BATCH TYPE REACTOR FOR MODIFICATION OF STARCH IN SOLID PHASE

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Experimental batch type reactor of 100 kg/charge was constructed for making solid phase reactions. The reactor is a horizontal cylinder equipped with impeller and chopper to perform the proper motion and prevent the agglomeration of fine solid materials. Spraying nozzle is used to distribute the dissolved component. The reactor has heating jacket with controler to reach the optimum temperature for the reaction. Biodegradable anionic flocculant (Greenfloc®) was developed and produced in this reactor by modification of nativ starch. Conditions of production, behaviors and usage of the floculant in waterworks are also summerised in this paper.

1. Introduction

Processing of fine grain solid materials often requires some different consequent 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, 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.

We have performed experiments using this reactor for the modification of starch. The aim of the modification was to produce starch based flocculants. In this paper we shall present the main parameters of the reactor and the production.

2. Experimental reactor

We have developed and constructed an experimental batch type reactor of 100 kg/charge (Fig.1.), that is suitable for performing solid phase reactions especially when the main component is a fine grain solid material (generally lower than 200 μm). The form of reactor is a horizontal cylinder closed at both ends. Its diameter is D=0.9 m, length L=0.9 m, and volume is V=0,45 m^3. The adequate motion of the particles is ensured by an impeller. The rotation speed of the impeller can be set in 8-90 rpm range depending on technological aims. The even distribution of the dissolved reagents on the

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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. Overagglomeration is prevented by a high rotation speed chopper (2440 rpm) placed at the bottom of the reactor.

Fig.1.

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 ^{o}C. The technological flow sheet of the reactor is shown in Fig.1.

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 eliminated by a vacuum pump and then condensed.

3. Starch based flocculant

By chemical modification of starch we have produced natural based flocculants with this reactor.

Flocculants are so called polyelectrolytes, water soluble polymers with ionic charge. The particles in aqueous suspension can be agglomerated by various mechanisms. Flocculants neutralise the identical charges of repelling particles and hence stop repulsion. Another mechanism is bridge-forming, that is the big polymer molecule binds particles to itself with the help of its functional groups.

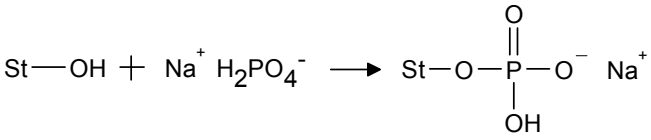
Starch in its original form is not water-soluble and has no functional groups with charges. It is a mixture of two polymers: amylose and amylopectin, and the mass of molecules ranges from 50,000 to millions.

Starch can be converted into flocculants by substituting a part of the OH^{-}-groups in the monomer units of the polymer chain 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. Cationic flocculants are suitable for the neutralisation of particles with a negative charge, while anionic ones are for those with a positive charge.

The flocculants used in today's industry are mostly synthetic products, such as polyacrylamid, polyethylene-oxide, etc. These are very effective, but may contain toxic monomer residuals and after disposed of in the environment they are not biodegradable. 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, where in the clarification step anionic flocculants are used. Al^{3+} or Fe^{3+}-salts are added to the water to be treated, and polyelectrolytes improve the sedimentation of the forming flocs.

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



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

4. Production of modified starch

The chemical reaction is performed in the solid phase. Apart from the starch all other components are water-soluble, therefore we add their aqueous solution to the starch before the reaction.

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

1. Spraying in the aqueous solution of the reagents and mixing it with the starch;
2. Drying the impregnated starch;
3. Heating up to the optimal reaction temperature;
4. Performing the phosphorilation reaction.

At the first step it is very important to add as little water as possible into the reactor for keeping the flowability of the particles during the operation as well as for reducing the energy demand of drying.

The temperature of drying and hence the speed of drying is restricted by the fact, that starch, in presence of water, gelatinises at a higher temperature. (Native starch at ca. 70 ^{o}C, modified could differ.) Gelatinised starch is impossible to handle in such an apparatus.

During the experimental production of Greenfloc 213A anionic flocculant we have measured and controlled the temperature of the reactor wall (t_w), as well as the temperature inside the reactor (t_{in}). During the drying period the wall temperature was set to t_w=80 ^{o}C, and no significant gelatinisation was experienced. The remaining (3-5 m%) humidity was eliminated in the heating-up phase at a wall temperature of t_w=120 ^{o}C. The phosphorilation reaction was performed at a wall temperature of t_w=140 ^{o}C. The temperature change in time can be seen on Fig. 2.

During the chemical reaction the building-in of phosphate groups and the degradation of polymer molecule take place simultaneously. However flocculants have to be of high molecular mass for bridge-forming. Therefore the temperature and time of the reaction have to be optimised.

Fig.2.

