EFFECT OF CATIONIZATION ON THE FUNCTIONAL PROPERTIES OF STARCH

Sanda Pilipović, Tatjana Botić, Borislav N. Malinović, Tijana Đuričić, Aleksandra Borković, Dajana Dragić, Ana Velemir

University of Banja Luka, Faculty of Technology, Stepe Stepanovića 73, 78 000 Banja Luka, Bosnia and Herzegovina, sanda.bjelosevic@tf.unibl.org, tatjana.botic@tf.unibl.org, borislav.malinovic@tf.unibl.org, tijana.djuricic@tf.unibl.org, aleksandra.borkovic@tf.unibl.org, dajana.dragic@tf.unibl.org, ana.velemir@tf.unibl.org

ORIGINAL SCIENTIFIC PAPER

ISSN 2637-2150
e-ISSN 2637-2614
UDC
DOI:
COBISS.RS-ID

Received: 21 August 2026.
Revised: 09 November 2026.
Accepted: 11 November 2026.
Published: 30 November 2026.
https://stedjournal.com/

Corresponding Author: Sanda Pilipović, University of Banja Luka, Faculty of Technology, Stepe Stepanovića 73, 78 000 Banja Luka, Bosnia and Herzegovina, sanda.bjelosevic@tf.unibl.org

Copyright © 2026 Sanda Pilipović et al.; published by UNIVERSITY PIM. This work licensed under the Creative Commons Attribution-NonCommercial-NoDerivs 4.

Citation: Pilipović, S. et al. (2026). Effect of Cationization on the Functional Properties of Starch. *STED Journal, 8*(2), 1-18.

ABSTRACT

Native starch exhibits limitations in its application in the chemical, food, and pharmaceutical industries due to unfavorable functional properties. These properties can be improved through chemical modification. This study investigates the effect of cationization conditions on swelling power (g/g), water absorption capacity (g/g), and solubility (%) of modified cationic starch compared to native starch. Cationization was performed using 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) in alkaline aqueous-alcoholic medium, with CHPTAC to anhydroglucose unit (AGU) molar ratios ranging from 0.08 to 0.23 and reaction times from 30 to 150 min. In general, increasing the CHPTAC/AGU molar ratio and prolonging the cationization reaction time result in cationic starch with a higher degree of substitution, which directly contributes to increased swelling power and water absorption capacity. However, no direct relationship is observed between these reaction conditions and solubility. The greatest increases in swelling power and water absorption capacity, by 16.5-fold and nearly 28-fold , respectively, were observed for the sample synthesized at 50 °C for 2.5 h using a CHPTAC/AGU molar ratio of 0.18. Solubility also exhibits changes. After modification, about one quarter of the starch mass became water-soluble, whereas the native starch contained only 1.66% of water-soluble components.

Keywords: native starch, cationization, swelling power, water absorption, solubility.

INTRODUCTION

Starch is a polysaccharide composed of linear amylose and highly branched amylopectin. Amylose consists of D-glucose units linked by α-(1→4) glycosidic bonds, whereas amylopectin also contains α-(1→4), and α-(1→6) glycosidic linkages, which are responsible for its branched structure. This molecular structure makes starch a naturally occurring polymer with considerable potential for applications in the chemical, food, and pharmaceutical industries.

The major advantages of starch include its wide availability from various botanical sources, low cost, excellent biodegradability and biocompatibility, as well as non-toxicity [1]. However, native starch exhibits several inherent limitations that restrict its practical applications, including low solubility, retrogradation, syneresis, thermal degradation, and high viscosity after gelatinization [2], [3]. To improve its functional properties and broaden its range of applications, native starch must be modified [4]. Starch modification not only improves its functional properties, such as swelling power, solubility, thermal stability, paste properties, and resistance to retrogradation [5], but also increases its commercial value. In fact, the market price of modified starch is reported to be nearly three times higher than the price of native starch [6].

Starch can be modified by physical, chemical, enzymatic, or genetic methods, as well as by combinations of these approaches [5], [7], [8]. Among them, chemical modification is considered as a non-destructive approach because it preserves the starch polymer backbone. At the same time, hydroxyl groups serve as reactive sites for the introduction of functional substituents [3]. One of the most widely applied chemical modification methods is cationization. Cationic starch has found extensive applications in the paper and textile industries, oil drilling operations, surface coating formulations, personal care products, adhesive formulations, and wastewater treatment. It is particularly employed as a flocculating agent for coal suspensions and various other contaminants, while its applications have recently expanded to pharmaceutical drug delivery systems, tissue engineering, and biomedicine [9], [10], [11], [12], [13], [14], [15], [16], [17].

Starch cationization can be performed by wet, semi-dry, or reactive extrusion processes [18], while more recent approaches involve microwave-assisted or ultrasound-assisted techniques [19]. Wet cationization may be carried out either under homogeneous conditions, typically using dimethyl sulfoxide (DMSO), or under heterogeneous conditions in aqueous or aqueous-alcoholic suspensions, most commonly containing methanol, ethanol, or isopropanol [20]. Reactions performed in aqueous media require the addition of salts, such as sodium sulfate, to prevent starch gelatinization, whereas cationization in aqueous-alcoholic systems avoids using gelatinization inhibitors [21], [22]. The most commonly used cationizing reagents are 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) and its reactive epoxide 2,3-epoxypropyltrimethylammonium chloride (EPTAC). In alkaline media, CHPTAC is converted into its reactive epoxide intermediate, which subsequently reacts with starch hydroxyl groups through an S_N2 substitution mechanism [18], [23].

Cationization improves several important functional properties of starch, including water absorption capacity, swelling power, solubility, emulsion stability, resistance to syneresis, and stability under alkaline conditions [24], [25]. The functional characteristics of the resulting cationic starch are influenced by several factors, including the botanical source of starch, the amylose/amylopectin ratio, the type of cationizing reagent, and the reaction conditions [26].

Numerous studies have investigated the cationization of different starches under various reaction conditions. In his works, Kweon [22], [27], [28] performed the cationization process in an aqueous-alcohol medium, examining normal corn and waxy corn starch, then barley starch and pea starch. The author determined the degree of substitution (DS) and the efficiency of the cationization reaction (RE), varying the concentration of alcohol in the aqueous-alcohol medium, the reaction time, the temperature of the reaction, as well as the concentration of CHPTAC. He also examined how cationization affects the swelling power and solubility of starch. Bhirud [20], similarly to Kweon, also investigated the cationization of native starches from various sources (barley, waxy corn, potato, wheat, waxy barley, and pea). The study examined several reaction parameters, including the starch-to-aqueous phase ratio (1:1 and 3:1 (w/w)), the presence or absence of Na_2SO_4 as a gelatinization inhibitor, CHPTAC concentration (0.05 and 0.10 mol/L), and

reaction time (30-180 min). Different types of alcohol (ethanol, isopropanol, and methanol) at various concentrations (15%, 25%, 35%, 45%, 55%, 65%, 75%, and 84%) were also investigated to provide an aqueous-alcoholic reaction medium. The effects of these parameters on the resulting DS were evaluated. Almonaityte [29] investigated the cationization of potato starch using a semi-dry method with CHPTAC, both in the presence and absence of CaO as an additive. The study focused on the effect of the reaction mixture composition (anhydroglucose unit (AGU):CHPTAC:NaOH:CaO) on the DS and RE, as well as the subsequent effects on various properties of cationic starch, including the solubility index. Md Nasir [30] investigated the effects of CHPTAC concentration, NaOH concentration, and reaction time on DS and optimized the reaction conditions using response surface methodology (RSM). Rahayu [31] investigated cassava starch as a raw material for cationic starch production, examining the effect of reaction temperature (50-90 °C) on DS and RE. Karić [8], on the other hand, investigated starch cationization primarily without the use of organic solvents, focusing on the effects of reaction conditions, including temperature, cationizing reagent concentration, the presence and concentration of a catalyst, and the presence of a natural plasticizer, on material properties, including swelling capacity and solubility. Liu [32] investigated starch cationization to improve its solubility under medium and low temperatures, whereas Lappalainen [23] employed this modification to enable the use of starch as a biomass-based alternative to oil-based chemicals. Lekniute-Kyzike [14] conducted a comprehensive investigation into the effects of starch cationization on its pasting and swelling properties. Kuo [33], [34], similarly to other researchers, performed starch cationization using CHPTAC, determined the DS and RE, and investigated the effects of reaction conditions on the physicochemical properties of the resulting products. Different reaction media and methods for the production of highly substituted cationic starch were investigated by Heinze [21]. Cationization was carried out in an aqueous solution, under homogeneous conditions in DMSO, and under fully heterogeneous conditions in an ethanol-water mixture. Various types of native starch were examined, along with the effects of reaction conditions, such as the CHPTAC/AGU molar ratio and NaOH concentration, on reaction yield and efficiency.

