

Extrusion of Cross-Linked Hydroxypropylated Corn Starches

II. Morphological and Molecular Characterization¹

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ABSTRACT

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A series of cross-linked hydroxypropylated corn starches were extruded with a Leistritz micro-18 co-rotating extruder. Extrusion process variables including moisture (30, 35, and 40%), barrel temperature (60, 80, and 100°C), and screw design (low, medium, and high shear) were investigated. Scanning electron microscopy (SEM) of extruded starches showed a gel phase with distorted granules and granule fragments after extrusion at 60°C. After extrusion at 100°C only a gel phase was observed with no granular structures remaining. High performance size exclusion chromatography (HPSEC) equipped with multiangle laser light-scattering (MALLS) and refractive index (RI) detectors showed extruded starches degraded to different extents, depending on extrusion conditions. The average molecular weight of the amylopectin of unextruded native corn starch was 7.7×10^6 . Extrusion at 30% moisture, 100°C, and

high shear reduced the molecular weight of amylopectin to 1.0×10^8 . Hydroxypropylated normal corn starch extruded at identical conditions showed greater decreases in amylopectin molecular weight. With the addition of cross-linking, the amylopectin fractions of the extruded starches were less degraded than those of their native and hydroxypropylated corn starch counterparts. Similarly, increasing moisture content during extrusion lowered amylopectin degradation in the extruded starches. Increasing temperature during extrusion of cross-linked hydroxypropylated starches at high moisture content (e.g., 40%) lowered amylopectin molecular weights of the extruded starches, whereas increasing extrusion temperature at low moisture content (30%) resulted in less degraded molecules. This difference was attributed to the higher glass transition temperatures of the cross-linked starches.

Extrusion has become a common processing method for starch-based foods and for producing pregelatinized starches (Snyder 1984, Mercier et al 1979, Harper 1992, Linko 1992, Govindasamy et al 1997). The effects of extrusion on native starches have been well studied. Extrusion of native starches has been reported to cause decreases in crystallinity (Mercier et al 1979), intrinsic viscosity (Colonna and Mercier 1983, Colonna et al 1984, Diosady et al 1985), and paste viscosity (Seiler et al 1980, Colonna et al 1984, Gomez and Aguilera 1984, Mason and Hosney 1986). During the extrusion process, thermal energy, shear, and pressure cause reductions in molecular size (Mercier 1977, Colonna and Mercier 1983, Colonna et al 1984, Davidson et al 1984a, Davidson et al 1984b, Diosady et al 1985, Jackson et al 1990, Wen et al 1990, Mitchell and Areas 1992). Extrusion variables including starch moisture content, barrel and die temperatures, screw design, screw speed, and starch type have been shown to affect the molecular weight of extruded starches (Colonna and Mercier 1983, Colonna et al 1984, Diosady et al 1985, Jackson et al 1990, Wen et al 1990, Tayeb et al 1992, Politz et al 1994).

Molecular degradation in extruded native starches has been examined using intrinsic viscosity, gel permeation chromatography (GPC), and high performance size exclusion chromatography (HPSEC) (Chinnaswamy and Hanna 1990, Jackson et al 1990, Wasserman and Timpa 1991, Harper 1992, Politz et al 1994). HPSEC, equipped with light scattering and refractive index detectors (RI), is a method for determination of absolute molecular weight and size of synthetic polymers and biopolymers such as starches (Podzimek 1994, Fishman et al 1996, Yokoyama et al 1998).

In this study, the effects of extrusion variables on granular morphology and molecular weight of the starch components of native and cross-linked (0.0–0.028% POCl₃) hydroxypropylated (8%) corn starches were examined. Extrusion variables, including starch moisture content, screw design, extrusion temperature, and level of cross-linking in the modified corn starches, were investigated.

MATERIALS AND METHODS

Preparation of cross-linked (0, 0.014, 0.024, and 0.028% POCl₃) hydroxypropylated (8% propylene oxide) starches and extrusion variables (moisture, screw designs, and temperature profiles) were reported earlier (McPherson et al 2000).

Scanning Electron Microscopy (SEM)

Extruded starches (0.5 g) were suspended in water (10 mL) and gently agitated at 20°C (20 min) to disperse the gelatinized material. A drop of the suspension was placed on a glass slide, spread with a spatula, and examined under a light microscope (Nikon Labophot, Nikon, Garden City, NY). The remaining granules were counted in 10 fields and compared with that in the respective unextruded parent starch to arrive at an approximate percentage of granules remaining after extrusion. A drop of the starch suspension was placed on a glass cover slip, spread with a spatula, and allowed to dry. The cover slip was then attached to an aluminum stub with double-sided tape, and colloidal silver was applied between the edge of the cover slip and the aluminum stub. The specimens were then sputter-coated with gold/palladium (60/40). The mounted specimens were observed using a scanning electron microscope (JEOL model 1850, Tokyo, Japan) at the Bessey Microscopy Facility, Iowa State University (Ames, IA).

