Carbohydrate Polymers 74 (2008) 673–679

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Synthesis and flocculating properties of cationic starch derivatives

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ARTICLE INFO

Article history:
Received 27 February 2008
Received in revised form 13 April 2008
Accepted 15 April 2008
Available online 25 April 2008

Keywords:
Starch
Irradiation microwave
Flocculation
Transmittance
Jar test

ABSTRACT

A series of cationic starch derivatives were synthesized by grafting cationic moiety such as glycidyl octyl dimethylammonium chloride (GODAC), glycidyl dodecyl dimethylammonium chloride (GDDAC), and glycidyl tetradecyl dimethylammonium chloride (GTDAC) on the starch backbone using NaOH as a catalyst. Products obtained were characterized by FT-IR and CP/MAS ^{13}C NMR analysis. Compared to conventional methods such as Kneading Device as reactor and wet (solvent) conditions, microwave irradiation has not any remarkable effects on the crystallinity of starch and surface structure as indicated by Scanning electron microscopy (SEM) and X-ray diffraction. Flocculation performance of these starch derivatives was evaluated in terms of the transmittance of supernatant liquid in Kaolin suspension by jar tests. In the case of S-GDDAC, the transmittance of supernatant liquid was 92.7 for microwave irradiation, 77.6 for Kneading Device as reactor and 58.3 for wet (solvent) condition, respectively. Among three cationic starches obtained with microwave irradiation, the transmittance of supernatant liquid for S-GTDAC with longer chains was 93.9 higher than other two (90.4 for S-GODAC and 92.7 for S-GDDAC) and the flocculation performance was superior to the commercially available flocculant (MP-584). Also, effects of addition dosage, sedimentation time and flocculating time on flocculation performance of S-GTDAC were investigated. Results showed that the transmittance of supernatant liquid for S-GTDAC was increased with the increase of sedimentation and flocculating time. And there was an optimal addition dosage of 0.29 g/L when S-GTDAC was employed under the experimental conditions.

1. Introduction

Flocculants are the materials, which are used, in fast solid–liquid separations by an aggregation process of colloidal particles, the process is termed as flocculation. Commercial forms of synthetic flocculants may contain toxic monomers from the synthesis and additives. Furthermore, new alternatives to synthetic polymers must be developed due to scarcity of oil resources. An important member of renewable primary products such as cellulose and chitosan, especially low-cost starch, are alternatives to synthetic flocculants. In recent years, considerable attention has been paid on starch derivatives used as flocculants and chelating agents to remove heavy metals.

Starch is one of the most abundant natural polymers in the world. In its crude form, starch is a mixture of two polymers of anhydroglucose units, amylose and amylopetin. Chemically modified starches are generally made by treating starch with agents that can reaction with hydroxyl groups or grafting with other polymers. Such starches have physicochemical properties that differ significantly from the parent starch, thus widening their usefulness in many applications in food manufacturing and other industrial processes (Prakash, Solanki, & Prasad Rao, 2007; Rvanitoyannis, 1999). Earlier in 1970, graft copolymers of starch and poly (2-hydroxy-3-methacryloyloxy propyltrimethyl-ammonium chloride) were prepared and were used as flocculating agents (Fanta, Burr, Russell, & Rist, 1970). It was also found that starch-g-polyacrylamide copolymer showed good flocculation ability because of synergistic characteristics in flocculation (Karmakar & Singh, 1997). Now many graft starch copolymers have been synthesized and flocculation were tested (Chan & Chiang, 1995; Hao, Chang, Duan, & Zhang, 2007; Khalil & Aly, 2001a, 2002b; Yao, 1992). These polyacrylamide grafted copolymers showed about the same flocculation action as the common synthetic polymer flocculants for relatively low negatively charged colloids. But for highly negatively charged colloidal particles, cationic polymers are more efficient. In addition, they also possess a bad biodegradability. In many countries, the disposal of flocculated sludge with polyacrylamide derivatives has been limited and will be strictly prohibited (Semsar, Scholz, & Kulicke, 2007).

Cationic starch derivatives possessing positively charged groups (such as amino, imino, ammonium etc.) were effective flocculants over a wide range of pH. They are non-toxic, easily biodegradable and can be used to treat organic and inorganic matter in wastewater carrying negative charge (Heinze, Haack, & Rensing, 2004; Jaernstroem, Lason, & Rigdahi, 1995; Nystrom, Backfolk, Rosenholm, & Nurmi, 2003; Pal, Mal, & Singh, 2005). In addition, introduction of a cationic group to starch gives good mineral binding

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doi:10.1016/j.carbpol.2008.04.026

properties. Conventionally cationic starch can be prepared by reaction of starch with *N*-3-Chloro-2-hydroxypropyl) trimethyl ammonium chloride in aqueous base or organic solvents. However, in the abovementioned process a large amount of solvent has to be used and serious environmental pollution may be caused. Also, the chain length of cationic moiety was limited.