In this study, the effect of cationization on DS and RE, and on the functional properties of cationic wheat starch, primarily swelling power, water absorption capacity, and solubility, was investigated in comparison with native wheat starch. Aqueous-alcoholic medium was selected for the synthesis to prevent starch gelatinization during the reaction. The synthesis parameters varied were the molar ratio of CHPTAC to AGU of starch (0.08-0.23) and reaction time (30-150 min). Cationization of native starch should improve swelling power, water absorption capacity and solubility.

METHODOLOGY SECTION

The experimental part of this study involved the synthesis of 20 samples of cationic starch (CS1–CS20), divided into four sets, with the synthesis conditions presented in Table 1. Cationization was confirmed by Fourier transform infrared (FTIR) spectroscopy based on the observed changes in the characteristic absorption bands. The degree of substitution, cationization reaction efficiency, and functional properties, including swelling power (SP), water absorption capacity (WAC), and solubility (SOL), were determined for each synthesized sample.

Materials and Chemicals

Native wheat starch was supplied by *Fidelinka Skrob* (Subotica, Serbia), a manufacturer of starch and starch-derived products.

The cationizing reagent CHPTAC, was purchased from *Sigma-Aldrich* (Merck Group, Darmstadt, Germany) as a 60% (w/w) aqueous solution. Isopropanol, sodium hydroxide (NaOH), acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl) were obtained from *Lach-Ner* (Neratovice, Czech Republic). At the same time, copper sulfate ($CuSO_4$) was purchased from *Merck*

(Darmstadt, Germany) and potassium sulfate (K_2SO_4) was purchased from *Centrohem* (Stara Pazova, Serbia).

Synthesis of Cationic Starch

Cationic starch was synthesized via a two-step process, following methods described by Stojanović [35] and Bhirud [20], with minor modifications. In the first step, native wheat starch was alkalized with NaOH by stirring in a three-necked round-bottom flask at room temperature for 20 minutes, using an aqueous-alcoholic reaction medium containing 75% (v/v) isopropanol, with a starch-to-liquid phase ratio of 1:1 (w/w) [20]. In the second step, etherification (cationization) of the starch was carried out at 50 °C, maintained using a water bath. The cationizing reagent was added dropwise to the reaction mixture. The reaction time was measured from the moment all the CHPTAC had been added to the mixture, while the amount of reagent varied depending on the desired CHPTAC/AGU molar ratio. The reaction times and CHPTAC/AGU molar ratios employed for each synthesized sample are presented in Table 1. The CHPTAC/AGU molar ratio was calculated as the ratio of the amount of CHPTAC to the amount of AGU in the native starch. For calculation purposes, the molar mass of the AGU was taken as 162 g/mol, corresponding to the repeating unit ($C_6H_{10}O_5$) in the starch polymer chain [29]. After completion of the cationization reaction, the reaction mixture was cooled and neutralized with acetic acid. The modified starch was precipitated and washed with isopropanol. The precipitated cationic starch was separated by filtration, and the resulting filter cake was first air-dried and then dried in an oven at 105 °C until constant mass was achieved. Finally, the dried starch samples were ground, transferred into glass containers, and stored until further characterization.

Table 1. Sample designation and starch cationization reaction conditions

Cationic starch sample designation	CS1	CS2	CS3	CS4	CS5	Set I
Reaction time (min)	30	60	90	120	150	
CHPTAC/AGU molar ratio	0.08	0.08	0.08	0.08	0.08	
Cationic starch sample designation	CS6	CS7	CS8	CS9	CS10	Set II
Reaction time (min)	30	60	90	120	150	
CHPTAC/AGU molar ratio	0.13	0.13	0.13	0.13	0.13	
Cationic starch sample designation	CS11	CS12	CS13	CS14	CS15	Set III
Reaction time (min)	30	60	90	120	150	
CHPTAC/AGU molar ratio	0.18	0.18	0.18	0.18	0.18	
Cationic starch sample designation	CS16	CS17	CS18	CS19	CS20	Set IV
Reaction time (min)	30	60	90	120	150	
CHPTAC/AGU molar ratio	0.23	0.23	0.23	0.23	0.23	

FTIR Analysis

The synthesized cationic starch samples (CS1–CS20) were characterized by Fourier-transform infrared (FTIR) spectroscopy using a *Bruker Tensor 27* spectrometer manufactured by *Bruker Optik GmbH*, over the spectral range of 400-4000 cm^{-1}, at a spectral resolution of 4 cm^{-1}, with 16 scans per sample. A background spectrum was recorded prior to sample measurement. Sample CS19, which exhibited the most prominent characteristic peaks, was selected for the

identification of characteristic absorption bands and to demonstrate successful starch cationization. In addition to the cationic starch samples, native starch and CHPTAC were also characterized by FTIR spectroscopy.

Determination of the Degree of Substitution and Cationization Reaction Efficiency

The degree of substitution of cationic starch was determined indirectly from the nitrogen content measured by the Kjeldahl method [36], following the procedures reported by Lekniute-Kyzike [15] and Almonaityte [29]. The DS values were calculated using Equation (1), as proposed by Heinze [21] and Rahayu [31]. In equation (1), N represents the nitrogen content determined by the Kjeldahl method (%), 162 is the molecular weight of the AGU (g/mol), 1400 corresponds to the molecular weight of nitrogen multiplied by 100, and 151.5 is the molecular weight of the attached cationic substituent (g/mol).

The cationization reaction efficiency was calculated using Equation (2), where n represents the amount of CHPTAC (mol) used for the cationization of one mole of AGU [29,37].

$$DS = \frac{162 \cdot N}{1400 - 151{,}5 \cdot N} \tag{1}$$

$$RE = \frac{DS}{n} \cdot 100\ [\%] \tag{2}$$

Determination of Swelling Power, Water Absorption Capacity, and Solubility

Water absorption is one of the most important functional properties of starch, reflecting the extent of starch-water interactions. Since numerous experimental approaches have been proposed for its evaluation, selecting an appropriate method is essential for obtaining meaningful results [38]. Different studies have reported water-related properties in terms of swelling power, water binding capacity, water absorption index, or water absorption capacity, with variations in both definitions and calculation methods [39], [40], [41], [42], [43], [44]. The principal distinction among these methods lies in whether the water-soluble fraction of starch is considered during the calculations.

In the present study, SP, WAC, and SOL of both native and cationic starch samples were determined using modified procedures described by Lekniute-Kyzike [14] and Han [45]. Starch suspensions containing 2% (w/w) of starch (0.4 g of sample (M_0) in 20 mL distilled water) were prepared in centrifuge tubes. The suspensions were mixed using a vortex mixer at 1800 rpm for 1 min, followed by hydration at room temperature for 30 min. Subsequently, the samples were centrifuged at 4000 rpm for 15 min. After centrifugation, the supernatant was carefully decanted into a glass dish, dried at 105 °C to constant mass, and weighed (M_2). The swollen starch sediment was immediately weighed (M_1). The complete experimental procedure is illustrated in Figure 1. SP, WAC, and SOL were calculated using Equations (3), (4), and (5), respectively. The definitions of each parameter are provided below. All measurements were performed in duplicate, and the results are expressed as mean ± standard deviation.

