

## Factors influencing production of cationic starches

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### Abstract

The main factors – the amount of catalyst NaOH, the temperature and composition of reaction mixture – influencing the effectiveness of starch cationization with glycidyltrimethylammonium chloride (GTAC) were investigated. It was found that cationic or cross-linked cationic starches with preserved microgranules, a degree of substitution from 0.2 to 0.85 and reaction efficiency from 82% to 93% could be obtained during etherification of starch or cross-linked starch with a mixture containing GTAC, “free” water and 0.04–0.08 mol/AGU sodium hydroxide in heterogeneous condition. The activation energy of the GTAC main reaction is lower than that of the side reactions, thus starch cationization at a lower temperature proceeds with higher reaction efficiency.

The amount of NaOH in the cationization mixture has a great influence on the rate of the main and side reactions of GTAC. Only the main reaction – cationization of starch – proceeds when all the NaOH present in the reaction mixture is adsorbed from the liquid phase by the starch. The duration of this “first reaction stage” decreases with increasing reaction temperature and the amount of NaOH in the reaction mixture. NaOH present in the liquid phase of the reaction mixture catalyzes the side reactions of GTAC and changes their character.

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### 1. Introduction

In recent years, cationic starches (CS) with a high degree of substitution (DS) are of increasing interest. CS with DS from 0.2 to 0.9 is the most promising candidate to replace synthetic flocculants or sorbents in various industrial applications (Bendoraitiene, Klimaviciute, Sableviciene, & Zemaitaitis, 2005; Crini, 2006; Haack, Heinze, Kulicke, & Oelmeyer, 2002; Klimaviciute, Riauka, & Zemaitaitis, 2007). Due to the use of renewable resources as a main raw material and a higher biodegradability of the products, production of CS becomes the subject of sustainable or “green” chemistry. In economic terms, the microgranular CS as flocculants and sorbents is still competitive with the synthetic products despite the higher doses required. The cost of the native starch is below the cost of synthetic reagents, and the cost of the cationization agent mainly influences the price of CS. Therefore, in the manufacture of modified starch, the ultimate requirement is high efficiency of the cationization reaction.

CS are commonly prepared by the reaction of starch with glycidyltrimethylammonium chloride (GTAC) or 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) in homogeneous or heterogeneous (water suspension, suspension in organic solvents or mixture of water and organic solvents) conditions or by cationization of starch in the “dry” state (Haack, Heinze, & Rensingm, 2004; Haack et al., 2002). If CHPTAC is used, higher amounts of alkaline agents are required, since part of it is consumed for the formation of epoxy groups. However, starch undergoes pasting if high amounts of alkali are present in the reaction mixture and the structure of starch grains is destroyed. Therefore, CHPTAC might be used only for the synthesis of CS with a low content of quaternary ammonium groups (DS < 0.1).

Heinze and co-workers (Haack et al., 2004) obtained starch derivatives containing high amounts of quaternary ammonium groups (DS up to 1.1) by etherification of

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potato, maize and wheat starch both with CHPTAC and GTAC in heterogeneous and homogeneous conditions. When starch was modified with CHPTAC in ethanol/water suspension the DS of the obtained CS depended on the molar ratio of the reagents and the type of starch and varied between 0.03 and 0.88. However, reaction efficiency (RE) was below 47% in all cases. The higher RE was achieved when starch was modified with GTAC. The DS of CS obtained in heterogeneous conditions (water suspension) varied between 0.38 and 1.05 with the RE from 40% to 76%. When starch was dissolved in dimethylsulphoxide modification with GTAC proceeded in homogeneous conditions, CS with DS from 0.37 to 0.57 was obtained with a similar RE as in the case of the heterogeneous conditions. CS with DS  $\sim$  1.5 was obtained only by two-stage modification, when cationic starch was additionally alkylated with a large amount of GTAC (10 mol GTAC/AGU). An increase in the amount of NaOH as a catalyst of cationization reaction did not enhance the yield, because the side hydrolysis reactions of epoxy groups were intensified when the amount of NaOH exceeded 0.4 mol/AGU.

