 (1965).
9. MOORE, C. A. Use of x-ray diffraction for the quantitative analysis of naturally occurring multicomponent mineral system. Southeast. Geol. 6: 139 (1965).

[Received February 7, 1973. Accepted April 25, 1973]