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INVESTIGATION OF SOLID-PHASE STARCH MODIFICATION REACTIONS

J. DENCS, G. NOS, B. DENCS and G. MARTON

University of Veszprem, Veszprem, Hungary

Anionic flocculants were produced by solid-phase chemical modification of starch. On the basis of their favourable properties (non-toxic, environmentally degradable), their application is very advantageous in drinking water treatment, food industry and pharmaceutical industry for removing colloid size particles from suspensions. A pilot scale plant was built for the production of the flocculant. The main part of the plant is a multifunctional batch type reactor in which all steps of the dry modification technology can be carried out. The scaling-up of the reactors requires thorough knowledge of the kinetics of the reactions taking place in the equipment. The starch modification reaction consists of the phosphorylation and degradation of the starch. The results of the kinetic investigation carried out in the laboratory and in the batch-type pilot-scale plant will be presented in this paper.

Keywords: multifunctional reactor; reaction kinetics; starch phosphorylation; flocculating agent.

INTRODUCTION

Flocculating agents are widespread used to enhance filtrating and settling aqueous suspensions. Flocculants are so-called polyelectrolytes, water-soluble polymers with 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 by its functional groups. Cationic flocculants are suitable for the neutralization of particles with a negative charge, while anionic ones are for those with a positive charge.

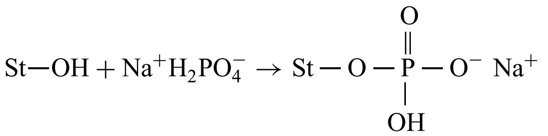
The flocculants used in today's industry and water treatment systems are mostly synthetic products, such as polyacrylamide, polyethylene-oxide and, their derivatives. In the clarification step of the drinking water treatment usually anionic flocculants are used. Al^{3+} or Fe^{3+} salts are added to the water to be treated, and the synthetic polyelectrolytes improve the sedimentation of the forming hydroxide flocs after the flocs adsorbed the colloid size particles. These are very effective, but may contain toxic monomer residuals, and after disposal in the environment they are not biodegradable. The drawbacks could be eliminated by developing and using natural-based polyelectrolytes, e.g. starch could serve as a backbone and ionic groups linked to it as charge carriers.

SOLID PHASE PHOSPHORYLATLON OF STARCH

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 100,000,000. Starch can be converted into flocculants 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 derivative increases. Depending on whether we build anionic or cationic functional groups into the starch chain, we will get anionic or cationic flocculants. The starch derivative if produced with the proper reagent is non-toxic and indeed biodegradable. The objective then is to produce natural-based flocculants for those fields where its beneficial properties are really an advantage. Such a field is drinking water treatment.

It was reported by Dencs *et al.* (2000, 2001) that at the Department of Chemical Engineering Science of the University of Veszprem a research group developed some starch-based anionic flocculants and a technology for producing starch derivatives by a dry modification process. One of the products was registered by the name of Greenfloc 213A and the Hungarian authorities allowed its use in the drinking water treatment. This flocculant is a starch phosphate.

By building phosphate groups into the starch, anionic derivatives can be produced:



$$\mathrm{St{-}OH} + \mathrm{Na^+H_2PO_4^-} \rightarrow \mathrm{St-O-\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{\underset{|}{P}}}}-O^-\ Na^+}$$

The building-in of phosphate groups can be made more effective by the use of N-containing catalysts.

The chemical reaction is performed in the solid phase. Apart from 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.

During the chemical modification the substitution and the degradation of polymer molecules take place simultaneously. However flocculants have to be of high molecular weight for bridge forming and at the same time ionic for good solubility. Therefore the temperature and time of the reaction have to be optimized. The optimal reaction conditions were defined by parallel investigation of the two chemical reactions and flocculation properties.

As a result of the laboratory experiments we developed a method for preparation of the Greenfloc 213A flocculant. At the transferral of the modification technology from the laboratory scale to the pilot-scale plant, a problem arose: the time of the drying period in the multifunctional reactor is much longer than in the laboratory. The objective of this kinetic investigation was to clear up the influence of the longer residence time and possibly irregular temperature on the quality of the product.

BATCH TYPE MULTIFUNCTIONAL REACTOR

Processing of fine-grain solid materials often requires some different consecutive or simultaneous technological steps such as mixing of powders, spraying of liquids, mixing of powders and liquids, agglomeration of powders, disintegration of agglomerates, atmospheric or vacuum drying, or chemical reaction in solid phase. To reduce the costs of production in small factories, it seemed practical to develop a reactor in which all the above-mentioned processes can be executed.