High Performance Size Exclusion Chromatography (HPSEC)

Starch (0.5 g, dsb) was solubilized in dimethyl sulfoxide solution (DMSO, 90%) (50.0 mL) in a boiling water bath for 1 hr with constant stirring, and continuously stirred for 24 hr at room temperature. Starch was precipitated from an aliquot of DMSO solution (1.0 mL) with excess absolute ethyl alcohol and centrifuged at $6,750 \times g$ for 15 min. The precipitated amorphous starch pellet, which had been defatted, was resolubilized in deionized water (10 mL, 95°C) and stirred with a magnetic stirrer in a boiling water bath for 30 min. Starch solutions were then filtered using a 5.0- μ m syringe filter. The filtrate was injected (100 μ L) into an HPSEC system. This system consisted of an HP 1050 isocratic pump (Hewlett Packard, Valley Forge, PA), refractive index (RI) detector (model HP1047A, Hewlett Packard, Valley Forge, PA), and a multiangle laser light-scattering (MALLS) detector (model Dawn F, Wyatt Tech., Santa Barbara, CA) with a helium-neon laser light source ($\lambda = 632.8$ nm) and a K-5 flow cell. The columns used were Shodex OH pak KB-G, KB-806, and KB-804 (Shodex Denko, Tokoyo, Japan) HPSEC columns connected

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in series and kept at 55°C. The mobile phase was distilled, deionized, and degassed water passed through in-line filters (0.2 and 0.1 μm) in series, at a flow rate of 0.7 mL/min.

The electronic outputs of the RI and MALLS detectors were collected by ASTRA software (ver. 4.10, Wyatt Tech., Santa Barbara, CA). Peaks were assigned using the RI chromatograms. A second-order fit in the Berry analysis method (ASTRA) had the least statistical error for determination of amylopectin weight average molecular weight. Because of the reduced sensitivity of MALLS for small molecular weight species, the molecular weight of the peak two (amylose and degraded amylopectin fragments) of extruded starches was calculated from the refractive index signal using a calibration curve constructed from a series of pullulan molecular weight standards (22.0, 47.3, 112.0, 212.0, 404.0, and 788.0 × 10³) (Viscotek, Houston, TX).

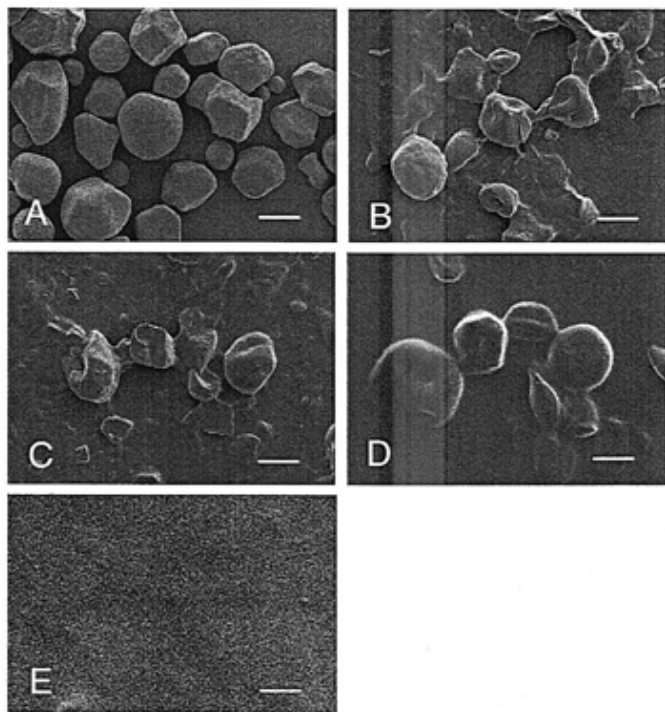


Fig. 1. Scanning electron micrographs of native corn starch (A); native corn starch extruded at 40% moisture, 60°C, and low shear (B); native corn starch extruded at 30% moisture 60°C, and high shear (C); cross-linked (0.028% POCl₃), hydroxypropylated corn starch at 40% moisture, 60°C, and low shear (D); and cross-linked (0.028% POCl₃), hydroxypropylated corn starch at 40% moisture, 100°C, and low shear (E). Bar = 10 μm.

Glass Transition Temperature of Starches Determined by Differential Scanning Calorimetry (DSC)

A comparison study on glass transition temperatures of the native and chemically modified starches was conducted by using a differential scanning calorimeter (DSC-7, Perkin Elmer Corp., Norwalk, CT) equipped with an Intracooler II System and Pyris thermal analysis software (Perkin-Elmer). Starch and water mixtures were prepared by mixing starch with water at 70:30 (w/w, dsb) in screw-capped glass vials. The starch and water mixtures were thoroughly mixed by placing the vials on a ball-mill tumbler at room temperature for 4 hr, and equilibrated for additional 48 hr. The starch mixtures were then weighed and sealed in aluminum pans and equilibrated at room temperature for 2 hr before analysis. An empty aluminum pan was used as the reference. Indium and zinc were used as reference standards. The initial scan was made from 25 to 120°C at 10°C/min followed by cooling to 5°C. The second scan was made from 5 to 120°C at 5°C/min. Moisture content of the starch sample was determined by puncturing the sealed DSC pan after scanning and drying at 100°C for 8hr in a convection oven. The glass transition temperature was determined from the midpoint of the baseline shift (Zeleznaek and Hosney 1987). All samples were examined in triplicate.

