

Note on the Reaction of Corn Starch with Chloromethylphosphonic Dichloride in Pyridine¹

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Chloromethylphosphonic dichloride has potential as a reagent for the introduction of phosphorus into starch, because of the presence of reactive chlorine atoms. Two of these are attached to the phosphorus atom and undergo reactions typical of an acid chloride, giving, with alcohols and amines, the corresponding esters and amides. A third chlorine atom attached to the methylene group is relatively inactive and undergoes replacement reactions only at elevated temperatures.

With such a reagent, starch may be slightly cross-linked to produce derivatives capable of forming viscous aqueous dispersions, or insoluble products in the case of high substitution.

Our first experiments were conducted by the pasting method usually used for preparing cellulose derivatives (1). When we tried to react unswollen corn starch with chloromethylphosphonic dichloride and urea, partially degraded products were obtained. However, the use of starch gelatinized in pyridine (2) to increase its reactivity was successful, and in this manner we were able to prepare several phosphorus derivatives.

MATERIALS AND METHODS

The starch employed was an ordinary dent corn starch, Pearl 3001, Globe Brand, supplied by Corn Products Co.

The chloromethylphosphonic dichloride was a product of Stauffer Chemical Co. and was used without further purification. Pyridine was dried with sodium hydroxide and distilled before use.

Esterification

The reactions were carried out in a 1-liter, three-necked flask (ground-glass joints) equipped with distilling condenser, mercury-sealed stirrer, and dropping funnel according to Mullen and Pacsu (2).

Fifty grams of starch was gelatinized by heating with 500 ml. of 2:3 water-pyridine azeotrope. Water was removed by azeotropic distillation with addition of dry pyridine to maintain the same solid-liquid ratio. The distilling condenser was then replaced by a reflux condenser and chloromethylphosphonic dichloride was added, in amounts seen below, to the anhydrous dispersed starch. The mixture was allowed to react for 1 hr. at reflux temperature.

The reaction mixture was filtered on a sintered-glass funnel, washed

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several times with alcohol-water, then with alcohol, and dried in a vacuum desiccator over calcium chloride.

Analytical Procedure

Determination of phosphorus content was performed by the Kjeldahl gravimetric method (3). Total chlorine was determined as chloride by mineralization with metallic sodium (4) and titration by the Volhard method.

Brabender Viscosity

Viscosity was determined in a single-velocity Brabender Viscograph (manufactured by Brabender, Duisburg).

The aqueous starch dispersions (3% dry-starch basis) were heated at a constant rate to 95°C., cooled to 35°C., and maintained at this temperature for 1 hr.

Anionic Character

The intensity of staining by methylene blue (C.I. 922) and safranin O (C.I. 841) evaluated under the microscope was used to determine the ionic charge of the derivatives (5).

RESULTS AND DISCUSSION

The products obtained by reacting nondefatted dent corn starch swollen in pyridine with various quantities of chloromethylphosphonic dichloride have quite different properties.

Reaction of starch with 0.5% by weight of chloromethylphosphonic dichloride yielded a product having 0.024% phosphorus. This corresponds to a degree of substitution (D.S.) of 0.0013 (D.S. in moles of phosphorus per moles of anhydroglucose unit). The product is slightly anionic, swells in cold water, disperses in hot water, and burns like natural starch. Reaction with 4% by weight of the acid chloride gave a starch phosphonate containing 1.0% phosphorus and 1.1% chlorine, corresponding to a D.S. of 0.06. This product is more anionic than the former one and disperses partially in cold water and completely in hot water, giving a very thick paste. It is more flame-resistant than starch.

When samples of the above starch derivatives were cooked in water at 95°C., in the proportion of 3 parts starch to 100 parts water, and the dispersions were compared with a corresponding dispersion prepared from an unreacted dent corn starch which had been gelatinized in dry pyridine, it was found that the starch derivatives produced more-viscous pastes than the unreacted starch. An aqueous dispersion of the product of intermediate degree of substitution (D.S. 0.06) was much more viscous than that produced with the lowest-D.S. starch product. After 10 days at room temperature the viscosities of these pastes remained practically unchanged.

As shown by the graph of the Brabender viscosities in Fig. 1, the paste of the product with a D.S. 0.06 (4% reaction with chloromethylphosphonic

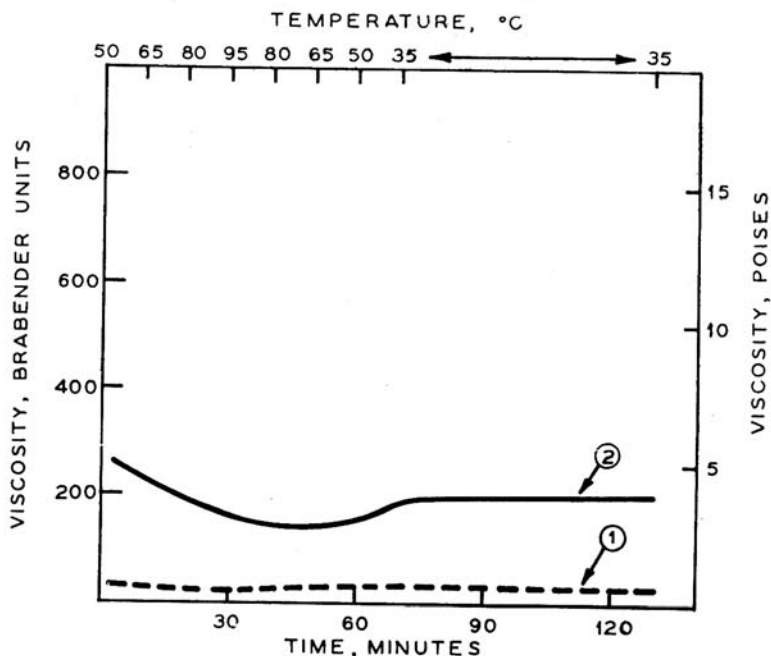


Fig. 1. Brabender viscosity of pregelatinized dent corn starch, 1, and of its reaction product with 4% chloromethylphosphonic dichloride, 2.

dichloride) shows a higher viscosity than the unreacted corn starch, and remains unchanged during the 1-hr. period at 35°C.

Cross-linking is indicated by the higher viscosity of the paste of the starch phosphonate. Absence of a gelatinization peak is due to the fact that pregelatinized starches were used.

The product obtained by reacting starch with 50% by weight of the phosphonic reagent contained 10% phosphorus and 9.3% chlorine, which corresponds to a D.S. of 0.75. It is very anionic, insoluble in cold and hot water, and nonflammable.

When this product was tested as a flame-proofing agent for rigid urethane foam it was found that the large proportions required to obtain flame resistance produced undesirable brittleness in the foam.

Analysis of the two more highly substituted derivatives shows an approximate ratio of 1:1 of phosphorus and chlorine. These results and the insoluble nature of the product of highest D.S. suggests progressive cross-linking of the anhydroglucose units of starch by the acid chlorides of chloromethylphosphonic dichloride. Apparently, the chlorine of the chloromethyl group did not react with starch under the conditions used.

Even without any data on the proportion of bound phosphorus involved in cross-bonding, the viscous paste obtained in the Brabender Visco-graph with the product of D.S. 0.06 strongly suggests that only a very minor portion of the bound phosphorus was engaged in cross-bonding of the starch.

Acknowledgment

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