Crosslinking of Starch by Alkaline Roasting

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Synopsis

Dry mixtures of starch with various bases were roasted in air. The effects of roasting were determined by a viscosity method. The results suggest that roasting at alkaline pH's produces covalent crosslinks. The author speculates that the crosslinks result from a combination of autoxidation and aldolization.

Introduction

Preliminary experiments performed by me suggest a surprising conclusion: heating dry starch in air—at an alkaline pH—produces covalent crosslinks. After presenting the evidence, I shall speculate on the nature of the postulated crosslinks and the mechanism of their formation.

Much work has been done on the aerobic alkaline heating of *wet* polysaccharides;[1,2] little on *dry* polysaccharides. I hope this publication will stimulate others to investigate this subject more thoroughly.

Roasting and pyrolysis of starch should not be confused. My roasting experiments were conducted below the temperature (about 220°C) at which starch begins to pyrolyze.

Commercial dextrinization employs acidic rather than alkaline roasting. Even when commercial dextrinization involves the addition of bases like trisodium phosphate—as in the case of certain British gums—roasting occurs entirely at acidic pH's: the amount of base does not suffice to raise the acidic pH of commercial starch to an alkaline level.   In my experiments I added enough base to accomplish this.

Procedure

The procedure involved heating a dry mixture of starch and base in a thin layer at 140–160°C., then determining the effects of roasting by a viscosity method.

The following directions for a typical pair of products illustrate the procedure. Mix 1000 g. of commercial corn starch (pH 4.9) for about $^1/_2$ hr. with 1500 ml. of a solution (the *impregnating solution*) containing 0.3% sodium bicarbonate. (Determine all pH's on a 6% aqueous suspension.) Using a water aspirator, filter through a Büchner funnel. After breaking the filter cake into small pieces, dry it overnight in a forced-air oven at 50°C.

Determine its moisture content by heating a sample 4 hr. in a convection oven at 130°C.; calculate the moisture content from the loss in weight (found, 7.0%). Also measure the pH (*initial pH*) of the material (found, 9.9). Grind the material to a fine powder in a Raymond Hammer Mill. Place the powder (spread in layers about $3/16$ in. thick) in a forced-air oven at room temperature. Raise the temperature of the oven as quickly as possible (about 1 hr.) to 140°C. and keep it at this temperature (*roasting temperature*). When the oven first reaches 140°C., determine the moisture content of the material (found, 0%). Six hours after the oven reaches 140°C., remove a portion of the material (Product I6, Table I); determine its pH (*final pH;* found, 8.0). Two hours later remove the rest of the material (Product I8); determine its pH (found, 7.7). Measure the viscosity of the products by means of a C.W. Brabender Visco-Amylo-Graph:[3] prepare an aqueous suspension of a portion of I6; adjust the pH with acetic acid to 3.0; by adding water, adjust the concentration of I6 to 6% (dry basis); place the suspension in the Visco-Amylo-Graph; start the automatic mixing (at the constant rate of 75 rpm) and maintain continuous mixing; raise the temperature from 25 to 95°C. at a rate of 1.5°/min.; (47 min. is required to reach 95°C.); hold the temperature at 95°C. for 60 min.; the instrument continuously graphs viscosity against time; measure the viscosity of I8 similarly.

TABLE I
Description of Products

Product	Impregnating solution	Initial pH	Final pH	Roasting time, hr.[a]
I6	0.3% $NaHCO_3$	9.9	8.0	6
I8	0.3% $NaHCO_3$	9.9	7.7	8
A[b]	None	—	—	0
B[c]	None	—	—	0
Corn starch	None	—	—	0

[a] At 140°C.

[b] Corn starch crosslinked by reaction with 0.3 wt.-% epichlorohydrin.

[c] Same as A but with 0.4 wt.-% epichlorohydrin.