RESULTS AND DISCUSSION

Morphology of Extruded Starch

The scanning electron micrographs (SEM) of native corn starch and representative extruded starches are shown in Fig. 1. Native

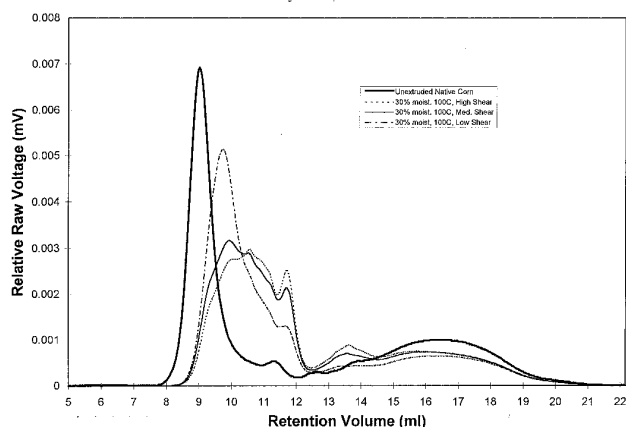


Fig. 2. Normalized chromatograms of unextruded native corn starch and extruded native corn starches at 30% moisture and 100°C at low, medium, and high shear (detected by refractive index).

TABLE I
Weight Average Molecular Weights (M_w) of Amylopectin and Peak Two (Amylose and Degraded Amylopectin) and Gyration Radii of Amylopectins of Extruded Native Corn Starches^a

Starch Moisture Content (%)	Extrusion (°C)	Level of Shear	Amylopectin Weight Av M_w ($M_w \times 10^8$) ^b	Gyration Radii of Amylopectin (R_z) (nm) ^b	Peak Two Weight Av. M_w ($M_w \times 10^5$) ^c
Unextruded			7.7 ± 0.6 ^d	368.6 ± 16.5	5.5 ± 0.2
30	60	Low	3.2 ± 0.2	296.1 ± 14.2	6.3 ± 0.1
30	80	Low	2.6 ± 0.0	226.7 ± 33.1	6.7 ± 0.0
30	100	Low	1.5 ± 0.0	223.8 ± 6.6	5.9 ± 0.2
30	100	Med.	1.1 ± 0.0	240.4 ± 7.1	7.0 ± 0.0
30	60	High	2.6 ± 0.2	296.1 ± 58.0	7.0 ± 0.1
30	80	High	1.4 ± 0.1	242.1 ± 13.5	7.0 ± 0.2
30	100	High	1.0 ± 0.1	229.2 ± 0.9	7.3 ± 0.2
40	60	Low	6.0 ± 0.2	363.5 ± 67.2	4.1 ± 0.2
40	100	Low	4.4 ± 0.3	300.0 ± 20.5	5.9 ± 0.2
40	100	High	1.9 ± 0.0	268.2 ± 2.5	5.2 ± 0.2

^a Average of at least two replicates.

^b Molecular weight determined by light scattering and refractive index detectors.

^c Molecular weight determined by pullulan standard curve with refractive index detector.

^d Standard error.

corn starch granules were polyhedral in shape and had axial diameters of 5–20 μm (Fig. 1a) as has been reported by Jane et al (1994). Starches extruded at low temperature (60°C) were found to have relatively small amounts of distorted and broken granular fragments. These results agreed with those of DSC and X-ray diffraction patterns of starches extruded at 60°C, which showed remaining crystallinity (McPherson et al 2000). Native corn starch extruded at 40% moisture, 60°C, and low shear (Fig. 1b) showed remaining distorted granules and some fractured granules ($\approx 42 \pm 8\%$ granules remained). That extruded at 30% moisture, 60°C, and high shear (Fig. 1c) showed substantially fractured granules ($\approx 21 \pm 6\%$ granules remained). The hydroxypropylated (8%) corn starch extruded at 30% moisture, 60°C, and high shear showed residual swollen, distorted, and fractured granules (data not shown). The highly cross-linked (0.028% POCl₃) hydroxypropylated (8%) corn starch extruded at 40% moisture, 60°C, and low shear levels showed disrupted swollen granules (Fig. 1d) ($\approx 14 \pm 2\%$ granules remained). Extrusion of this starch at 40% moisture, 100°C, and low shear displayed only a continuous gel phase with no remaining granular structure (Fig. 1e). All starches showed no remaining granular structure after extrusion at 100°C. Extrusion of starch at high temperatures (>100°C) has been reported to completely destroy granular structure of native starches (Mercier et al 1979, Richmond and Smith 1985).

Molecular Weight Distributions of Extruded Starches

Native starch. The HPSEC chromatogram of the unextruded native starch showed two major peaks corresponding to amylopectin and amylose, with retention volumes of 7.6–11.8 and 11.9–

20.7 mL, respectively (Fig. 2). The extruded starches displayed multiple peaks, resulting from degradation during extrusion. Degradation has been reported in both the amylopectin and amylose fractions of extruded starches (Colonna et al 1984, Wen et al 1990). As a consequence, the molecular weight of amylopectin decreased and shifted to higher retention volumes. Therefore, the second major peak in the HPSEC chromatograms of the extruded starches is referred to as peak two because it is composed of a mixture of amylose and degraded amylopectin molecules. The weight average molecular weights of native corn amylopectin and amylose were 7.7×10^8 and 5.5×10^5 , respectively (Table I). Previously reported molecular weight values for amylopectin and amylose using HPSEC vary with sample preparation, size exclusion chromatography columns, mobile phase, and detection systems. The molecular weights of corn amylopectin and amylose from various sources have been reported to range from 1.5×10^7 to 2.27×10^8 and 1.36 to 4.89×10^5 , respectively (Politz et al 1994, Fishman et al 1996, Mua and Jackson 1997, Bello-Perez et al 1998, Yokoyama et al 1998).

