# EFFECT OF CHEMICAL MODIFICATIONS ON THE ULTRASTRUCTURE OF CORN, WAXY MAIZE, AND TAPIOCA STARCHES[1]

J. F. CHABOT, L. F. HOOD, and J. E. ALLEN, Department of Food Science, Cornell University, Ithaca, NY 14853

## ABSTRACT

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Unmodified and modified tapioca, corn, and waxy maize starches were examined with light and electron (scanning and transmission) microscopy. Modified starches investigated included those cross-linked with $POCl_3$ or epichlorohydrin, and/or derivatized with propylene oxide or acetic anhydride. Only slight differences were noted in the structure of granules cross-linked with different reagents. Some samples of uncooked modified starches showed granule breakage and partial gelatinization. Gelatinized preparations of unmodified tapioca consisted of few granules and a mass of interconnected fibrils of variable dimension. Hydroxypropyl distarch phosphate and acetylated distarch glycerol from tapioca had intact granules containing a diffuse material as well as intergranular fibrils. Unmodified waxy maize and all modified waxy maize starches had little or no extragranular fibrillar material. Unmodified and modified corn had small granules embedded in a fine fibrillar matrix. Some of the modified granules also had diffuse fibrillar material in the central cavity of the granule. Chemical modification of corn and tapioca starch caused a reduction in the amount of extragranular starch, with the maintenance during cooking of an intact envelope around a fibrillar filled cavity.

Structure, swelling properties, and stability of starch granules are important in determining how they function during food processing. For example, the texture of baked goods is dependent on the type of starch used, both with respect to amylose/amylopectin ratios and to the botanical origin of the granule (1).

Chemical modification of starches is used to achieve properties needed for food processing and storage (2). Cross-linking starch increases the stability during cooking, especially under shear or acid conditions. Derivatizing starch inhibits the association of amylose in the cooked starch paste.

Relatively little is known about the effect of chemical modification on starch granule structure. Hood *et al.* (3) have described the ultrastructure of hydroxypropyl distarch phosphate from tapioca and compared it to unmodified tapioca. The scanning electron microscope has only recently been utilized for the study of the ultrastructure of gelatinized starch. Miller *et al.* (4) examined structural changes associated with viscosity measurements in wheat starch paste. Hill and Dronzek (5) studied wheat, corn, and potato starches during early gelatinization and found an exudate coming from the granules at low temperatures and associated this with the loss of polarization crosses. At higher temperatures, they found total disruption of the granules.

In this study we examined the structure of several types of modified and unmodified starches: tapioca, waxy maize, and corn. Special emphasis was placed on how modification affects the structure of the cooked granule.

## MATERIALS AND METHODS

Flasks containing starch suspensions (1%) were immersed in a water bath or

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placed on a hot plate at a temperature of 80°–95° C for 5–10 min. The solutions were stirred gently to keep the starch granules in suspension. After the heat treatment, no polarization crosses were seen and the granules were swollen. For more controlled heating, 1% starch solutions were cooked using a Brabender amylograph with 1.5° C rise per min. However, this method subjected the paste to high shear forces and disrupted the swollen granules in some unmodified waxy maize and tapioca starch preparations.

Material for light microscopy was stained with iodine solution and examined with a Leitz Ortholux microscope. Material for scanning electron microscopy was removed with a spatula, placed on aluminum specimen mounts using double sided sticky tape, frozen in liquid nitrogen and freeze-dried. Specimens were coated with carbon and gold-palladium and examined with a Mini-SEM scanning electron microscope.

Modified and unmodified starch samples were provided by National Starch and Chemical Corp., A. E. Staley Manufacturing Co., and Stein, Hall and Co., Inc. Starches were modified with epichlorohydrin, propylene oxide, acetic anhydride, and/or phosphorous oxychloride.