Microwave-assisted synthesis has attracted considerable attention in recent years. Compared with the conventional mode, a microwave-assisted reaction has advantages of energy saving, high conversion, and rapidity. The avoidance of volatile organic solvents in organic syntheses is the most important goal in green chemistry. During ultrafast synthesis using microwave irradiation, reactions are completed in minutes compared to hours and days using the conventional methods. For this reason, microwave irradiation is widely applied in starch modification (Biswas, Shogren, Kim, & Willett, 2006; Guo, Shu, Ben, & Jin, 2006; Jyothia, Rajasekharanb, Moorthya, & Sreekumara, 2005; Lewandowicza et al., 2000; Singh & Tiwari, 2008; Staroszczyk, Tomasik, Janas, & Poreda, 2007).

In this paper, cationic starch grafted three different long-chain quaternary ammonium salts were synthesized with microwave-assisted method and simultaneously compared with other two conventional ones in terms of flocculation ability. It was found that etherification could be completed in a very short reaction time under milder conditions with microwave irradiation as expected. Starch derivatives obtained were characterized by FT-IR, CP/MAS ^{13}C NMR, X-ray, and SEM analysis. Also flocculation properties of cationic starch were evaluated in terms of the transmittance of the kaolin supernatant liquid.

2. Materials

Cornstarch used for this study was supplied by Tianjin Huanglong Starch Co., Ltd. PR China. Sodium hydroxide, ethanol, and epoxychloropropane were obtained from Tianjin University Kewei Co. Ltd. Dimethyl laurylamine, Dimethyl octylamine, and Dimethyl tetradecylamine were obtained from Tianjin Angel Chemicals Group Co. Ltd. PR China. A Galanz (Model No. WD700S-1, 1000W) domestic microwave (MW) oven was used for the experiment.

3. Experimental

3.1. Synthesis of cationic etherifying agents

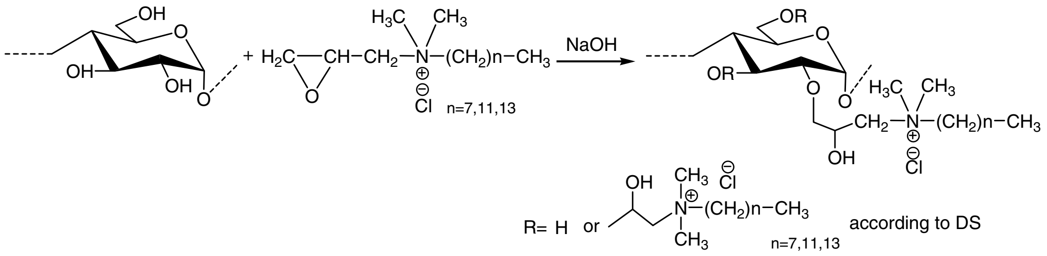
Three cationic etherifying agents (CEA) such as glycidyl octyl dimethylammonium chloride (GODAC), glycidyl dodecyl dimethylammonium chloride (GDDAC), glycidyl tetradecyl dimethylammonium chloride (GTDAC) were synthesized according to our earlier literature (Pan, Cheng, Wei, & Zhu, 2007).

3.2. Synthesis of cationic starch with microwave irradiation

Typically, 1 mL aqueous sodium hydroxide (0.5 g/mL) was added to the reaction vessel containing starch (5 g). The mixture was stirred thoroughly and then put into microwave (MW) oven for 1 min. GODAC (1.41 g) was added to above mixture and stirred to form a smooth colloid. The whole mixture was put into microwave (MW) oven again for another 2 min and finished reaction. The product obtained was cooled to room temperature and dissolved in definite amount of deionized water. The solution was neutralized with HCl (1 M) to pH 7 in ice-water bath and the product was isolated by precipitation in ethanol. Finally the filtered product was purified by dialysis against water and lyophilized. The cationic starch product starch grafted glycidyl octyl dimethylammonium chloride (S-GODAC) was obtained as a white powder. Similarly, starch grafted glycidyl dodecyl dimethylammonium chloride (S-GDDAC) and starch grafted glycidyl tetradecyl dimethylammonium chloride (S-GTDAC) can also be synthesized according to this method. The synthetic pathway and conditions was shown in Scheme 1 and Table 1, respectively.

