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A novel way to obtain effective cationic starch flocculants

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ABSTRACT

A novel way to obtain an effective flocculant based on biodegradable starch was found. The medium-substituted (DS from 0.10 to 0.54) cationic starches (CS) with preserved microgranular form was synthesised by the reaction of potato starch with 2,3-epoxypropyltrimethylammonium chloride using the semi-dry process. The cationic starch derivatives were characterised by Fourier Transform infrared spectroscopy, X-ray diffraction and ^{1}H-NMR, and their pasting and swelling properties were investigated. High-performance flocculant was obtained using intense mechanical shearing of aqueous cationic starch slurry. Swollen CS microgranules were crushed by the applied mechanical shearing and low-viscosity, stable CS aqueous dispersions were prepared. Sheared CS have a higher accessibility to polyanions, a lower molecular weight and a markedly higher flocculation efficiency—a lower minimum dose, while maintaining wide flocculation window. The flocculation mechanism of the kaolin suspension by sheared CS was proposed.

Keywords: Cationic starch; Mechanical shearing; Flocculation; Kaolin suspension; Flocculation mechanism

1. Introduction

Growing requirements for the environmentally friendly phase separation technologies including purification of various wastes promote the interest in the application of process-enhancing aids derived from renewable raw materials, such as chitin, cellulose or starch. Native starch has been known as a flocculant long ago, but its low cost does not recompense the insufficient flocculative performance at comparatively large quantities used. The chitin derivative chitosan is expensive; in addition, such an amino polysaccharide has a limited application because the pH control and adjustment in the suspension to be sedimented is usually needed. Cationic starches (CS) with quaternary ammonium groups are effective over wide range of pH. Because of their low cost, non-toxicity and biodegradability, CS have attracted considerable attention in the recent years as an alternative for inorganic and synthetic organic flocculants in liquid–solid separation processes, more specifically in wastewater treatment and papermaking industries. However, the problem of comparatively large quantities of CS needed in flocculation still exist; therefore, many scientific investigations have been carried out in

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order to increase flocculation efficiency of starch derivatives.

In water treatment, cationic starch acts as a flocculant where the degree of substitution of its hydroxyl groups by cationic moieties is higher than 0.1. The CS is obtainable by etherification of native starch with a cationisation agent such as N-(3-chloro-2-hydroxypropyl)trimethylammonium or 2,3-epoxypropylthrimethylammonium chloride in the presence of organic or inorganic bases in different reaction media [1–5]. Using starches from different botanical sources and by varying the conditions of cationisation—the amount of catalyst and cationisation agent, water content in a mixture, reaction temperature and time [1,6–8], CS derivatives of different solubility in water could be obtained [3,9]. The flocculation properties of CS mainly depend on the content of incorporated cationic groups, their molecular weight and solubility [3,10,11]. According to the common opinion, the optimal dose of a flocculant required to destabilise suspensions decreases with increasing DS, molecular weight or solubility of CS [12–14], although the literature survey has also disclosed the fact that the efficiency of a flocculant does not directly correspond to the amount of incorporated cationic groups. This finding was noticed in different experiments: in dispersion destabilisation by commercial Catisol 9 flocculant [12], in flocculating microalgae with commercial Greenfloc 120 and Cargill C*Bond HR 35.849 flocculants [15], where the difference of DS only 1.4 times results in lowering the optimal dose at least three times. Such results suggest that optimal dose should be influenced not only by DS but also by additional factors. Therefore, the origin of such a discrepancy needs more detailed studies.

In addition to the optimal dose, another parameter —the width of the flocculation range (flocculation window)—is also useful in practice for the evaluation of flocculation behaviour of polyelectrolytes [12,16,17]. This is the range between the minimum and the maximum quantity of a flocculant, the addition of which makes possible the optimal separation. The wider the flocculation window, the lower the risk of re-stabilisation of the particles due to charge reversal and more reliably the process can be controlled. In addition, wider flocculation window minimises the influence of the interfering factors: pH change, variation of the ionic strength or variation of the solid material concentration. Herein, the widening of the flocculation window has been an increasingly important feature for investigation. Bratskaya et al. [18] have proclaimed that amphiphilic starch derivatives with a high amount of hydrophobic moieties showing a strong hydrophobic association are effective only at significantly higher doses, but in wider concentration range compared to cationic starch of the same DS. Lekniute et al. [19] have prepared starch ampholytes by the succinylation of precationised starch. The main advantage of such derivatives is their wider flocculation window. A similar feature has been noticed for non-stoichiometric polyelectrolyte complexes formed by mixing two water-soluble polymers possessing oppositely charged polyions at various ratios [17,20,21]. However, the products and methods mentioned above cannot be broadly used in practice because of their high cost, complicated synthesis or technical implementation problems.