## RESULTS

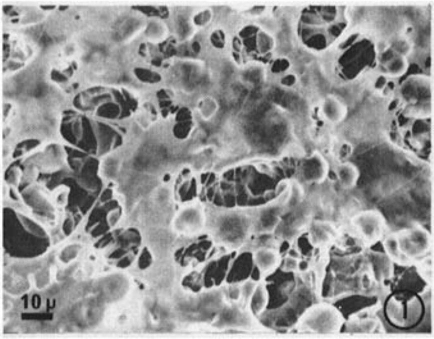
### Tapioca

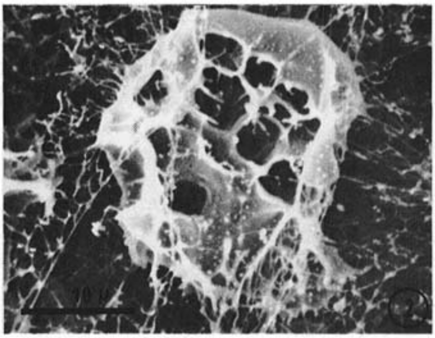
Uncooked tapioca granules were round with 1-5 indentations on one side. Both modified and unmodified granules had a smooth surface with no indication of the pitting seen by Hall and Sayre (6). Most modification procedures seemed to have little effect on granule morphology. In some of the modified samples, partial gelatinization was seen with the light microscope; another sample showed extensive damage with many granule fragments. Only samples with minimal change from the unmodified state were investigated further.

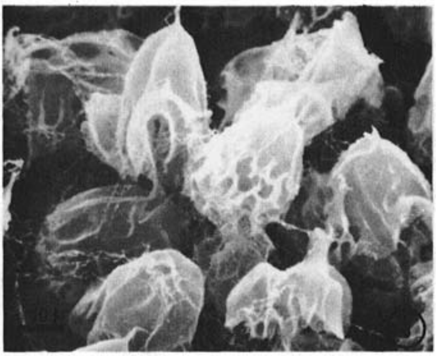
Unmodified tapioca granule structure changed markedly during cooking. As the temperature increased material leached out of the granules, the granules lost their polarization crosses and eventually swelled. In samples removed from the Brabender amylograph at 65° C, granules were present but were surrounded by a matrix of strands and sheets (Fig. 1). Granule swelling had begun before any rise in viscosity was recorded on the Brabender. No intact swollen granules were evident at peak viscosity but rather a honeycomb arrangement of sheets of nongranular starch was evident.

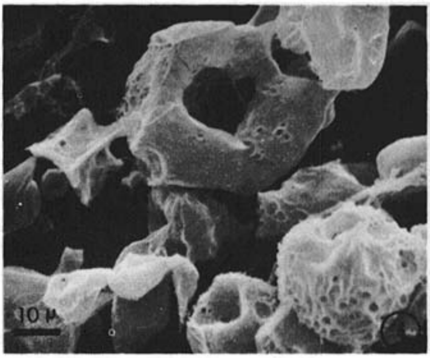
When unmodified tapioca was cooked under mild conditions some intact granules or identifiable granule ghosts were present at 80°–90° C. Extragranular starch formed more thread-like structures in contrast to the solid sheets formed after Brabender cooking. Figure 2 shows a partially disintegrated granule with direct continuity between the granule surface and the strands of the matrix. By prolonging the cooking time the granules were totally disrupted.

All of the cross-linked, substituted starches behaved in a similar manner during cooking. Granules expanded to become sac-like structures. Amylose, stained blue with iodine, was present in the interior of the sacs and a variable amount was seen between the granules in the solution. Scanning electron micrographs revealed intact granules surrounded by a matrix of fibrils (Fig. 3). The granule surface was folded with more folds present toward the former flat







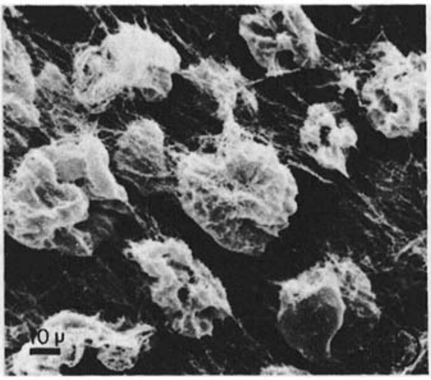



Fig. 1. Unmodified tapioca starch cooked to 65° C in Brabender. Most granules were not yet swollen. Exudate was present. 400×. Fig. 2. Unmodified tapioca starch cooked to 80°−90° C in flask. Granule structure was open with extragranular fibrils evident. 1500×. Fig. 3. Hydroxypropyl distarch phosphate tapioca cooked to 95°C in flask. Granules swelled but remained intact. Folds were present in the envelopes. 600×. Fig. 4. Unmodified corn starch cooked to 80°C in Brabender. Limited swelling. Little extragranular fibrillar material was present. "Donut" shape was common in some corn samples. 600×. Fig. 5. Unmodified corn starch cooked to 95°C in Brabender. Swollen granules beginning to disintegrate. Extragranular fibrils were present. 400×.

end. Holes were evident in the surface although not as much as in the unmodified granules. Cross-linking substantially reduced the open meshwork nature of the swollen envelope.