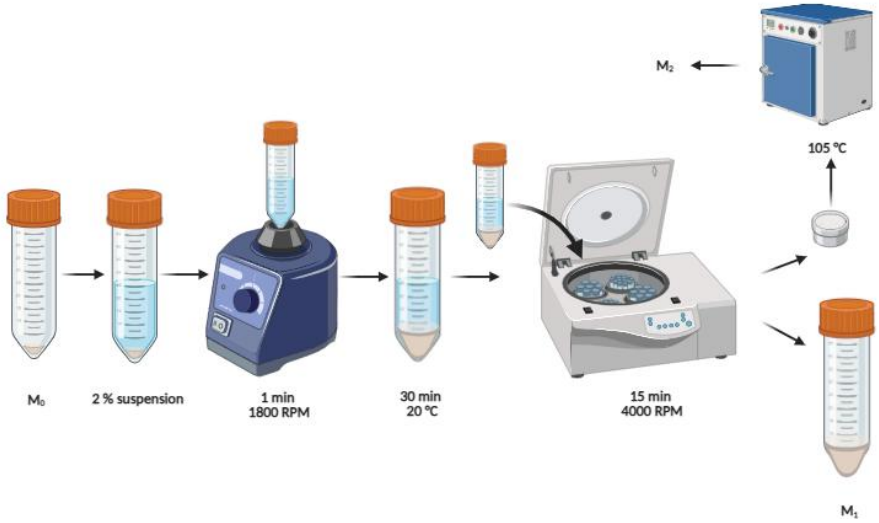

Figure 1. Determination of swelling power, water absorption capacity, and solubility

Swelling Power (SP)

SP is defined as the ratio between the mass of swollen starch granules (g) and their dry mass (g). It represents the mass of hydrated starch granules (M_1) relative to the dry mass of the insoluble starch fraction ($M_0 - M_2$) [43], [44] and was calculated using Equation (3) [45].

$$SP = \frac{M_1}{M_0 - M_2} \left[\frac{g}{g}\right] \quad (3)$$

M_0 - initial dry mass of the starch sample [g]
M_1 - mass of the swollen starch sediment obtained after centrifugation [g]
M_2 - mass of the dried soluble starch fraction recovered from the supernatant after centrifugation [g]

Water Absorption Capacity (WAC)

WAC represents the amount of water absorbed (g) per gram of the water-insoluble dry starch fraction and was calculated according to the Equation (4), proposed by Han [45].

$$WAC = \frac{M_1 - (M_0 - M_2)}{M_0 - M_2} \left[\frac{g}{g}\right] \quad (4)$$

M_0 - initial dry mass of the starch sample [g]
M_1 - mass of the swollen starch sediment obtained after centrifugation [g]
M_2 - mass of the dried soluble starch fraction recovered from the supernatant after centrifugation [g]

Solubility (SOL)

SOL is defined as the percentage of dry soluble matter present in the supernatant relative to the total dry mass of the starch sample [14], [43], [44], [45] and was calculated according to Equation (5).

$$SOL = \frac{M_2}{M_0} \times 100\ [\%] \quad (5)$$

M_0 - initial dry mass of the starch sample [g]
M_2 - mass of the dried soluble starch fraction recovered from the supernatant after centrifugation [g]

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

Cationic starch can be obtained by reacting native starch with CHPTAC under alkaline conditions and elevated temperature due to the rapid conversion of CHPTAC into an epoxide intermediate formed in situ, followed by a reaction between the hydroxyl groups of starch and the epoxide ring [8], [18]. This is shown and confirmed by the FTIR spectra obtained in Figure 2. The most convincing evidence can be obtained by comparing the FTIR spectra of native starch before modification (NS), the synthesized cationic starch (CS), and the cationizing reagent used for modification (CHPTAC).

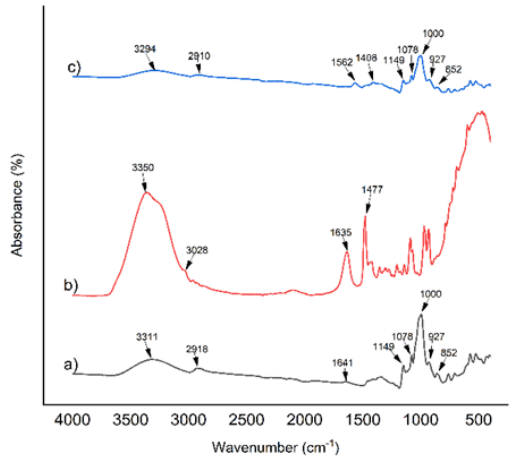

Figure 2. FTIR spectra of a) native wheat starch (NS), b) CHPTAC, and c) cationic starch (CS19)

Native starch (black spectrum line in Figure 2) exhibits several characteristic peaks. The broad absorption band at 3311 cm^{-1} corresponds to O-H stretching vibrations, whereas the band at 2918 cm^{-1} is also attributed to stretching vibrations, in this case of C-H bonds within methylene groups [37]. C-O-C bonds produce signals in several different wavenumber ranges depending on is it a starch triplet that builds glycosidic bonds within the amylose and amylopectin chains, resulting in peaks at 1149 cm^{-1} and 927 cm^{-1}, or the C-O-C bond within the pyranose ring, represented by peaks at 1078 cm^{-1} and 852 cm^{-1}. The peak at 1000 cm^{-1} is attributed to C-OH bond vibrations [46].

The peaks at 1641 cm^{-1} and 1562 cm^{-1} indicate the presence of bound water molecules in native and modified cationic starch, respectively, due to their hygroscopic nature. A corresponding peak is also observed in CHPTAC at 1635 cm^{-1}, since the reagent is supplied as a 60% (w/w) aqueous solution. This peak is the most intense compared with those observed for native and cationic starch, which were dried before FTIR analysis, resulting in lower absorption-band intensities [8], [30].

The cationizing reagent, CHPTAC (red spectrum line in Figure 2), exhibits several peaks characteristic of its chemical structure. The stretching and deformation vibrations of methyl groups within the quaternary ammonium group, $(CH_3)_3N^+$ appear at 3028 cm^{-1} and 1477 cm^{-1} [46], [47].

Cationic starch (blue spectrum line in Figure 2) retains most of the peaks characteristic of native starch, although some are slightly shifted, e.g., from 3311 cm^{-1} to 3294 cm^{-1} and from 2918 cm^{-1} to 2910 cm^{-1}, while others exhibit reduced intensity, such as the peak at 1000 cm^{-1}. This primarily indicates that the main polysaccharide backbone of starch remained preserved during modification [17]. The main difference between the spectra of native and cationic starch is the appearance of characteristic peaks associated with cationic starch synthesized using CHPTAC. In particular, a peak appears at 1408 cm^{-1}, which, as previously explained for the FTIR spectrum of CHPTAC, is attributed to vibrations of methyl groups within the quaternary ammonium moieties. This peak provides clear evidence that the cationic moiety was incorporated into the starch backbone, indicating the successful synthesis of cationic starch [29], [46].

Effects of reaction conditions on the DS and RE of cationic starches

The degree of substitution of cationic starch can be varied depending on several factors, including the molar ratio of the cationizing reagent to the anhydroglucose unit of starch, the NaOH/cationizing reagent molar ratio, the volume and type of reaction medium, reaction temperature and time, and the type of native starch [18], [20]. In the present study, the following reaction conditions were kept constant: pH=12, selected to provide adequate epoxide stability while maintaining a sufficiently high pH for its formation from CHPTAC, a temperature of 50 °C, which proved to be optimal, a starch-to-liquid-phase ratio of 1:1 (w/w), which gives a high RE [22], [28], and a NaOH/CHPTAC molar ratio of 2:1. The reaction was carried out in a 75% (v/v) isopropanol solution, although 65% (v/v) proved to be more effective, 75% (v/v) was chosen because in preliminary studies it showed less swelling tendency of starch [20]. The synthesis parameters investigated in this study were the CHPTAC/AGU molar ratio and reaction time, and the obtained results are presented in Table 2.