Earlier, members of our research group have synthesised CS with preserved microgranular form in the conditions of reaction in heterogeneous medium [22]. When such CS are dispersed in cold water they exhibit a higher flocculation efficiency, faster sedimentation rates, but at the expense of higher optimal doses as compared with dissolved cationic starch. Based on such an experience, one can prognosticate that some possibilities to make the flocculation behaviour better lie in the methods of flocculant preparation for use. The aim of our present work is to investigate the structural features and flocculative properties of medium-substituted CS whose aqueous slurries were subjected to an intense mechanical treatment. The desired issue is lowering the demand of the flocculant amount upon flocculation and the risk of re-stabilisation if it is overdosed.

2. Materials and methods

2.1. Materials and chemicals

The Antanavas Starch Plant (Lithuania) supplied the native potato starch (intrinsic viscosity $[\eta] = 0.39$ l/g). 2,3-Epoxypropyltrimethylammonium chloride (EPTMAC, 70%), toluidine blue O, lithium bromide, kaolin with the average particle size 0.9 μm (ζ-potential of −31 mV) and dimethyl sulfoxide (DMSO, Chromasolv® Plus, for HPLC ≥99.7%) were supplied by Sigma–Aldrich. Dextran sulphate with the molecular weight 500,000 was obtained from the Loba Feinchemie. All chemicals were of analytical grade.

2.2. Synthesis of CS

CS were obtained by the etherification of potato starch with EPTMAC in the presence of NaOH as a catalyst (the molar ratio AGU: EPTMAC: NaOH: H_2O was 1: (0.10–0.57): (0.038–0.040): (3–4.5) at 45°C for 48 h. After the reaction, CSs were washed with a water–isopropanol mixture and dried. The nitrogen

content of cationic starch derivatives was estimated by the Kjeldahl method after purification by the Soxhlet extraction with methanol for 16 h. The degree of substitution according to cationic groups (DS) was calculated from the nitrogen content:

$$DS = \frac{162 \cdot N}{1,400 - 151.5 \cdot N}$$

where N is the Kjeldahl nitrogen, %.

2.3. Characterisation of starch and its derivatives

2.3.1. FT-IR spectroscopy

The Fourier Transform infrared (FT-IR) spectra of native starch and cationic starch microgranules were recorded with a FRONTIER spectrophotometer (Perkin Elmer, USA).

2.3.2. Wide angle X-ray diffraction

X-ray diffraction (XRD) diffractograms were recorded with a DRON–6 multipurpose diffractometer (Russia) [23]. The crystallinity (%) of samples was calculated by the diffraction peaks' integration based on the Gaussian function fitting [24].

2.3.3. ^1H nuclear magnetic resonance (^1H NMR) spectroscopy

^1H NMR spectra were recorded at 300 MHz on a Varian Unity Inova spectrometer and at 400 MHz on a Bruker Avance 400 spectrometer. Samples for the NMR-spectroscopy were dissolved in DMSO-d6.

2.3.4. Size exclusion chromatography

The molecular weight of cationic starch samples was determined with the size exclusion chromatography (SEC) system (Viscotek 270 Dual Detector, Malvern Instruments Ltd) which contains a refractive index and light scattering (right-angle (RALS) and low-angle (LALS) light scattering) detection. The eluent was DMSO with 0.05 M LiBr at a flow rate of 0.3 ml/min, and two Viscotek-A columns (A2,500 and A5,000) were used in a series. Columns and detectors were operated at 60 and 50°C, respectively. The calibration was performed with a pullulan standard (PUL-110 K), provided by the Malvern. Data were recorded and the molecular weights were calculated with the Malvern OmniSEC software version 4.7.

2.3.5. Pasting properties

The pasting properties of native and CS were studied using a Brabender Micro-Viscoamylograph (Germany). Briefly, 2% w/w (dry basis) native and cationic starch slurry was heated from 1 to 95°C at a heating rate of 3°C/min.

2.3.6. Swelling power and solubility index

The swelling power (SP) and solubility index (SOL) were determined using modified methods of Chaisawang [25] and Mandala [26]. Native and cationic starch suspensions of 0.1–1% and 0.05–0.1% w/w concentration, respectively, were put in centrifuge tubes and kept in a water bath at temperatures of 5, 20, and 75°C for 30 min with minimum shear conditions. After, the centrifuge tubes were immediately immersed into ice bath (5°C) for 5 min to quickly cool the suspension. After cooling, the samples were centrifuged at 8,000 rpm at 5°C for 30 min. The precipitated paste was separated from the supernatant and weighted. Both phases were dried to a constant weight in a hot air oven at 105°C. All measurements were done in triplicate. The SP is the wet weight ratio of the precipitated starch gel to its dry weight, whereas the SOL is the percentage of the dry mass of solubles in the supernatant to the dry mass of a whole starch sample.