**Corn**

Uncooked corn starch consisted of polygonal and spherical granules that stained deeply blue with iodine solution. Sizes ranged from 10 $\mu$m small spheres to large irregular granules, 25–40 $\mu$m in diameter. Figure 4 illustrates a preparation of unmodified corn starch at 80° C from the amylograph. A variety of shapes was present. Slight swelling had begun, emphasizing the hollow belt type of formation. Spherical granules were swollen and slightly folded. Figure 5 illustrates a sample removed from the Brabender amylograph after 10 min at 95° C. Swollen sacs with many extragranular fibrils were evident. Some granule disintegration had begun.

Modified corn starches showed greater swelling than unmodified, with formation of spheres and retention of amylose in the center. Substituted, non-cross-linked starch formed very large balloons that stained only pale blue with iodine. In the scanning electron microscope, these appeared as spheres with folds and some disintegration and fraying around the edges. The level of cross-linking affected the degree of swelling, with highly cross-linked samples showing slightly more folding and less swelling. No other structural differences could be related to the type of chemical used. Granules cross-linked with phosphorous oxychloride and substituted with propylene oxide, and cooked to 95° in the amylograph are seen in Fig. 6. Swollen sacs were present with extragranular fibrils. Starch cross-linked with phosphorous oxychloride is seen in Fig. 7. Sacs were formed, and in this case part of the wall has been torn off revealing the fibrillar component in the interior. The outer wall was smooth surfaced, but it was in direct contact with extragranular fibrillar material.

**Waxy Maize**

Uncooked waxy maize granules were polygonal, similar to corn, but stained light brown rather than blue with iodine solution. Cooked unmodified waxy maize granules had a curly appearance, and stained brown. In the scanning electron microscope the folded morphology of the envelope was emphasized, although this varied in degree. Only a few fibrils were seen between the granules, but the granules were in contact with each other and some stretching and fraying of edges was noted (Fig. 8). After cooking in the Brabender, very little intact granule structure of the unmodified waxy was seen. There were only very elongated stretched bands of starch.

All of the modified waxy maize preparations looked similar after gentle cooking. Figure 9 shows an epichlorohydrin cross-linked-propylene oxide substituted waxy maize granule. The envelope was very convoluted and folded. This varied slightly from one granule to another. Practically no extragranular fibrillar material was present. Brabender cooking of modified waxy resulted in some alteration of granule structure, with the granules becoming elongated and stretched. No central cavity could be detected, as was seen in the modified corn and tapioca starches.

## DISCUSSION

The gelatinization process, especially as noted with the light microscope, includes loss of birefringence, leaching of amylose into solution, and tangential swelling, resulting in a small bladder (7). At first some amylose is retained in the interior cavity, but rupture, collapse, and dissolution of the swollen starch granule occur during prolonged heating. Cross-linking restricts the swelling of starch granules and makes the swollen granules more resistant to degradation. Although the peak viscosity of the cooked paste is lower in comparison to non-cross-linked starch, the higher viscosity is maintained for a longer time than with unmodified starches. The extent of cross-linking can be varied using different agents or reaction conditions. At very high levels of cross-linking, granule swelling may be repressed. The starches we examined had moderate to low levels

