Starch Characterization of Nixtamalized Corn Flour[1]

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ABSTRACT

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Commercial nixtamalized corn flours used to prepare tortilla and tortilla chips were analyzed for particle size distribution, composition, and functionality. Changes in starch crystallinity, solubility, and kernel microstructure were evaluated in commercial samples of raw corn, alkaline-cooked and steeped corn (nixtamal), ground nixtamal (masa), and nixtamalized corn flour (NCF). The coarse, intermediate, and fine particle size fractions of NCF had similar chemical composition and distribution of anatomical parts. Starch in the large particles of NCF was less damaged during grinding and was more soluble after autoclaving and sonication. Starch in the intermediate and smaller particle size fractions was more mechanically damaged, gelatinized, and retrograded, as indicated by decreased starch solubility (after autoclaving and sonication). NCF drying, the last thermal operation during processing, caused partial starch gelatinization and retrogradation, decreasing starch crystallinity. Thus, starch functionality was modified during NCF preparation, which negatively affected the rheological characteristics of rehydrated NCF; that is, it decreased the cohesiveness and plasticity of the NCF and the shelf life of baked products, so that tortillas became stale sooner.

The traditional nixtamalization process to produce tortilla dough (masa) has been modified to produce convenient and functional nixtamalized corn flour (NCF) (Serna-Saldivar et al 1990). Corn is cooked in a lime-water solution and steeped for a short time or is alkaline-cooked more intensively to avoid steeping. After washing to remove excess lime and loose pericarp fragments, the cooked corn is stone-ground or hammer-milled. Cooking, steeping, and grinding release starch granules from the endosperm and cause partial starch gelatinization and limited starch retrogradation (Gomez et al 1990). Drying, the most critical operation, is usually done in large tunnels or drying towers in which hot air flows countercurrent to the masa (Serna-Saldivar et al 1990). The dried material is ground, and the particles are separated by size. Oversized particles are reground. Different particles are blended to obtain NCF with optimum particle size distribution for different applications. For example, soft tortillas require a fine-particle-size flour, whereas corn chips and tortilla chips require a coarse-particle-size flour (Montemayor and Rubio 1983). Tortilla NCF is formulated to develop flexibility and cohesiveness in tortillas, whereas tortilla chip NCF is formulated to promote crispiness in chips after frying.

Tortilla manufacturers know that rehydrated NCF has different rheological properties than fresh masa (L. W. Rooney, *personal communication*). Rehydrated NCF is less plastic and cohesive than fresh masa. Also, the products made from NCF stale faster. Fresh masa contains 52–54% moisture, 12–25% small endosperm and germ pieces, 19–31% free starch granules and cell fragments, and 3–5% dispersed solids and free lipids (dissolved solids) (Pflugfelder et al 1988). Water, dispersed starch polymers, and partially gelatinized starch form a continuous thin film that entraps kernel pieces during masa kneading (Gomez et al 1990). Although several studies of nixtamalization have heen reported (Molina et al 1977, Bazua et al 1979, Bedolla 1983, Bedolla and Rooney 1984, Gomez et al 1987, Serna-Saldivar et al 1990), there is limited information about the effects of processing on starch properties and the relationship of these properties to NCF functionality. Therefore, the purpose of this study was to characterize the starch in NCF to understand how starch changes during NCF production.

MATERIALS AND METHODS

Sample Preparation

NCFs for tortilla and tortilla chip preparations were obtained in 1987 from a commercial Texas plant. NCFs were hand sieved using U.S. standard sieves No. 60 (250 μm) and No. 100 (150 μm). Each fraction was quantitatively collected to determine particle size distribution (Bedolla and Rooney 1984).

Raw corn, cooked corn, masa, and NCF were also obtained from a commercial Texas plant. Samples were collected, frozen, freeze-dried for 24 hr, ground, and sieved through a No. 60 sieve for analysis.

Analytical Methods

The moisture content of NCF was determined by drying to a constant weight in a forced air oven at 105°C (AACC 1983). Samples were analyzed for nitrogen by Kjeldahl digestion (AACC 1983) and for ammonia by an automated colorimetric assay (Technicon 1978). Protein was calculated as N × 6.25. Crude fat in the samples was measured by ether extraction using Goldfish apparatus and evaporation of the solvent (AACC 1983). Ash in the samples was determined after incinerating at 500°C (AACC 1983).

