Corn Starch Changes During Tortilla and Tortilla Chip Processing[1]

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ABSTRACT

Structural and molecular changes of corn starch during tortilla chip processing were evaluated by X-ray, liquid chromatography, viscosity, and microscopic techniques. Cooking disrupted the crystalline structure of corn starch. The starch then recrystallized or annealed during steeping to form a new polymeric structure. Grinding of cooked corn released starch granules from the endosperm and reduced their crystallinity. Tortilla baking caused significant losses in starch crystallinity, and frying of tortilla chips caused further gelatinization and the formation of amylose-lipid complexes. Starch solubilization was unchanged after alkaline cooking and increased after steeping. The physical disruption of the kernel caused by grinding further increased the starch solubilization in masa. Baking and frying reduced starch solubility. Steeping and alkaline cooking caused swelling and agglomeration of starch granules throughout the endosperm. Grinding the nixtamal caused complete physical disruption of kernels, resulting in dispersion of swollen starch granules. Tortilla baking caused partial to complete starch gelatinization. Tortilla frying resulted in total gelatinization in the internal areas of the chip, but starch granules on both surfaces of the chips displayed strong birefringence.

Mexican food products, such as tortillas, tortilla chips, corn chips, and taco shells, are made from corn by the nixtamalization process (Serna-Saldivar et al 1990). This process involves alkaline cooking, steeping, washing, and stone-grinding of the kernels to produce masa. Corn masa is kneaded and molded, then baked on a hot griddle to produce table tortillas, which are baked and fried for tortilla chips and taco shells, fried for corn chips, or dried to produce nixtamalized corn flour.

Changes in corn during tortilla processing (such as structural alterations on the outside surface of corn and in the cell walls of the corneous and floury endosperm and the retention of most of the germ, aleurone, and some pericarp layers) have been reported (Paredes-Lopez and Saharopulos 1982, Gomez et al 1989). Starch behavior during processing has been documented only during cooking, steeping, and grinding (Gomez et al 1990). These authors indicated that several granular and molecular forms of starch occurred in masa as a result of incomplete gelatinization and retrogradation. Pflugfelder et al (1988) and Gomez et al (1989) reported losses of starch birefringence (which is related to starch gelatinization) during commercial nixtamalization of corn, i.e., more than 47% loss of birefringence was found in coarse masa made from soft endosperm under severe heat treatment. Starch granules in tortilla and tortilla chip masas made under less severe conditions lost 5–15% birefringence.

Starch commonly exists in two polymorphic forms: crystal lattices A and B (Katz and van Itallie 1930). X-ray diffraction shows the differences in these crystalline forms and yields useful evidence regarding changes in the structure of starch during processing. Starch is insoluble in cold water, but can be solubilized during thermal, chemical, or mechanical gelatinization. High-pressure size-exclusion chromatography (HPSEC) effectively separates macromolecular starch systems on the basis of their effective diameters and molecular weights (Jackson et al 1988). Differences in size and shape of starch granules during processing can be followed with microscopic techniques (Snyder 1984).

The objectives of the present work were to determine structural and molecular changes that starch underwent during tortilla chip processing and to relate these changes to product quality. Starch changes after alkaline cooking, steeping, grinding, baking, and frying were analyzed by X-ray diffraction, HPSEC, viscosity, and microscopic techniques.

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MATERIALS AND METHODS

Sample Preparation

Commercial white, food-quality corn (Asgrow 405W) (3 kg) was cooked for 60 min in 9 L of boiling water containing 30 g of calcium oxide. The cooked grain was steeped for 16 hr. Nixtamal was ground to produce masa, which was molded and baked (40 sec) into tortillas in a three-tier, gas-fired oven with a moving belt (top belt: 370°C, medium belt: 320°C, and bottom belt: 425°C). Tortillas were rested for about 30 min and deep fat fried at 190°C for 1 min in fresh peanut oil (Serna-Saldivar et al 1989).

X-ray diffraction and light microscopy evaluations were conducted on lyophilized samples ground to pass through 150-μm mesh.

