

Investigation of Reactions Occurring at Starch Phosphorylation

Monika Meiczinger,* Judit Dencs, Gyula Marton, and Bela Dencs

University of Veszprem, POB 158, H-8201 Veszprem, Hungary

Environmentally friendly, biodegradable biopolymers can be prepared via the chemical modification of starch. These biopolymers are able to partially or totally substitute synthetic additives used today in the chemical or environmental technologies. Through the building of ionic function groups into polymeric chains of the starch ion exchangers, flocculants or dispersants can be produced. In this paper, we examine water-soluble ionic derivatives called polyelectrolytes. By phosphorylating starch while preserving or maybe increasing the molecular weight of the native starch polymers, anionic flocculating agents can be prepared. If the polymer chains degrade during the reaction, the products will act as dispersing agents in aqueous suspensions. It is apparent that, during the phosphorylation reaction, the changes in the molecular weight distribution and the ionic charge of the polymers have crucial importance. In our experiments, we investigated the solid-phase reactions by following the change in the molecular weight distributions, using size exclusion chromatography, and the change in the charge densities, using a particle charge detector. The efficiency of the products was tested in the laboratory, and the results were evaluated by means of severity parameters.

1. Introduction

Currently, many additives are utilized in chemical and environmental technologies (e.g., water clarification, wastewater treatment, water supply, and cooling and heating systems) to influence the behavior of the suspended particles in the water. These materials are usually synthetic polymers; they are very effective, but they may be harmful to the environment and human health.

Our raw material, starch, is a natural polymer, and, using its "skeleton", environmentally friendly, biodegradable biopolymers can be prepared, which are able to partially or totally substitute synthetic additives recently used in many technologies. The nontoxic character of the starch derivatives is of great importance in water treatment.

Depending on the conditions of modification reactions, these products have different features and different potential application areas. In this paper, we examine water-soluble, ionic derivatives: polyelectrolytes. By building ionic function groups into the starch polymers, water-soluble ionic polymers can be produced, which can act as flocculating or dispersing agents, according to their molecular weight, ionic character, and charge density.

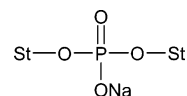
Starch in its original form is not water-soluble and has no functional groups with charges. It is a mixture of two polymers (amylose and amylopectin), and the molecular weight of the polymers ranges from 50 000 to hundreds of millions. Starch can be converted to polyelectrolytes by substituting some of the OH⁻ groups in the anhydroglucose monomer units with ionic functional groups. As a result of the substitution, the water solubility of the starch derivatives increases. Depending on whether we build anionic or cationic functional groups into the starch chain, we will obtain anionic or cationic polyelectrolytes. The starch derivatives pro-

duced through the use of proper reagents are nontoxic and, indeed, biodegradable.

At the Department of Chemical Engineering Science of the University of Veszprem, a research group has developed some starch-based anionic additives and a technology for producing these starch derivatives using a dry solid-phase modification process. The modification reaction is phosphorylation, and the products are starch phosphates:



The chemical reaction is performed in the solid phase. Besides the starch, all other components are water-soluble; therefore, their aqueous solution was added to the starch before the reaction. The impregnation is followed by drying and heat treatment. The phosphorylation proceeds at a reasonable rate at 140–150 °C; therefore, during the chemical modification, the phosphate substitution, as well as the degradation and polymerization, of polymer molecules occur. During the phosphorylation at alkaline pH, distarch phosphates are produced via the binding of ester molecules. In this way, the molecular weight becomes higher.



1.1. Flocculating Agents. Flocculants are water-soluble polymers that are characterized by very high molecular weight and ionic charge. The particles in aqueous suspension can be agglomerated by various mechanisms. Flocculants neutralize the identical charges of repelling particles and, hence, stop repulsion. Another mechanism is bridge forming, where the big polymer molecule binds particles to itself, using its functional groups. Cationic flocculants are suitable for the neu-

* To whom correspondence should be addressed. Phone/fax: +36 88 422022/4931. E-mail: moni@meiczinger.hu.

tralization of particles with a negative charge, whereas anionic flocculants are suitable for those with a positive charge.

