Pasting Behavior of Dicarboxyl Starches Prepared from Cross-Linked Cornstarch

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STARCHES treated with minor quantities of epichlorohydrin have been reacted consecutively with periodic and chlorous acids to give cross-linked dicarboxyl starches. The highly specific nature of these oxidants permits convenient and accurate control of the degree of carboxylation, even at the low levels of modification (0.5 to 5.7 dicarboxyl units per 100 repeating units) described in the present work. All products in this range of modification retain the usual starch granule form.

At these levels of modification dicarboxyl starches made from unmodified cornstarch (*3*) swell rapidly when dispersed in hot water and initially produce high viscosities. At elevated temperatures, however, the highly swollen granules rapidly disintegrate to nonviscous solutions. In contrast, epichlorohydrin cross-linked starches of very slight degrees of modification—e.g., 1200 anhydroglucose units per cross link—gelatinize with difficulty and produce partially swollen granules which are highly resistant to further swelling or rupture.

In a search for combinations of carboxylation and cross linking that would result in resistant granules having a high water-holding capacity, useful viscometric properties were found for a given level of carboxyl content within a relatively narrow range of cross linking. The pasting properties of these products are described.

MATERIALS AND METHODS

Commercial cornstarches were used throughout. Typical analyses are: ash 0.03%, nitrogen 0.04%, phosphorus 0.02%, absolute methanol extracts (reflux) 0.81%, and moisture 9 to 12%.

Epichlorohydrin (Shell Chemical Corp.) was redistilled and the fraction in the boiling range 114.5° to 116.5° C. (literature, 117° C. at 756 mm. of mercury) was collected for use.

Sodium metaperiodate of high purity was prepared by electrolytic oxidation of iodine (*4*).

Sodium chlorite (Olin Mathieson Chemical Corp., analytical grade) was used without further purification.

The carboxyl content of the cross-linked dicarboxyl starches was determined by a previously described method (*3*). The extent of cross linking was calculated from the quantity of epichlorohydrin that had reacted with the starch (*2*). The analysis was by difference through determination of unreacted epichlorohydrin at the conclusion of the reactions. Alkali treatment of the filtrates of the reaction mixtures converted unreacted epichlorohydrin to glycerol, which was then oxidized with excess periodate to produce formaldehyde. The formaldehyde was then determined by chromotropic acid analysis.

Preparative Procedures. Illustration of the various steps in the preparation of cross-linked dicarboxyl starches is exemplified by the preparation of a 5% dicarboxyl starch having 305 AGU (anhydroglucose units) per cross link as described below.

The cross-linking reaction, a modification of the one proposed by Caldwell (*1*), was performed in a gas-tight system to prevent loss of epichlorohydrin through volatilization. One hundred grams of cornstarch were slurried in 150 ml. of an aqueous stock alkali solution which contained 1.33 grams of sodium hydroxide and 33.4 grams of anhydrous sodium sulfate. A fresh solution of epichlorohydrin (0.187 gram) in 50 ml. of the aqueous stock alkali solution was slowly added to the mechanically stirred starch slurry. The reaction was continued for 18 hours at 25° ± 0.3° C. The slurry was then neutralized with 6*N* sulfuric acid from an initial pH of approximately 11 to 6.0; the product was separated by filtration and was washed once with water.

For periodate oxidation, the wet, cross-linked starch was suspended in 550 ml. of water and a solution of sodium periodate (6.61 grams in 700 ml. of water) was slowly added with stirring at room temperature. When qualitative tests on the slurry supernatants, using potassium iodide and a starch solution buffered with sodium bicarbonate, were negative for free iodine, the reactions were considered complete. After the cross-linked periodate oxystarch was separated by filtration, it was washed once with water.

Final oxidation with chlorous acid (*3*) was accomplished as follows: The wet, cross-linked periodate oxystarch in 186 ml. of water was mechanically stirred (in a well-ventilated fume hood) and 54 ml. of an aqueous solution containing 22.23 grams of sodium chlorite were added, followed by addition of 7.1 ml. of glacial acetic acid. After 3 hours, reaction time at room temperature the product was isolated by filtration, washed twice with water, and suspended in 20% methanol. An aqueous solution of 0.5*N* sodium hydroxide was added to neutralize the carboxyl groups at a pH of approximately 9. Following an additional wash with 20% methanol, the product was filtered and air-dried for 24 hours. Although 20% methanol washes prevent swelling of the less resistant granules in the product, for oxidations below the 4% level only water is required for washing.

