

Modification of Wheat Starch by Initiating Systems Used for Graft Polymerization¹

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ABSTRACT

Treatment of wheat starch with ceric ammonium nitrate in dilute nitric acid or with ferrous ammonium sulfate-hydrogen peroxide, under conditions used for graft polymerization but in the absence of monomer, gave products only partially dispersible in 90:10 (by volume) dimethyl sulfoxide-water. With ceric ion-nitric acid, the amount and intrinsic viscosity of the dispersible fraction depended on both the degree of swelling of the starch (used with ceric ammonium nitrate solution) and on whether the acidic reaction mixture was neutralized before isolation of the product. Dilute nitric acid in the absence of ceric ammonium nitrate gave a completely dispersible product whose intrinsic viscosity slowly decreased with reaction time. Electron beam irradiation of wheat starch also gave a completely dispersible and apparently degraded product. In contrast to their behavior in dimethyl sulfoxide-water, starches treated with ceric ion-nitric acid or the ferrous ion-hydrogen peroxide system were more readily dispersed in water than untreated wheat starch.

Previous publications⁽¹⁾ have discussed starch graft polymerizations from the standpoint of variations in molecular weight and frequency of grafted branches with changes in reaction conditions. Changes in the properties of starch resulting from reactions caused by the various initiating systems have not been reported. Since the properties, and consequently the possible commercial utility, of a starch graft copolymer would be influenced by any chemical modification of the polysaccharide moiety which might accompany grafting, this aspect of the graft polymerization reaction was investigated.

MATERIALS AND METHODS

Materials

The starch used was unmodified wheat starch (Supergel) from Industrial Grain Products, Ltd., Montreal, Quebec.

¹Contribution from the Northern Regional Research Laboratory, Peoria, Ill. 61604. This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture. Mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture.

Initiator solution was prepared by dissolving 13.9 g. of ceric ammonium nitrate in 250 ml. of 1N nitric acid.

Ferrous ammonium sulfate hexahydrate and 30% hydrogen peroxide were Baker Analyzed Reagent Grade.

Reaction with Dilute Nitric Acid

A stirred slurry of 21.9 g. (dry basis) of starch in 500 ml. of water (0.135 mole anhydroglucose unit, AGU) was sparged with nitrogen for 1 hr. at 25° or 60°C. and the temperature adjusted to 25°C. Seven and one-half milliliters of 1N nitric acid was added and samples were removed from the stirred mixture (pH 1.9) after 1 and 3 hr. The pH of some samples was adjusted to 6.0 with sodium carbonate solution, and the products were isolated by filtration or centrifugation, washed, and air-dried.

Reaction with Ceric Ammonium Nitrate in Dilute Nitric Acid

Four starch slurries (two with 25°C. pretreatment and two with 60°C. pretreatment) were prepared in the same manner as described for nitric acid reactions. Initiator solution (7.5 ml.; 7.6×10^{-4} mole Ce^{+4}) was then added, the reaction mixtures (pH 1.9) were stirred for 3 hr. at 25°C., and 1.0 g. of hydroquinone was finally added to terminate the reaction. One reaction mixture derived from swollen starch and one from unswollen starch were neutralized to pH 6.0 with sodium carbonate solution and the products separated by filtration or centrifugation. Products were isolated from the other two slurries without pH adjustment. All four products were washed first with water and then with ethanol and finally air-dried.

In each of the four reactions, the recovery of starch was more than 98%. About 3.5 g. of each product was accurately weighed into a 1-liter volumetric flask and diluted nearly to the mark with a 90:10 (by volume) dimethyl sulfoxide (DMSO)-water solution. This mixture was stirred magnetically at room temperature for several days until the solid had disintegrated to a swollen gel. The flask was then diluted to the mark, the mixture centrifuged ($1,600 \times g$ for 35 min.), and the clear supernatant decanted. A portion of the supernatant was evaporated to near dryness and the solid precipitated with ethanol. From the weight of the washed and dried precipitate, the percent solid remaining in suspension after centrifugation (percent dispersible) was calculated. Sulfur analysis of one precipitated fraction showed little or no DMSO. Intrinsic viscosities (dl./g.) of the precipitated dispersible fractions were determined at 25°C. in 90:10 DMSO-water with Cannon-Fenske viscometers.