The starch content was measured after autoclaving (to gelatinize the starch) and hydrolysis (to glucose) with amyloglucosidase (Diazyme L-200, Miles Lab., Inc., Elkhart, IN.), using an automated colorimetric method involving immobilized hexokinase (Khan et al 1980, Technicon 1978). The enzyme-susceptible starch ratio (ESS), a measure of the extent of starch damage, was determined by digesting ungelatinized samples with amyloglucosidase for 30 min at 60°C (Khan et al 1980, Bedolla and Rooney 1984).

The pasting viscosity of samples (10.0% solids) was determined using a Brabender Viscoamylograph (type VAV, model 3042, C.W. Brabender Instruments, Inc.) equipped with a 700-cmg sensitivity cartridge and an amylograph cup rotating at 75 rpm. The amylograph cycle was set for 30 min of heating from 50 to 95°C, 20 min of holding at 95°C, and 30 min of cooling from 95 to 50°C.

Dough consistency was determined with a Brabender Farinograph (AACC 1983), using 25 g of flour (dwb) and 20 g of water. Water absorption capacity, expressed as the amount of water per 100 g of flour required to develop a maximum resistance value of 300 farinograph units (FU), was also determined using the farinograph. Molina et al (1977) suggested that this viscosity gives a good approximation of the amount of water needed to develop adequate machinability of rehydrated masa.

Starch solubility at 120°C of defatted NCF was measured by high-performance, size-exclusion chromatography (HPSEC) (Jackson et al 1988). Tortilla NCF (0.25 g) or tortilla chip NCF (0.35 g) was moistened with 0.5 ml of methanol and brought to 100 ml with water. Suspensions (10 ml) were gelatinized, equilibrated, sonicated, centrifuged, filtered through a 5.0-μm nylon filter, and injected into the HPSEC system.

The starch crystallinity of NCF and flour prepared from raw corn, nixtamal, and masa equilibrated at 91.0% relative humidity was determined with Cu Kα radiation on a Philips X-ray diffrac-

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tometer. Operation was at 35 kV and 15 mA over 2-32°, and "d" spacing was computed according to Bragg's law.

Loss of birefringence was evaluated in a glycerol-water (50:50) suspension of ground samples that had been sieved through a U.S. standard sieve No. 230 (63 μm). Sieving removed most of the larger endosperm pieces from the starch granules. Microscopic examinations were done on a Zeiss Universal microscope using a polarizing filter (Snyder 1984).

Samples were mounted with double sticky tape on an aluminum stub, coated with 200 Å of gold-palladium, and viewed on a JEOL JSM25 scanning electron microscope at an accelerating voltage of 12.5 kV.

Statistical analyses were perfomed using PC-SAS (SAS Institute, 1985).

RESULTS AND DISCUSSION

Particle Size Distribution of Nixtamalized Corn Flours

NCF used to prepare tortilla chips and taco shells contained a high proportion (77.1%) of coarse particles retained on No. 60 sieve (i.e., >250 μm), whereas tortilla NCF contained about 42% coarse particles (Table I). Thus, tortilla NCF is milled into smaller particles than tortilla chip NCF, as reported earlier by Montemayor and Rubio (1983). Particle size distribution is currently the most important criterion for NCF applications (Bedolla and Rooney 1984). Large particles are required for textural characteristics of fried products (i.e., crispiness), since large particles disrupt the dough network, reduce blistering, and decrease oil uptake during frying. The smaller particles are responsible for most of the water uptake, viscosity, cohesiveness, plasticity, and smoothness (Gomez et al 1987).

Chemical Composition of Nixtamalized Corn Flour

The moisture content of NCF was 10.3% ± 0.5. Commercial NCF usually contains <11% moisture to maintain adequate shelf life for several months (Gomez et al 1987). The chemical composition of tortilla and tortilla chip NCFs did not differ from that of raw corn flour (Table II). Thus, the concentration of macrocomponents was not affected by the NCF process. Protein, fat, ash, and starch contents were also uniformly distributed in the different particle size fractions of NCF (Table II). The uniformity resulted from extensive mixing during the several unit operations, e.g., hammer-milling, sieving, regrinding and particle-blending, used to formulate NCF.

