

SOME FACTORS AFFECTING THE TENSILE STRENGTH OF STARCH FILMS¹

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ABSTRACT

The effects of starch variety, granule modification, and humidity on the strength and elongation of starch films were investigated. Film strength of different varieties increased with increased amylose content. Waxy maize films gave lower elongation than films of nonwaxy varieties. Corn starches that had been acid-modified, hypochlorite-oxidized, hydroxyethylated, heat-moisture-treated, or cross-bonded with epichlorohydrin (0.24% or less) to impart widely different solubility and viscosity properties showed only moderate differences in strength and elongation. Corn starch cross-bonded with 0.48% epichlorohydrin did not form a continuous film. Increasing the solubility of corn starch by a high-shear treatment in dilute paste form resulted in slightly increased film strength and markedly improved elongation. Humidity (i.e., film moisture) was the most important factor. Increasing humidity from 35 to 65% decreased film strength by 43%.

With the exception of some high-amylose varieties, starch does not form tough, pliable, unsupported films. Nevertheless, it has found extensive use in the formulation of adhesives and sizes to improve the mechanical properties of items such as paper, paperboard, and textiles in which the film-forming ability of the starch is important. Very often the starch is modified (for example with acid or hypochlorite) to reduce the viscosity of its pastes and to impart other desirable flow properties. Much emphasis has been placed on the paste viscosity requirements for the various end uses and on methods for attaining them. With few exceptions (2,9,10,12), relatively little account has been taken of how the various kinds of modification might affect the film-forming properties of the starch. Once the requirements of proper distribution of starch substance on or within a given substrate, adhesion to the substrate, etc., have been met, the film properties of the starch should thereafter determine the extent of improvement in mechanical properties imparted to the substrate.

It was our object to determine the extent to which starch variety, kind and degree of modification in granule form, and humidity affect the tensile strength and ultimate elongation of starch films.

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Materials and Methods

Waxy maize and high-amylose corn starch were obtained from National Starch and Chemical Co., tapioca and potato starch from Morningstar-Paisley, Inc., and wheat starch from Ogilvie Flour Mills, Fort William, Ontario. Unmodified corn starches (A, B, C) and oxidized and hydroxyethylated corn starch were from Clinton Corn Processing Co.

Heat-moisture treatment was carried out by heating 500 g. of unmodified corn starch containing 30% moisture in a 6-qt. pressure cooker for 24 hours at 90°C. after the manner of Sair and Fetzer (11).

Acid-modified starches were prepared on a pilot-plant scale from a common sample of unmodified corn starch by treatment with dilute hydrochloric acid according to current commercial practice.³

Cross-bonded starches were prepared with epichlorohydrin. Sodium hydroxide solution (115 ml.), 0.75N, was added dropwise with rapid stirring to 835 g. of corn starch (sample C) slurried in 1,165 ml. of water. The desired amount of epichlorohydrin was added, and the slurry stirred for 16 hours at 23°C. The slurry was then adjusted to pH 5.2 with concentrated hydrochloric acid solution and filtered, and the filter cake was washed with 1,000 ml. of water and air-dried at room temperature.

Predispersed corn starch was prepared from unmodified corn starch (sample A). Starch (20 g.) was cooked in 1,000 ml. of water for 20 minutes at 99°C. The resulting hot paste was agitated in a Waring Blendor for 3 minutes to complete the dispersion of swollen granules. The resulting starch sol was filtered and the filtrate poured into 2,000 ml. of methanol to precipitate the starch. The precipitate was allowed to settle and the supernate removed by decantation. The precipitate was washed once with absolute methanol and dried over anhydrous calcium sulfate under reduced pressure.

Starch Analyses. Intrinsic viscosities were determined in normal sodium hydroxide solution.⁴ Starch (1.2 g., dry basis) was suspended in 100 ml. of distilled water and 100 ml. of 2N sodium hydroxide solution added during stirring. The mixture was stirred 10 minutes to disperse the starch and the dispersion filtered through a fine glass-wool plug in the stem of a funnel. With unmodified starches, it was necessary to vigorously shake the suspensions for 30 seconds to complete the dispersion of starch before filtering. Efflux times were determined

³For a description of different commercial starch modification processes and of terms such as "fluidity" and "degree of substitution" (DS), refer to Kerr, Ralph W., *Chemistry and Industry of Starch*, 2nd ed., Academic Press, Inc. (1950).