Throughout a number of experiments the products were filtered and washed with 80% ethanol, to prevent possible losses of any carboxyl-rich water-soluble fragments. Essentially neutralized products were obtained. When similar products isolated with and without alcohol are compared, only slight differences in pasting behavior are observed. Nonalcoholic products give somewhat higher and more stable viscosities.

Pasting Curves. The Corn Industries Research Foundation (C.I.R.F.) viscometer was used to obtain a continuous pasting history of the various dicarboxyl starches evaluated. The value of this viscometer lies in its ability to compare pasting characteristics, so that differences observed can be interpreted in terms of the variables involved. Unless otherwise specified, the slurries of the various products at room

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temperature and at a concentration of 2.0 ± 0.1% in distilled water were added to the viscometer with the stirrer speed set at 24 r.p.m. and that of the propeller at 60 r.p.m. The water jacket surrounding the sample was kept at a temperature of 92.0° C.

Reproducibility of pasting curves of a given sample based on values of maximum viscosity was found to be 2.26% (coefficient of variation). Of the various chemical reactions involved in the preparation of cross-linked dicarboxyl starches, cross linking is by far the most critical step in terms of reproducibility.

Cross-Linking Reaction. The reaction rate of epichlorohydrin with starch, under the conditions described earlier was studied (Figure 1). Over the range of 300 to 2500 AGU per cross link, it has consistently been found that approximately 80% of the epichlorohydrin added reacted after 18 hours. Degrees of cross linking are expressed here in terms of epichlorohydrin reacted, rather than of the amounts of epichlorohydrin originally added.

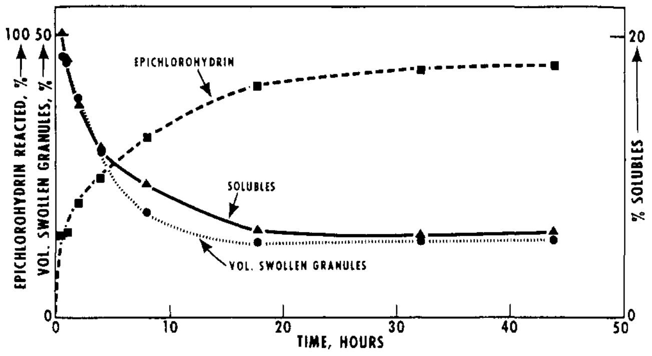

Figure 1. Rate of reaction of starch with sufficient epichlorohydrin to obtain 600 AGU per cross link, and changes in solubility and water-holding capacity of cross-linked starch closely parallel one another

Also in Figure 1 are shown the progressive changes in two physical properties of the cross-linked starch which parallel the cross-linking reaction rate. The volume of the swollen granules was determined by pasting a 2% slurry of the sample in a graduated, conical centrifuge tube in a boiling water bath for 30 minutes, cooling, centrifuging for 10 minutes (gravitation factor of 1500), and calculating the percentage of the total volume occupied by the swollen granules. The supernatant solutions were analyzed by anthrone analysis to determine the percentage of dicarboxyl starch solubilized (% solubles). Good agreement was obtained in determinations in which both anthrone and evaporation to dryness with direct weighing were used.

Small changes in cross linking produced relatively large changes in the physical properties of the pasted dicarboxyl starches (Figure 2). Curve 7 in Figure 2 corresponds to the 32-hour sample in Figure 1. After 45 hours of reaction the product was too highly cross linked to provide a measurable viscosity.

To prevent possible evaporation losses closed systems were preferred for cross-linking reactions. At 25° C. in an open system, 18 hours of reaction produced less than one half of the theoretical cross linking and left only a trace of unreacted epichlorohydrin. Incompleteness of the reaction was deduced from the pasting behavior of the isolated product.

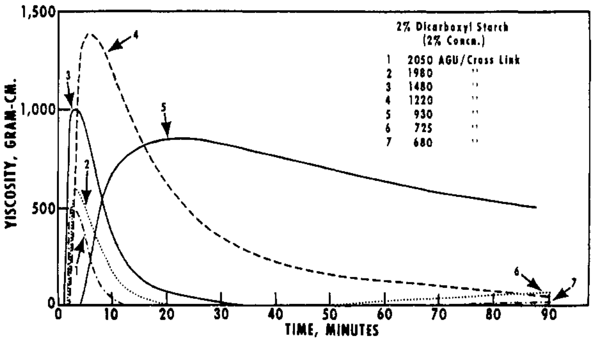

Figure 2. Progressive changes in degree of cross linking at various times of reaction produce relatively large changes in C.I.R.F. viscometer curves of 2% dicarboxyl derivatives

PRODUCTS AND PROPERTIES

The products had oxidation levels and extents of cross linking ranging, respectively, from 0.5 to 5.7% and from 300 to 2500 AGU per cross link. In appearance, the dried substances resembled ordinary cornstarch and microscopic examination revealed the presence of the usual granule form. Starches of 5% dicarboxyl content after equilibration at 21° C. and 65% relative humidity, had a moisture content of 15 to 16%. Aqueous 2% suspensions in distilled water had pH values of 8.4 to 9.0; however, the pH values dropped to the range 6 to 7 on pasting. The neutralized (sodium salts) dicarboxyl starches with moisture contents up to 15% showed little change in viscosity characteristics after 1.5 years.