2.4. Preparation of cationic starch colloidal dispersions

Cationic starch microgranules (1% w/w) were swollen to the equilibrium state in distilled water (20°C) and then processed by mechanical shearing at 15,000 rpm with an Ultra-Turrax T25 digital (IKA, Germany) device at room temperature to obtain colloidal dispersions.

2.5. Characterisation of cationic starch slurry and dispersions

2.5.1. Dynamic viscosity

The dynamic viscosity of CS aqueous slurry and colloidal dispersions was measured with the rotational viscometer Rheotec RC02-R (Germany) at 20°C, using a TR8 spindle. The measurements were performed with 1% w/w (by dry basis) of CS.

2.5.2. Polyelectrolyte titration

For the determination of the accessibility of CS cationic groups (%) to polyanions, the polyelectrolyte titration was done [3,19].

2.5.3. Particle size and ζ-potential

The particle size and the ζ-potential of sheared CS particles and destabilised kaolin floccules in aqueous medium were measured using DelsaNano C instrument (Beckman Coulter, Japan).

2.5.4. Optical microscopy and scanning electron microscopy

The optical observations were carried out using an Olympus CX31 optical microscope (Philippines) under 100-time magnification. The photograph of CS slurry in water was taken with an Olympus camera.

For the scanning electron microscopy (SEM) analysis, the freeze-dried native and modified starches were examined on a FEI Quanta 200 FEG.

2.6. Flocculation experiment

The flocculation experiment with a model kaolin suspension was done, and the residual turbidity (RT, %) of kaolin suspension after addition of cationic starch flocculant was evaluated [19].

3. Results and discussion

3.1. Chemical and structural characteristics of cationic starch derivatives

2-hydroxypropyltrimethylammonium starch chloride (cationic starch, CS) is prepared by the etherification of native potato starch with EPTMAC in the presence of NaOH as a catalyst (Fig. 1).

Synthesis of medium-substituted CS in the conditions preserving the microgranular form can be performed with a reaction efficiency of greater than 82% [6].

The introduction of quaternary ammonium groups into starch was evidenced by NMR spectroscopy (Fig. 2). The signal at 2.5 ppm (A) in the ^{1}H NMR spectra of native starch (Fig. 2(a)) was assigned to a hydrogen atom of the solvent DMSO-d6. In the spectra, the resonances of starch chain protons denoted to 2–6 can be identified in the region of 3.1–3.8 ppm (B), and other peaks from starch −OH groups and proton 1—in the region of 4.2–5.7 ppm (C). Compared to the native starch, the cationic starch exhibited an additional peak at 3.18 ppm (D) (Fig. 2(b)), which was ascribed to the $(CH_3)_3\,N^+$ group [7,27].

The FT-IR spectra of native and CS with a various degree of substitution were also recorded and are shown in Fig. 3(a). All the spectra showed a typical peak of starch backbone—wide hydroxyl band around 3,300 cm^{-1}, the spectral patterns near 1,000 cm^{-1} (C–O–C), 1,148 cm^{-1} (C–O) and 2,928 cm^{-1} (C–H). The presence of an additional band at 1,477 cm^{-1}, assignable to the C–N stretching vibration, in the spectra of CS is a proof of the incorporation of cationic moiety onto the starch backbone [27,28]. With an increase in the DS of CS, the intensity of this peak increased. The alteration of the peak intensity put into relative adsorption data is shown in Table 1.

The granular form of native starch after its chemical modification was claimed to be preserved [6]; however, some changes in the structure of microgranules was observed after cationisation (Fig. 3(b)). The polysaccharide crystallinity decreased gradually from the initial value with increasing the degree of substitution and CS with DS = 0.54 possessed only 8% of crystallinity (Table 1). These changes may be explained by the fact that the structure of cationic starch microgranules disintegrates during cationisation, mainly, due to the changes in intermolecular interactions, first of all due to the rupture of H-bonds in amorphous and then in weak crystalline regions and finally at the surface of starch crystallites. All these variations could be associated with cationic groups linking to the polysaccharide chains.

The chemical starch modification is accompanied by the alteration of macromolecular interactions. These changes affect the characteristics of starch–water dispersions. The pasting behaviour of 2% suspensions of native starch and CS was evaluated (Table 1) and the

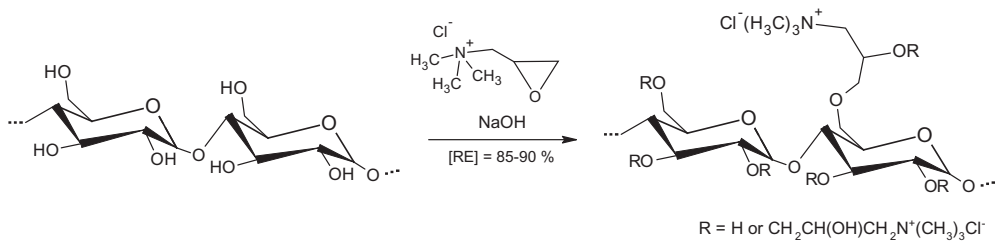


Fig. 1. Reaction scheme of cationic starch synthesis.