Samples of raw corn, cooked corn, nixtamal, masa, tortilla, and tortilla chip were ground with ethanol (96%) in a Waring Blendor for 1.0 min. The suspensions were fractionated into dissolved solids and particulates by centrifuging (3,000 $\times$ g for 20 min). The ethanol phase was discarded, and the residue was dried at 50°C for 30 min and ground in a coffee mill. HPSEC analysis was conducted on the ethanol-washed residue.

X-Ray Diffraction Analysis

X-ray diffraction patterns of samples were determined with monochromatic Cu Kα radiation on a Philips X-ray diffractometer at 35 kV and 15 mA. Lyophilized samples were placed on the 1-cm^2 surface of a glass slide and equilibrated overnight at 91.0% rh and run at 2–32° (diffraction angle 2Θ). The "d" spacing was computed according to Bragg's law (Gomez et al 1991).

HPSEC Analysis

Suspensions containing about 0.05 g of sample in 10 ml of water were cooked at 100°C for 10 min. Suspensions were cooled, equilibrated to 55°C in an oven, sonicated for 18 sec, and centrifuged at 3,000 $\times$ g for 10 min. Filtered ($<$5.0-μm nylon filter) aliquots of 25 μl were injected into the HPSEC system and analyzed following the procedure described by Jackson et al (1988).

Viscosity

The viscosities of corn samples were determined by using a Rapid Visco Analyzer (3C, Newport Scientific PTY. Ltd., Sydney, Australia). A slurry (30 g, 15% solids) was heated from 50 to 95°C, cooked at 95°C for 4 min, and cooled from 95 to 50°C.

Microscopy Techniques

Loss of birefringence was evaluated in water-glycerol (50:50) suspensions of flour from grain, nixtamal, masa, tortilla, and tortilla chip. Samples were sieved to remove the larger endosperm pieces, leaving mostly starch granules or particles smaller than

150 μm. Bright-field and polarized-light microscopic examinations were performed using a Zeiss Universal microscope equipped with a 100-W tungsten light source (Snyder 1984).

Raw corn, nixtamal, masa, and tortilla for observation by scanning electron microscopy (SEM) were dried in a vacuum oven at 4°C overnight and viewed on a JEOL JSM-25 scanning electron microscope at an accelerating voltage of 15 kV. Defatted tortilla chip samples were viewed on a JEOL T330A scanning electron microscope at an accelerating voltage of 15 kV. Samples were mounted with conductive adhesive and coated with 200 Å of gold-palladium. Comparable magnifications and positions of samples were photographed.

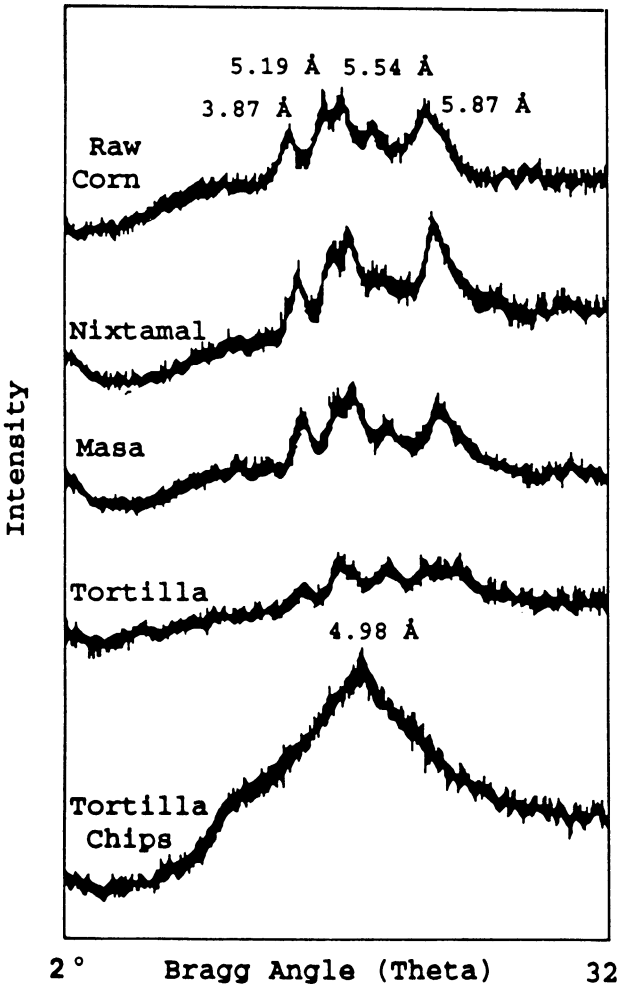

Fig. 1. X-ray diffractograms of raw corn, cooked corn, nixtamal, masa, tortilla, and tortilla chips. Maximum intensity = 2,000 count per second.