Reaction with Ferrous Ammonium Sulfate-Hydrogen Peroxide

The procedure was similar to that used with ceric ammonium nitrate-nitric acid. One gram of 30% hydrogen peroxide (8.8×10^{-3} mole) was added to the nitrogen-sparged starch slurries followed by 0.2 g. of ferrous ammonium sulfate hexahydrate (5.1×10^{-4} mole) dissolved in a minimum of water. The pH was 2.8. Reaction times were 3 hr.

Determination of Dispersibility in Water

A method developed by Rankin and co-workers (2) was used. A stirred 2% slurry of starch in water was adjusted to pH 7.0, heated for 30 min. at 92° to 100°C., cooled to room temperature, and centrifuged at $750 \times g$ for 15 min. A

TABLE I. DEGRADATION OF WHEAT STARCH (INTRINSIC VISCOSITY 1.73) BY DILUTE NITRIC ACID^a

Time at 25°C. hr.	Intrinsic Viscosity ^b	
	Unswollen	Swollen (60°C.)
1	1.53	1.64
3	1.41	1.49

^aReaction mixture: 21.9 g. (dry basis) starch, 500 ml. water, and 7.5 ml. 1N nitric acid; pH adjusted to 6.0 before isolation.

^bDI./g. determined at 25°C. in 90:10 (by volume) dimethyl sulfoxide-water.

portion of the supernatant was freeze-dried, and the percent solid remaining in suspension after centrifugation (percent dispersible) was then calculated from the weight of freeze-dried solid. As an estimate of solubility, the percent transmission of the supernatant was determined at 650 m μ .

RESULTS AND DISCUSSION

We have used ceric ammonium nitrate in dilute nitric acid to initiate graft polymerization of acrylonitrile onto starch (1). To determine how dilute nitric acid influences starch properties, aqueous slurries of wheat starch (either unswollen or swollen by heating the slurry to 60°C.) were stirred at 25°C. with an amount of nitric acid equal to that used in ceric-initiated graft polymerization. Portions of each reaction mixture (pH 1.9) were removed after 1 and 3 hr. and neutralized to pH 6.0; the intrinsic viscosities of the isolated starch samples were determined in 90:10 (by volume) DMSO-water. This solvent system was chosen since it completely dispersed both untreated and acid-treated starch and had less tendency than aqueous alkali to degrade partially oxidized starch samples, which might be encountered later. Intrinsic viscosities (Table I) decreased with increasing reaction time and were relatively independent of granule swelling.

When ceric ammonium nitrate in dilute nitric acid was reacted with swollen or unswollen starch (Table II), a significant percentage of the product could be removed from 90:10 DMSO-water as a highly swollen gel on centrifugation at 1,600 X g for about 35 min. Both the amount of the dispersible fraction and its intrinsic

TABLE II. PROPERTIES OF WHEAT STARCH TREATED WITH CERIC AMMONIUM NITRATE-NITRIC ACID^a

Starch	pH Adjusted to 6.0 ^b	Fraction Dispersible in 90:10 DMSO-Water	
		% of Total	Intrinsic Viscosity ^c
Unswollen	Yes	86	1.21
Swollen ^d	Yes	53	1.54
Unswollen	No	28	1.51
Swollen ^d	No	28	1.83

^aReaction mixture: 21.9 g. (dry basis) starch (intrinsic viscosity 1.73), 500 ml. water, 7.5 ml. initiator solution (13.9 g. ceric ammonium nitrate in 250 ml. of 1N nitric acid).

^bpH adjusted before isolation of product.

^cDetermined as in Table I.

^dSwollen by heating in water at 60°C.