Results and Conclusions

Figure 1 shows the change in viscosity with time during the viscosity measurement; it shows curves for untreated (commercial) corn starch; two roasted products, I6 and I8; and two chemically crosslinked products, A and B. A and B (Table I) were prepared by covalently crosslinking corn starch with epichlorohydrin; the reaction was conducted in aqueous suspension according to a conventional method.[4]

By comparison with corn starch we see that the covalent crosslinks in A retarded both the rise and fall in viscosity. An increase in the crosslink density, as in B, retarded the rise further; also it prevented any drop within the observation period. Curves A and B exemplify the general effect of
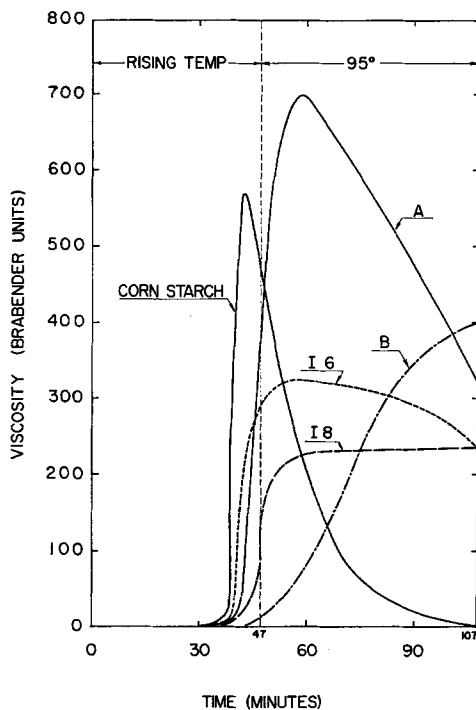
TIME (MINUTES)

Fig. 1. Change in viscosity with time during the viscosity measurement. Dispersions contained 6% starch and had a pH of 3.0. For a description of products see Table I.

covalently crosslinking starch; other crosslinking agents (e.g., phosphorus oxychloride and cyanuric chloride) afford similar curves.

Product I6 (Fig. 1) resembles A in its retarded rise and fall; I8 resembles B in its retarded rise with no fall. (The slight degradation of I6 and I8 during roasting probably explains why they have lower maximums than A and B.) These experiments (and an unreported series of similar ones) suggest that alkaline roasting produces covalent crosslinks.

Could these crosslinks be only *secondary* bonds—for example, hydrogen bonds? An increase in secondary bonds probably could not explain the results. Probably too few secondary bonds would survive the conditions of the viscosity measurement to affect the results: though at pH's close to neutrality corn starch still has a high viscosity at the end of the measurement,[5] at pH 3.0 (Fig. 1) it has no viscosity that the Visco-Amylo-Graph can detect; yet bulk corn starch has a high density of hydrogen bonds. Apparently at this pH even the strongest of secondary bonds—hydrogen bonds—cannot survive. Actually, evidence[6] suggests that roasting dry starch *decreases* secondary bonding (unlike the case of moist starch[7]). Tentatively I conclude that these crosslinks are indeed covalent.

From my other (unreported) experiments I tentatively conclude further: (1) *All* bases catalyze the covalent crosslinking: trisodium phosphate, disodium phosphate, and sodium carbonate also apparently produced

crosslinking. (*2*) The rate of crosslinking decreases with pH: it apparently decreased as initial pH decreased from 10.5 (the highest tried) until at 7 it became practically zero and remained so at acidic pH's. (*3*) Crosslink density increases with duration of roasting: for example, I8 appeared more crosslinked than I6. (*4*) Alkaline roasting crosslinks any type of starch: potato and waxy maize starch also appeared to crosslink. (*5*) The rate of crosslinking increases with temperature: 160°C. showed a rate apparently about eight times that of 140°C. (*6*) Crosslinking involves oxidation: the addition of antioxidants (e.g., sodium sulfite) apparently retarded crosslinking.