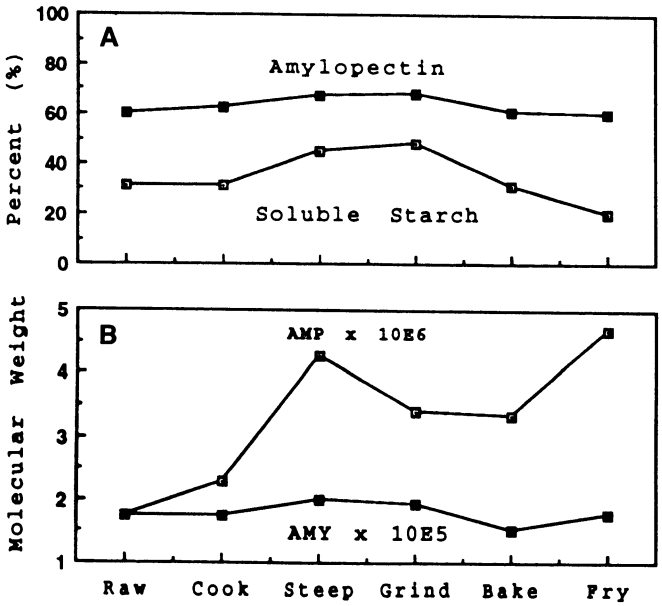

Fig. 2. Starch properties of raw corn, cooked corn, nixtamal, masa, tortilla, and tortilla chips. AMP = amylopectin, AMY = amylose.

RESULTS

Changes in Starch Crystallinity

The crystallinity of corn starch decreased during tortilla processing (Fig. 1). Raw corn contained A-type starch with "d" spacing ranging from about 5.8 to 3.9 Å. Cooking reduced the intensity of the major peaks, indicating that the crystalline starch structure was partially disrupted. After steeping to produce nixtamal, however, the native starch crystallinity was recovered. Alterations in starch crystallinity caused by cooking were corrected by a recrystallization process or annealing during steeping. Grinding the nixtamal to produce masa did not cause significant changes in starch crystallinity, even though the nixtamal (50% moisture) was exposed to mechanical shearing and warm temperatures (45–50°C).

Corn masa was exposed to high temperatures (320–420°C) for 20–45 sec during baking into tortilla (Fig. 1). Most of the starch crystallinity of corn was lost during baking. The hot metalic surfaces facilitated extensive cooking of starch because the masa disks were only 2–3 mm thick. Fried tortilla chips displayed an amorphous X-ray pattern with a peak around 4.5–4.7 Å. The location of this peak, however, was slightly displaced from the strong 4.4-Å peak characteristic of the V-type amylose-lipid complex pattern (Zobel 1964).

Changes in Starch Solubility

Soluble solids extracted at 100°C from raw and cooked corns contained 31.4% soluble starch (Fig. 2A). Low-molecular-weight amylopectin (1.75 × 10E6 to 2.28 × 10E6) accounted for about 60% of the starch and resulted from milling damage to the endosperm starch (Fig. 2B). Apparently, the potential for starch dispersion was not affected by alkaline cooking.

Nixtamal contained 44.7% soluble, dispersed starch (Fig. 2A), primarily (about 67.0%) composed of polymers of high-molecular-weight (HMW) amylopectin (4.26×10^6) and HMW amylose