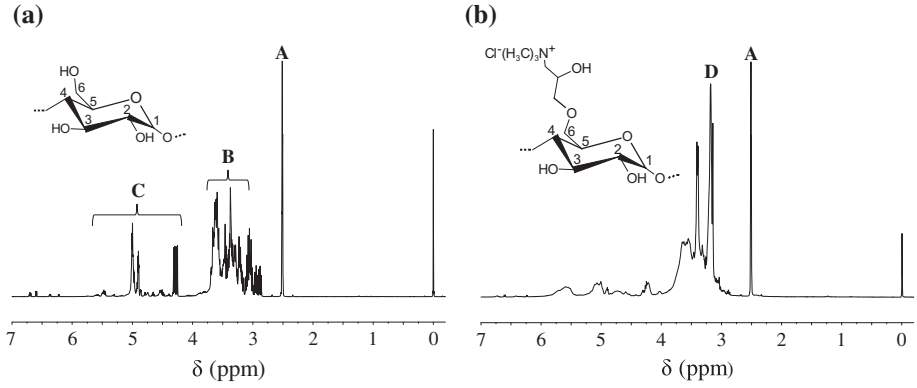


Fig. 2. ^{1}H NMR spectra of native starch (a) and cationic starch (b) with DS = 0.30.

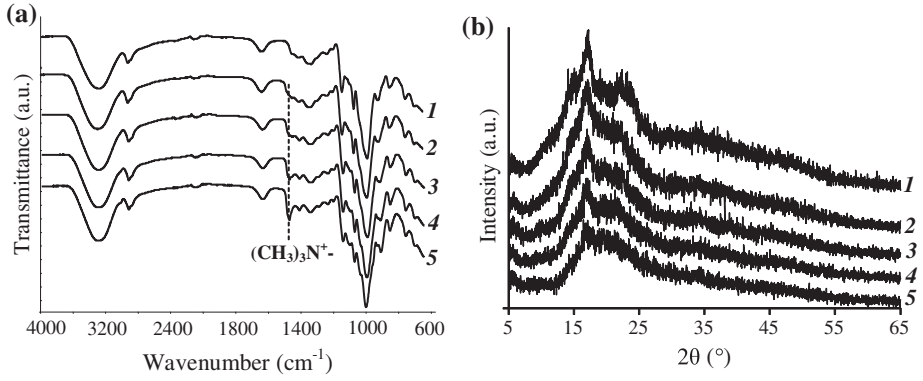


Fig. 3. FT-IR spectra (a) and XRD pattern (b) of native starch (1) and its cationic derivatives: $CS_{0.10}$ (2); $CS_{0.19}$ (3); $CS_{0.30}$ (4); $CS_{0.54}$ (5).

Table 1
Characteristics and properties of native starch and CS

Starch derivative	DS[a]	Relative adsorption[b], a.u.	Crystallinity, %	Pasting properties		SP at 75℃, g/g	SOL at 75℃, %
				T_p, ℃	η_{final}, BU		
Starch	0	0	23 ± 1.2	73	147	47 ± 4	21 ± 4
$CS_{0.10}$	0.10	0.02	19 ± 0.9	37	320	918 ± 66	43 ± 4
$CS_{0.19}$	0.19	0.10	18 ± 0.9	11	312	871 ± 21	52 ± 1
$CS_{0.30}$	0.30	0.19	16 ± 0.8	7	320	826 ± 31	54 ± 3
$CS_{0.54}$	0.54	0.30	8 ± 0.5	<3	308	663 ± 52	61 ± 4

[a]According to *N* content (by Kjeldahl).
[b]The peak height ratio (1,477 cm^{-1}/1,148 cm^{-1}) of FT-IR spectra.

Brabender viscosity curves (viscograms) of native starch and CS are shown in Fig. 4(a). As is known, native potato starch granules are insoluble in cold water due to the hydrogen bonds formed either directly via the neighbouring hydroxyl functional groups of the starch molecules or indirectly via water bridges. The determined pasting temperature (T_p) of potato starch is 73℃ (Table 1). CS have a much lower pasting temperature than native starch, because cationic groups readily disrupt the weak bonding among the CS chains. The T_p of CS decreased with increasing DS when DS changed from 0.10 to 0.54 and