Pasting behavior of cross-linked dicarboxyl starches was diverse. For a given level of oxidation there exists a range of cross linking within which pasting characteristics vary from readily dispersible with initially high, unstable viscosity to very slow swelling with greatly improved viscosity stability. Figure 3 shows the relationship (at 2% concentration) of the swelling time (time in minutes in the C.I.R.F. viscometer when a measurable viscosity was first observed) to cross linking and oxidation level. Figures 4 and 5 show the series of pasting curves obtained at 92° C. for oxidation levels of 1 and 4%, respectively, as the degree of cross linking was varied.

Factors Influencing Pasting Properties. CONCENTRATION. Concentration-viscosity relationships were examined both in the pasting process at 92° C. and at room temperature as "cold pastes." To cover a wide range of concentrations within the viscosity limits of the viscometer, starches of 0.5 and 1.0% dicarboxyl content were used (Figure 6). Viscosity values were obtained from the pasting curve maxima at approximately 92° C. For a given level of oxidation, the slopes of the curves are not appreciably affected by a change in cross linking, but are displaced. The expected displacement is toward a lower maximum viscosity with an increasing amount of cross linking. As the level of oxidation increases, regardless of cross linking, proportionally greater

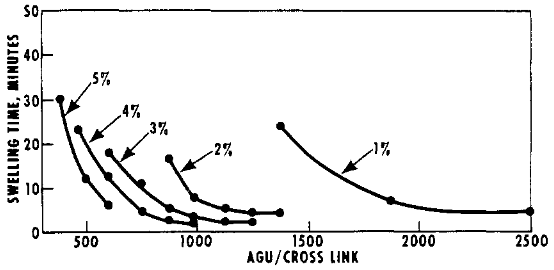

Figure 3. Relationship of degree of cross linking, level of oxidation, and swelling time shown here allows selection of a number of combinations of cross linking and oxidation to obtain a given degree of dispersibility

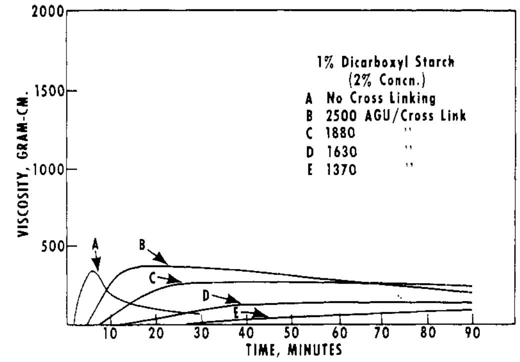

Figure 4. Variation of pasting behavior of 1% dicarboxyl starches for several levels of cross linking

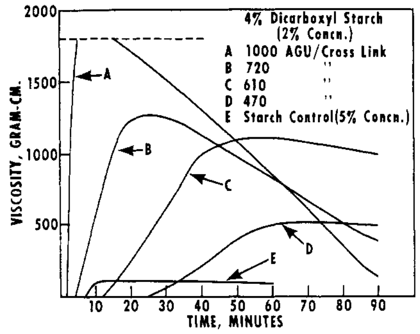

Figure 5. Variation of pasting behavior of 4% dicarboxyl starches for several levels of cross linking

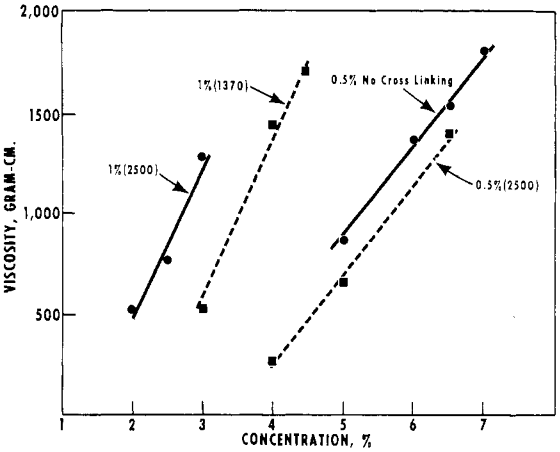

Figure 6. Relationship of concentration to maximum viscosity obtained in the C.I.R.F. viscometer at 92° C. for several combinations of variables

changes in viscosity are produced by similar variations in concentration. Extrapolation of the curves to the abscissa gives the approximate minimum value of the concentration at which a measurable viscosity can be obtained. At higher concentrations, less time is required to produce a measurable viscosity and the rate of viscosity rise to maximum is much greater.