⁴The method is a variation of one now under collaborative study by the member companies of the Corn Industries Research Foundation.

at starch concentrations from 0.1 to 0.45 g./100 ml. in No. 75 Cannon-Ubbelohde dilution viscometers.⁵ Plots of reduced viscosity vs. concentration were extrapolated to infinite dilution to calculate intrinsic viscosity.

Iodine affinities were determined as described by Lansky *et al.* (6). "Apparent amylose" contents of the starches were calculated from the iodine affinities, assuming that pure amylose bound 200 mg. of iodine per g. of starch and neglecting the iodine bound by the amylopectin component. Starch solubilities were determined at 99°–100°C. as described by Leach *et al.* (7).

Film Preparation. Starch pastes were prepared by cooking the requisite amount of starch in distilled water for 20 minutes at 99°–100°C. The amounts of starch used were sufficient to give pastes viscous enough to inhibit flow to the point where a wet film laid down on the silicone-treated casting surface (see below) would not draw up into isolated puddles owing to interfacial tension effects. The pastes were deaerated by alternate application and release of a vacuum while contained in a suction flask immersed in a boiling water bath. High-amylose corn starch paste was prepared by heating a 10% suspension while stirring in a steam-jacketed pressure vessel. The suspension was brought to 140°C., held for 15 minutes, and then cooled to 100°C. before being withdrawn for casting. Pastes of oxidized starches were cooled to 70°C. before they were cast. All others were cast without cooling.

The films were cast on 8-in. by 30-in. plate glass coated with a silicone resin release agent. The plates were prepared by masking off with tape to leave an exposed rectangular surface 5 in. by 14 in. in the center. The exposed surface was painted with a 3% solution of Dow Corning Resin R-671 in toluene, air-dried, and cured for 1 hour at 215°C. Removal of the tape left a border of untreated glass surface around the treated area.

Films were cast using a 6-in. Boston Bradley applicator adjusted to give a film 0.025 mm. thick when dry. Wet films were applied to cover the entire silicone-treated surface and to extend 0.5 in. beyond the untreated border on all sides. This provided secure anchoring for the film pieces around their entire periphery so that upon drying they would not release spontaneously, with consequent curling and distortion.

All films were air-dried, released, and cut into strips for testing in a room maintained at 73° ± 1°F. and 50 ± 2% relative humidity. Be-

⁵ Cannon Instrument Co., State College, Pa.; catalog No. CUDC.

fore the dried films were released, cellophane tape was placed around their edges. The tape border was then cut through its center, and the film piece then could be released without danger of shattering.

Ten strips 19 mm. by 102 mm. were cut from each film piece and were equilibrated before testing for at least 24 hours at the desired temperature and humidity. All tests were performed at 73°F. and 50% humidity except where noted. After tempering, each strip was weighed to the nearest 0.1 mg. and its cross-section calculated, assuming a uniform density for all films of 1.53 g./cc.

Tensile and Elongation Tests. Tensile strength and elongation at break were determined in a Thwing Albert Electro Hydraulic Tester, Model 30-LT. Jaw span was 2.5 inches. Average loading rate was 2 kg. per minute. Tensile strengths were not corrected for elongation. Occasionally film pieces broke in the tester at values considerably below the average of their class, presumably because of flaws which were not readily apparent because of the opacity of most of the films. Therefore, data which were lower than the average value by more than three standard deviations were rejected as nonrepresentative and new averages were calculated. The coefficient of variation of single tensile determinations was $\pm 6\%$. Elongation results were relatively much more variable owing to the extreme brittleness of most of the films, so that, in interpretation of the data, no significance is attached to differences of less than 1% elongation. The data presented represent the average of from 7 to 70 determinations. Usually, the results of 20 determinations on strips cut from films cast at two different times were averaged.

Film Moistures. Moisture content of the films tested at different humidities were determined using the broken pieces of film from tensile tests. The pieces from at least ten film strips were pooled and moisture determined by heating in a vacuum oven for 4 hours at 120°C.