The optimal reaction conditions were defined by flocculation experiments (jar-test) and the examination of the molecular mass distribution of the derivatives. Fig.3. shows size exclusion (HPSEC) chromatogram of the native starch and the anionic flocculant derived from it. The area beneath the curve is proportional to the amount of material, that can be dissolved under same conditions. The average molecular weight, calculated from the diagrams by calibration, hardly decreased throughout the reaction, but the solubility of the polymers of higher molecular weight increased.

Fig.3.

In the course of liquid spraying and heat treatment the physical properties of the solid modified starch also changes significantly. The mean particle size increased from 35-40 μm to 580 μm. The product does not contains big lumps, more than 90 w/w% of the flocculant is in 100-2000 μm size range. The low moisture content and the relatively high bulk density ensure good free-flowing properties of the product.

Fig.4.

From the starch derivatives we recommend Greenfloc 213A for drinking water treatment. Following the lab-scale experiments this product has been tried at industrial scale in various water plants [1]. As results show in the Table 1. the product is suitable for the substitution of synthetic flocculants.

4. Conclusions

- The reactor could be operated without any problem, and all steps of the technology could be carry out according to the expectations.
- The flocculant, produced by the reactor had the same characteristics and efficiency as the product made in the laboratory.
- In spite of the long operating time the costs of production of starch-based flocculant are favorable.

Reference

1. Dencs, J., Marton, G.: Application of starch based anionic flocculant in the water treatment. Biomass for Energy and Industry. 10th European Conference Technology Exhibition. Würzburg, 8-11 June 1998.

Table 1. Results of the experiment in Lazberc
(1 November - 31 December 1997)*

Property	Removal percent after sedimentation		
	1-16 Nov. by synthetic flocculant	17 Nov.-8 Dec. by Greenfloc 213A	9-31 Dec. by synthetic flocculant
Turbidity, NTU	89.6	87.5	84.0
COD, mg/L	43.8	43.2	32.4
Algae, 10^6/L	92.8	93.6	92.0
Al(III), mg/L	99.96	99.96	99.94
Temperature, ^oC	6-7	4-6	3-4

*Coagulant: BOPAC (poly-aluminium-chloride)

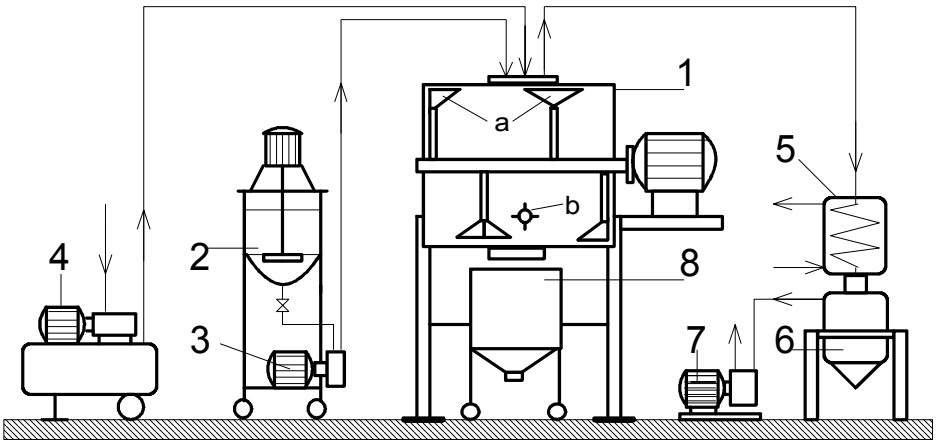


Fig. 1. Flow Sheet of Solid Phase Reactor

1-Reactor with electric heating jacket, a- Impeller, b- Chopper
2-Liquid tank with heating jacket, 3-Liquid pump, 4-Compressor
5-Condenser, 6-Container for condensed vapour, 7-Vacuum pump
8-Container for product