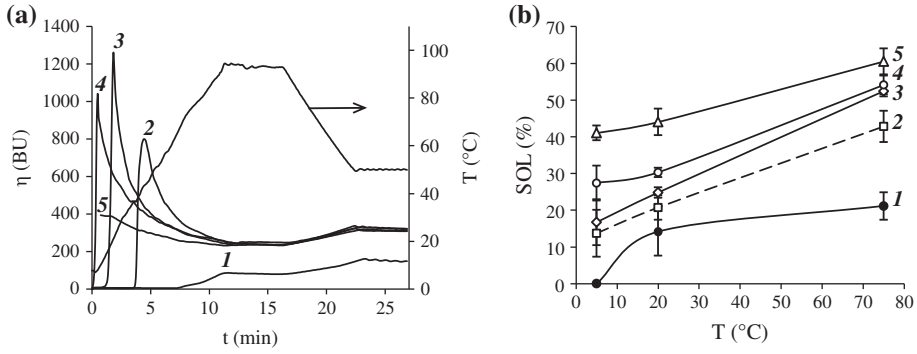


Fig. 4. Viscograms (2% suspensions) (a) and solubility index (SOL) (b) of native starch (1) and CS with DS: 2—0.10; 3—0.19; 4—0.30; 5—0.54. Error bars represent standard deviations.

the pasting temperature decreased by 36–70˚C from the initial value, respectively. The determination of final viscosity (η_{final}) at 50˚C also revealed great differences of CS from native starch—η_{final} of CS is twice as high (Table 1). A certain observation can be made from the obtained results: hydrophilicity of CS increases with increasing the amount of ionogenic groups bonded. Repulsion of the charged (cationic) groups forces the macromolecules to expand and water molecules to hydrate them. For this reason, the paste of CS with DS ≥ 0.19 can be prepared even at room temperature.

The introduction of cationic groups into starch influences not only the pasting behaviour of CS derivatives, but also their swelling and solubility. The effects of DS on the SP and SOL at the balance state were determined (Table 1, Fig. 4(b)). The SP of native potato starch granules at 75˚C is 47 g/g, meanwhile the SP of CS is even 14–20 times higher. It was noticed that SP decreased with the increase of DS from 0.10 to 0.54 of CS. Meanwhile, the SOL increases with increasing the DS of CS, also due to a higher temperature, and at 75˚C the solubility of $CS_{0.54}$ reaches 61%.

3.2. Mechanical treatment of cationic starch in cold water

In spite of the high hydrophilicity of CS, their initial granular form during cationisation is preserved. From the previous data, we see that CS granules are not homogeneous and consist of polysaccharide regions of different modification levels or orderliness (Table 1). The microgranules in cold water divide into two parts—to microgel particles of various size (Fig. 5(a) and (b)) and to the soluble CS macromolecules which have leached out from the granules; in such a way an aqueous slurry is composed. The soluble part of CS at 20˚C varies from 21 to 44%, subjected to the degree of substitution from 0.10 to 0.54, respectively (Fig. 4(b)). CS microgel particles still have an insufficient hydration of macromolecules and, therefore, a limited functional value in flocculation.

The objective of this part of work was to investigate the influence of the mechanical treatment on the state and properties of medium-substituted CS. CS microgranules without the application of external heat were treated with water and processed using shear forces (shearing). During this process, the swollen granules began to rupture and break down, yielding a low viscosity opalescent colloidal dispersion composed of dissolved macromolecules and submicroparticles of cationic polysaccharide. A sheared CS dispersion possessing some new quality was obtained.

The mechanical treatment initiated huge changes in the dynamic viscosity of the aqueous CS slurry and in the accessibility of CS cationic centres to polyanions (Fig. 6).

Fig. 6 shows the dynamic viscosity of the 1% $CS_{0.19}$ aqueous slurry/dispersion and the accessibility of cationic centres to polyanions as a function of the shearing time. As is seen in Fig. 6, a sharp reduction in dynamic viscosity of CS slurry occured during the first five minutes of shearing (from 2,960 to 49 mPa·s) and with the additional shearing time did not further reduced, which indicates that a stable colloidal dispersion was formed. Not all the cationic groups in CS microgels can be easily reached by the macroions, presumably, due to the steric hindrance. The accessibility of cationic centres in the $CS_{0.19}$ slurry was only 18%, but during the first 5 min of the mechanical treatment it suddenly increased 3.5 times—to 64% and reached 87% after 20 min of shearing. A comparison of the accessibility and the dynamic viscosity in the graph indicates the same characteristic reflection point at 5 min in the time-dependence curves. The only difference is that the viscosity values after such a point lie on the plateau, meanwhile the accessibility

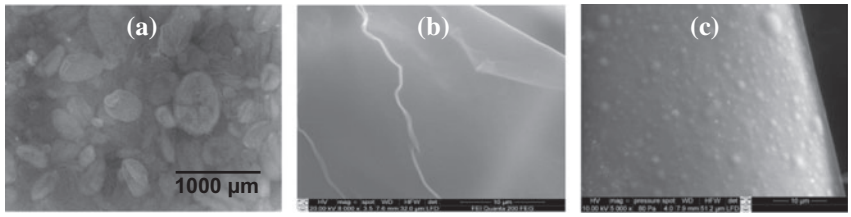


Fig. 5. Optical microscopy picture of $CS_{0.19}$ microgranules gelatinised in water before shearing (a) and the SEM pictures of freeze-dried $CS_{0.19}$ before (b) and after shearing (c).