To prepare starch-based flocculants, we must achieve the highest molecular weight possible during the conversion and make a water-soluble product. Under these obviously conflicting requirements, the optimal reaction parameters must be determined by parallel investigation of the chemical reactions and flocculation properties.

If the chemicals used at the conversion are acceptable, in regard to food quality requirements, the product is nontoxic (similar to some pudding powders) and biodegradable as starch. Given this information, the main application areas are drinking water treatment, the food industry, and biotechnology.

1.2. Scale Inhibitors. Control of scale formation on heat-transfer surfaces is one of the main problems in technologies that use water as a heating or cooling medium. Forming scale on the surfaces impedes the rate of the heat transfer; in addition, the scale deposits increase the danger of the corrosion. The main scale-forming constituents are calcium, magnesium, and iron salts, oxides, and hydroxides. Recently, phosphates, polyphosphonates, and complexing agents have been used to inhibit or prevent scale formation, but they can hydrolyze and their consumption is relatively high.

The antiscalants act via three different mechanisms: (i) prevention of the formation of crystal seeds by complexing the cations; (ii) dispersion of the colloid-sized particles; and (iii) inhibition of the scale formation, because of coprecipitation with the salts.

Starch can be converted to antiscalants via phosphorylation: the starch phosphate scale inhibitors are water-soluble derivatives with rather low molecular weight. To prepare scale inhibitors from starch via the phosphorylation reaction, we must build phosphate groups into the starch polymers and, at the same time, degrade them to the required degree. The degree of the polymerization (DP) of the products can be influenced by changing the strength of the reaction parameters: the concentration of the reagents, as well as the pH, temperature, and duration of the heat treatment.

2. Experimental Section

In the laboratory experiments, native starch samples were impregnated with an aqueous solution of the reagents in grinders, and the drying and phosphorylation was performed at different temperatures (130–160 °C) in heating blocks. The duration of the heat treatments was in the range of 30–240 min.

2.1. Materials. The raw material Meritena 300 corn waxy starch was supplied by Hungrana (Hungary); all of the other ingredients used at the phosphorylation in laboratory scale were of analytical grade. The chemicals used in the analysis were purchased from Merck AG and were of analytical reagent grade.

2.2. Methods. 2.2.1. Determination of Molecular Weight Distribution. The starch phosphate samples were dissolved in distilled water at 95 °C for 24 h. The molecular weight distribution was measured by high-performance size exclusion chromatography/multiple-angle laser light scattering/refractive index (HPSEC/MALLS/RI) analysis: this process involved a high-performance liquid chromatography (HPLC) system (LaChrom, Merck–Hitachi) that consisted of 2×30 cm \times 7.8 mm \times 8 μ m PLaquegel-OH mixed columns

(Polymer Laboratories), 5 μ L of a 1 mg/mL sample injected, 1 mL/min of a pH 11 buffer eluent, a 30 °C thermostat, and RI detectors and MALLS detectors (model PD 2020, Precision Detectors). The parameters of the molecular weight distribution were determined using Discovery 32 software.

The molecular weight distribution of the polymers was characterized by the following parameters: the weight-average molecular weight (M_w), which is very sensitive to the fractions of high molecular weight; the number-average molecular weight (M_n), which is sensitive to low molecular weight; and the so-called polydispersity ($D = M_w/M_n$).

2.2.2. Determination of Charge Density. The charge density of the polyelectrolytes was measured by conducting polyelectrolyte titrations, using a particle charge detector and an automatic titrator (model Müték PCD 02, Müték Analytic GmbH). The titrations were made with poly-DADMAC cationic polyelectrolyte.

2.2.3. Flocculation Characteristics. The flocculation properties of the derivatives were measured by a quick test that was developed at our department. Ten milliliters of a kaolin suspension (concentration of 5 g/L) was placed into test tubes; 0.1–0.5 mL of flocculant solution (concentration of 1 g/L) then was added, and the mixture was thoroughly mixed. A few seconds after the mixing stopped, flocs appeared and settled into the lower portion of the tubes. Their settling time was measured.