For the starch modification we have developed and constructed a pilot-scale batch-type reactor of 100 kg charge^{-1} which is suitable for performing solid-phase reactions, especially when the main component is a fine-grain solid material (Figure 1). The shape of reactor is a horizontal cylinder closed at both ends. Its diameter is $D = 0.9$ m, length $L = 0.9$ m, and volume $V = 0.45\,\mathrm{m}^3$. Adequate motion of the particles is ensured by an impeller. The rotation speed of the impeller can be set in an 8–90 rpm range depending on technological aims. The even distribution of the dissolved reagents on the surface of particles of the main component is carried out by a pneumatic nozzle. In the course of spraying the agglomeration of particles also takes place. Over-agglomeration is prevented by a high rotation speed chopper (2440 rpm) placed at the bottom of the reactor.

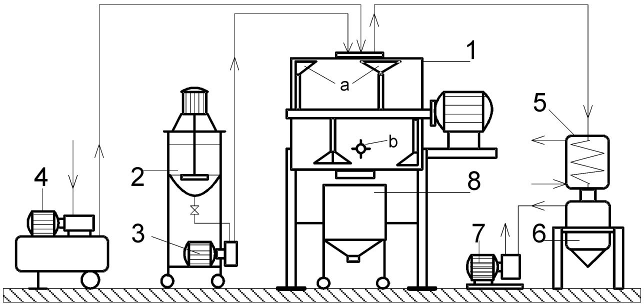


Figure 1. Flow sheet of the pilot scale plant. 1, reactor, a-impeller, b-chopper; 2, liquid tank; 3, liquid pump; 4, compressor; 5, condenser; 6, container for condensed vapour; 7, vacuum pump; 8, container for product.

The reactor is equipped with proper insulation and an electric heating jacket to ensure the heat energy input required for the reaction. The maximum temperature is 180°C. Belonging to the reactor there is a liquid tank with a heating jacket to dissolve reagents and a compressor to provide compressed air for spraying. The vapour formed during the heat treatment (drying, heating, chemical reaction) is removed from the reactor by a ventilator and then condensed.

EXPERIMENTAL

In the laboratory experiments native starch samples were impregnated with the aqueous solution of the reagents in mortars, and the drying and phosphorylation was carried out at different temperatures (120–160°C) in the oven. The duration of the heat treatments ranged from 15 to 480 minutes.

In the pilot-scale experiments samples were taken from the reactor during the production of the anionic flocculant. The substitution was followed by determination the bound phosphorus content of the starch phosphate. At the same time the degradation reaction was examined through the analysis of the molecular weight distribution of the derivatives. The flocculation properties were tested by settling standard kaolin suspension.

MATERIALS AND METHODS

Chemicals

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 at the analysis were bought from Merck AG in analytical reagent grade.

Analysis of the Bound Phosphorus Content

The free phosphate content of the samples was separated from the bound phosphate by extraction three times repeated with 80% methanol–20% water mixture. The bound phosphorus was analysed according to Radley (1976). All organic material of the solid residue was burned, and the P content was determined from the ash as molybdivanadophosphoric acid by a Biochrom 4060 spectrophotometer (Pharmacia AG) at 460 nm.

Determination of the 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 HPSEC/MALLS/RI analysis. The HPLC system (LaChrom, Merck-Hitachi) comprised $2 \times 30\,\mathrm{cm} \times 7.8\,\mathrm{mm} \times 8\,\mu\mathrm{m}$ PLaquagel-OH mixed columns (Polymer Laboratories), $10\,\mu\mathrm{L}$ $1\,\mathrm{mg\,mL^{-1}}$ sample injected, $1\,\mathrm{mL\,min^{-1}}$, pH 11 puffer eluent, 60°C thermostat, RI and MALLS (PD 2020, Precision Detectors) detectors. The parameters of the molecular weight distribution were determined by Discovery 32 software.

The molecular weight distribution of the polymers was characterized by 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 ($D = M_w/M_n$).

Flocculation Characteristics

The flocculation properties of the derivatives were measured by a quick test developed at our department. Ten millilitres of kaolin suspension ($5\,g\,L^{-1}$) were put into test tubes, 0.1–0.5 mL of flocculant solution ($1\,g\,L^{-1}$) was added and the mixture was thoroughly mixed. Some seconds afterwards flocs appeared and settled into the lower part of the tubes. The time of the appearance of the flocs and the time of their settling were measured.