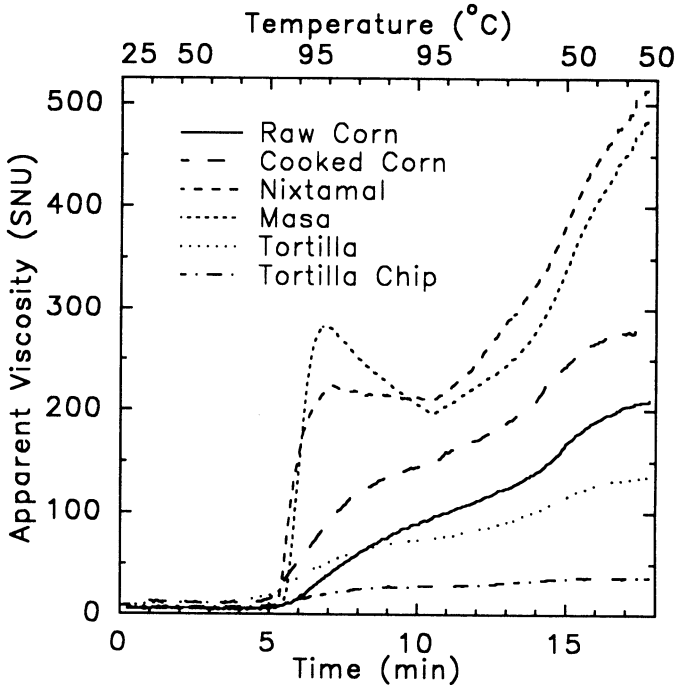

Fig. 3. Pasting properties of raw corn, cooked corn, nixtamal, masa, tortilla, and tortilla chips. SNU = stirring number.

(2.00×10^5) (Fig. 2B). Solubilization of HMW amylopectin might have resulted from swollen starch granules susceptible to laboratory grinding during preparation of the sample for analysis.

The soluble starch increased to 47.6% in masa (Fig. 2A). This soluble starch was composed of HMW amylopectin (about 67.8%). Again, solubilization of amylopectin might have resulted from the disruption of swollen starch granules by stone-milling for masa production and from laboratory grinding.

In tortillas, the cooked, steeped, and ground corn was exposed to high temperatures (180°C). Baking caused some additional starch gelatinization, because thin, high-moisture masa disks were heated above the gelatinization temperature. However, the amount of solubilized starch was reduced (31.4%), probably as a result of starch retrogradation and interactions with lipids (Fig. 2A).

Further reduction in starch solubility to 20.0% was observed in tortilla chips (Fig. 2A). The reduction in starch solubility was attributable to structure shrinkage because of fast dehydration during frying and to amylose-lipid interactions. Rapid water removal from the tortilla decreased the volume of gelatinized starch, which enhanced starch retrogradation during frying.

Pasting Properties

The viscograms of nixtamal and masa differed significantly from those of raw and cooked corn, tortilla, and tortilla chips. (Fig. 3). Neither raw nor cooked corn had a peak viscosity at 95°C. Swelling and gelatinization of starch were restricted because the granules were tightly locked within endosperm cells (Gomez et al 1989). Nixtamal and masa had peak viscosities at 95°C. During cooking, nixtamal starch was very resistant to breakdown, keeping a constant viscosity, whereas the viscosity of masa decreased because of shearing. Both samples increased in viscosity during cooling (setback). Tortilla and tortilla chips developed low viscosity during heating and cooking. The viscosity of tortillas increased during cooling, whereas the tortilla chip viscosity remained unchanged during cooling.

Changes in Starch Birefringence During Tortilla Processing

Starch granules in raw corn exhibited birefringence, i.e., each granule displayed a clear maltese cross under polarized light (Fig. 4). The majority of the starch granules in nixtamalized samples were swollen, adhered to other granules, and exhibited partial or total birefringence. However, the maltese crosses of starch granules were less distinct than those of raw kernels. Snyder (1984) indicated that surface gelatinization causes individual starch granules to stick together and form aggregates. The initial stage of starch gelatinization is indicated by a darkened and enlarged hilum when viewed in nonaqueous medium; the interference cross begins to fade and eventually disappears as starch gelatinization proceeds.

The kernel was physically torn apart by the mechanical cutting and shearing actions of the grinding stones during the conversion of nixtamal to masa. In masa samples, the starch was no longer adherent, and approximately 4–7% of the starch granules lost birefringence. Many of the starch granules in masa appeared irregular in shape when compared to raw and nixtamalized samples, and often only the external part (<60–70% of total area) of the granule exhibited birefringence.