The viscosity of a cold paste is dependent upon its pasting history, so that duplication of a given cold paste viscosity would require standardization of the pasting time, rate and extent of heating, and stirring conditions. To evaluate the viscosity-concentration relationships for cold pastes, three cross-linked dicarboxyl starches having 1, 3, and 5% oxidation levels were pasted at 5% concentration. The pasting process was continued for only a short time beyond initial gelatinization. They were then cooled to 25° C., and the Brookfield viscosities (spindle speed of 20 r.p.m.) were observed. Figure 7 gives the plots of the viscosities of the three products *vs.* concentration. Because of the short duration of the pasting process these viscosities are, no doubt, close to the maximum obtainable.

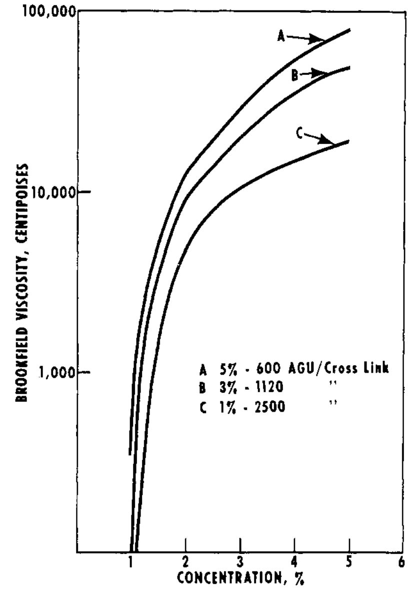

Figure 7. Variation of the cold paste viscosity (25° C.) with paste concentration is similar to that found for many natural and synthetic gums

TEMPERATURE. When the cross-linked dicarboxyl starches are pasted in the C.I.R.F. viscometer at 92° C. and below, changes occur in pasting characteristics, particularly in viscosity stability and rate of swelling. Results of pasting a cross-linked, 5% dicarboxyl starch at five different temperatures are illustrated in Figure 8. As the temperature decreases, the maximum paste viscosity remains nearly the same, and the stability becomes excellent. Similar trends were obtained with a cross-linked 1% dicarboxyl starch.

pH. Dicarboxyl starches slurried in distilled water at 2% concentration have pH values in the range 8.4 to 9.0. The cooled pastes have pH values from 6 to 7. Changes in

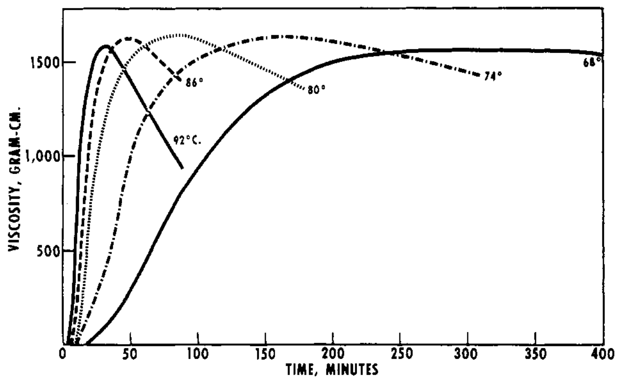

Figure 8. C.I.R.F. viscometer pasting curves at various bath temperatures of a cross-linked 5% dicarboxyl starch at 2% concentration which shows the trend toward more stable viscosity and slower rates of swelling at lower temperatures

pasting behavior over a broad range of pH values were determined.

Figure 9 shows the various pasting curves obtained with a cross-linked, 5.5% dicarboxyl starch (600 AGU per cross link) in which the paste pH values ranged from 4.0 to 10.6. The adjustments in pH were made by addition of acid or alkali to the slurries prior to pasting.

Low pH values result in formation of carboxylic acid from the carboxylate. The hydrophylic nature of the granule is thus reduced and longer times of heating are required to initiate gelatinization. The inherent stability to scission of the dicarboxylated starch chain is also reduced at a low pH and this fact, together with the hydrolytic nature of the acidic medium, results in ultimate fragmentation of the granule.