DS and RE as a function of CHPTAC/AGU molar ratio

The degree of substitution can be readily adjusted by varying the molar ratio of the cationizing agent to the anhydroglucose unit of starch [26]. As can be observed from the graphs in Figure 3, increasing the amount of cationizing reagent resulted in an increase in DS, which can be explained by the greater availability of reagent molecules in the vicinity of the starch chains [18]. In other words, the higher CHPTAC concentration may have enhanced its effective reaction at the activated sites on starch [32]. For example, comparison of CS4 and CS9 shows that increasing the molar ratio from 0.08 to 0.13, at a reaction time of 2 h, resulted in 1.5 times increase in DS. This indicates that, at the same reaction time, increasing the amount of CHPTAC can produce cationic starch with a substantially higher DS, thereby allowing the reaction time to be shortened. An increase in both DS and RE with increasing CHPTAC/AGU molar ratio during the cationization of wheat starch in an aqueous-alcoholic medium using CHPTAC was also reported by Heinze [21]. However, a slight decrease in RE was observed in the present study when the CHPTAC/AGU molar ratio increased from 0.18 to 0.23, as you can see in Figure 3 on each graph. This may be attributed to the increased number of cationic groups on the starch, which could reduce reaction efficiency due to electrostatic repulsion between groups carrying the same charge. This, in turn, may affect the utilization of CHPTAC and the reactive epoxide formed from it [32].

Based on the obtained results, a CHPTAC/AGU molar ratio of 0.18 was identified as optimal, because it gives approximately equal values of DS while achieving the highest RE values. More specifically, for each reaction time investigated (30, 60, 90, 120, and 150 min), the CHPTAC/AGU molar ratio of 0.18

resulted in the highest reaction efficiency percentages compared with cationization performed at molar ratios of 0.08, 0.13, and 0.23. Furthermore, the advantage of using a molar ratio of 0.18 rather than 0.23 lies in the lower consumption of the cationizing reagent.

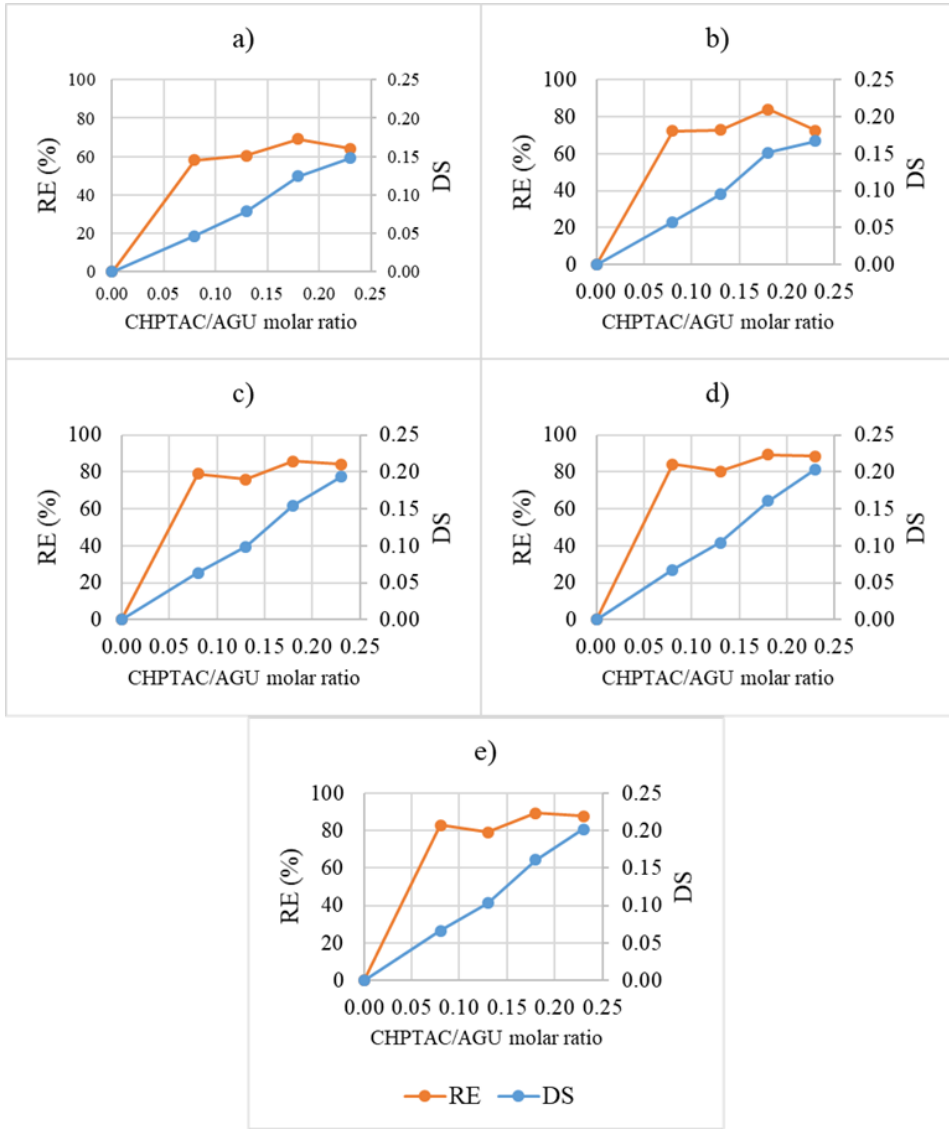

Figure 3. Effects of CHPTAC/AGU molar ratio on cationization at reaction times of: a) 30 min, b) 60 min, c) 90 min, d) 120 min, and e) 150 min. The data points at a CHPTAC/AGU molar ratio of 0 represent native starch (DS = 0 and RE = 0)

DS and RE as a function of reaction time

Figure 4 shows an increase in DS with increasing reaction time, from 30 to 120 min, at a constant CHPTAC/AGU molar ratio. For example, for cationic starch synthesized at a CHPTAC/AGU molar ratio of 0.18, DS increased by approximately 30% when the reaction time was increased from 30 to 120 min, whereas for starch synthesized at a CHPTAC/AGU molar ratio of 0.08, the increase was as high as 45% over the same reaction-time interval. An increase in the DS

of wheat starch in an aqueous-alcoholic medium was also observed by Bhirud [20], with the increase being more pronounced up to 3 h, after which the change in DS became slower. The graphs presented by Bhirud closely resemble those shown in Figure 4. However, in the present study, a slight decrease or nearly constant DS and RE values were observed at each CHPTAC/AGU molar ratio when the reaction time was extended from 2 to 2.5 h. Based on these results, it can be concluded that 2 h was the most appropriate reaction time for the synthesis of cationic starch under the conditions applied in this study, which is also consistent with the findings of Wang [48]. This behavior may be attributed to a decrease in the amount of CHPTAC, or more precisely, the reactive epoxide, after 2 h of reaction. Previous studies have also reported that DS, and consequently RE, initially increase with reaction time, whereas longer reaction times do not result in significant further reaction progress and may instead lead to deetherification of the polysaccharide, thereby reducing DS [18]. This is likely the case in this study as well. Furthermore, as the reaction proceeded, the number of available reactive sites on the starch gradually decreased, resulting in lower utilization efficiency of the etherifying agent, i.e., the cationizing reagent [32]. Another possible reason for the slight decrease in DS and RE with increasing cationization time is the stability of the formed epoxide. Namely, the epoxide may undergo a secondary reaction leading to diol formation. Epoxide degradation depends on the reaction time, and the resulting diols are unable to react with starch, thereby reducing the reaction efficiency [18].