Baking masa into tortillas caused several microstructural changes in starch birefringence and the physical appearance of corn components. These changes were due primarily to the intense heat, which further gelatinized the starch. The masa particles in the tortillas were cooked more in the center of the tortilla than on the edges. This was reflected by the differences in birefringence observed in these areas.

Up to 95% of birefringence in the starch granules was lost

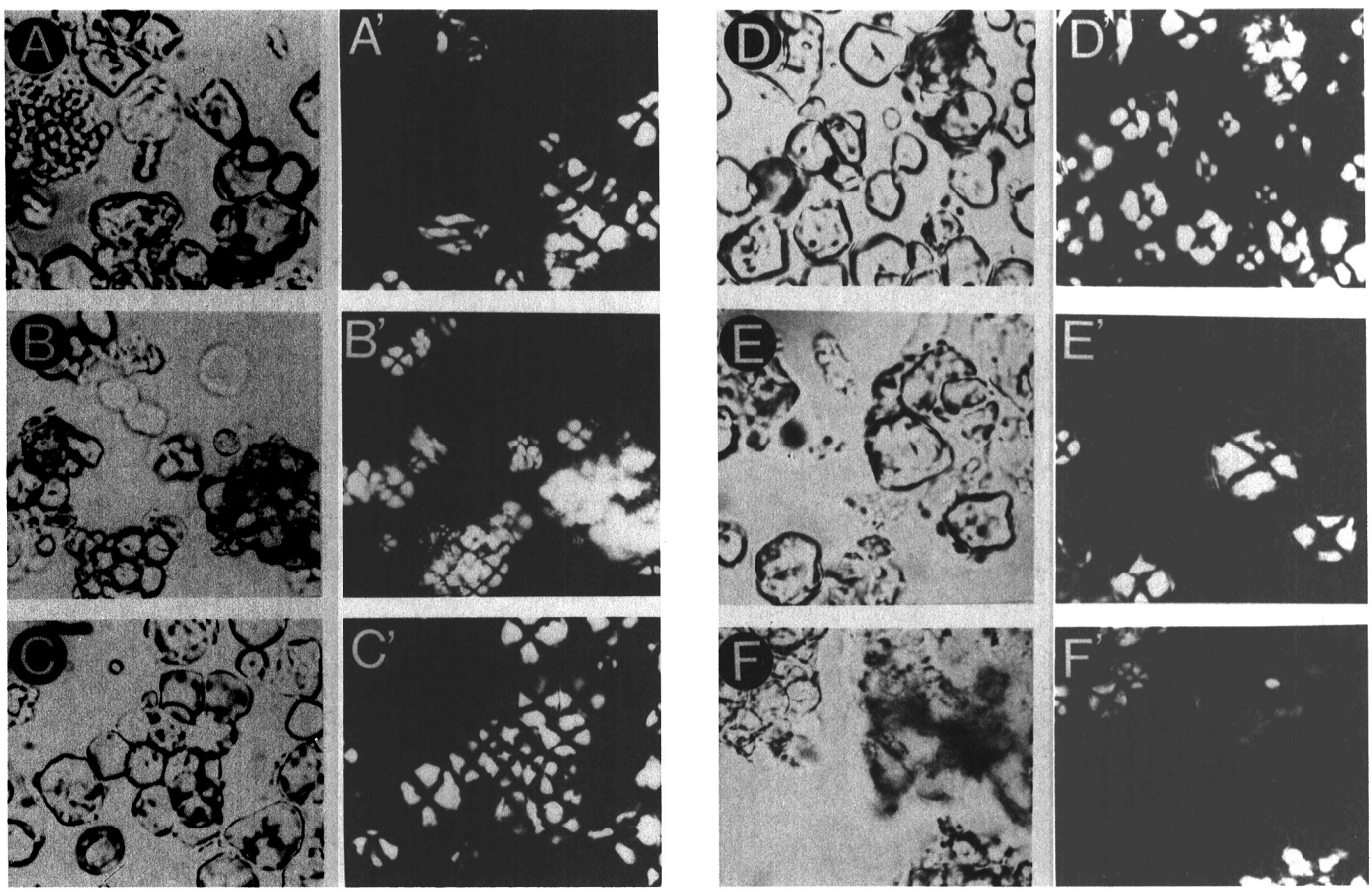

Fig. 4. Loss of birefringence in corn flour samples. **A** and **A'**, raw corn; **B** and **B'**, cooked corn; **C** and **C'**, nixtamal; **D** and **D'**, masa; **E** and **E'**, tortilla; **F** and **F'**, tortilla chips. **A–F**, bright-field; **A'–F'**, polarized.

after the tortillas were fried into tortilla chips. However, some starch granules located on the outside surfaces of the chips displayed strong birefringence, presumably because they were the first part dehydrated during baking and insufficient water was present for gelatinization during frying.