TABLE I
Particle Size Distribution of Tortilla and Tortilla Chip Nixtamalized Corn Flours (NCFs)[a]

Particle Size (μm)	NCF for Tortilla (%)	NCF for Tortilla Chips (%)
> 250	41.9 ± 1.6	77.1 ± 4.2
< 250, > 150,	23.2 ± 3.5	11.2 ± 1.7
< 150	34.9 ± 2.6	12.2 ± 2.2

[a] Results are expressed as averages of six replicates ± standard deviation.

Physicochemical Properties of Nixtamalized Corn Flours and Their Fractions

The ESS of NCF was larger than that of raw corn (Table II), i.e., some starch granules were gelatinized and/or damaged during processing. The ESS of large particles of NCF was not significantly different than that of fine particles. Masas with low ESS values (undercooked masas) generally have low cohesiveness or pasting behavior, whereas masas with high ESS (overcooked masas) are sticky due to an excessive amount of gelatinized starch (Gomez et al 1987).

The amylograph viscosity of tortilla NCF was higher than that of tortilla chip NCF (Fig. 1A), suggesting that NCF viscosity (10% w/v) increased with smaller particle size distribution. Both tortilla and tortilla chip NCFs developed a peak viscosity at 95° C, which remained constant during the cooking period.

The relative contributions of the fine (<150 μm), intermediate (>150, <250 μm), and coarse (>250 μm) fractions of NCF to the development of viscosity are shown in Fig. 1B. The pasting

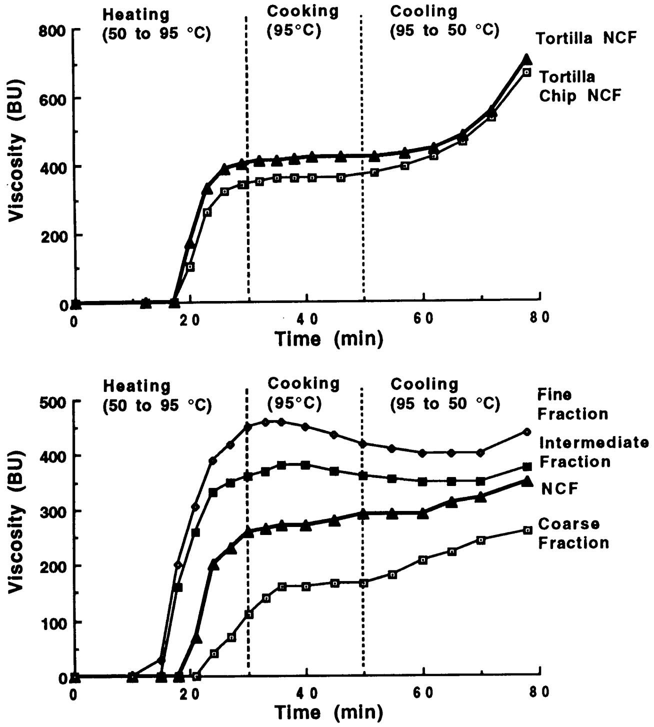

Fig. 1. Brabender amylograms of tortilla and tortilla chip nixtamalized corn flours (NCFs) (**A**) and tortilla chip nixtamalized corn flour and its fractions (**B**).

TABLE II
Chemical Composition of Tortilla and Tortilla Chip Nixtamalized Corn Flours (NCFs)[a]