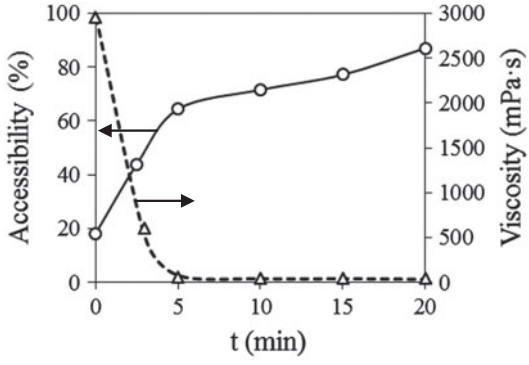
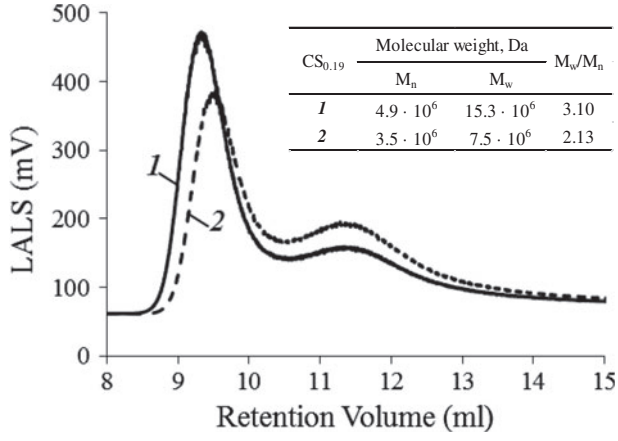


Fig. 6. Dynamic viscosity and the accessibility of cationic groups to polyanions of $CS_{0.19}$ slurry/dispersion dependence on shearing time; T = 20°C; ○ - accessibility; △ - viscosity.



$CS_{0.19}$	Molecular weight, Da		M_w/M_n
	M_n	M_w	
1	$4.9 \cdot 10^6$	$15.3 \cdot 10^6$	3.10
2	$3.5 \cdot 10^6$	$7.5 \cdot 10^6$	2.13

Fig. 7. Chromatograms of $CS_{0.19}$ before (1) and after (2) shearing.

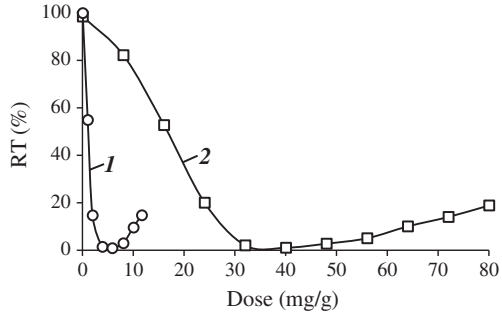


Fig. 8. Residual turbidity dependence on $CS_{0.19}$ dose: 1—sheared; 2—non-sheared.

continuously increases with increasing shearing time. It may be suggested that some qualitative changes in the sheared CS colloidal dispersion take place during the intense mechanical treatment. Presumably, when the microgel particles of CS are subjected to shearing forces, the weak hydrogen bonds and also covalent ones are being disrupted. Sheared product is nonhomogeneous. It is composed of swollen microgranule fragments, submicroparticles of CS and dissolved CS macromolecules.

Such an opinion can be supported by size exclusion chromatography analysis. The chromatogram and Table with the average molecular weight in Da of $CS_{0.19}$ before and after shearing are given in Fig. 7 (curves 1 and 2, respectively). The substantial changes of LALS signals after shearing can be indicated—curve shifts to the right, towards higher retention volume zone, the height of the first peak decreases and the height of the second one increases, and the molecular weight of the sheared $CS_{0.19}$ by weight (M_w) decreased by half compared to the non-sheared CS (from $15.3 \cdot 10^6$ to $7.5 \cdot 10^6$ Da). This means that after mechanical treatment the size of CS macromolecules varies and the hydrodynamic volume of them is smaller, and that molecules with a higher molecular weight during shearing are disrupted more. This can be explained by the destruction of the large branched amylopectin macromolecules due to the disruption of covalent bonds and, as a result, formation of new macromolecules with a lower molecular weight. It is reasonable to suggest that such a process increases the mobility of the polymer chains and, therefore, facilitates the approach for the oppositely charged macroions to certain centres or the structure domains.

Table 2
Characteristics of cationic starch derivatives before and after 15 min of shearing.