Changes in Starch Structure During Tortilla Processing

Alkaline cooking and steeping of corn to produce nixtamal caused swelling of starch granules throughout the kernel (Fig. 5A–C). In the peripheral and corneous endosperm, starch granules were modified very little and remained packed together as in the original cell. Irregular and swollen starch granules were observed in corn masa (Fig. 5D). A cohesive, gluelike structure appeared to hold the masa pieces together. This glue probably is composed of a mixture of gelatinized and dispersed starch, hydrated and denatured protein matrix, and free and emulsified lipids.

SEM evaluations showed that the central, internal area of corn tortillas (Fig. 5E) had misshapen starch granules, whereas granules seen in the outer edges of tortillas (Fig. 5F), which received more severe heat treatment during baking, were more uniform, smoother, and more amorphous.

When tortillas were fried into tortilla chips (Fig. 5G and H), the surface structure was completely changed and most of the starch granules were gelatinized, losing their integrity. The internal tortilla chip contained gel pieces, and the starch was completely gelatinized.

Structural Description of the Nixtamalization Process

Alkaline cooking and steeping of corn causes water and calcium to be taken up by the corn grain. The alkaline solution degrades and solubilizes cell wall components, resulting in partial removal of the pericarp, softening of the endosperm structure, and denaturing of the protein matrix (Gomez et al 1989). Starch granules undergo limited swelling as a result of the physical constraints of the endosperm cells and the insufficient heat and moisture levels reached during cooking and steeping. A very small amount of amylose leaching occurs after starch swelling and contributes to the formation of a network that connects cellular components. According to Robles et al (1988), the gelatinization of starch during alkaline cooking and steeping of corn is inhibited by amylose-calcium interactions. Amylose and amylopectin retrograde during corn steeping, resulting in the recovery of some of the native starch crystallinity (as documented by X-ray diffractograms). Donovan et al (1983) indicated that holding a suspension of starch just below the gelatinization temperature gives rise to more perfectly ordered crystals. French (1984) reported that the annealing process at 50°C permitted realignment of starch chains in the amorphous phase, as well as some additional recrystallization. Donovan et al (1983) and Robles et al (1988) reported that the starch recrystallization results in higher melting points and increased pasting temperatures, which reduce starch solubility.

Masa grinding disrupts the grain structure, releasing starch granules from the endosperm cells and dispersing cellular components and starch polymers. From the physicostructural point of view, masa can be considered to be a network of solubilized starch polymers (continuous phase) supporting dispersed, uncooked and swollen starch granules, cell fragments, and lipids (dispersed phase) (Gomez et al 1990) (Fig. 6A). Swollen and partially gelatinized starch granules act as deformable particles in a network of dispersed starch polymers, allowing tortilla shaping during kneading, and gas retention and puffing during baking. Further starch gelatinization occurs (<5%) because of a combination of high water content, previously damaged and swollen starches, warm-to-high temperatures (56–60°C), and physical shear. This additional gelatinization contributes to the development of adhesive properties among cellular components, i.e., among cell walls, protein matrix, and starch. Amylose retrogradation occurs during masa cooling, yielding a more rigid gel network (Gomez et al 1990). Ring (1985) defined starch retrogradation as the change in starch gels, such as chain aggregation and/or recrystallization, occurring immediately during cooling.