2.2.4. Scale Inhibition Characteristics. The antiscalant efficiency of the products was evaluated by conductivity titration (model MPC227, Mettler Toledo). The supersaturation level of CaCO₃ in the water was determined in the presence of a specified amount of scale inhibitor and also without it.¹ The relative degree of the supersaturation (S_r) can be calculated from these data.

3. Results and Discussion

Tailor-made starch-based flocculants and antiscalants can be produced by phosphorylation of starch in the solid phase. The conditions of the reactions are dependent on the quality of the products to be prepared. The most important properties of these products that determine their efficiencies in the aimed applications are the molecular weight distribution and charge density.

Our earlier results demonstrated that, during the solid-phase phosphorylation, at least two reactions occur: phosphate groups are built into the starch polymers and the polymers degrade. The former reaction was investigated in detail.^{2,3} The building-in of phosphorus can be described using first-order kinetics; the kinetic parameters determined can be used to calculate the conversion in a pilot-scale batch-type reactor. The final point of the heat treatment, which is of great importance, with respect to the product quality, can be calculated fairly well.⁴

During the improvement of the product's quality, the introduction of a polymerization reaction into the reaction system was suggested to compensate for the undesirable degradation. Monitoring the influence of the complex heterogeneous reaction system on the efficiency became increasingly difficult. Therefore, we try to apply, as a reaction ordinate, the severity parameter adopted in the literature for describing such complex systems. In this way, we can compare reactions that produce flocculants and antiscalants.

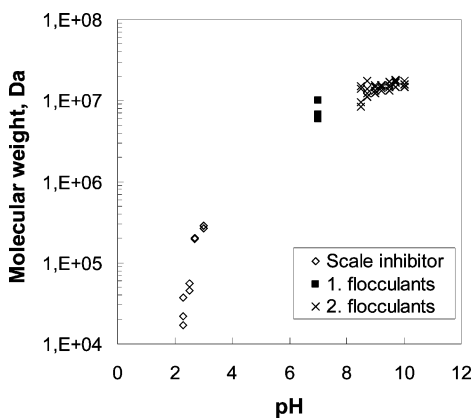


Figure 1. Effect of pH on the molecular weight (M_w) of starch derivatives.

The severity factors combine the effect of the different operational variables into a single parameter. Overend and Chornet⁵ used the reaction ordinate R_o to map the destructuring, diaggregation, and depolymerization of lignocellulosics:

$$R_o = \exp\left(\frac{T - 100}{14.75}\right)t$$

where T is the temperature (in units of °C) and t is the reaction time (in minutes). Chum et al.⁶ used this expression in their studies, together with an extended severity parameter R' for acid-catalyzed organosolv delignification ($R' = R_o[H^+]$), because the role of the acidity should be taken into consideration in the severity parameter.

We used a similar extended severity parameter R' for investigations of the dry-phase phosphorylation of starch. It is known, and our results also verified, that the most important property of these starch derivatives—molecular weight distribution—is determined by the pH of the chemical modification. In Figure 1, the molecular weights of all products can be found in three groups, according to the pH; the influences of other variables are limited. Therefore, only the parameters T , t , and C_P were included in the severity parameter investigations:

$$R_o = \exp\left(\frac{T - 100}{15}\right)t$$

$$R' = R_o C_P$$

where C_P represents the amount of phosphate added, relative to the amount of starch (given in units of g (PO_4) per g starch).

3.1. Flocculating Agents. The purpose of our experiments is to improve the quality of the flocculants produced at pH 7, as previously discussed (see data labeled “1. flocculants” in Figure 1), by increasing the molecular weights and charge density. It is known from the literature⁷ that, when phosphorylating the starch at an alkaline pH value, distarch phosphates are produced. We tried to involve the alkaline reaction into the modification to make flocculants of higher molecular weight. The newly developed flocculants are denoted as “2. flocculants” in Figure 1.