Cationic starch derivative	Amount of cationic groups in CS, mg-equ/g			Dynamic viscosity[a] of 1% CS, mPa·s		Particles of sheared CS in dispersion		
	Theoretical according to DS	Accessible to polyanions (experimental value)				Size, nm	PI	ζ-potential, mV
		Slurry (non-sheared)	Dispersion (sheared)	Slurry	Dispersion			
$CS_{0.10}$	0.56	0.06	0.42	14,650	49	1,100	0.414	+34 ± 2
$CS_{0.19}$	1.04	0.19	0.80	2,960	49	750	0.344	+41 ± 1
$CS_{0.30}$	1.45	0.27	1.23	4,300	39	560	0.364	+46 ± 1
$CS_{0.54}$	2.22	0.41	1.92	4,075	33	530	0.329	+51 ± 1

[a]5 N/m^2 shear stress.

It has been found that the opalescent colloidal $CS_{0.19}$ dispersion has a higher flocculation efficiency than that of CS slurry (Fig. 8) and is suitable for destabilising the model kaolin suspensions. The minimum dose (at which RT ≤ 5%) of the sheared $CS_{0.19}$ flocculant decreased 10 times after shearing. The considerable difference between the CS dispersion and slurry suggests, that using mechanical shearing, the flocculation performance of CS may have been improved.

Table 2 summarises the main characteristics of CSs with the DS from 0.10 to 0.54 in slurries and dispersions, obtained after 15 min of shearing (a 1% CS concentration was used). The mechanical treatment of the CS aqueous slurries has been carried out without the application of external heat. The shearing time is long enough to obtain the shear stable cationic starch dispersions (Fig. 6).

When the CS with DS ≥ 0.19 are mixed with cold water (20˚C), the translucent slurries are obtained; their dynamic viscosity is about 3,000–4,000 mPa·s, and the accessibility of CS cationic groups to polyanions reaches 18–19%. An exception is $CS_{0.10}$: aqueous slurry is opaque; it consists of less swollen CS granules (due to a higher pasting temperature (Table 1)) and has only 10% of accessible cationic groups. The viscosity of $CS_{0.10}$ slurry is significantly higher—approximately 15,000 mPa·s. When such CS (DS 0.10–0.54) slurries are affected by shear forces, the amount of accessible cationic groups increases even to 75–86%, meanwhile the dynamic viscosity decreases dramatically to 49–33 mPa·s.

The mechanical treatment of cationic starch in cold water causes the changes of slurry—a colloidal opalescent dispersion is obtained with smaller particle size which varies from 1 μm to 500 nm (submicroparticles). Submicroparticles of sheared CS have the polydispersity index value (PI) greater than 0.3, which indicates wide size distribution. In all cases the positive ζ-potential value of the particles has been determined (Table 2). These submicroparticles are visualised in the SEM picture of freeze-dried CS (Fig. 5(c)).

3.3. Flocculation properties of sheared CS

In order to obtain exhaustive information on the flocculating performance of sheared cationic starch derivatives, the flocculation of kaolin suspension has been examined. The quality of CS as flocculants after their mechanical treatment is characterised by the minimum dose of the flocculant (*C*, mg/g) and by the width of the flocculation window (*W*), which shows the range of cationic starch concentrations where the residual turbidity upon sedimentation less than 5% can be reached. The lower *C* and the wider *W*, the more effective flocculation can be expected.

The data on residual turbidity as a function of the flocculant dose and the minimum required dose of flocculant (see Table) are presented in Fig. 9(a). A steep decrease in the turbidity occurs after addition of the first portions of sheared cationic starch dispersion and is followed by a zone of effective flocculation. From the obtained results we can see that with increasing DS from 0.10 to 0.54 the minimum dose of the flocculant decreases (*C* shifts to the left), meanwhile the flocculation window narrows. The minimum dose *C* of $CS_{0.54}$ is almost three times lower and flocculation window *W* is twice narrower than that of $CS_{0.10}$. Taking into account the high affinity of CS to a substrate and the correlation between cationic starch DS and the required minimum flocculant dose, we can conclude that electrostatic interactions are the main driving force in the flocculation of kaolin suspensions.

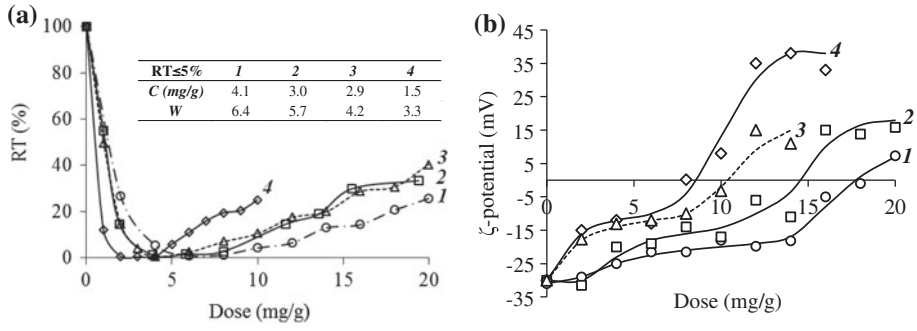


Fig. 9. Dependence of residual turbidity (a) and ζ-potential of kaolin particle surface (b) on the dose of sheared cationic starch whose DS: 1—0.10; 2—0.19; 3—0.30; 4—0.54.