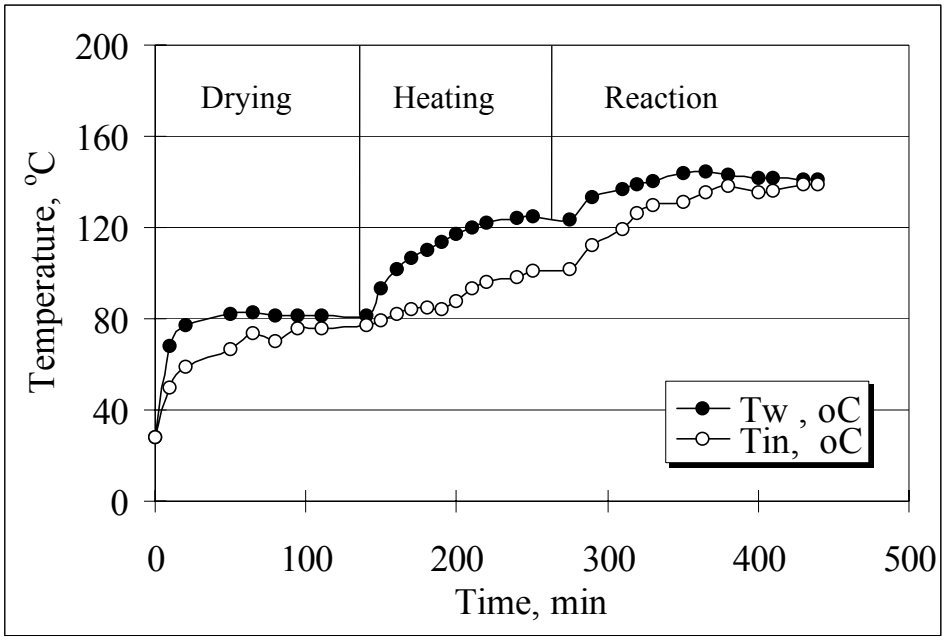


Fig. 2. Temperature change in time at the wall of reactor and inside the reactor

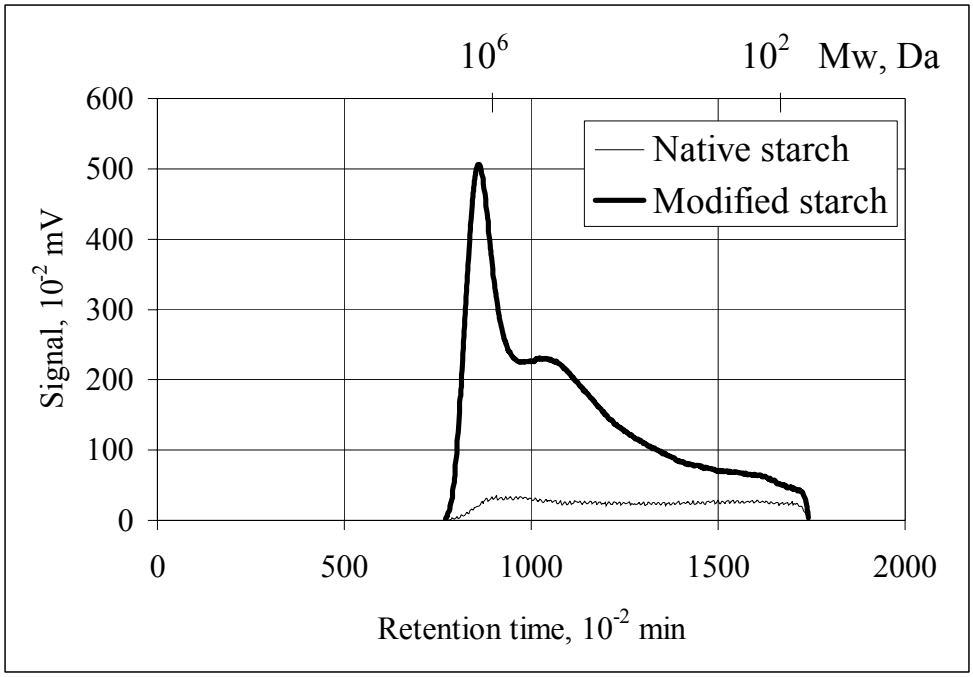


Fig. 3. Size exclusion chromatogram of native and modified starches

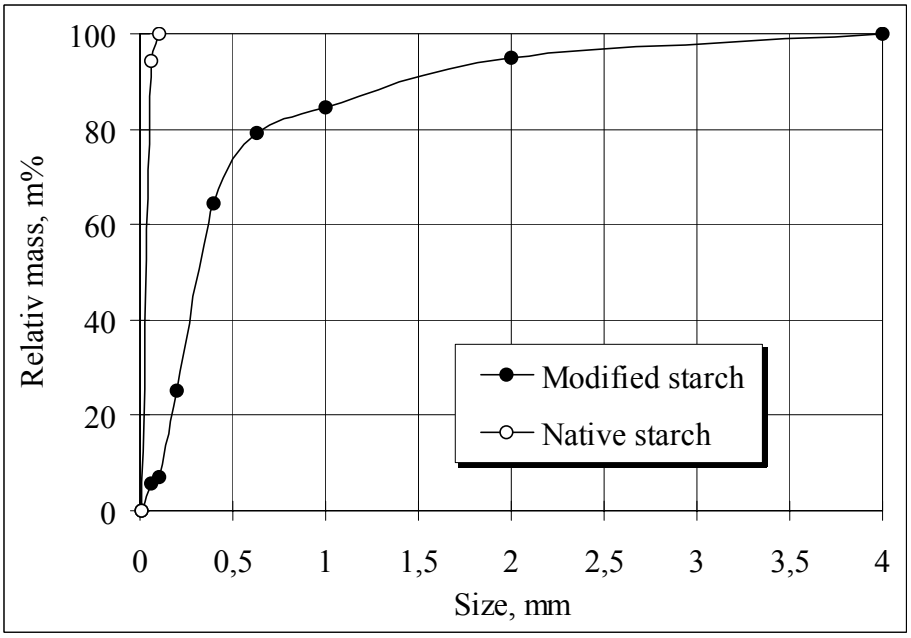


Fig. 4. Cumulative particle size distribution curves of native starch and modified starch