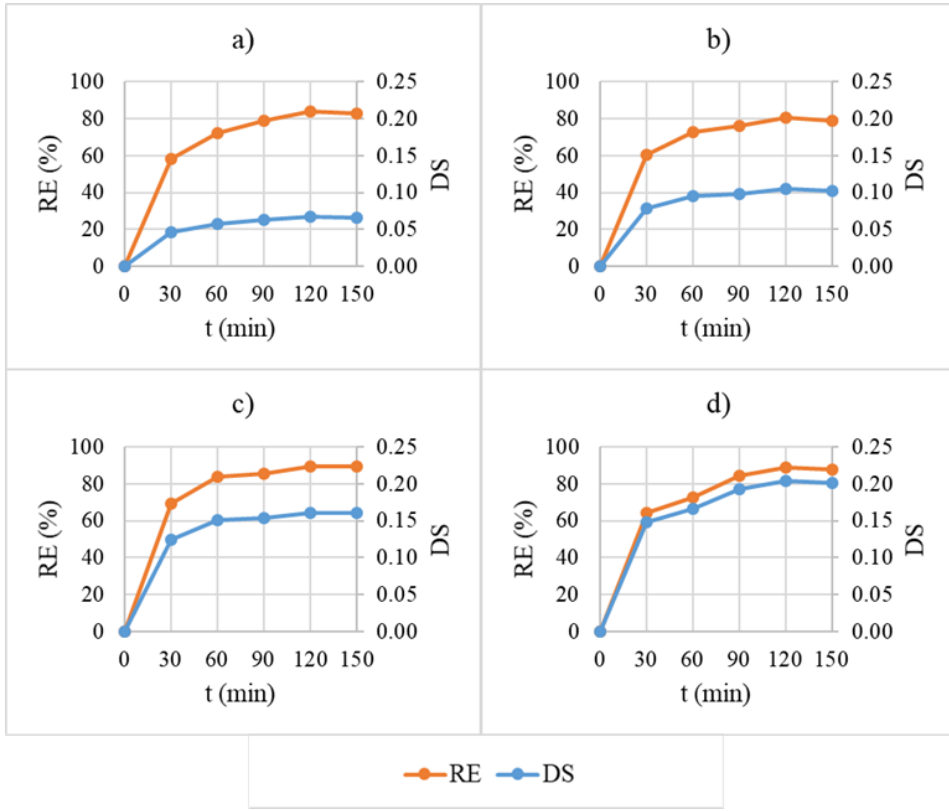

Figure 4. Effects of reaction time on cationization at CHPTAC/AGU molar ratios of: a) 0.08, b) 0.13, c) 0.18, and d) 0.23. The data points at a reaction time of 0 min represent native starch (DS = 0 and RE = 0)

SP, WAC and SOL of cationic starch

The swelling power obtained for native wheat starch was very low, amounting to only 2.37 g/g. This can be explained by the ability of amylose to form amylose-lipid complexes, which inhibit swelling in water by entangling amylopectin molecules. Wheat starch, along with corn and rice starches, has a relatively high fat content, reported by Schmidt [39] to be approximately 0.47%, supporting the possibility of amylose-lipid complex formation [49]. Table 2 shows an increase in SP for the synthesized cationic starch samples compared with native starch. Water absorption capacity, and consequently swelling power, is influenced by the interaction forces between starch components, where weaker interactions result in a higher capacity [50]. In the present case, the cationic groups apparently facilitated the opening of starch granules, reduced interactions between starch components, and promoted water penetration [27], thereby increasing the SP and WAC of cationic starch samples compared to native starch.

Table 2. Characteristics and properties of native starch (NS) and cationic starch (CS)

Sample designation	DS	RE (%)	SP (g/g)	WAC (g/g)	SOL (%)
NS	0.0000	0.00	2.37±0.07	1.37±0.07	1.66±0.13
CS1	0.0465	58.10	4.72±0.35	3.72±0.35	14.00±0.69
CS2	0.0578	72.27	5.85±0.17	4.85±0.17	15.15±1.89
CS3	0.0632	78.97	8.07±0.28	7.07±0.28	12.51±0.39
CS4	0.0673	84.08	9.87±0.36	8.87±0.36	12.15±0.26
CS5	0.0665	83.07	7.98±0.26	6.98±0.26	14.73±0.46
CS6	0.0786	60.43	13.51±0.46	12.51±0.46	17.25±5.92
CS7	0.0948	72.95	13.63±0.08	12.63±0.08	18.80±0.17
CS8	0.0987	75.92	14.13±0.52	13.13±0.52	21.10±1.01
CS9	0.1046	80.50	27.54±0.93	26.54±0.93	16.74±0.35
CS10	0.1030	79.24	29.45±0.96	28.45±0.96	24.74±3.27
CS11	0.1245	69.18	16.77±1.35	15.77±1.35	22.21±0.66
CS12	0.1514	84.11	26.96±0.53	25.96±0.53	24.81±0.13
CS13	0.1544	85.79	33.53±0.71	32.53±0.71	20.81±0.52
CS14	0.1610	89.45	36.73±2.28	35.73±2.28	22.28±1.24
CS15	0.1607	89.29	39.05±2.15	38.05±2.15	23.78±1.42
CS16	0.1475	64.13	18.22±0.94	17.22±0.94	20.22±1.65
CS17	0.1669	72.56	17.13±0.12	16.13±0.12	24.61±0.24
CS18	0.1936	84.17	31.64±1.32	30.64±1.32	21.26±1.18
CS19	0.2040	88.68	35.13±1.18	34.13±1.18	18.63±1.65
CS20	0.2019	87.77	35.96±0.97	34.96±0.97	16.14±0.48

SP of cationic starch samples increased with increasing amount of cationizing reagent used in the reaction until a critical point in the modification of the starch granules was reached [29]. At a constant reaction time, this occurred at a CHPTAC/AGU molar ratio of 0.18 (Figure 5a, left). For all samples synthesized at a CHPTAC/AGU molar ratio of 0.18 (CS12-CS15), except for the sample synthesized for 30 min (CS11), the experimentally determined DS values ranged from 0.151 to 0.161 (Table 2). This indicates

that, under the other cationization conditions applied in this study, the achieved DS range was the most favorable for increasing SP. CHPTAC/AGU molar ratio of 0.18 also proved to be the most suitable when investigating the effect of reaction time (Figure 5a, right). It should also be noted that the highest RE of 89.45% was achieved at this molar ratio for sample CS14 (Table 2).