Extrusion of native corn starch at 30% moisture and 100°C with increasing shear degraded the amylopectin and caused the peak to broaden and shift to higher retention volumes (8.5–12.5 mL) (Fig. 2). Residence time of the starch in the extruder barrel increased as shear increased and likely contributed to molecular degradation. The amylopectin molecular weight decreased as shear increased ($1.5, 1.1,$ and 1.0×10^8 for low, medium, and high, respectively) (Table I). As a result of increasing shear and degraded amylopectin molecules shifting to higher elution volumes, peak two molecular weight increased ($5.9, 7.0,$ and 7.3×10^5 for low, medium, and

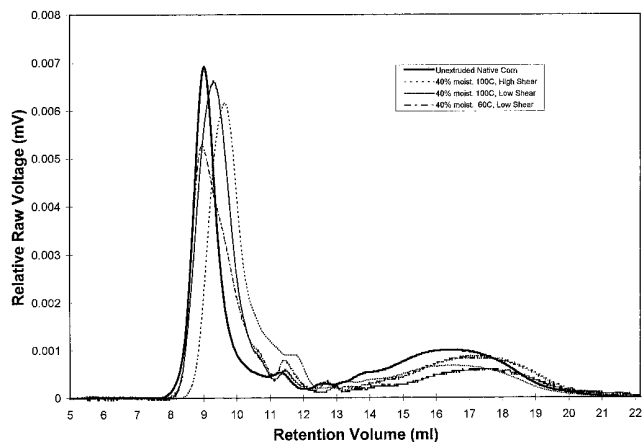


Fig. 3. Normalized chromatograms of unextruded native corn starch and extruded native corn starches at 40% moisture and low shear at 60 and 100°C and at 40% moisture and high shear at 100°C (detected by refractive index).

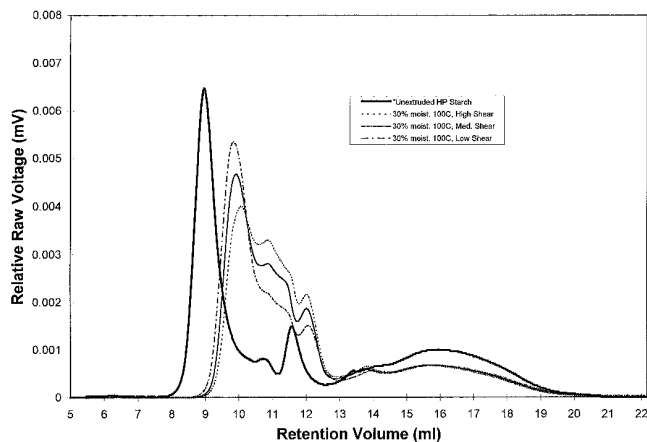


Fig. 4. Normalized chromatograms of the unextruded hydroxypropylated (8%) and extruded hydroxypropylated (8%) corn starches at 30% moisture and 100°C at low, medium, and high shear (detected by refractive index).

TABLE II
Weight Average Molecular Weights (M_w) of Amylopectin and Peak Two (Amylose and Degraded Amylopectin) and Gyration Radii of Amylopectins of Extruded Hydroxypropylated (8%) Corn Starches^a

Starch Moisture Content (%)	Extrusion (°C)	Level of Shear	Amylopectin Weight Av M_w ($M_w \times 10^8$) ^b	Gyration Radii of Amylopectin (R_z) (nm) ^b	Peak Two Weight Av. M_w ($M_w \times 10^5$) ^c
Unextruded			6.5 ± 0.6^d	369.6 ± 27.0	5.5 ± 0.2
30	60	Low	2.7 ± 0.0	308.0 ± 29.3	5.8 ± 0.1
30	80	Low	2.4 ± 0.0	242.1 ± 11.3	6.3 ± 0.0
30	100	Low	1.3 ± 0.1	208.1 ± 11.9	5.3 ± 0.2
30	100	Med.	0.6 ± 0.0	178.9 ± 3.4	6.6 ± 0.1
30	60	High	0.8 ± 0.0	253.5 ± 0.7	7.3 ± 0.2
30	80	High	0.5 ± 0.2	222.5 ± 4.2	7.1 ± 0.2
30	100	High	0.4 ± 0.0	131.8 ± 6.4	6.9 ± 0.1
40	60	Low	3.7 ± 0.3	357.4 ± 44.5	5.2 ± 0.1
40	100	High	1.3 ± 0.1	194.0 ± 10.8	6.1 ± 0.0

^a Average of at least two replicates.

^b Molecular weight determined by light scattering and refractive index detectors.

^c Molecular weight determined by pullulan standard curve with refractive index detector.