RESULTS AND DISCUSSION

Figure 2 shows the building-in of the phosphorus into the starch during the time at different temperatures. Increasing the intensity (duration and temperature) of the heat treatment increased the degree of substitution. Unfortunately, the more intensive heat treatment involves the degradation of the starch molecules; the number of polymers of low molecular weight increases and the average molecular weight decreases. It is well known that these molecules can act as dispersing agents, which is why it is very important to avoid their formation.

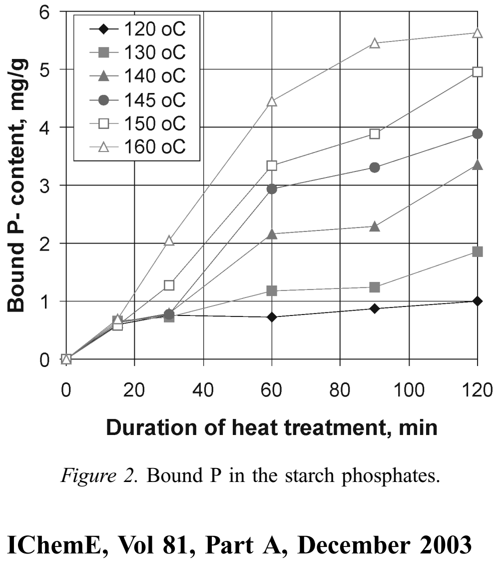


Figure 2. Bound P in the starch phosphates.

Figure 3 shows the change in the weight average molecular weight of starch phosphates during heat treatment. The native corn waxy starch is not soluble under the conditions of the standard sample preparation, which is why we accept, according to Willett *et al.* (1997), $M_w = 10^8$ Da as the initial molecular weight. In the diagram the molecular weights measured at 15 min at lower temperatures are less than the molecular weights at 30 min, thus apparently the molecular weight can grow. The explanation of this phenomenon is that the solubility of the starch phosphate polymers present in the sample depends on the phosphate bound to the starch (degree of substitution). The HPSEC/MALLS/RI analytical method was developed for analysis of phosphorylated starch. Under standard sample preparation the low phosphate content only allows polymers of lower molecular weight to dissolve. According to our experiments 0.5–1 $mg\,g^{-1}$ P-content makes it possible for polymers of $M_w = 10^8$ to dissolve, thus above this P-content the data are acceptable.

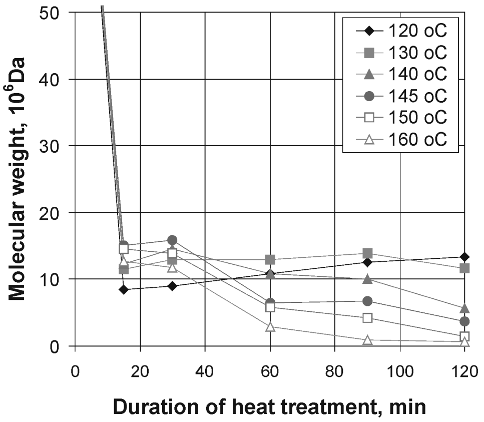


Figure 3. Average molecular weight of the starch phosphates.

As a consequence of the opposite effects of the increasing bound P-content and decreasing average molecular weight, the settling time—which characterizes the flocculating efficiency—has a minimum value (Figure 4).

Evaluating molecular weight distributions and the flocculation efficiencies of the derivatives, we could draw an average molecular weight vs. bound P-content diagram (Figure 5), on which a limited area contains the characteristics of the products resulting from the given raw material composition. In the diagram we can determine the range where the 'best products' can be found. The average molecular weights of these derivatives range from 6 to 10×10^6 Da; the P content is 1.5–3.0 $mg\,g^{-1}$. The products of $2–4 \times 10^6$ Da molecular weight and 3.0–4.0 $mg\,g^{-1}$ P content showed rather good flocculation effects, but the flocs were smaller.

Using the results of the laboratory-scale experiments, important conclusions can be drawn regarding the operation of the pilot-scale plant.

The steps to be carried out in the batch type multifunctional reactor are the following:

- spraying in the aqueous solution of the reagents and mixing it with the starch;
- drying the impregnated starch;

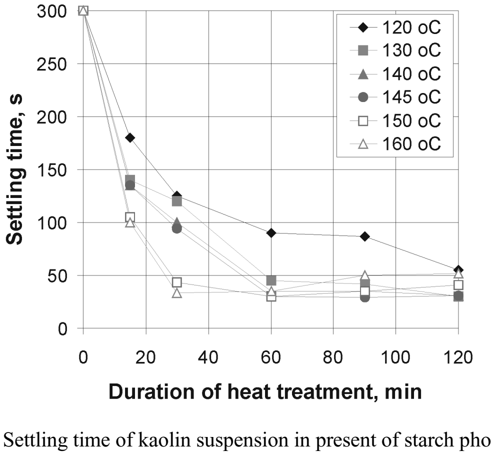


Figure 4. Settling time of kaolin suspension in present of starch phosphates.