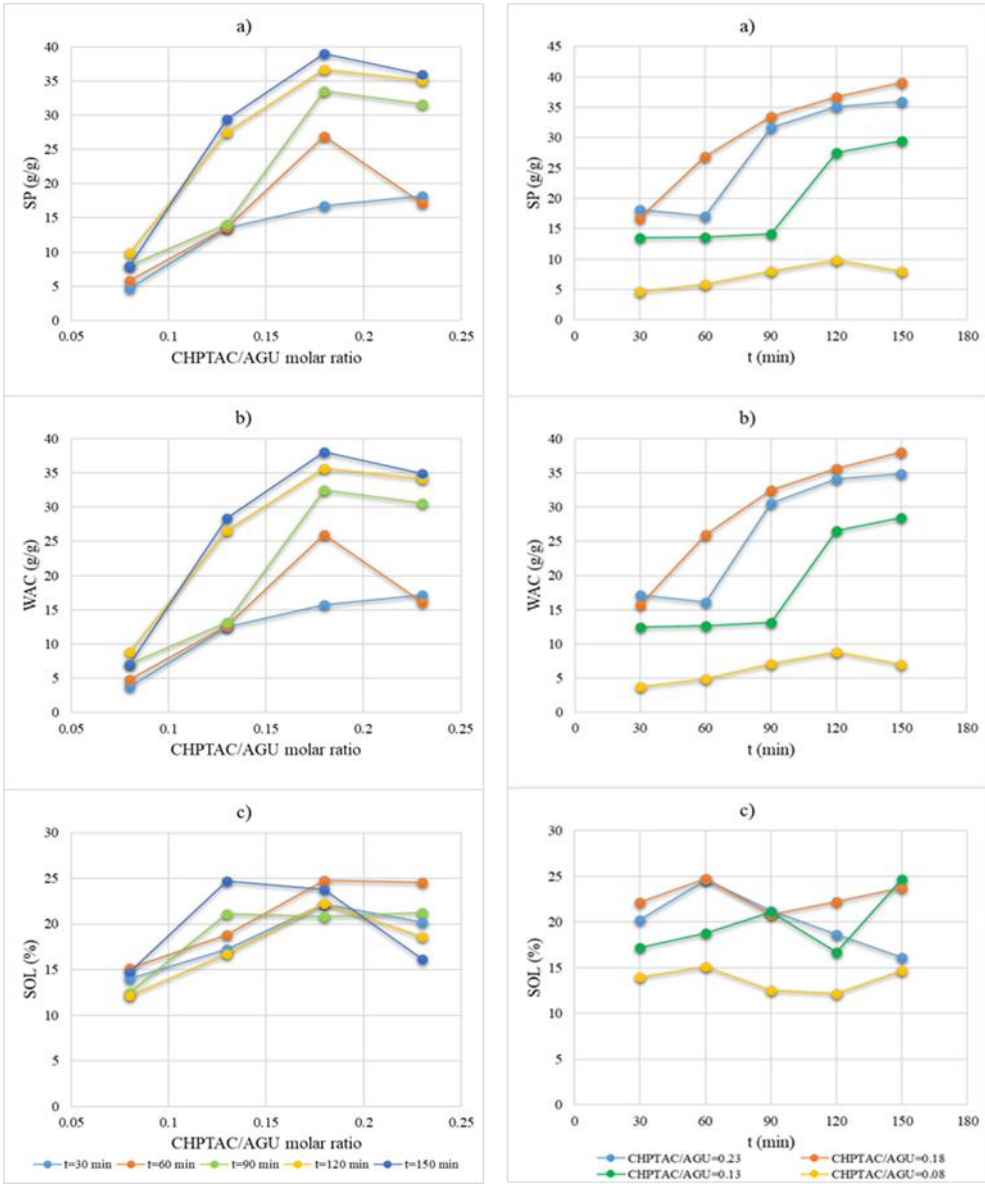

Figure 5. Effects of CHPTAC/AGU molar ratio (left) and reaction time (right) on a) SP, b) WAC and c) SOL of cationic starch

When starch is added to water, water molecules pass through the surface of the starch granules into their interior, continue to penetrate, and eventually reach the amorphous regions of the starch granules, thereby hydrating them. As a result, the starch granules gradually expand and increase in volume. The water-absorbing behavior of

starches acts as a pre-swelling stage [38]. For this reason, the WAC values obtained for all cationic starch samples and native wheat starch followed the same trend as SP, which is consistent with the findings of Han [45]. But for comparison, it is useful to consider the results reported by Zhang [42], who determined the water absorption capacity of native wheat starch at room temperature after 30 minutes without stirring, which represents practically the same conditions as those used in the present study. The WAC value reported for native wheat starch, expressed as the mass of the wet sediment relative to the total dry mass of the starch sample, was approximately 1.00 g/g, which agrees reasonably well with the experimentally determined value obtained in this study, which amounts to 1.37 g/g (Table 2). It is also important to note that, although Zhang [42] expressed WAC relative to the total sample mass, i.e., both the water-soluble and water-insoluble fractions, whereas in the present study it was expressed relative to the water-insoluble starch fraction, the values can be compared as long as starch solubility is low, which is the case here [39].

The solubility of native starch obtained in this study was 1.66%. Very low solubility, i.e., the fact that wheat starch is practically insoluble in water at 25 °C, was also reported by Schmidt [39]. According to this author, the low solubility of native wheat starch, as well as cereal starches in general, is associated with their relatively high fat content. This was also mentioned when discussing the low SP of wheat starch. In addition, at higher lipid contents an insoluble layer of pure lipids and surrounding starch granules, thereby preventing water penetration and consequently reducing solubility [49]. However, starch cationization can contribute to an increase in its SOL (Table 2), as also reported in studies [29], [51], although no consistent pattern in the effect of cationization on the solubility of cationic starch was observed [27]. More specifically, no clear trend was observed regarding the effects of the CHPTAC/AGU molar ratio and reaction time on SOL (Figure 5c, right and left). Although there is no observed growth trend, an increase in SOL occurs because cationic groups introduced into the starch structure can substantially disrupt or reduce the crystalline regions of starch, thereby increasing its solubility [1].

Regarding the relationship between SP and SOL, at room temperature, as in the present study, as well as at all temperatures below the gelatinization temperature of wheat starch (45-50 °C), swelling can occur without dissolution [52]. This may explain why some cationic starch samples with very high SP values, such as CS15 (39.05 g/g), CS14 (36.73 g/g), CS20 (35.96 g/g), CS19 (35.13 g/g), and CS13 (33.53 g/g), did not exhibit a proportional increase in SOL, with corresponding values of 23.78%, 22.28%, 16.14%, 18.63%, and 20.81%, respectively.

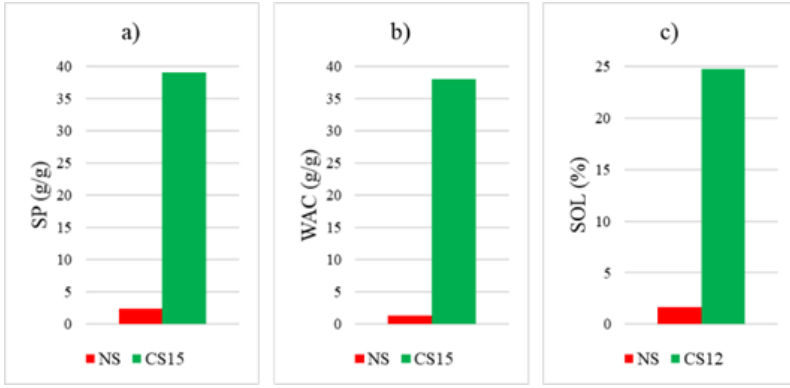

Figure 6. Comparison of a) SP, b) WAC and c) SOL of NS and CS samples with the highest value for each functional property

The maximum increases in SP (from 2.37 g/g to 39.05 g/g) and WAC (from 1.37 g/g to 38.05 g/g) shown on Figure 6a and b were achieved for sample CS15, synthesized for 150 min at a CHPTAC/AGU molar ratio of 0.18, whereas the highest solubility was obtained for sample CS12, which exhibited a 15-foldhigher solubility than NS (Figure 6c).

CONCLUSION

The results of this study demonstrated that the cationization reaction time and the CHPTAC/AGU molar ratio influenced the functional properties of cationic wheat starch, particularly its swelling power, water absorption capacity, and solubility. In general, increasing the CHPTAC/AGU molar ratio and prolonging the reaction time led to higher degrees of substitution, which were generally associated with increased swelling power and water absorption capacity. However, no consistent direct relationship was observed between the cationization conditions and solubility, although the solubility of all modified starch samples was higher than that of native starch. A CHPTAC/AGU molar ratio of 0.18 was identified as the most favorable among the investigated ratios, providing the highest reaction efficiency values at each reaction time while yielding comparable degrees of substitution. This finding indicates that satisfactory functional properties can be achieved with lower consumption of the cationizing reagent than at a molar ratio of 0.23. Increasing the reaction time up to 120 min resulted in increases in both the degree of substitution and the cationization reaction efficiency, which were accompanied by increases in swelling power and water absorption capacity. Extending the reaction time from 120 to 150 min did not result in further increases in either the degree of substitution or reaction efficiency and had only a slight additional effect on swelling power and water absorption capacity. Therefore, a reaction time of 120 min was considered the most appropriate for cationic starch synthesis under the conditions investigated in this study. Depending on the intended application, cationic starch with specific swelling power and solubility characteristics can be obtained by adjusting the reaction conditions while limiting cationizing reagent consumption and reaction time. Furthermore, the use of an aqueous-alcoholic reaction medium helped prevent premature starch gelatinization, facilitating the cationization process.