Particle Size (μm)	Moisture (%)	Protein (%)	Fat (%)	Ash (%)	Starch (%)	ESS[b]
Raw corn flour	10.0 ± 0.2	10.3 ± 0.3	4.3 ± 0.1	1.2 ± 0.2	74.4 ± 0.9	351.3 ± 14.5
Tortilla NCF	10.1 ± 0.4	9.3 ± 0.4	4.0 ± 0.2	1.4 ± 0.1	73.3 ± 1.2	471.8 ± 23.0
> 250	10.6 ± 0.3	9.7 ± 0.5	3.2 ± 0.3	1.2 ± 0.2	71.9 ± 0.6	438.7 ± 18.9
< 250, > 150	9.8 ± 0.4	10.9 ± 0.7	4.2 ± 0.1	1.4 ± 0.2	73.4 ± 0.8	470.6 ± 16.4
< 150	9.9 ± 0.4	8.3 ± 0.4	4.8 ± 0.5	1.6 ± 0.1	73.5 ± 1.1	458.5 ± 24.3
Tortilla chip NCF	10.5 ± 0.6	8.3 ± 0.4	2.6 ± 0.2	1.5 ± 0.1	72.9 ± 1.4	449.4 ± 15.6
> 250	11.2 ± 0.5	9.2 ± 0.5	3.7 ± 0.4	1.4 ± 0.2	71.9 ± 0.4	448.3 ± 23.8
< 250, > 150	10.1 ± 0.3	8.9 ± 0.7	4.2 ± 0.1	1.3 ± 0.2	73.8 ± 0.6	499.2 ± 19.4
< 150	10.5 ± 0.4	9.4 ± 0.2	3.1 ± 0.5	1.4 ± 0.1	74.5 ± 1.0	459.7 ± 12.5

[a] Results are expressed as average of three replicates ± standard deviation.

[b] Enzyme-susceptible starch ratio, expressed as milligrams of glucose per gram of starch.

curve for the fine fraction resembles amylograms of uncooked corn starch (Moore et al 1984). However, the pasting viscosity of the coarse fraction was initially low but increased steadily, reaching a peak viscosity during cooking. The fraction of intermediate particle size had viscosity behavior similar to that of the fine fraction. Although the starch concentration in the NCF fractions remained constant (about 74%), the fine and intermediate fractions contained a high proportion of small particles and probably free starch granules that contributed to the increased viscosity during heating. Slow water diffusion into coarse particles and limited swelling of starch granules within endosperm cells probably were responsible for the slower viscosity development of the coarse fraction during the heating period.

The farinograph mixing behavior of NCF was also affected by the type of NCF (Fig. 2). Tortilla and corn chip flours showed good stability after 15 min of mixing. The particle size distribution of NCF caused the variation in masa consistencies, since equal water-flour ratios were utilized. Consistencies for tortilla NCF were about 700 FU, whereas consistencies for tortilla chip NCF were >600 FU.

Water absorption capacities, determined using the farinograph, ranged from 110 to 115 g of water per 100 g of flour for tortilla NCF and 85–105 g/100 g for tortilla chip NCF. As expected, the water-holding capacity of NCF increased with smaller particle size.

Starch Solubility of Commercial Nixtamalized Corn Flour

Heating and sonication increased the solubility of native corn starch more than they increased the solubility of starch extracted from tortilla and tortilla chip NCF (Fig. 3). This indicated that some starch gelatinization and retrogradation had occurred during NCF production. Tortilla chip NCF yielded more solubilized and dispersed starch than did tortilla NCF. As indicated above, tortilla NCF contained more fine particles than did tortilla chip NCF. Probably, starch granules in tortilla NCF were more gelatinized because they were exposed to water, heat, and mechanical damage during the process to a greater extent than starch granules enclosed in coarse endosperm particles. This was confirmed when fine, intermediate, and coarse fraction of NCF were analyzed (Fig.