TABLE III. PROPERTIES OF WHEAT STARCH TREATED WITH FERROUS AMMONIUM SULFATE-HYDROGEN PEROXIDE^a

Starch	pH Adjusted to 6.0 ^b	Fraction Dispersible in 90:10 DMSO-Water	
		% of Total	Intrinsic Viscosity ^c
Unswollen	Yes	21	0.55
Swollen ^d	Yes	17	0.77
Unswollen	No	22	0.62

^aReaction mixture: 21.9 g. (dry basis) starch (intrinsic viscosity 1.73), 500 ml. water, 1.0 g. hydrogen peroxide (30%), 0.2 g. ferrous ammonium sulfate hexahydrate.

^bInitial pH was 2.8. pH adjusted before isolation of product.

^cDetermined as in Table I.

^dSwollen by heating in water at 60°C.

viscosity were influenced by the degree of swelling of the starch granules and by whether the acidic reaction mixture was neutralized on completion of the reaction. When the pH was adjusted to 6.0 with sodium carbonate solution before the product was isolated, a larger percentage was dispersible in 90:10 DMSO-water and the intrinsic viscosity of the dispersible fraction was lower than observed when the product was isolated, washed, and dried without addition of base. Granule swelling influenced the amount of the dispersible fraction only when reaction mixtures were neutralized to pH 6.0; however, in both pairs of reactions, increased swelling led to higher intrinsic viscosities for dispersible fractions. To determine the influence of hydroquinone (added to terminate the reaction with ceric ion), the third reaction of Table II was repeated without hydroquinone addition. No large differences in the two products were observed (32% dispersible in 90:10 DMSO-water; $[\eta] = 1.53$).

Brockway (3,4) used ferrous ion and hydrogen peroxide to initiate graft polymerizations onto starch. We, therefore, investigated the reaction of this system with starch (Table III) and found that product properties did not depend on granule swelling and on neutralization before isolation as much as with ceric ammonium nitrate. In each reaction, about 80% of the product was removed from 90:10 DMSO-water by centrifugation and the solid was not so highly swollen as when the ceric reagent was used. The intrinsic viscosities of the dispersible fractions, however, were appreciably lower than those for dispersible fractions derived from ceric-treated starch.

Reyes and co-workers (5) used gamma or electron beam irradiation to initiate graft polymerizations onto starch. Irradiation reportedly degrades the polysaccharide into smaller fragments (6,7), and we have confirmed this degradation by examining intrinsic viscosities in 90:10 DMSO-water of irradiated starch samples kindly provided by Dr. Z. Reyes. A sample of wheat starch ($[\eta] = 1.42$), which was irradiated (electron beam) to a dose of 2 Mrad, was completely dispersible in DMSO-water and had an intrinsic viscosity of 0.61.

The less-than-total dispersibility of starch samples in 90:10 DMSO-water after treatment with ceric ammonium nitrate-nitric acid or ferrous ammonium sulfate-hydrogen peroxide suggested a cross-linking reaction with these two initiating systems, as did paste viscosities in 90:10 DMSO-water (curves, Fig. 1, obtained on a Brabender amylograph). The product from the reaction of unswollen

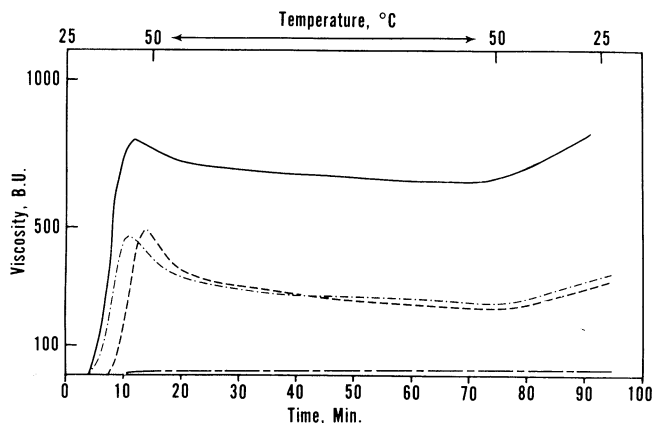


Fig. 1. Brabender amylograms in 90:10 dimethyl sulfoxide-water. Concentration, 4%; 700 cm./g. cartridge; 100 r.p.m.; dashed line, untreated wheat starch; solid line, unswollen wheat starch treated with ceric ammonium nitrate-nitric acid; -.-. unswollen wheat starch treated for 3 hr. with nitric acid; ---- unswollen wheat starch treated with ferrous ammonium sulfate-hydrogen peroxide. For the three treated starches, there was no pH adjustment before isolation of product.