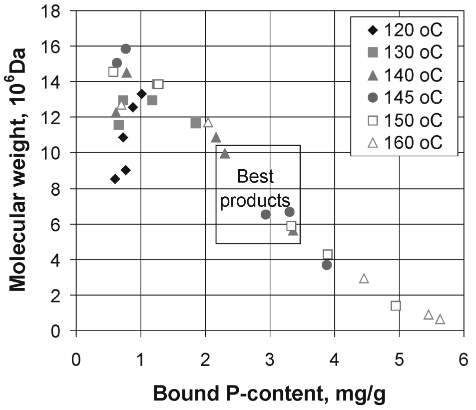


Figure 5. Properties of the best starch phosphates.

- heating up to the optimal reaction temperature;
- performing the phosphorylation reaction.

It is very important to use as little water as possible to maintain the flow of the particles during the operation as well as to reduce the energy demand of drying. The temperature of drying and hence the speed of drying is restricted by the fact that starch, in the presence of water, gelatinizes at a higher temperatures. Gelatinized starch is impossible to handle in such an apparatus. The phosphorylation and the degradation reactions can take place during the drying process, and their rates influence the quality of the products. The knowledge of the kinetics of these reactions provides an opportunity to optimize the heat treatment process.

Provided that the phosphorylation reaction is characterized by first-order kinetics, the reaction rate constants (k) were determined as a function of the temperature (T) from the data of substitution measurements. In Figure 6 ln(k) vs. $1/T$ values were plotted. From the Arrhenius equation

$$k = k_\infty e^{(E_a/RT)}$$

k_∞ frequency factor and E_a activation energy were determined: $k_\infty = 4.17 \times 10^{13}\,h^{-1}$ and $E_a = 1.14 \times 10^5\,J\,mol^{-1}$, where the gas constant $R = 8.314\,J\,mol^{-1}\,K^{-1}$.

Using the kinetic parameters we could predict the degree of phosphorylation in the pilot-scale reactor during the whole heat treatment process. We measured the temperature in the reactor at time t and took samples from the modified starch. The moisture content, bound phosphorus content, the molecular weight distribution and the flocculating efficiency of the samples were determined. In the course of the HPSEC/MALLS/RI analysis a value occurred in the chromatogram which is characteristic of the water solubility of the samples, the area of the refractive index signal. Figures 7–9 show the change of these properties during the heat treatment in the pilot-scale reactor; the period marked in the diagrams was necessary in the laboratory experiments for optimal conversion.

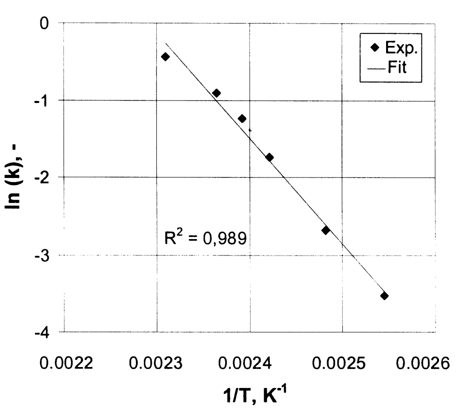


Figure 6. Starch phosphorylation: ln(k) vs. $1/T$.

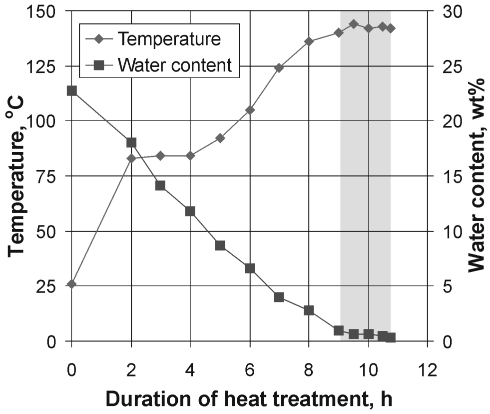


Figure 7. Change in the temperature and the water content in the pilot-scale reactor.