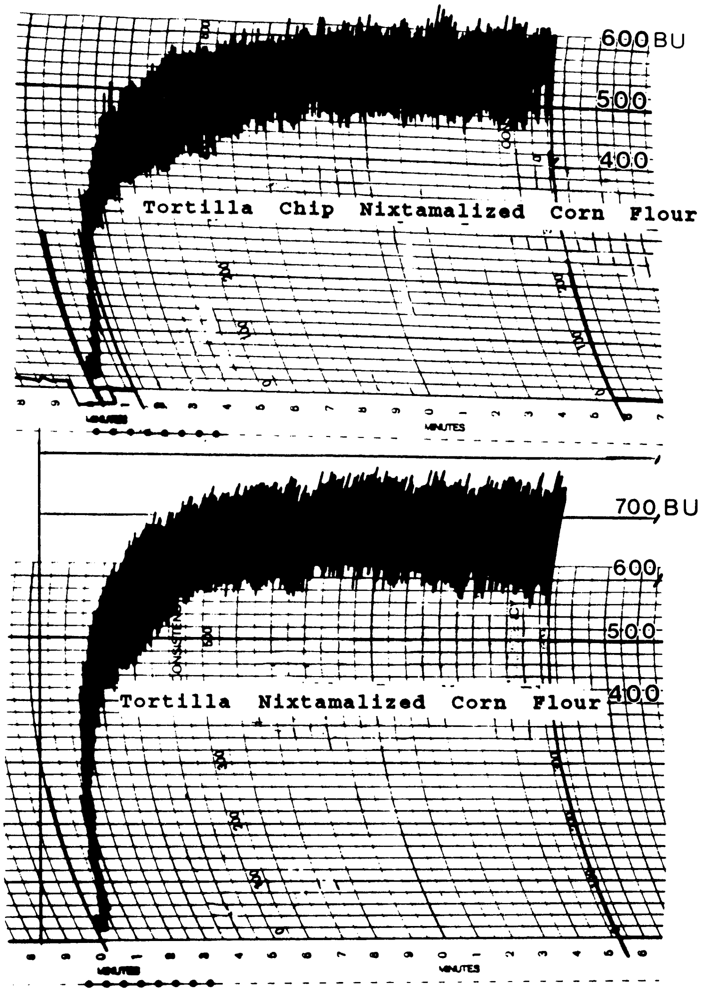

Fig. 2. Brabender farinograms of tortilla and tortilla chip nixtamalized corn flours.

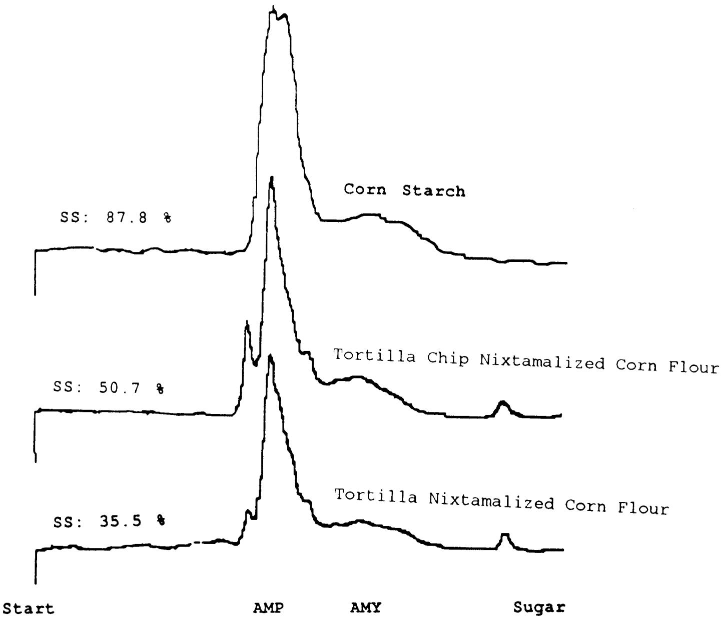

Fig. 3. Solubilized starch (SS) in tortilla and tortilla chip nixtamalized corn flours extracted at 120°C. SS (g/100 g of sample) includes amylopectin (AMP) and amylose (AMY). Average molecular weights are 2.0×10^{-7} for AMP and 4.7×10^{-5} for AMY.