DECLARATIONS OF INTEREST STATEMENT

The authors affirm that there are no conflicts of interest to declare in relation to the research presented in this paper.

LITERATURE

1. Xie, Q., Fan, B., Tao, R., Wang, F., & Sun, Y. (2025). A Comprehensive Review of Starch: Structure, Properties, Chemical Modification, and Application in Food Preservation. *Food Frontiers, 6*(4), 1645–1657. https://doi.org/10.1002/fft2.70040
2. Ondaral, S., Kurtuluş, O., Öztürk, G., Ergün, M., & Yakın, İ. (2018). Aldehyde Starch Complexes: Adsorption on Cellulose Model Film and Performance as a Strength Additive for Papermaking. *BioResources, 13*(2), 4470-4483. https://doi.org/10.15376/biores.13.2.4470-4483
3. Compart, J., Singh, A., Fettke, J., & Apriyanto, A. (2023). Customizing Starch Properties: A Review of Starch Modifications and Their Applications. *Polymers, 15*(16), 3491. https://doi.org/10.3390/polym15163491
4. Sun, J., Fang, T.-S., Chen, Y.-X., Tsai, Y.-C., Liu, Y.-X., Chen, C.-Y., Su, C.-Y., & Fang, H.-W. (2023). Improving the Physical Properties of Starch-Based Powders for Potential Anti-Adhesion Applications. *Polymers, 15*(24), 4702. https://doi.org/10.3390/polym15244702
5. Suri, S., & Singh, A. (2023). Modification of starch by novel and traditional ways: Influence on the structure and functional properties. *Sustainable Food Technology, 1*(3), 348–362. https://doi.org/10.1039/D2FB00043A
6. Adewale, P., Yancheshmeh, M. S., & Lam, E. (2022). Starch modification for non-food, industrial applications: Market intelligence and critical review. *Carbohydrate Polymers, 291*(1), 119590.

https://doi.org/10.1016/j.carbpol.2022.119590

7. Falua, K. J., Pokharel, A., Babaei-Ghazvini, A., Ai, Y., & Acharya, B. (2022). Valorization of Starch to Biobased Materials: A Review. *Polymers, 14*(11), 2215. https://doi.org/10.3390/polym14112215
8. Karić, N., Stanišić, T., Đolić, M., Vukčević, M., Ristić, M., Perić-Grujić, A., Marinković, A., & Trivuna, K. (2021). Synthesis and Characterization of Cationic Starch for Application in the Wastewater Treatment. *Proceedings of the 34th International Congress on Process Industry*, *34*(1), 49–54. https://doi.org/10.24094/ptk.021.34.1.49
9. Pal, S., Mal, D., & Singh, R. P. (2005). Cationic starch: An effective flocculating agent. *Carbohydrate Polymers, 59*(4), 417–423. https://doi.org/10.1016/j.carbpol.2004.06.047
10. Pal, S., Sen, G., Karmakar, N. C., Mal, D., & Singh, R. P. (2008). High performance flocculating agents based on cationic polysaccharides in relation to coal fine suspension. *Carbohydrate Polymers, 74*(3), 590–596. https://doi.org/10.1016/j.carbpol.2008.04.007
11. Patra, A. S., Patra, P., Chowdhury, S., Mukherjee, A. K., & Pal, S. (2020). Cationically functionalized amylopectin as an efficient flocculant for treatment of coal suspension. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 586*, 124229. https://doi.org/10.1016/j.colsurfa.2019.124229
12. Zhang, S., Ma, H., Gao, N., & Qiao, Y. (2025). Enhanced flocculation performance and coal slurry water by using starch-based flocculant with rich charges and its flocculation mechanism. *Journal of Environmental Management, 381*, 125112. https://doi.org/10.1016/j.jenvman.2025.125112
13. Khachan, M. M., Bhatia, S. K., Bader, R. A., Cetin, D., & Ramarao, B. V. (2014). Cationic starch flocculants as an alternative to synthetic polymers in geotextile tube dewatering. *Geosynthetics International, 21*(2), 119–136. https://doi.org/10.1680/gein.14.00003
14. Lekniute-Kyzike, E., Bendoraitiene, J., Danilovas, P. P., & Zemaitaitis, A. (2016). A novel way to obtain effective cationic starch flocculants. *Desalination and Water Treatment, 57*(50), 23728–23738. https://doi.org/10.1080/19443994.2016.1138892
15. Lekniute-Kyzike, E., Bendoraitiene, J., Navikaite-Snipaitiene, V., Peciulyte, L., & Rutkaite, R. (2023). Production of Cationic Starch-Based Flocculants and Their Application in Thickening and Dewatering of the Municipal Sewage Sludge. *Materials, 16*(7), 2621. https://doi.org/10.3390/ma16072621
16. Chatterjee, S., Mahmood, S., Hilles, A. R., Thomas, S., Roy, S., Provaznik, V., Romero, E. L., & Ghosal, K. (2023). Cationic starch: A functionalized polysaccharide based polymer for advancement of drug delivery and health care system - A review. *International Journal of Biological Macromolecules, 248*, 125757. https://doi.org/10.1016/j.ijbiomac.2023.125757
17. Posada-Vélez, M. C., Millán-Malo, B. M., Barrón-García, O. Y., Gaytán-Martínez, M., & Buitrón, G. (2026). The Reactive Extrusion Cationization of Starches as a Novel Physicochemical Surface Modification Method. *Biopolymers, 117*(3), e70093. https://doi.org/10.1002/bip.70093
18. Prado, H. J., & Matulewicz, M. C. (2014). Cationization of polysaccharides: A path to greener derivatives with many industrial applications. *European Polymer Journal, 52*, 53–75. https://doi.org/10.1016/j.eurpolymj.2013.12.011
19. Muñoz Prieto, E., Palacios Alquisira, J., & Rius Alonso, C. (2013). Microwave and ultrasound activation effect on cationization of corn and potato starches. *Ciencia en Desarrollo, 4*(1), 151-173 https://doi.org/10.19053/01217488.483
20. Bhirud, Prakash. R., Sosulski, Frank W., Tyler, Robert T., & Kweon, Meera. (1998).

Aqueous alcoholic aklaline process for cationization and anionization of normal, waxy, and high amylose starches from cereal, legume, tuber and root sources (Patent No. US5827372A). https://patents.google.com/patent/US5827372A