When phosphorylating the starch at higher pH, three parallel reactions occur: (a) a building-in of phosphate groups, (b) degradation, (c) polymerization. Therefore, all of the properties that determine the product quality

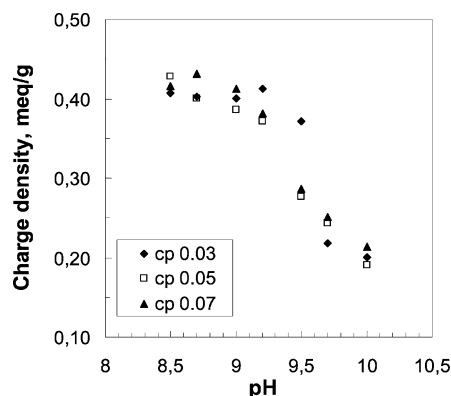


Figure 2. Effect of pH and the reagent/starch ratio (C_P) on the charge density of starch derivatives.

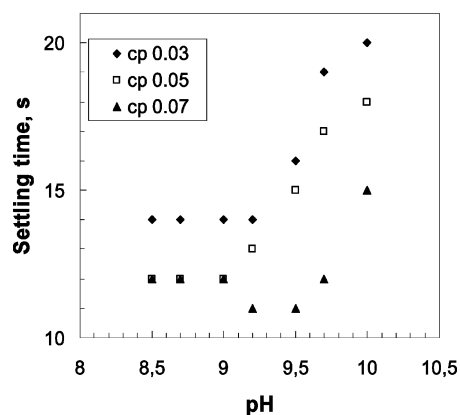


Figure 3. Effect of pH and the reagent/starch ratio (C_P) on the efficiency (settling time).

and the efficiency are changing, according to more difficult functions than without polymerization.

Based on the results of our preliminary experiments, the investigations were made in the following range of variables: pH, 8.5–10; C_P , 0.03–0.07 g PO_4 /g starch; temperature, 140–150 °C; and reaction time, 60–90 min. According to these parameters, the value of R' was in the range of 20–100.

The results are illustrated in Figures 2–4. To produce better flocculants, the pH value of the impregnating solution and the ratio of phosphate/starch (C_P) were increased. It was found that the charge density of the derivatives decreased by increasing the pH value, and a higher charge density was measured when more phosphate salt was applied (see Figure 2).

The settling capabilities of the flocculants were tested by flocculation experiments (see Figure 3). The increased reagent ratio has an advantageous effect on the settling time. The results show that there are optimal pH values at all phosphate/starch ratios. This phenomenon is due to the fact that the solubility of the products decreases at larger pH values (see Figure 4). The solubility of the derivatives was measured by an indirect method. The area below the RI chromatogram obtained by HPSEC–MALLS analysis is proportional to the solubility of the starch derivatives. If the concentration of the modified starch solution is larger, the RI signal is increased.

We evaluated the results of the complex reaction system using the extended severity parameter as a reaction coordinate. The results are illustrated in Figures 5 and 6, by means of data series at pH 8.7. Similar functions were determined when other series

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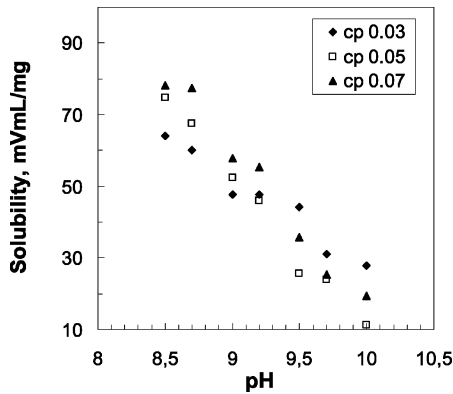


Figure 4. Effect of pH and the reagent/starch ratio (C_P) on the solubility of starch derivatives.