Discussion

How might alkaline roasting produce the postulated covalent crosslinks? Perhaps a combination of oxidation and aldolization produces them (Fig. 2): oxidation by air probably produces many interior carbonyl groups; some of these probably aldolize intermolecularly; these aldol links would crosslink the starch.
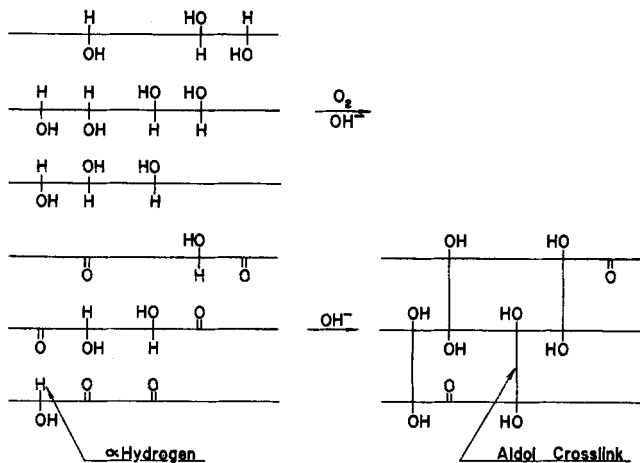

Fig. 2. Crosslinking by alkaline roasting: postulated mechanism. Autoxidation followed by aldolization produces a three-dimensional network. The scheme shows portions of three starch molecules; it omits some hydroxyls.

Several things support this explanation: (*1*) air readily oxidizes polysaccharides under alkaline conditions, producing interior carbonyls;[2,8-10] (*2*) apparently antioxidants retard crosslinking by alkaline roasting (as mentioned), bolstering the belief in autoxidation; (*3*) aldol condensation occurs readily in carbonyl-containing carbohydrates under alkaline conditions[11]; (*4*) aldol links withstand acid and heat—conditions of the viscosity measurement; (*5*) the increase in rate of crosslinking with pH (pre-

viously mentioned) probably reflects the fact that an increase in pH increases the rates of both autoxidation[8-10] and aldolization.[12]

Let us consider an alternative explanation.   Could the crosslinks be ester links incorporating the bases as integral parts?   This seems unlikely.   True, certain *esters* of carbonic acid (e.g., ethylene carbonate) can form carbonate crosslinks with starch;[13] these never were used.   But bicarbonate and carbonate *salts* probably cannot form ester crosslinks under the conditions of alkaline roasting; these did serve as bases.   Also certain *anhydrides* of *ortho*-phosphate salts (e.g., sodium metaphosphate) can form phosphate crosslinks with starch;[14] these never were used.   But *ortho*-phosphate *salts* (e.g., disodium phosphate) probably cannot form ester crosslinks under alkaline conditions;[15] these did serve as bases.   The crosslinks produced by alkaline roasting probably are aldol rather than ester links.
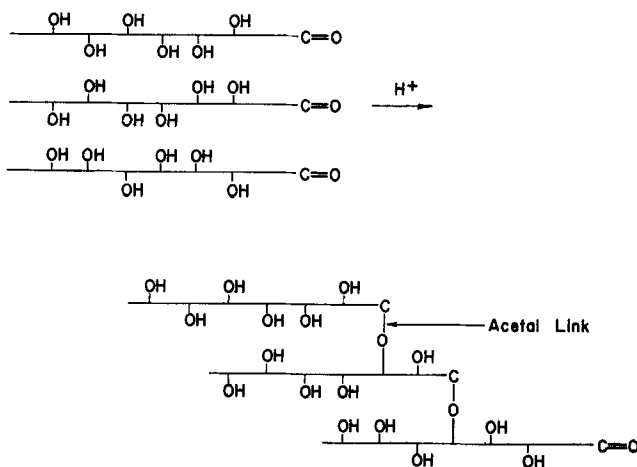

Fig. 3. Branching by acidic roasting: postulated mechanism.   Terminal carbonyls form acetal links.   The scheme shows portions of three starch molecules.

Previous reports[1,2] of aerobic alkaline heating of polysaccharides do not mention crosslinking.   Perhaps the presence of water in these experiments explains this: more degradation occurs in the presence of water; extensive degradation probably would obscure crosslinking.