^d Standard error.

high shear, respectively) and developed a pronounced shoulder at an elution volume of 13.2 mL. Increasing extrusion temperature of native corn starch at 30% moisture decreased the amylopectin molecular weight at low shear (3.2, 2.6, and 1.5×10^8 , for 60, 80, and 100°C, respectively) and high shear (2.6, 1.4, and 1.0×10^8 , for 60, 80, and 100°C, respectively). Increasing extrusion temperature of native corn starch also increased peak two molecular weight. Amylopectin peaks of starches extruded at 30% moisture were broad, indicating the molecules were severely degraded during extrusion, whereas those extruded at 40% moisture content were less degraded and had a narrower molecular weight distribution, close to that of the unextruded corn starch amylopectin (Fig. 3). These results agreed with those of starches extruded at 40% moisture that displayed greater viscosity than those extruded at 30% moisture (McPherson et al 2000). For native corn starch, the greatest degradation of amylopectin occurred with extrusion at high shear, 30% moisture, and 100°C. This is in agreement with previous findings that the amylopectin of extruded corn starch is degraded most readily at low moisture and high shear conditions (Wen et al 1990, Politz et al 1994, Pan et al 1998).

Hydroxypropylated starch. Unextruded hydroxypropylated (8%) corn starch with no cross-linking displayed retention volumes of 7.8–12.4 mL and 12.4–19.9 mL for amylopectin and amylose, respectively (Fig. 4). The molecular weights of amylopectin and amylose were 6.5×10^8 and 5.5×10^5 , respectively (Table II). Extrusion of hydroxypropylated (8%) starch at 30% moisture content and 100°C with increasing shear produced amylopectins with lower molecular weights of 1.3, 0.6, and 0.4×10^8 for low, medium, and high shear, respectively, compared with 1.5, 1.1, and 1.0×10^8 for low, medium, and high shear, respectively, of their native corn starch counterparts. The lower onset gelatinization temperature of hydroxypropylated starch (50.6°C) than that of native

corn starch (66.1°C) (McPherson et al 2000) resulted in a higher degree of gelatinization and dispersion during extrusion and subsequently more molecular degradation from shear. Increasing extrusion temperatures at 30% moisture content resulted in decreased amylopectin molecular weight at both low shear (2.7, 2.4, and 1.3×10^8 for 60, 80, and 100°C, respectively) and high shear (0.8, 0.5, 0.4×10^8 for 60, 80, and 100°C, respectively). Similar temperature effects have been reported in native wheat starch (Diosady et al 1985) and in native corn (Chinnaswamy and Hanna 1990). Like that observed in native corn starch, extrusion at 40% starch moisture

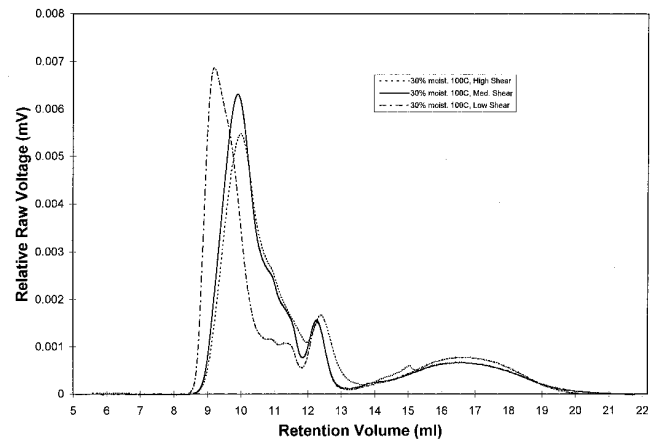


Fig. 5. Normalized chromatograms of extruded cross-linked (0.014% POCl₃) and hydroxypropylated (8%) and cross-linked (0.014% POCl₃) corn starches at 30% moisture, 100°C, and low, medium, and high shear (detected by refractive index).

TABLE III
Weight Average Molecular Weights (M_w) of Amylopectin and Peak Two (Amylose and Degraded Amylopectin) and Gyration Radii of Amylopectins of Extruded Cross-Linked (0.014% POCl₃) and Hydroxypropylated (8%) Corn Starches^a

Starch Moisture Content (%)	Extrusion (°C)	Level of Shear	Amylopectin Weight Av M_w ($M_w \times 10^8$) ^b	Gyration Radii of Amylopectin (R_z) (nm) ^b	Peak Two Weight Av. M_w ($M_w \times 10^5$) ^c
30	100	Low	5.0 ± 0.4^d	381.7 ± 4.6	3.6 ± 0.0
30	100	Med.	1.2 ± 0.1	292.3 ± 6.3	3.7 ± 0.1
30	60	High	1.1 ± 0.0	687.5 ± 69.7	4.5 ± 0.1
30	80	High	1.0 ± 0.3	424.6 ± 68.4	4.7 ± 0.3
30	100	High	1.3 ± 0.2	286.3 ± 25.2	3.9 ± 0.0
40	100	High	4.5 ± 0.2	450.5 ± 34.4	3.9 ± 0.0

^a Average of at least two replicates.

^b Molecular weight determined by light scattering and refractive index detectors.

^c Molecular weight determined by pullulan standard curve with refractive index detector.

^d Standard error.