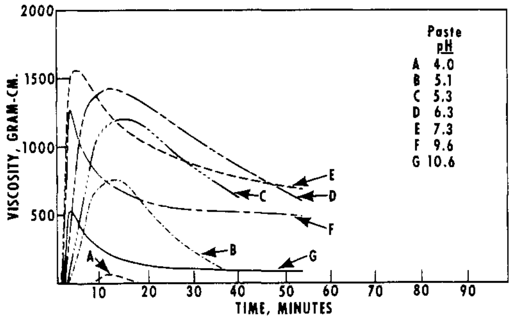

Figure 9. Effects of pH on C.I.R.F. viscometer pasting curves of a cross-linked 5.5% dicarboxyl starch are considerable over the paste pH range 4 to 10.6

Pasting in the presence of an increasing concentration of alkali results in a progressive decline of the maximum viscosity. However, there is a coincident trend shown towards greater stability. Part of the drop from maximum viscosity found in the more highly alkaline pasting curves (Figure 9) is a result of temperature because the sample had not yet reached 92° C.

A cross-linked 1% dicarboxyl starch exhibited similar trends in its pasting behavior over the same range of pH. However, the fall-off from maximum viscosity of this more starchlike material was decidedly less as the alkalinity increased. When measured at various pH levels cold paste viscosities show similar changes. The viscosity was relatively stable for a cross-linked 5% dicarboxyl starch over the range 6 to 9, being a maximum at pH 6.5.

Additives. The solution viscosities of starches containing ionizable groups are greatly reduced in the presence of electrolytes, as is generally found with high polymers of this nature. Pastes consisting of swollen granules of dicarboxyl starch are no exception. Regardless of whether the salt is added prior to, during, or after cooking to slurries or pastes of the dicarboxyl starches, large viscosity decreases result. The viscosity loss is reversible upon removal of the salts, indicating that granule damage does not occur. The effects produced are dependent both upon the relative number and kind of electrolytes involved. As expected, di- and trivalent ions (both positive and negative) exert greater effects than monovalent ions.

Figure 10 illustrates the pasting behavior of a cross-linked 5.7% dicarboxyl starch in the presence of various salts in low concentrations. Aside from over-all reduction of viscosity, other effects produced by electrolytes are: increased gelatinization time, slower rate of viscosity rise, and greater stability. A cross-linked 1% dicarboxyl starch behaved similarly. From 60 to 70% viscosity loss resulted when cold pastes were treated with as little as 0.1 mole of salt per mole of ionizable groups of the dicarboxyl starch. Other additives which influenced pasting behavior included sucrose, stearic acid, and casein. Sucrose increased both the viscosity and clarity of the pastes when present in 5 to 20% concentration on the basis of solution weight. The viscosity increase at the 20% level amounted to approximately 13%, and clarity was remarkably improved. Stearic acid (0.029% of solution weight) caused a slight decline in viscosity, as did the addition of casein (0.02%).

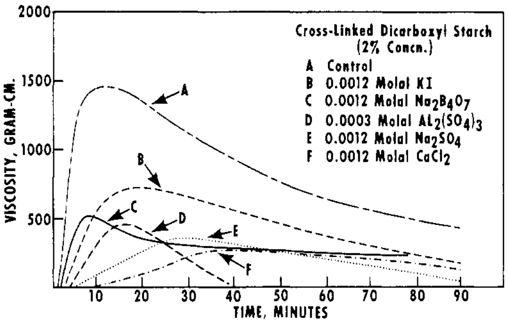

Figure 10. Pasting characteristics of cross-linked, dicarboxyl starches are extremely sensitive to small quantities of electrolytes

DISCUSSION

Aside from their potential usefulness, the dicarboxyl starches present an interesting study of the interplay of two opposing forces within the starch granule. Through the proper balancing of these forces, it has been possible to obtain a modified granule having a combined water-holding capacity and stability far exceeding that found in the parent starch granule or in dicarboxyl starches having no cross linking. The introduction of carboxylate groups even in very slight amounts results in a marked increase in the water-swelling ability of the granule. However, this enhanced affinity for water favors granule disruption, as less external energy is now required to overcome the cohesive forces within the granule. The forces of mutual repulsion in addition to the hydration effects hasten granule dissolution. Conversely, cross linking, most of which may occur on or near the granule surface, reinforces the granule and allows only limited hydration and swelling to occur.

The extremes of pasting properties of the cross-linked dicarboxyl starches are functions of both the variables of modification and of pasting. In view of the large number of possible combinations, an attempt has been made to present only general relationships and to define, where possible, the limits of variation associated with the individual variables. As a result it is believed that viscosity requirements for many specific or general applications can be anticipated in suitably modified products.

ACKNOWLEDGMENT

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