Results and Discussion

Effects of Variety. Tensile strength and elongation of films prepared from starches of different variety are shown in Table I. Intrinsic viscosities were determined as an index of molecular weight. There was no correlation between mechanical properties of the films and intrinsic viscosity. There was, however, good positive correlation between strength and apparent amylose content. The relationship between strength and amylose content was nonlinear. Differences in elongation between films of the nonwaxy varieties were not significant. Similar behavior of corn, potato, and sago starch films has been

TABLE I
TENSILE STRENGTH AND ELONGATION OF FILMS
OF STARCHES OF DIFFERENT VARIETY

STARCH	[η]	"APPARENT AMYLOSE"	TENSILE STRENGTH	ELONGATION
	dl/g.	%	kg./mm. ²	%
Waxy maize	1.50	0.8	3.49	1.7
Tapioca	2.03	16.6	4.40	3.4
Potato	2.20	19.3	4.42	3.1
Wheat	2.00	25.1	4.63	2.9
Corn (A)	1.73	27.0	4.61	2.5
High-amylose corn	1.35	50.5	5.03	2.5

observed by Neale (9). The waxy maize films were less extensible than the others, presumably owing to the lack of linear component, and were extremely brittle and thus difficult to handle. With regard to the effects of amylose content, our results agree qualitatively with those of Wolff *et al.* (12), who determined the tensile strength and elongation of films containing different proportions of butanol-fractionated corn amylose and amylopectin.

Effects of Starch Modification. Starch is modified commercially by treatment with warm dilute acid to reduce paste viscosity and so permit its use at higher solids content. It is also common practice to modify starch by treatment with hypochlorite, by hydroxyethylation, or by a combination of hydroxyethylation and acid-modification. Both acid-modification and oxidation reduce the molecular weight of starch and could, therefore, reduce its film strength (8). As shown in Table II, acid-modification of corn starch resulted in no significant decrease in strength even though a fivefold reduction in intrinsic viscosity was observed at the highest level of modification. In this respect, the behavior of corn starch films paralleled that of amylose films (12). Un-

TABLE II
EFFECTS OF ACID-MODIFICATION, OXIDATION, AND HYDROXYETHYLATION

STARCH	[η]	TENSILE STRENGTH	ELONGATION
	dl/g.	kg./mm. ²	%
Unmodified corn (B)	1.73	4.67	3.2
15-F Acid-modified	1.21	4.47	2.7
34-F Acid-modified	1.06	4.45	2.6
50-F Acid-modified	0.88	4.94	2.7
71-F Acid-modified	0.67	4.57	2.9
89-F Acid-modified	0.32	4.58	2.2
Hypochlorite-oxidized	0.47	4.87	3.0
Hypochlorite-oxidized	0.25	4.50	2.3
0.05-D.S. hydroxyethyl corn	1.66	4.74	2.5
0.05-D.S. hydroxyethyl, acid-modified corn	0.38	4.18	2.6

like amylose films, however, the corn starch films showed no significant change in elongation except, perhaps, at the highest level of modification. The films of the 50-F acid-modified corn starch were significantly stronger than the others.

Oxidation with hypochlorite to an intermediate degree slightly increased strength. More extensive oxidation decreased it. A similar effect due to oxidation has been noted by Ivanov and Demchenkov (5). Hydroxyethylation of unmodified corn starch had no apparent effect on its mechanical properties. However, a combination of hydroxyethylation and acid-modification reduced strength by 12%. This result may have been due to decreased intermolecular association of starch chains within the film as a consequence of steric hindrance by the substituent hydroxyethyl ether groups. By means of solubility analyses, Hull and Schoch (4) have shown that association in acid-modified starch films was substantially reduced by hydroxyethylation. Cushing and Schuman (1), in a study of polysaccharide additives in the wet end of papermaking, found that strength values of hand sheets sized internally with hydroxyethylated acid-modified starches were always slightly lower than when the corresponding non-derivatized acid-modified starches were used. It is possible that the mechanism responsible for intermolecular bonding within starch films may also be operative when starch is used for bonding cellulose, owing perhaps, to the similarity in chemical structure of starch and cellulose.