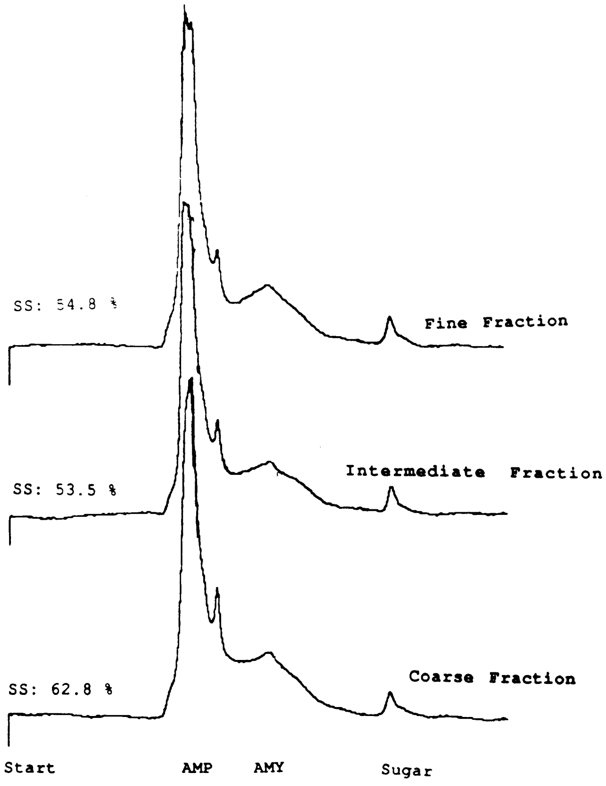

Fig. 4. Starch solubility in fine (<150 μm), intermediate (>150, <250 μm), and coarse (>250 μm) fractions of nixtamalized corn flour extracted at 120°C. Solubilized starch (SS) (g/100 g of sample) includes amylopectin (AMP) and amylose (AMY). Average molecular weights are 2.0×10^{-7} for AMP and 4.7×10^{-5} for AMY.

4). Smaller particles in the NCF were more exposed to water, heat, and mechanical damage during processing, decreasing their starch solubilization capacity. Thus, processing to NCF decreased the capacity of starch particles to undergo solubilization.

Processing of corn into NCF did not affect the average molecular weight of starch polymers (Figs. 3 and 4). Uncooked corn and processed samples contained amylopectin and amylose, with an average molecular weights of 2.0×10^7 and 4.7×10^5, respectively. Soluble and dispersed starch from tortilla and tortilla chip NCFs contained a normal amylopectin-amylose ratio (76:24).

Changes of X-Ray Pattern During the Process

Nixtamalization of corn during NCF production introduced few changes in the organization of starch polymers (Fig. 5). The crystallinity of starch in masa also was similar to that of raw corn, even though the corn in masa had been alkaline-cooked, steeped, and ground. However, starch crystallinity decreased during the drying of masa. Partial gelatinization of the masa starch resulted because hydrated endosperm pieces were exposed to high temperature. In contrast, conventional nixtamalization to produce fresh masa for tortillas significantly decreases the starch crystallinity of raw corn; that is, partial gelatinization takes place during alkaline cooking (Gomez et al 1990). Thus, the initial heat treatment is more severe for production of fresh corn masa than for production of NCF, as indicated by the changes in the starch crystallinity (and solubility).

The coarse particles of NCF contained starch with an X-ray pattern of sharper, more well-defined peaks than those in the starch in the fine fraction (Fig. 6). Hence, starch crystallinity decreased as particle size decreased due to the mechanical damage imposed during grinding and regrinding. Starch in the larger particles received less cooking and shear than starch in the smaller particles.

Microscopic Examinations

Granule birefringence decreased during processing into NCF (Fig. 7). NCF contains irregularly shaped starch granules with some of the spherical integrity destroyed.

Nixtamal contained starch granules inside endosperm cells that were more swollen than those starch granules in uncooked corn (Fig. 8A and B). After being ground into masa, the endosperm cells were disrupted and the starch granules were released. Most of the starch granules in masa lost their native, regular shape (Fig. 8C). Similar processing effects were observed on fresh masa (Gomez et al 1989). They indicated that fresh masa was held together as a cohesive, nonsticky dough by a mixture of dispersed solids in water that consisted of gelatinized starch, hydrated protein, lipids, and calcium salts. NCF contained some gelatinized, very distorted starch granules and agglomerated particles that were held together by a molten, "gluelike" material (Fig. 8D).