Baking resulted in grain components being set into the three-dimensional tortilla structure (Fig. 6B). Starch granules and endosperm pieces are glued together by amylose, protein, lipids,

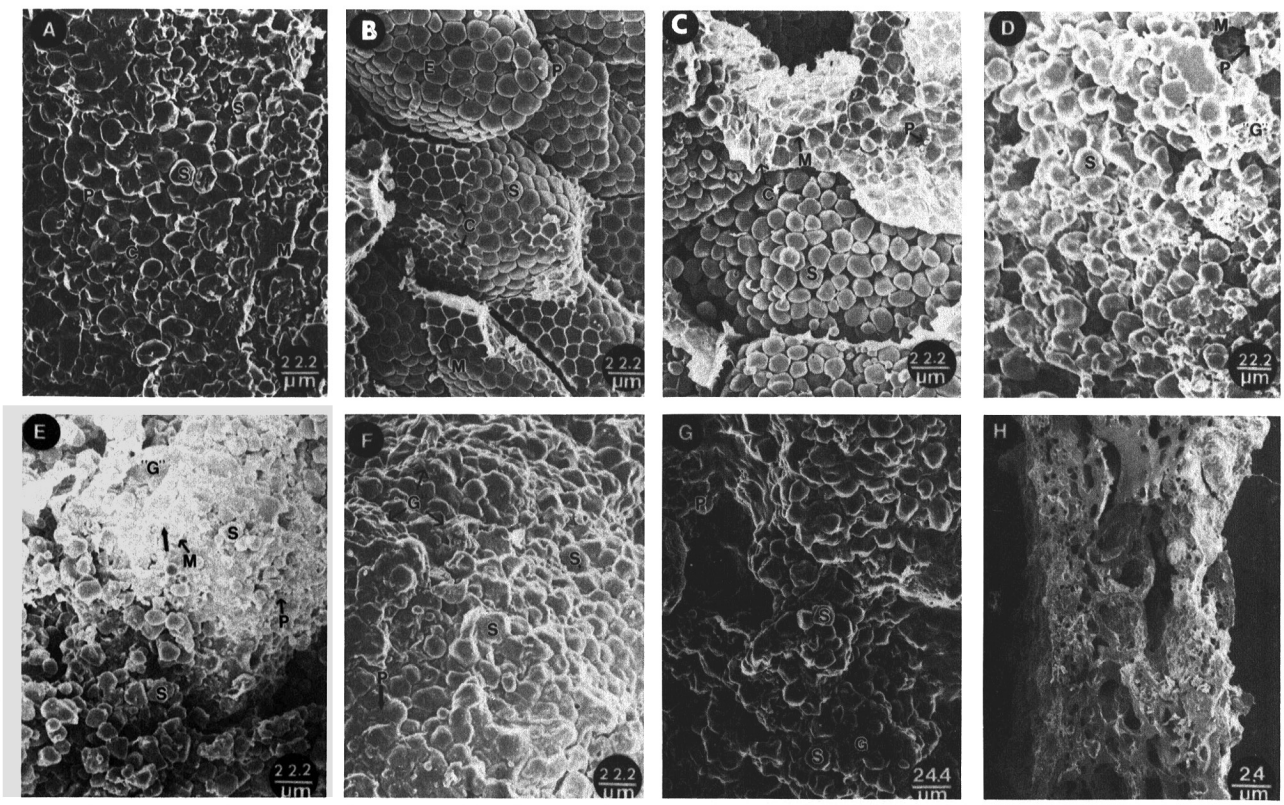

Fig. 5. Scanning electron micrographs of raw corn (**A**), nixtamal (floury endosperm) (**B**), nixtamal (corneous endosperm) (**C**), masa (**D**), tortilla (inside) (**E**), tortilla (outside) (**F**), tortilla chips (outside) (**G**), and tortilla chips (cross section) (**H**). C = Cell wall fragment, E = endosperm piece, "G" = gluelike substance, M = protein matrix, P = protein, S = starch.