21. Heinze, T., Haack, V., Rensing, S. (2004). Starch Derivatives of High Degree of Functionalization. 7. Preparation of Cationic 2-Hydroxypropyltrimethylammonium Chloride. *Starch/Stärke, 56*(2), 288–296.
22. Kweon, M. R., Bhirud, P. R., & Saskatoon, F. W. S. (1996). An Aqueous Alcoholic-Alkaline Process for Cationization of Corn and Pea Starches. *Starch - Stärke, 48*(6), 214–220. https://doi.org/10.1002/star.19960480604
23. Lappalainen, K. (2015). *Modification of native and waste starch by depolymerization and cationization: Utilization of modified starch in binding of heavy metal ions from an aqueous solution* [Doctoral dissertation, University of Oulu]. OuluREPO. https://oulurepo.oulu.fi/handle/10024/3569524. Bertolini, A. (Ed.). (2009). *Starches: Characterization, properties, and applications*. CRC Press. https://doi.org/10.1201/9781420080247
25. Šubarić, D., Babić, J., & Ačkar, Đ. (2012). Modificiranje škroba radi proširenja primjene. *Radovi Zavoda Za Znanstveni i Umjetnički Rad u Požegi, 1*(2012), 247–258.
26. Chemelli, A., Gomernik, F., Thaler, F., Huber, A., Hirn, U., Bauer, W., & Spirk, S. (2020). Cationic starches in paper-based applications—A review on analytical methods. *Carbohydrate Polymers, 235*, 115964. https://doi.org/10.1016/j.carbpol.2020.115964
27. Kweon, M. R., Sosulski, F. W., & Han, H. S. (1997). Effect of Aqueous Ethanol Cationization on Functional Properties of Normal and Waxy Starches. *Starch - Stärke, 49*(5), 202–207. https://doi.org/10.1002/star.19970490507
28. Kweon, M. R., Sosulski, F. W., & Bhirud, P. R. (1997). Cationization of Waxy and Normal Corn and Barley Starches by an Aqueous Alcohol Process. *Starch - Stärke, 49*(2), 59–66. https://doi.org/10.1002/star.19970490205
29. Almonaityte, K., Bendoraitiene, J., Babelyte, M., Rosliuk, D., & Rutkaite, R. (2020). Structure and properties of cationic starches synthesized by using 3-chloro-2-hydroxypropyltrimethylammonium chloride. *International Journal of Biological Macromolecules, 164*, 2010–2017. https://doi.org/10.1016/j.ijbiomac.2020.08.089
30. Md Nasir, N., Abdulmalek, E., & Zainuddin, N. (2020). Preparation and Optimization of Water-Soluble Cationic Sago Starch with a High Degree of Substitution Using Response Surface Methodology. *Polymers, 12*(11), 2614. https://doi.org/10.3390/polym12112614
31. Rahayu, S., Wirjosentono, B., Oktavia, E., Zuhra, C. F., Pasaribu, K. M., Rahman Piliang, A. F., Sihotang, N. S., Tarigan, J. B., Siow, J., Goei, R., Tok, A. I. Y., & Gea, S. (2024). Temperature-dependent etherification of cassava starch with CHPTAC for cationic starch production. *Case Studies in Chemical and Environmental Engineering, 10*, 100779. https://doi.org/10.1016/j.cscee.2024.100779
32. Liu, M., Wu, Z., Meng, Y., Wang, Z., He, X., Gu, J., Zhang, Y., Wang, L., & Qin, X. (2023). Cationic etherification modification of corn starch and its sizing property. *Textile Research Journal, 93*(15–16), 3680–3691. https://doi.org/10.1177/00405175231163869
33. Kuo, W.-Y., & Lai, H.-M. (2007). Changes of property and morphology of cationic corn starches. *Carbohydrate Polymers, 69*(3), 544–553. https://doi.org/10.1016/j.carbpol.2007.01.012
34. Kuo, W.-Y., & Lai, H.-M. (2009). Effects of reaction conditions on the physicochemical properties of cationic starch studied by RSM. *Carbohydrate Polymers, 75*(4), 627–635.

https://doi.org/10.1016/j.carbpol.2008.09.004

35. Stojanović, P. Ž. (2010). *Sinteza i karakterizacija nekih derivata skroba rastvorivih u vodi*. [Doktorska disertacija, Univerzitet u Beogradu, Tehnološko-metalurški fakultet]. http://eteze.bg.ac.rs/application/showtheses?thesesId=1181
36. International Organization for Standardization. (1978). ISO 3188:1978 Starches and derived products - Determination of nitrogen content by the Kjeldahl method - Titrimetric method.
37. Su, Y., Du, H., Huo, Y., Xu, Y., Wang, J., Wang, L., Zhao, S., & Xiong, S. (2016). Characterization of cationic starch flocculants synthesized by dry process with ball milling activating method. *International Journal of Biological Macromolecules, 87*, 34–40. https://doi.org/10.1016/j.ijbiomac.2015.11.093
38. Zhang, J., Tao, L., Yang, S., Li, Y., Wu, Q., Song, S., & Yu, L. (2024). Water absorption behavior of starch: A review of its determination methods, influencing factors, directional modification, and food applications. *Trends in Food Science & Technology, 144*, 104321. https://doi.org/10.1016/j.tifs.2023.104321
39. Schmidt, C., Brunner, M., Berger, C., Zahn, S., & Rohm, H. (2022). Solubility and swelling of soils from native starch. *International Journal of Food Science & Technology, 57*(10), 6755–6762. https://doi.org/10.1111/ijfs.15911
40. Mustafa, S., Elkatry, H. O., Oirdi, M. E., Sun, C., Zhu, Z., El-Beltagi, H. S., Ahmed, A. R., & Du, X. (2025). The relationship between fine structure and physicochemical properties of starches from wheat (Triticum aestivum L.) varieties. *Italian Journal of Food Science, 37*(2), 319–333. https://doi.org/10.15586/ijfs.v37i2.2868
41. Song, Z., Zhong, Y., Tian, W., Zhang, C., Hansen, A. R., Blennow, A., Liang, W., & Guo, D. (2020). Structural and functional characterizations of α-amylase-treated porous popcorn starch. *Food Hydrocolloids, 108*, 105606. https://doi.org/10.1016/j.foodhyd.2019.105606
42. Zhang, L., Zeng, L., Wang, X., He, J., & Wang, Q. (2020). The influence of Konjac glucomannan on the functional and structural properties of wheat starch. *Food Science & Nutrition, 8*(6), 2959–2967. https://doi.org/10.1002/fsn3.1598
43. Suhaimi, E. S. M., Ahmad, W. Y. W., & Lazim, A. M. (2016). Synthesis and physicochemical characterization of cationic polymeric surfactant from Dioscorea pyrifolia Starch. *Malaysian Journal of Analytical Sciences*, *20*(6), 1278-1285.
44. Mandala, I. G., & Bayas, E. (2004). Xanthan effect on swelling, solubility and viscosity of wheat starch dispersions. *Food Hydrocolloids, 18*(2), 191–201. https://doi.org/10.1016/S0268-005X(03)00064-X
45. Han, F., Liu, M., Gong, H., Lü, S., Ni, B., & Zhang, B. (2012). Synthesis, characterization and functional properties of low substituted acetylated corn starch. *International Journal of Biological Macromolecules, 50*(4), 1026–1034. https://doi.org/10.1016/j.ijbiomac.2012.02.030
46. Pigorsch, E. (2009). Spectroscopic Characterisation of Cationic Quaternary Ammonium Starches. *Starch - Stärke, 61*(3–4), 129–138. https://doi.org/10.1002/star.200800090
47. Etale, A., Nhlane, D., Mosai, A., Mhlongo, J., Khan, A., Rumbold, K., & Nuapia, Y. (2021). Synthesis and application of cationised cellulose for removal of Cr(VI) from acid mine-drainage contaminated water. *AAS Open Research, 4*, Article 4. https://doi.org/10.12688/aasopenres.13182.1
48. Wang, Y., & Xie, W. (2010). Synthesis of cationic starch with a high degree of substitution in an ionic liquid. *Carbohydrate Polymers - CARBOHYD POLYM, 80*, 1172–1177. https://doi.org/10.1016/j.carbpol.2010.01.042
49. Wang, S. (Ed.). (2020). *Starch Structure, Functionality and Application in Foods*.

Springer. https://doi.org/10.1007/978-981-15-0622-2

50. Abd El-Aal, M., Abouzeid, R., Koo, M. S., Shayan, M., Picha, D. H., & Wu, Q. (2025). Physicochemical and Structural Properties of Starches from Diverse Sweetpotato Genotypes Grown in Louisiana, United States. *ACS Food Science & Technology, 5*(9), 3563–3576. https://doi.org/10.1021/acsfoodscitech.5c00611
51. Chang, Y.-J., Choi, H.-W., Kim, H.-S., Lee, H., Kim, W., Kim, D.-O., Kim, B.-Y., & Baik, M.-Y. (2014). Physicochemical properties of granular and non-granular cationic starches prepared under ultra high pressure. *Carbohydrate Polymers, 99*, 385–393. https://doi.org/10.1016/j.carbpol.2013.09.010
52. Tyowua, A. T., Zhang, Z., & Adams, M. J. (2026). Swelling and dissolution of starch granules in water under low and high shear mixing. *Food Hydrocolloids, 170*, 111745. https://doi.org/10.1016/j.foodhyd.2025.11