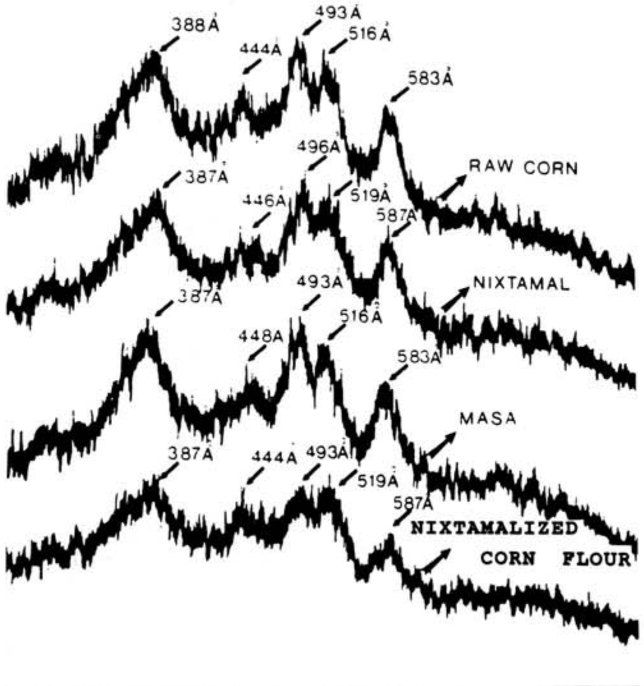

Fig. 5. Starch crystallinity in raw corn, nixtamal, masa, and nixtamalized corn flour, determined by X-ray analysis. Maximum intensity, 500 cp.

What is Nixtamalized Corn Flour?

NCF is a product from a modified "traditional" nixtamalization process. Corn is usually undercooked during NCF production. Undercooking of corn causes insufficient water absorption and weakening of the endosperm structure, restricted swelling of starch granules, and limited amylose leaching during the initial heating step. The shorter steeping time (another usual operation during NCF production) limits water redistribution and reorganization of the molecular structure of starch compared to that occurring in the preparation of fresh masa (Gomez et al 1990). Starch gelatinization is incomplete because the starch granules are within endosperm cells and exposed to very limited amounts of water during the shorter cooking and steeping operations. Grinding of nixtamal releases some starch granules from the endosperm and disperses some starch polymers from swollen and partially gelatinized starch granules. Rapid drying of masa causes further starch gelatinization and reorientation of starch polymers. Then, during storage, rehydration of NCF, and its utilization in tortilla or tortilla chip production, the partially gelatinized

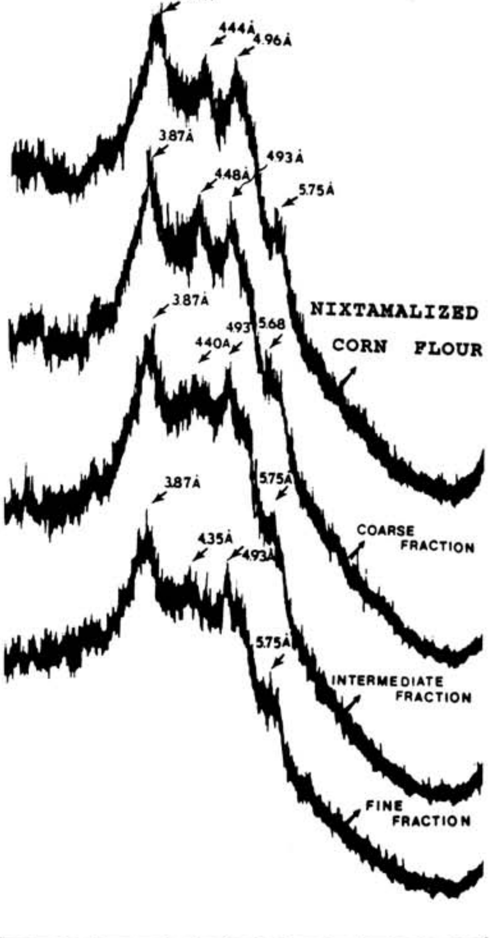

Fig. 6. Starch crystallinity in tortilla nixtamalized corn flour and its fractions, determined by X-ray analysis. Maximum intensity, 1,000 cp.