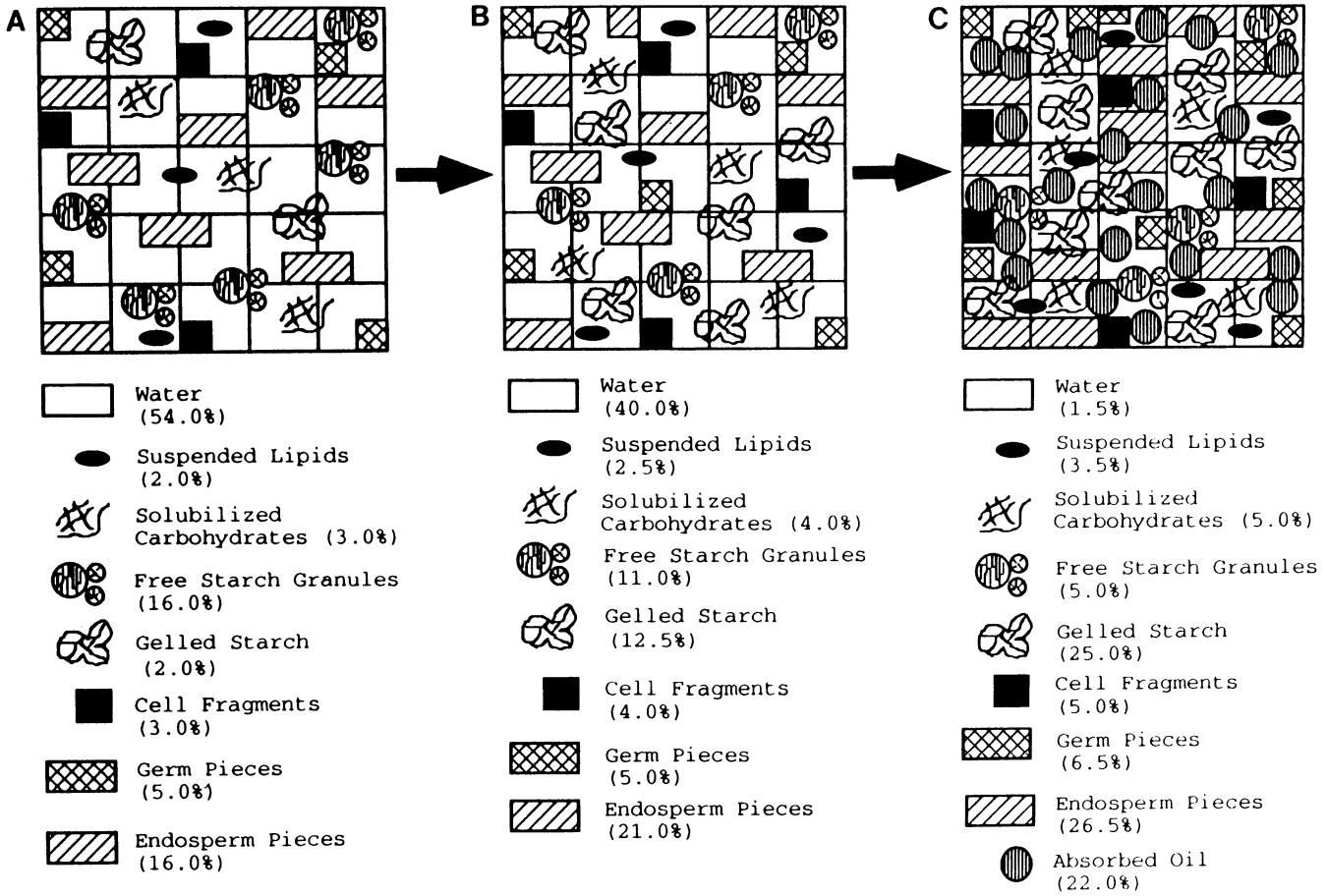

Fig. 6. Structural descriptions of masa (**A**), tortilla (**B**), and tortilla chips (**C**).

and cell wall components. Fast water evaporation from the tortilla surface and severe starch gelatinization (>40%) occur during the 45–60 sec of baking time. Granules on the tortilla surface are partially gelatinized and more dehydrated than those in the middle of the tortilla, where the starch is more gelatinized (shown less birefringence).

Tortillas are exposed to very high temperatures (190°C) in a nonaqueous medium during frying. A very low moisture content (<1.5%) in the tortilla chip results after frying (Fig. 6C). During tortilla frying, the oil fills most of the empty spaces of the tortilla structure, and the evaporation of water creates new empty spaces (with negative pressure), which forces further oil into the structure. Ultimately, the tortilla structure is oily, dehydrated, and set. Additional starch gelatinization occurs during the first 10–15 sec of frying, before most of the water is removed. Interactions between amylose and lipid during frying reduce the potential for dispersion of starch.

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