TABLE IV
Weight Average Molecular Weights (M_w) of Amylopectin and Peak Two (Amylose and Degraded Amylopectin) and Gyration Radii of Amylopectins of Extruded Cross-Linked (0.024% POCl₃) and Hydroxypropylated (8%) Corn Starches^a

Starch Moisture Content (%)	Extrusion (°C)	Level of Shear	Amylopectin Weight Av M_w ($M_w \times 10^8$) ^b	Gyration Radii of Amylopectin (R_z) (nm) ^b	Peak Two Weight Av. M_w ($M_w \times 10^5$) ^c
30	60	Low	3.3 ± 0.3^d	472.1 ± 49.0	3.1 ± 0.0
30	80	Low	4.3 ± 0.2	421.0 ± 12.7	3.2 ± 0.0
30	100	Low	6.9 ± 0.6	434.3 ± 15.3	3.5 ± 0.3
30	100	Med.	5.3 ± 0.4	465.4 ± 13.4	3.7 ± 0.0
30	60	High	0.7 ± 0.1	337.6 ± 10.6	4.0 ± 0.0
30	80	High	0.7 ± 0.0	411.1 ± 11.6	3.7 ± 0.0
30	100	High	1.7 ± 0.0	460.5 ± 51.6	4.0 ± 0.1
35	100	High	3.6 ± 0.1	400.1 ± 5.7	3.4 ± 0.0
40	60	Low	9.0 ± 0.8	410.6 ± 33.0	2.7 ± 0.1
40	80	Low	7.7 ± 0.1	340.7 ± 12.2	2.6 ± 0.0
40	100	Low	3.4 ± 0.1	379.5 ± 2.1	3.7 ± 0.0
40	100	High	6.7 ± 0.5	417.9 ± 10.6	3.4 ± 0.1

^a Average of at least two replicates.

^b Molecular weight determined by light scattering and refractive index detectors.

^c Molecular weight determined by pullulan standard curve with refractive index detector.

^d Standard error.

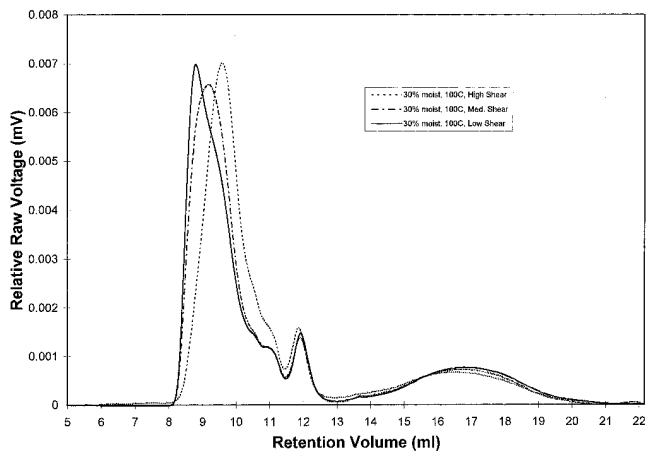


Fig. 6. Normalized chromatograms of extruded cross-linked (0.024% POCl₃) and hydroxypropylated (8%) corn starches at 30% moisture, 100°C and low, medium, and high shear (detected by refractive index).

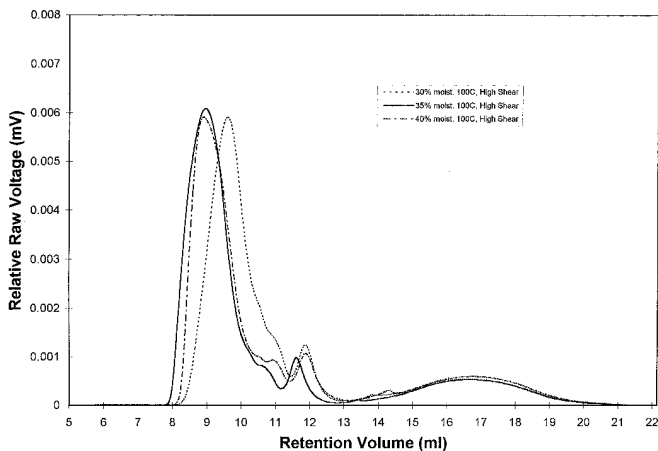


Fig. 7. Normalized chromatograms of extruded cross-linked (0.024% POCl₃) and hydroxypropylated (8%) corn starches at high shear, 100°C, and 30, 35, and 40% moisture (detected by refractive index).

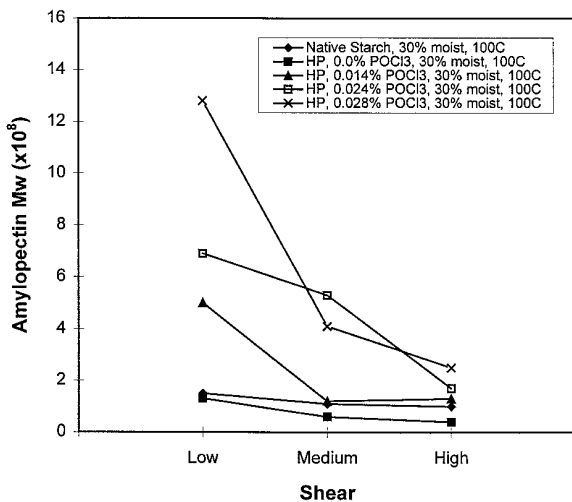


Fig. 8. Amylopectin molecular weights of starches extruded at 30% moisture and 100°C at low, medium, and high shear.

content resulted in less degraded amylopectin molecular weights and a narrower distribution of molecular weight (data not shown).