In comparison with the other methods, “dry” modification of starch has several advantages (Bischoff, Hellwig, & Rubo, 1992). The obtained product does not require washing and filtering, thus starch loss and water pollution are avoided. With special catalysts (Powdercat<sup>®</sup> Process) the reaction proceeds at room temperature and reduces the energy input. This method allows production of CS with DS up to 0.5 and a satisfactory yield.

Our earlier investigations demonstrated (Bendoraitiene, Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2006) that the reaction of GTAC with starch might proceed in the absence of the external catalyst if a particular quantity of “free” water is present in the system. The reaction is accelerated by alkaline agents, such as NaOH, KOH or other alkalis which act as catalysts for the reaction and deprotonate the hydroxyl groups of starch.

At the same time, alkalis accelerated (Bischoff et al., 1992; Buchberger, Pfeifer, & Schoftner, 2002; Goclik, Stach, & Mischnick, 2004) the side reactions of cationization agents subject to the conditions of the reaction. In an alkaline medium, hydrolysis of epoxy groups occurred and *N*-(2,3-dihydroxy)propyl-*N,N,N*-trimethylammonium chloride was produced. Water-soluble oligomers of GTAC are also found in the reaction mixture. *N*-(3-Hydroxy-1-propen)-*N,N,N*-trimethylammonium chloride was produced when starch was modified with GTAC in an organic solvent containing small amounts of alkali even at room temperature. Hellwig et al. (Bischoff et al., 1992) proposed that hydrolysis of GTAC is predominant in water, whereas *N*-(3-hydroxy-1-propen)-*N,N,N*-trimethylammonium chloride was found in the reaction mixture if starch was modified at a higher than room temperature under alkaline conditions.

The literature has no data about the best methods of obtaining CS with a high DS and are action efficiency above 60%. Furthermore, it was shown that CS with a pre-

served granular structure of native starch was a better adsorbent (Klimaviciute et al., 2007) and flocculant (Bendoraitiene et al., 2005). For these reasons, the production of CS with a high charge density requires choosing the conditions of cationization that preserve the starch microparticles unchanged, where only the main reaction of polysaccharide with GTAC occurred. The obtained products should contain only minor amounts of by-products and can be used without further purification. Discovery of conditions at which at least 80% of alkylation agent is used in the main reaction would enable to reduce the cost of CS and to compete with synthetic polymers.

The aim of the present work was to estimate the main factors, such as the amount of alkaline catalyst, the temperature and composition of the reaction mixture, that influence the effectiveness of starch cationization with GTAC under conditions preserving the microgranules of highly cationic starches unchanged.

## 2. Materials and methods

### 2.1. Materials

The Antanavas Starch Plant (Lithuania) supplied native potato starch (intrinsic viscosity  $[\eta] = 390$  ml/g). The aqueous solution of the cationic reagent, 2,3-epoxypropyltrimethylammonium chloride (glycidyltrimethylammonium chloride, GTAC or Quab 151<sup>®</sup>), was purchased from Degussa (Dusseldorf, Germany). The original solution contained 70% of active, 5% of inactive monomers and 22% of water (molar ratio of GTAC:H<sub>2</sub>O was 1:2.645). Epichlorohydrin (99%) was purchased from Sigma–Aldrich. All the other chemicals were of analytical grade.

*N*-(2,3-dihydroxy)propyl-*N,N,N*-trimethylammonium chloride was obtained under hydrolysis of GTAC in water at a temperature of 60 °C.

### 2.2. Preparation of cross-linked starch

The native potato starch was suspended in water in order to obtain the 50% (w/w) slurry. The macromolecules of starch were cross-linked by epichlorohydrin (EPI) in the presence of NaOH added until the pH value of the reaction mixture reached 11. The cross-linking at 45 °C was completed after 24 h. Cross-linked starch, water-washed and dried at 50 °C, was used for cationization.

As a mole of starch, the mole of anhydroglucoside unit (AGU) was used and the amount of EPI ranged from 0.002 to 0.3 mol/AGU. Cross-linked starches were denoted as CLS<sub>*x*</sub>, where *x* shows the amount of EPI (mol/AGU) used in the cross-linking reaction.

### 2.3. Preparation of cationic starches

Cationic starches were prepared by modifying native potato or cross-linked starch with a reaction mixture containing Quab 151<sup>®</sup> under heterogeneous conditions at 45,

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