Why does *acidic* roasting fail to produce covalent crosslinks?   Basically, the absence of oxidation probably causes the difference.   The work of others[8-10] suggests that bases—but not acids—catalyze autoxidation.   In the absence of oxidation each starch molecule (or fragment) after acidic roasting still has only one carbonyl (Fig. 3); this carbonyl (actually a hemiacetal hydroxyl) provides only a *single* site for attachment to another starch molecule (by acetalization); therefore such single carbonyls permit branching—as others[16-19] have shown—but not crosslinking into three-dimensional networks.

References

1. For a review see R. L. Whistler and J. N. BeMiller, *Advan. Carbohydrate Chem.*, **13**, 289 (1958).

2. For a review see J. N. BeMiller in *Starch: Chemistry and Technology*, R. L. Whistler and E. F. Paschall, Eds., Academic Press, New York, 1965, pp. 525–531.

3. R. J. Smith, in *Methods in Carbohydrate Chemistry*, R. L. Whistler, Ed., Academic Press, New York, 1964, Vol. 4, pp. 114–117.

4. M. Konigsberg (to National Starch Products, Inc.), U.S. Pat. 2,500,950 (1950).

5. F. E. Kite, E. C. Maywald, and T. J. Schoch, *Staerke*, **15**, 131 (1963).

6. J. R. Katz and A. Weidinger, *Z. Physik. Chem.*, **A184**, 100 (1939).

7. L. Sair and W. R. Fetzer, *Ind. Eng. Chem.*, **36**, 205 (1944).

8. D. Entwistle, E. H. Cole, and N. S. Wooding, *Textile Res. J.*, **19**, 527 (1949).

9. R. T. Bottle, G. A. Gilbert, C. T. Greenwood, and K. N. Saad, *Chem. Ind. (London)*, **1933**, 541.

10. R. I. C. Michie and S. M. Neale, *J. Polymer Sci. A*, **2**, 225 (1964).

11. J. C. Sowden, in *Carbohydrates*, W. Pigman, Ed., Academic Press, New York, 1957, pp. 113–114.

12. E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Henry Holt, New York, 1959, pp. 389–394.

13. J. W. Opie (to General Mills, Inc.), U.S. Pat. 2,767,171 (1956).

14. R. W. Kerr and F. C. Cleveland, Jr. (to Corn Products Co.), U.S. Pat. 2,884,413 (1959).

15. R. W. Kerr and F. C. Cleveland (to Corn Products Co.), U.S. Pat. 2,961,440 (1960).

16. J. D. Geerdes, B. A. Lewis, and F. Smith, *J. Am. Chem. Soc.*, **79**, 4209 (1957).

17. G. M. Christensen and F. Smith, *J. Am. Chem. Soc.*, **79**, 4492 (1957).

18. A. Thompson and M. L. Wolfrom, *J. Am. Chem. Soc.*, **80**, 6618 (1958).

19. M. L. Wolfrom, A. Thompson, and R. B. Ward, *Ind. Eng. Chem.*, **53**, 217 (1961).

Résumé

Les mélanges secs d'amidon avec diverses bases ont été chauffés à l'air. Les effets de ce chauffage ont été déterminés par la méthode viscosimétrique. Les résultats suggèrent que le chauffage à des pH alcalins produit des ponts covalents. L'auteur suggère que les ponts résulteraient de la combinaison de phénomènes d'autoxydation et d'aldolisation.

Zusammenfassung

Trockene Gemische von Stärke mit verschiedenen Basen wurden an Luft geröstet. Der Einfluss des Röstens wurde mittels einer Viskositätsmethode bestimmt. Die Ergebnisse zeigen, dass Röstung bei alkalischem pH covalente Vernetzungen erzeugt. Es wird vermutet, dass die Vernetzungen durch eine Kombination von Autoxydation und Aldolisierung zustande kommen.