In Figure 7 it can be seen that the drying period in the pilot-scale reactor is about 9 h (in the laboratory experiments the removal of the moisture content required 5–15 min). During this period the temperature in the reactor slowly approaches the desirable reaction temperature. Figure 8 shows the building in of phosphorus together with the change in the solubility. Since only the polymers dissolved in water can flocculate the colloid particles, the flocculation efficiency develops at the end of the heat treatment, decreasing the settling time to the desirable value (Figure 9). Because of the degradation of the polymers, the heat treatment at this point must be stopped.

Using the kinetic parameters of the phosphorylation reaction and the measured temperatures, we have calculated

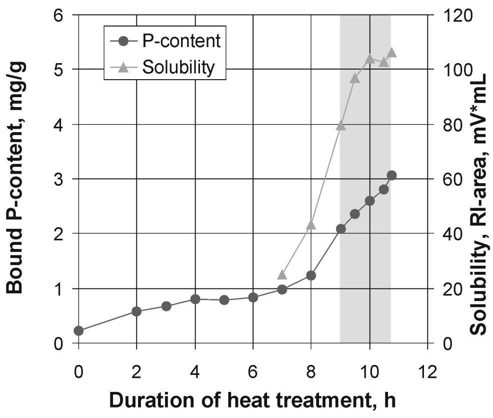


Figure 8. Change in the bound P content and the solubility in the pilot-scale reactor.

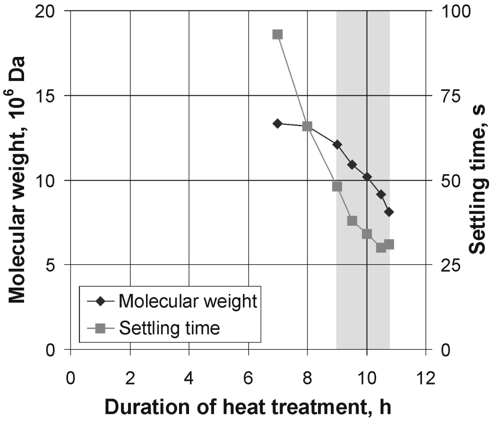


Figure 9. Changing of average molecular weight and the flocculating efficiency in the pilot-scale reactor.

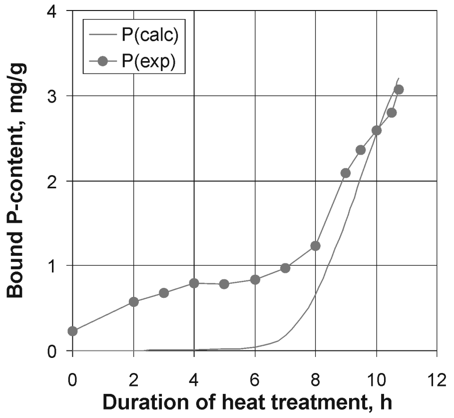


Figure 10. Comparison of the experimental and calculated phosphorus building in the pilot-scale reactor.

the expected concentrations for the pilot-scale reactor and compared them to the measured values. In Figure 10 the measured phosphorus content data are plotted; the continuous line shows the P content calculated from the kinetics. Although at the end of the heat treatment (in the critical range) the coincidence was rather good, it is obvious that the phosphate substitution is preceded by another reaction that is building phosphorus into the starch. According to the pH and temperature it could be a crosslinking reaction. The resolution of this problem will require further investigations.

CONCLUSIONS

Environment-friendly non-toxic anionic flocculating agents can be produced both in laboratory and at pilot-scale by a practically waste-free technology. All of the technological steps can be carried out in the batch-type multifunctional reactor, but as a consequence of the relatively lower heat input, the drying period of the heat treatment lasts longer than in the laboratory, and during this time some reactions can occur. In the course of the phosphorylation at least two reactions take place, the substitution of hydroxyl groups in the starch polymers by phosphate groups and the thermal degradation of the polymers. The building in of phosphorus can be described by first-order kinetics; the kinetic parameters determined can be used to calculate the conversion in the batch-type reactor. The final point of the heat treatment, which is of great importance with respect to product quality, can be calculated fairly well. The resolution of the problem of the parallel reactions requires further investigations.

NOMENCLATURE

k	reaction rate constant, h^{-1}
k_∞	frequency factor, h^{-1}
t	time, h
E_a	activation energy, $J\,mol^{-1}$
T	temperature, K
M_w	weight average molecular weight, Da
M_n	number average molecular weight, Da
D	polydispersity

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ADDRESS

Correspondence concerning this paper should be addressed to Dr J Dencs, Department of Chemical Engineering Science, University of Veszprem, H-8200 Veszprem, POB: 158, Hungary. E-mail: dencsj@almos.vein.hu

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