3.3. Synthesis of cationic starch with solvent method

Typically, 25 mL aqueous sodium hydroxide (0.08 g/mL) was added to the flask containing starch (5 g). The mixture was stirred thoroughly and activated at 50 °C for 1 h. Then GDDAC (18.86 g) dissolved in 10 mL deionized water was added into the starch paste above dropwise and stirring was continued for 8 h. Then, deionized water (25 mL) was added to stop the reaction. After cooled to room temperature, the reaction solution was neutralized



Scheme 1. Synthesis route of cationic starch derivatives.

Table 1
Optimal conditions for three cationic starch derivatives with different methods

Samples	Mol ratio (CEA/starch)	Time (min)	Water content (mL)	NaOH content (g)	DS$_{Cl}$	Transmittance (%)
S-GODAC[a,b]	0.3:1	2	0.5	0.25	0.0351	90.4
S-GDDAC[a,b]	0.2:1	4	0.5	0.25	0.0241	92.7
S-GTDAC[a,b]	0.2:1	6	1.0	0.25	0.0219	93.9
S-GDDAC[a,c]	2:1	480	25.0	2.0	0.0116	58.3
S-GDDAC[d,e]	0.25:1	420	20.0	20.0	0.0295	77.6

[a] The weight of starch was 5 g.
[b] Microwave irradiation.
[c] Wet method.
[d] The weight of starch was 200 g.
[e] Kneading Device as reactor.

with HCl (1 M) to pH 7 in ice-water bath and the product was isolated by precipitation in ethanol. Finally the filtered product was purified by dialysis against water and lyophilized. The cationic starch product starch grafted glycidyl dodecyl dimethylammonium chloride (S-GDDAC) was obtained as a white powder. Similarly, other two cationic starch derivatives can be synthesized.

3.4. Synthesis of cationic starch with Kneading Device as a reactor

Typically, 20 mL aqueous sodium hydroxide (1.0 g/mL) was sprayed on the surface of starch (200 g) in Kneading Device. The mixture was stirred and activated at 50 °C with a rotate velocity of 700r/min. then GDDAC 975.2 g) was added with three portions. After that the reaction was stirred for 7 h. Then cooled to room temperature, the reaction product was taken out and dissolved in deionized water. According to the methods mentioned above for solvent method, the product can be neutralized and purification. The cationic starch product starch grafted glycidyl dodecyl dimethylammonium chloride (S-GDDAC) was obtained as a white powder. Similarly, other two cationic starch derivatives can be synthesized.

3.5. Degree of substitution

The degree of substitution (DS) was calculated from the chloride analysis (DS_{Cl}) according to the following equations:

$$DS_{Cl} = \frac{M_{AGU} * Cl\%}{100M_{Cl} - M_{CEA} * Cl\%}$$

where M_{AGU} is the molar quantity of anhydroglucose units in starch, M_{CEA} is the molar quantity of cationic etherifying agent, M_{Cl} is the molar quantity of chloride atom.

3.6. FT-IR analysis

IR spectra were recorded on Fourier-transform infrared spectrometer (BIO-RAD EXCALIBUR FTS3000) in KBr discs.

3.7. CP/MAS ^{13}C solid-state NMR

Cross polarization/magic angle spinning (CP/MAS) ^{13}C solid-state NMR experiments were performed using a Varian Unity-Plus 300 spectrometer operating under a static field strength of 4.7 T at ambient temperature.

3.8. Wide angle X-ray diffraction (WAXD)

X-ray diffraction spectrometry was measured using a DMAX-RC powder diffraction meter with Cu radiation in the range 10–30θ at 40 kv and 30 mA.

3.9. Scanning electron microscopy (SEM)

SEM images were observed on a Philips XL-3 scanning microscope. Each starch sample was suspended in a bottle in which there was a small amount of ethanol by ultrasonography. The sample was mounted on glass plates and dried for removal of the ethanol, followed by coating with a thin layer of gold in a vacuum before examination.

3.10. Flocculation

Flocculation performance of the polymers was examined using Coagulation-Flocculation jar tests (Bratby, 1980, chap. 8): six beakers of 0.1% kaolin suspension prepared by mixing 1 g in 1000 ml of distilled water were used for flocculation studies. Immediately after the addition of the polymer flocculants, all the suspensions were stirred with magnetic bars at a constant speed of 120 r/min for 1 min, followed by a slow agitation at 40 rpm for 20 min (this period named flocculating time). The flocs were then allowed to settle down for 15 min (sedimentation time). At the end of the settling period, the transmittance of supernatant liquid at half height of the clarified layer was measured using a UVVIS spectrometer (722 S) at 620 nm. The dose of flocculants was varied in the range of 0.1–0.3%. Six replications of each test were carried out. The mean value obtained and standard deviation from the six replications was from 0.05 to 0.1.