In order to facilitate the interpretation of experimental data for sheared starch varying in charge density, simultaneously the electrokinetic effects of flocculant adsorption on kaolin particles have been examined. The data depicted in Fig. 9(b) show that the flocculation might be characterised by a few different segments. The steep decrease of the negative value at the first portions added is noticed only for the flocculants with the higher cationicity (Fig. 9(b), curves 3 and 4). All curves representing flocculation have horizontal segments varying in width depending on starch DS in negative ζ-potential zones. The horizontal segments between −23 and −12 mV of the ζ-potential in the curves approximately correspond to the zones defined by flocculation windows of CS derivatives. The higher dose depending on the modified starch DS is enough to cause the mutual repulsion of cationic groups and induce the re-stabilisation of the kaolin suspension. The negative ζ-potential values steeply decrease and further reverse the particle surface charge from negative to positive.

The different flocculation performance of the non-sheared and sheared CS might be explained bearing in mind the peculiarities of their water slurries/dispersions. With reference to the data mentioned above (see Part 3.2), one might conclude that the sheared cationic starch colloidal dispersion consists of the dissolved linear and branched cationic starch macromolecules of various molecular weight (Fig. 7) and of various size CS submicroparticles (Fig. 5(c), Table 2). By using such a heterogeneous sheared CS composition as a flocculant, many different proccesses/interactions between positively and negatively charged particles might be involved. It is reasonable to suggest that firstly the sheared CS adsorbs onto kaolin particles' surface by forming oppositely charged "patches", and then the flocculation is induced due to the electrostatic attraction between the flocculant, already adsorbed onto kaolin particle surface and a bare surface on another particle of kaolin. Dissolved CS macromolecules can easily reach the surface of a kaolin particle and adsorb on the outer surface, lie on it flat or penetrate into their pores. Presumably, dissolved macromolecules bearing a positive charge work efficiently in the charge neutralisation mechanism and cause a significant change of the ζ-potential value on a particle surface in the first portions of added flocculant. For CS submicroparticles it is more difficult to match the template of kaolin surface charges because of a mismatch in spacing among the cationic groups at CS particle surface and oppositely charged kaolin sites. The presence of flocculant submicroparticles in the flocculant–kaolin system induces a high-charge heterogeneity and creates many binding sites for inorganic particles with a bare surface. One can imagine that CS submicroparticle serves as an additional attraction centre for a few kaolin particles. Such an idea seems to be supported by the electrokinetic measurements and explains the existence of horizontal segments in ζ-potential curves in the negative values zone. It indicates to the great validity of the existence of many more 2-hydroxypropyl trimethylammonium groups available at the surface of CS particles. The mechanical shearing serves for increasing the surface area and opening these sites for binding.

On the basis of experimental results, it might be concluded that a compromise among the flocculant efficiency, cost and risk of overdose must be done. Sheared CS (DS ≥ 0.54) exhibit an excellent flocculative behaviour at a low dosage, but by using such flocculant, it is easier to overdose and re-stabilise the kaolin suspension. CS with DS = 0.10 can be characterised by wide flocculation window, but a large dose of material is needed to achieve an adequate sedimentation. The optimum seems to be the sheared CS with the DS between 0.19 ≤ DS ≤ 0.30.

The intensity of the shearing force to which the cationic starch–water mixture is subjected can vary

widely depending upon the ease of gelatinisation of a particular CS, its concentration, as well as the mechanical shear device equipment design and efficiency. Different devices for imparting a mechanical shearing other than described Ultra-Turrax device are possible, for example, dispersers, homogenisers or emulsifiers. In this case, the flocculation characteristics after subjecting the CS aqueous mixture to the shearing action must be routinely determined.

4. Conclusions

(1) CS with the medium degree of substitution (DS = 0.10–0.54) were obtained with a reaction efficiency of greater than 85% in such conditions that the granular form was preserved. The microgranules of cationic starch consist of the regions of different chemical modification level and orderliness. Their slurry in cold water was composed of dissolved CS macromolecules and CS granules swollen to the equilibrium state.
(2) After processing of CS aqueous slurry using shear forces the granules became disrupted, the accessibility of cationic groups increased more than 4 times, and a stable opalescent colloidal dispersion composed of CS macromolecules and submicroparticles (0.5–1 μm) was obtained.
(3) The minimum effective flocculation dose of sheared CS (DS from 0.19 to 0.30) decreased approximately 10 times compared to that of non-sheared CS while maintaining wide flocculation window.
(4) Results of ζ-potential measurements suggest that the charge patch flocculation mechanism is predominant in the flocculation of negatively charged particles with sheared CS.

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