Effects of Starch Solubility. Pastes of unmodified starches prepared at ordinary cooking temperatures contained appreciable amounts of swollen starch granules which were not completely dissolved. The inclusion of incompletely dispersed granules could conceivably produce localized stresses on drying and shrinkage of a film, leading to a weakened structure.

To determine the influence of solubility, corn starch was modified in three different ways: 1) by high-shear treatment in dilute paste form to give a predispersed starch (completely soluble at 99°C.), 2) by heat-moisture treatment to reduce solubility, and 3) by progressive cross-bonding with epichlorohydrin to obtain products with solubilities even lower than could be obtained by heat-moisture treatment. The latter treatments have been shown to reduce granule swelling as well as solubility (7). The high-shear treatment reduced the intrinsic viscosity of corn starch from 1.73 to 1.43 dl/g., presumably owing to depolymerization of the amylopectin component (6).

Hamerstrand *et al.* (3) showed that solubility was a good index

TABLE III
EFFECTS OF STARCH SOLUBILITY

STARCH	EPICHLOROHYDRIN	SOLUBILITY	TENSILE STRENGTH	ELONGATION
	%	%	kg/mm ²	%
Predispersed corn	...	100.0	4.94	4.9
Unmodified corn (C)	...	26.7	4.78	3.3
Heat-moisture-treated	...	22.0	4.68	3.2
Cross-bonded	0.03	16.5	4.76	2.9
Cross-bonded	0.12	8.6	4.80	3.9
Cross-bonded	0.24	4.0	4.66	3.8
Cross-bonded ^a	0.48	2.6	2.83	1.2

^a This starch did not give a continuous film.

of the relative degree of cross-bonding of corn starch treated with epichlorohydrin. On the basis of their findings and the results of our own solubility determinations (Table III), it was estimated that for the most highly cross-bonded starch (0.48% epichlorohydrin) the number of cross bonds was no greater than 1 per 300 anhydroglucose units.

Table III shows that film strength was virtually unaffected except at the two extremes of solubility. The predispersed corn starch gave films slightly stronger than unmodified starch. The films were also substantially more extensible. Heat-moisture treatment or cross-bonding had no effect until solubility was reduced to below about 4%. The result with corn starch cross-bonded with 0.48% epichlorohydrin

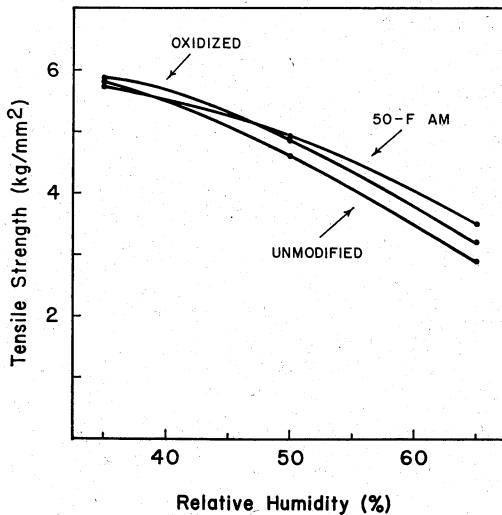


Fig. 1. The effects of humidity on the tensile strength of starch films.

was not indicative of the true inherent strength of the starch substance, since on drying, these films developed numerous small cracks.

Effects of Humidity. Figure 1 shows the effects of relative humidity on the strength of films of corn starch, 50-fluidity acid-modified starch, and hypochlorite-oxidized starch ($[\eta] = 0.47$ dl/g.). Moisture contents of the films at 35, 50, and 65% relative humidity averaged 11.8, 13.2, and 15.3% respectively. The average reduction in strength over this range of humidity was 43%. Differences in strength due to modification were accentuated at higher humidity. Thus, at 65% humidity the acid-modified starch gave films 21% stronger than those from unmodified corn starch. The strength differences at the higher humidity could not be accounted for on the basis of moisture content, since all contained the same moisture to within $\pm 0.2\%$. Average elongation of the films decreased from 3.5% at 35% humidity to 2.2% at 65% humidity.

It is apparent that the humidity-moisture relationships of starch films are extremely important factors governing their strength, more so than amylose content if tensile strength alone is considered. Modification in granule form, if not too extensive, is in comparison a relatively minor factor.

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