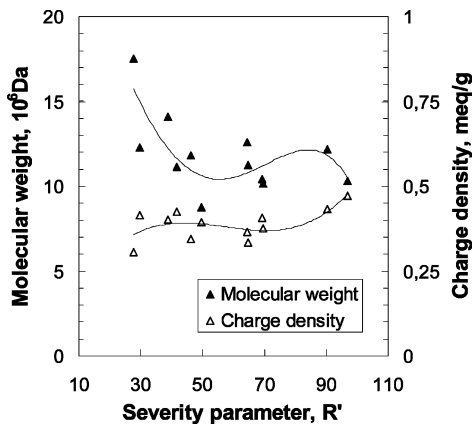


Figure 5. Effect of the extended severity parameter R' on the molecular weight (M_w) and on the charge density of the flocculants prepared at pH 8.7.

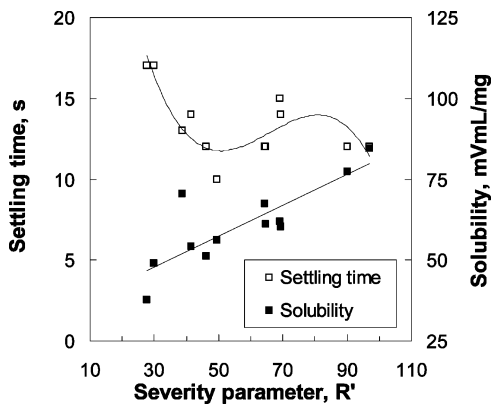


Figure 6. Effect of the extended severity parameter R' on the efficiency (settling time) and on the solubility of the flocculants prepared at pH 8.7.

were evaluated. All of the data points in the figures denote the property of a given product that was prepared according to the given severity parameter. Contrary to the pH 7 data, the average molecular weights of the products do not decrease monotonically along the R' parameter; because of the polymerization, a local maximum appears.

The charge density increases as the severity increases; however, the rate of growth is less at $R' = 60-70$, where the polymerization occurs: the phosphate groups that are built-in do not increase the charge but do cross-link the polymers.

The settling time, which is characteristic to the efficiency of the flocculants, has a minimum value at

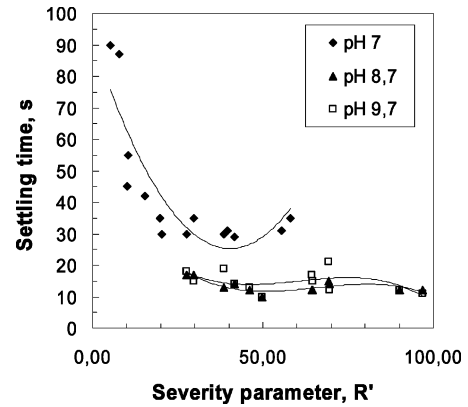


Figure 7. Effect of the extended severity parameter R' on the flocculation efficiency of starch phosphates at pH 7–9.7.

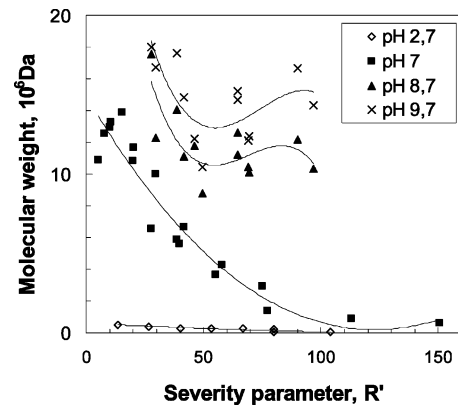


Figure 8. Effect of the extended severity parameter on the molecular weight (M_w) of starch phosphates at pH 2.7–9.7.

$R' = 45$, where the solubility of the polymers becomes high enough. At values of $R' > 90$, the settling capacity is good again; however, because of the degradation, the settling capacity worsens outside the experimental range.

The solubility of the products increase linearly, relative to the extended severity parameter R' .