Hydroxypropylated starch with a moderate level of cross-linking. Dispersed, unextruded cross-linked (0.014% POCl₃) hydroxypropylated (8%) starch could not be filtered through a 5.0- μ m

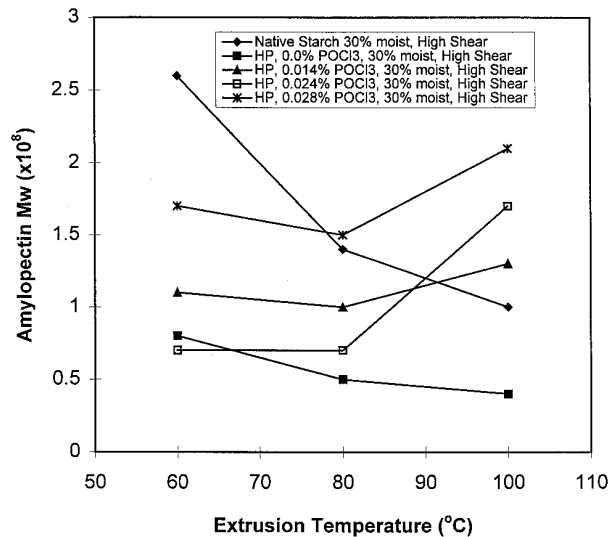


Fig. 9. Amylopectin molecular weights of starches extruded at 30% moisture and high shear at 60, 80, and 100°C.

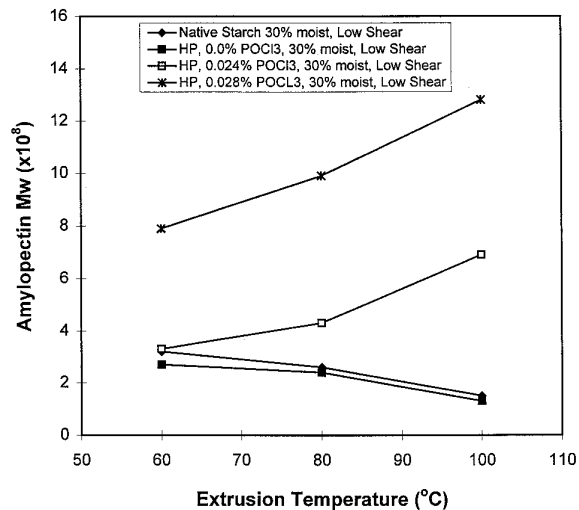


Fig. 10. Amylopectin molecular weights of starches extruded at low shear at 60, 80, and 100°C.

syringe filter. Therefore, the molecular weight of the unextruded cross-linked starches could not be obtained. After extrusion the cross-linked starches could be filtered and analyzed by HPSEC. Amylopectins of the extruded cross-linked starches had larger molecular weight than those of the native and hydroxypropylated starches extruded at the same conditions (Figs. 2–5). Extrusion of cross-linked (0.014% POCl₃) hydroxypropylated (8%) starch at 30% moisture and 100°C yielded amylopectin molecular weights of 5.0, 1.2, and 1.3 $\times 10^8$ for low, medium, and high shear, respectively (Fig. 5 and Table III), compared with 1.3, 0.6, and 0.4 $\times 10^8$ for low, medium, and high shear, respectively (Table II) of their hydroxypropylated corn starch without cross-linking counterparts. The amylopectin peaks of the extruded cross-linked (0.014% POCl₃) hydroxypropylated (8%) corn starches were not as broad as those of hydroxypropylated (8%) and native corn starches extruded at the same conditions (Figs. 2–5), indicating the cross-linking prevented the amylopectin molecules from being highly degraded as those of the non cross-linked starch counterparts (Figs. 2 and 4). The substantially lower molecular weight of the peak two in the extruded cross-linked (0.014% POCl₃) hydroxypropylated (8%) corn starch than that of the amylose of the unextruded native corn starch might be a result of high molecular weight amylose being

TABLE V
Weight Average Molecular Weights (M_w) of Amylopectin and Peak Two (Amylose and Degraded Amylopectin) and Gyration Radii of Amylopectins of Extruded Cross-Linked (0.028% POCl₃) and Hydroxypropylated (8%) Corn Starches^a

Starch Moisture Content (%)	Extrusion (°C)	Level of Shear	Amylopectin Weight Av M_w ($M_w \times 10^8$) ^b	Gyration Radii of Amylopectin (R_z) (nm) ^b	Peak Two Weight Av. M_w ($M_w \times 10^5$) ^c
30	60	Low	7.9 ± 0.2	417.4 ± 22.3	2.9 ± 0.0
30	80	Low	9.9 ± 0.3	474.5 ± 39.7	2.8 ± 0.1
30	100	Low	12.8 ± 0.8 ^d	575.9 ± 34.5	3.2 ± 0.0
30	100	Med.	4.1 ± 0.0	381.4 ± 4.2	3.4 ± 0.1
30	60	High	1.5 ± 0.0	353.2 ± 29.7	3.1 ± 0.0
30	80	High	1.7 ± 0.1	382.1 ± 32.1	3.3 ± 0.1
30	100	High	2.5 ± 0.1	422.3 ± 14.1	3.5 ± 0.1

^a Average of at least two replicates.

^b Molecular weight determined by light scattering and refractive index detectors.

^c Molecular weight determined by pullulan standard curve with refractive index detector.

^d Standard error.

preferentially cross-linked to the amylopectin and eluted with amylopectin (Jane et al 1992). Cross-linked starches are produced for food and industrial applications in which shear resistance is needed (Hullinger 1967, Wurzburg 1986).