wheat starch with dilute nitric acid gave a Brabender curve similar to that for untreated wheat starch. However, unswollen wheat starch treated with ceric ammonium nitrate-nitric acid (product isolated without neutralization) had a much higher Brabender viscosity than untreated starch and showed less viscosity loss with prolonged stirring at 50°C. Unswollen wheat starch treated with ferrous ammonium sulfate-hydrogen peroxide and isolated without neutralization remained as grainy particles and, therefore, showed only a low Brabender viscosity. Kite et al. (8) studied a series of cross-linked waxy sorghum starches in water and also found that Brabender viscosities first increased due to cross-linking and then, after a certain number of cross-links had been produced, decreased owing to restricted granule swelling.

The dispersibilities in water of the various starch samples, including irradiated starch, are shown in Table IV. Percent dispersibility refers to the percentage of the

TABLE IV. DISPERSIBILITY^a OF STARCH SAMPLES IN WATER

Treatment of Wheat Starch ^b	Dispersible in Water %	Transmission of Supernatant (650 m μ) %
Untreated	53	55
HNO ₃	52	75
Ce ⁺⁴ -HNO ₃	70	39
Fe ⁺² -H ₂ O ₂	99	25
Electron beam ^c	86	62

^a2% Aqueous slurry. Experimental procedure given in Materials and Methods.

^bUnswollen starch treated with HNO₃, Ce⁺⁴-HNO₃, or Fe⁺²-H₂O₂ for 3 hr. and isolated without neutralization.

^cIrradiated to a dose of 2 Mrad.

sample that remained suspended after heating a 2% aqueous slurry to near reflux, cooling it to room temperature, and centrifuging (see Materials and Methods). The chemically treated ($\text{Ce}^{+4}\text{-HNO}_3$ or $\text{Fe}^{+2}\text{-H}_2\text{O}_2$) starch samples that showed only limited dispersibility in 90:10 DMSO-water were more highly dispersed in water than untreated or nitric acid-treated wheat starch. In fact, the ferrous ion-hydrogen peroxide-treated starch, which was the least dispersible in DMSO-water, was also the most highly dispersed when treated with water alone. Brabender amylograms in water (90°C. max.) showed a lower paste viscosity for the ceric ammonium nitrate-nitric acid-treated material than for untreated or nitric acid-treated starch. The evidence suggests, therefore, that if cross-links are formed by reaction of starch with either ceric ion-nitric acid or ferrous ion-hydrogen peroxide, they are susceptible to cleavage when the products are heated in water.

The chemical nature of any cross-links would be difficult to establish with certainty because of the small amounts of reactants employed compared to starch (e.g., 5.56×10^{-3} mole Ce^{+4} /AGU). One possibility, however, is that hydroxyl groups are oxidized to carbonyl groups, possibly with some opening of the glucopyranose ring (9,10). As with dialdehyde starch (11), hemiacetal or acetal linkages could then form by reaction of carbonyl groups with hydroxyls on neighboring starch molecules. The acidic reaction conditions should favor hemiacetal and acetal formation, and it might be expected that such linkages would hydrolyze in hot water.

It is apparent from our data that different initiating systems used for graft polymerization will variously influence the physical properties of starch and that the properties of treated starch will also vary according to the solvent used to effect dispersion. Choice of initiator should, therefore, be carefully considered when one attempts to synthesize a graft copolymer that will have a particular set of properties in a given solvent system.

Acknowledgment

We are indebted to Z. Reyes, Stanford Research Institute, for samples of irradiated starch.

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[Received July 7, 1969. Accepted August 20, 1969]