Figure 7, using the severity parameter as a reaction coordinate, shows that, in the applied range of reaction parameters, the settling is always faster in the presence of flocculants that have been produced in an alkaline medium than in the case of derivatives that have been obtained at neutral pH. These results are attributed to the higher molecular weight (Figure 8). To achieve further improvement in the flocculation capacity, the solubility must be increased.

3.2. Scale Inhibitors. To prepare scale inhibitors, the starch polymer had to be degraded to a great extent. This was achieved via acidic hydrolysis; the pH value of the impregnating solution was set, using phosphoric acid. Phosphoric acid has two roles here: (i) it is the phosphorylating agent and (ii) by setting the pH value, it has great influence on the quality of the products.

Investigations were made in the following range of variables: pH, 2.3–3.0; C_P , 0.04–0.10 g PO_4 /g starch; temperature, 140–150 °C; and reaction time, 60–90 min. The extended severity parameter R' was in the range of 20–200.

The results are illustrated in Figures 9 and 10, using the data series at pH 2.7. The molecular weight of the products decreases along the severity parameter, whereas the charge density increases until all of the phosphate is built into the product. This results in a maximum in

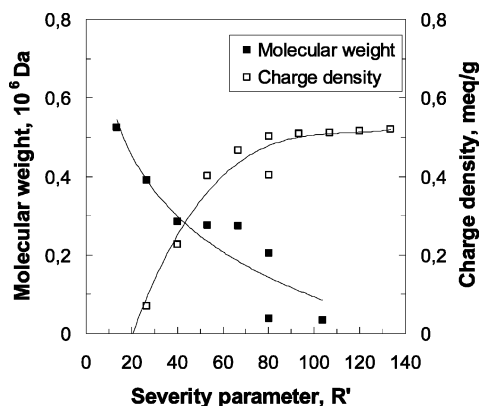


Figure 9. Effect of the extended severity parameter on the molecular weight (M_w) and on the charge density of scale inhibitors prepared at pH 2.7.

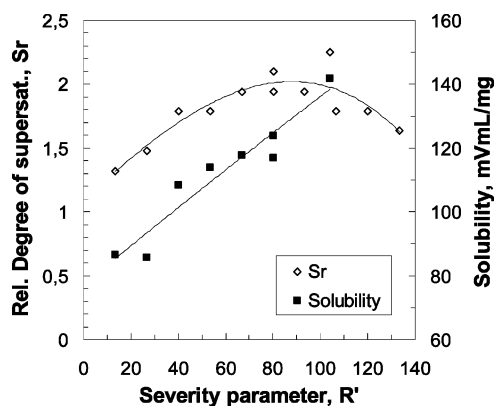


Figure 10. Effect of the extended severity parameter on the efficiency (settling time) and on the solubility of the scale inhibitors prepared at pH 2.7.

the relative degree of supersaturation (which characterizes the efficiency) at the severity parameter range of $R' = 60$ – 80 , because, here, the products have optimal molecular weights.

The efficiency of the starch phosphate antiscaling agents were also investigated in a laboratory-scale recirculated heating–cooling system. These products decrease the precipitation of CaHPO_4 salt from the saturated aqueous solution by 80%–95% at a dosage of 10 ppm.

4. Conclusion

Tailor-made biodegradable polyelectrolytes–floculants and scale inhibitors–can be produced via the solid-

phase phosphorylation of starch. During the modification, at least three reactions happen: phosphorylation, thermal degradation, and cross-linking of the polymers. The results of our experiments have demonstrated that the most important parameter of the modification is the pH value. At alkaline pH values, where the cross-linking occurs, better flocculants can be prepared than in a neutral medium. At acidic pH values, antiscaling agents can be produced using acidic hydrolysis.

The other parameters of the complex reaction system (reagent rate, reaction temperature, and duration of reaction) were summarized in an extended severity parameter (R'). Both types of products can be characterized by average molecular weight, charge density, solubility, and, as a consequence, the settling or antiscaling efficiency. The changes of these properties were investigated as a function of the extended severity parameter R' . The optimal R' ranges were determined, and through application of the recovered reaction parameters, the product development becomes easier.

Acknowledgment

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