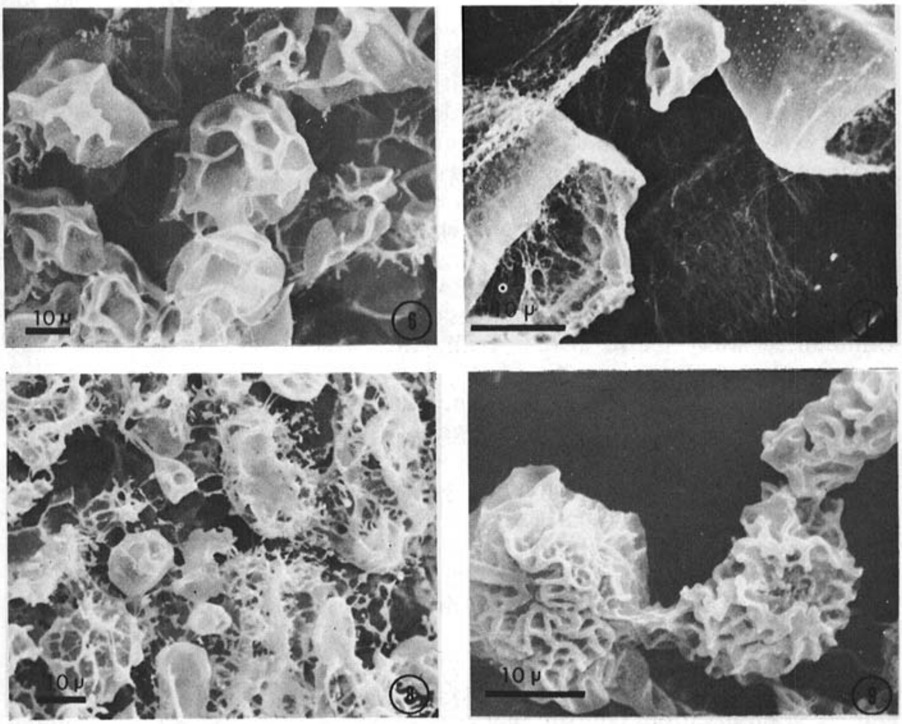



Fig. 6. Hydroxypropyl distarch phosphate corn cooked to 95°C in Brabender. Granules formed folded balloons with less disintegration than unmodified granules. 600×. Fig. 7. Distarch phosphate corn cooked to 90°C in flask. Envelopes of swollen granules were ripped open, revealing inner fibrillar material. 1250×. Fig. 8. Unmodified waxy maize starch cooked to 95°C in flask. Granules disintegrated after gelatinization. 650×. Fig. 9. Hydroxypropyl distarch glycerol waxy maize cooked to 95°C in flask. Granule envelope was extensively folded. Granule structure was stable. Little extragranular fibrillar material was present. 1300×.

of cross-linking suitable for use in food products. We saw no substantial differences in structure of the granules related to the type of cross-linking agent used; thus, granules cross-linked with phosphorous oxychloride or epichlorohydrin looked similar. The type of derivitizing agent also had little or no effect. There were substantial differences in the structure of the unmodified cooked tapioca, corn, and waxy maize granules versus the cross-linked, substituted granules.

Water is an integral part of the structure of a cooked starch granule. Dehydration procedures present the possibility of inducing changes in the granule structure. We have found that chemical dehydration procedures result in substantial shrinking of the granule and precipitation of material. Freeze-drying avoids shrinkage and the three-dimensional structure is thereby effectively preserved. Artifacts such as ice crystal damage are still possible. Rapid freezing should help to control this. Granules may be slightly elongated in the freeze-dried samples, and some fibers are insoluble when water is again added. However, the general pattern of granule structure and extragranular material fits well with light microscope observations.

Cooked granules, especially unmodified waxy maize and tapioca, are very fragile and easily subject to mechanical deformation. Hill and Dronzek (5) found a three-dimensional granule structure only in the early stages of gelatinization and found flattened discs as remnants of swollen granules. Like them, we found a leaching of material from the granules around the gelatinization temperature. However, they used a centrifugation step prior to freeze-drying, a step that may have damaged the swollen granules.

The Brabender amylograph subjects starch pastes to large shear forces. We were surprised to find no intact granules of unmodified tapioca at peak viscosity. Unmodified waxy maize also lost all granule structure shortly after peak viscosity was reached.

Miller *et al.* (4) found a complex filamentous network in cooked wheat starch. Potato, waxy maize, and wheat starch granules had open filamentous structures after cooking in a Brabender and freeze-drying. In our results, a filamentous network was prevalent in corn and tapioca and was partially reduced in the modified samples. Waxy maize and especially the cross-linked waxy showed little or no extragranular fibrils. Cross-linking starch reduced the amount of granule swelling and reduced the peak viscosity of a paste. However, the maintenance of a high viscosity was directly correlated with the retention of intact granules.

The scanning electron microscope should prove useful in evaluating the effect of various chemical modification agents on the structure of gelatinized granules. Our SEM observations confirm that cross-linked granules remain intact under prolonged cooking. Three-dimensional details of granule structure are made vividly clear and the relation between granules and extragranular fibrils becomes evident.

**Acknowledgment**

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