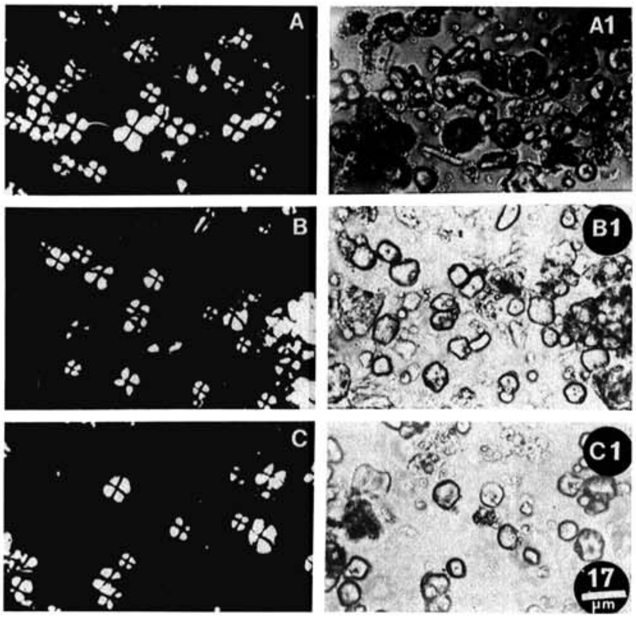

Fig. 7. Loss of birefringence in raw corn (**A**), nixtamal (**B**), and tortilla nixtamalized corn flour (**C**), using polarized (left) and brightfield (right) light microscopy.

starch granules provide nuclei for starch recrystallization or retrogradation.

The rheological characteristics of masa prepared from NCF are not quite like those of fresh masa (Gomez et al 1990; L. W. Rooney, *personal communication*), and the baked tortillas are dryer and stale faster (Bedolla and Rooney 1984). Recrystallization and/or retrogradation of starch decreases the cohesiveness of rehydrated NCF. Improved mechanical properties of rehydrated NCF result from the combination of mechanically damaged and partially gelatinized starches, the particle size distribution of NCF, and added hydrocolloids.

We postulate that starch retrogradation occurs very rapidly in corn tortillas because crystalline areas of starch remaining after NCF preparation act as nuclei for further molecular starch associations. Rehydration of NCF and baking of tortillas are unable to destroy these nuclei. The tortilla thinness and the high surface area favor rapid evaporation of water. Therefore, any additive that binds water and interrupts starch crystal growth will improve the rollability or decrease the firmness and crumbliness of corn tortillas made from NCF.

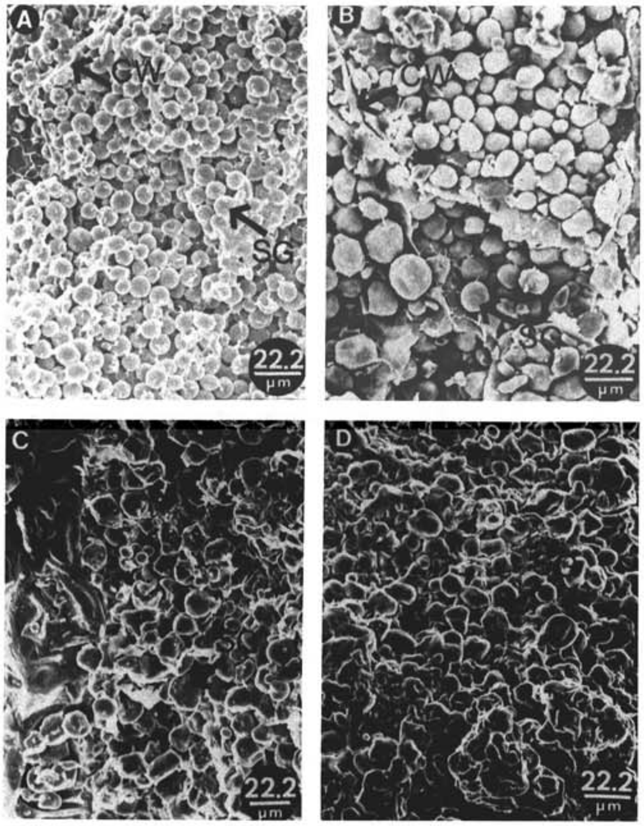

Fig. 8. Scanning electron micrographs of raw corn (**A**), nixtamal (**B**), masa (**C**), and tortilla nixtamalized corn flour (**D**). CW = cell wall, SG = starch granule.

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