Hydroxypropylated starch with a higher level of cross-linking. Amylopectin molecular weights were 6.9, 5.3, and 1.7 × 10⁸ for low, medium, and high shear, respectively, for cross-linked (0.024% POCl₃) hydroxypropylated (8%) corn starch extruded at 30% moisture and 100°C (Table IV). The amylopectin of extruded cross-linked (0.024% POCl₃) hydroxypropylated (8%) corn starch displayed decreased molecular weight with increasing shear (Fig. 6). Extrusion of cross-linked (0.024% POCl₃) hydroxypropylated (8%) corn starch at 40% moisture also yielded less degraded amylopectin compared with their counterparts extruded at 30% moisture. Increases in starch moisture content during extrusion at 100°C and high shear resulted in increasing amylopectin molecular weights (1.7, 3.6, and 6.7 × 10⁸ for 30, 35, and 40% moisture content, respectively) (Table IV and Fig. 7). This agreed with the positive effect of the moisture content on the hot paste viscosity and final viscosity of extruded cross-linked hydroxypropylated (8%) starches (McPherson et al 2000). The differences are attributed to a decrease in friction during extrusion at increased moisture content (Lai and Kokini 1991).

In contrast to the results of extruded native and hydroxypropylated corn starches, extrusion of cross-linked hydroxypropylated corn starches at 30% moisture yielded increased amylopectin molecular weight as temperature increased at both low and high shear (Tables I–V). Extrusion of cross-linked (0.024% POCl₃) hydroxypropylated (8%) corn starch at 30% moisture yielded increasing amylopectin molecular weights as temperature increased at low shear (3.3, 4.3, and 6.9 × 10⁸ for 60, 80, and 100°C, respectively) and high shear (0.7, 0.7, and 1.0 × 10⁸ for 60, 80, and 100°C, respectively) (Table IV). This agreed with the reported increased average viscosity of starches extruded at 30% moisture with increasing temperature of extrusion (60–80°C) (McPherson et al 2000). However, extrusion of cross-linked (0.024% POCl₃) hydroxypropylated (8%) corn starch at 40% moisture and low shear yielded decreased amylopectin molecular weight with increasing temperature (9.0, 7.7, and 3.4 × 10⁸ for 60, 80, and 100°C, respectively). Amylopectin molecular weight of cross-linked (0.028% POCl₃) hydroxypropylated corn starch decreased with increasing shear (12.8, 4.1, and 2.5 × 10⁸ for low, medium, and high shear, respectively) during extrusion at 100°C and 30% moisture (Table V). Increasing the temperature of extrusion at 30% moisture yielded increased amylopectin molecular weights of the cross-linked (0.028% POCl₃) hydroxypropylated corn starch.

Extrusion of the starches at 100°C and 30% moisture decreased amylopectin molecular weight as shear increased (Tables I–V and Fig. 8). The amylopectin of native corn starch was not degraded to the same magnitude as that of the hydroxypropylated (8%) corn starch. This difference was attributed to the lower gelatinization

temperature of the hydroxypropylated (8%) starch, which resulted in higher degrees of gelatinization and dispersion during extrusion. The highly dispersed starch molecules were more susceptible to shear degradation. The magnitude of amylopectin molecular weight change, from low to high shear, became more drastic as the level of cross-linking increased. At low shear the chemical cross-links were able to prevent severe molecular degradation, whereas at medium and high shear substantial degradation occurred to the large cross-linked amylopectin molecules. These results agreed with the average viscosity of extruded starches decreasing more for chemically modified starches than for the native starch counterparts as shear increased (McPherson et al 2000).

Extrusion of native corn and hydroxypropylated corn starches at 30% moisture yielded decreased amylopectin molecular weights as temperature increased (Tables I and II) (Figs. 9 and 10). Extrusion of cross-linked (0.024% POCl₃) hydroxypropylated corn starch at 30% moisture showed that amylopectin molecular weights were less degraded when the extrusion temperature increased (60–100°C), whereas at 40% moisture amylopectin molecular weights were more degraded with increasing temperature (Table IV). This effect can be attributed to the higher glass transition temperatures of the cross-linked starches. The glass transition temperatures of native, hydroxypropylated, and cross-linked (0.014 and 0.028% POCl₃) hydroxypropylated (8%) corn starch were 29.1, 28.3, 43.2, and 67.2°C, respectively. The moisture contents of the starch samples (prepared with 30% water content), measured by puncturing the sealed DSC pans, were 26%. The glass transition temperature of polymers is known to increase with the addition of cross-linking (Nielsen 1974). At 60°C of extrusion temperature, the highly cross-linked starch was likely to be in the glassy state, and the rigid molecules were more susceptible to shear degradation. When the temperature of extrusion increased, the cross-linked molecules became rubbery, and degradation decreased.

CONCLUSIONS

Extrusion of starches produced substantial morphological changes in granular structure. Starches extruded at 60°C showed distorted and fragmented granules, whereas those extruded at 100°C showed no granular structure and were completely amorphous. Extrusion conditions showed large effects on the molecular weights of the extruded starches. Increasing starch moisture content reduced amylopectin degradation during extrusion. Cross-linking prevented amylopectin degradation. However, the magnitude of amylopectin degradation increased at higher levels of cross-linking as shear increased. Increasing temperature of extrusion decreased amylopectin molecular weight of extruded native and hydroxypropylated corn starches, whereas the opposite effect was observed in cross-linked hydroxypropylated starches as a result of glass transition temperature.

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