4. Results and discussions

4.1. Synthesis of cationic starch

Table 1 shows the optimal conditions and flocculation properties for three cationic starches with microwave-assisted method. In the experiments, orthogonal Test was employed to examine the influence of various factors on the flocculation efficiency. The preferable transmittance of S-GDDAC prepared using Kneading Device (KD) as reactor, wet (solvent) method and microwave irradiation were 77.2, 58.3, and 92.7, respectively. Obviously, flocculation properties of S-GDDAC prepared with microwave irradiation were remarkably superior to ones with conventional ones. Details about flocculation property of cationic starch derivatives can be seen in Part 4.4. Even if the reaction time is prolonged to 8 and 10 h for conventional Kneading Device and wet methods, no significant increase in the flocculation efficiency can be further observed. Thus, a shorter reaction time and higher flocculation efficiency make microwave-assisted synthesis attractive for practical purposes.

4.2. FT-IR analysis

The Spectra of starch, cationic starch derivatives S-GODAC, S-GDDAC, and S-GTDAC are indicated in Fig. 1a–d. The broad band (Fig. 1a) at 3400 cm^{-1} is due to the stretching mode of the O–H groups. Peaks at 1154, 1082, and 1022 cm^{-1} are the characteristic absorption bands of starch backbone. For cationic starch derivatives S-GODAC, S-GDDAC, and S-GTDAC (Fig. 1b–d), besides the broad band at 3400 cm^{-1} is for the O–H stretching vibrations, the presence of additional bands at near 1458 cm^{-1} assignable to the stretching mode of C–N of cationic starch, which was not

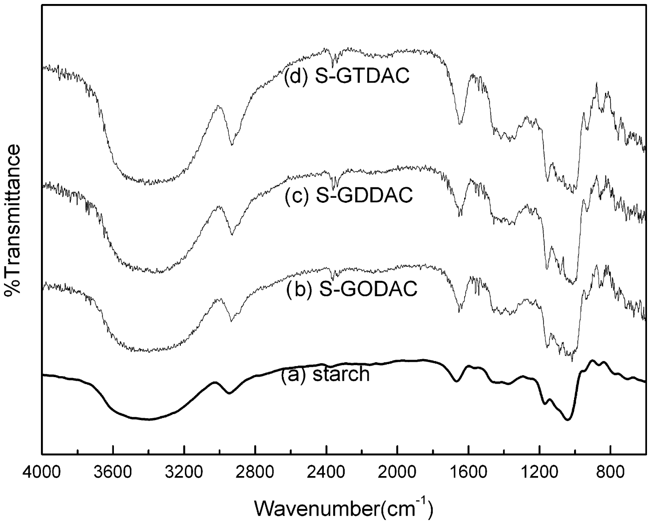


Fig. 1. FT-IR Spectrum of starch and cationic starch derivatives.

present in unmodified starch ((Fig. 1a). Also, peaks at 720 cm^{-1} contributed to the vibration of $-(CH_2)_n-(n \geqslant 4)$. These results indicated that cationic moieties had been well introduced into starch backbone by etherification. In addition, three cationic starch derivatives had similar CP/MAS ^{13}C solid-state NMR spectra. Typically, the following signals were recorded. Peaks in 101.4 (C_1), 81.7 (C_4), 72.6 ($C_{2,3,5}$), 62.1 ppm (C_6) were corresponding to anhydroglucose units of the starch backbone in CP/MAS ^{13}C NMR spectrum. Peaks near 31 ppm were the fragments of methylene of the long-chain cationic etherifying agents. These data further confirmed the formation of starch ethers. But other signals related to cationic moiety was too weak and cannot be detected by CP/MAS ^{13}C NMR, therefore, it was not possible to determine which starch hydroxyl was the preferred target for etherification.

4.3. X-ray and SEM analysis

Fig. 2 shows the X-ray spectrum of starch and cationic starch derivatives prepared with different methods. As shown in Fig. 2, both the unmodified and the modified starch prepared with microwave irradiation all displayed the typical A-type patterns.

But the corresponding peaks disappeared for cationic starch prepared using Kneading Device as reactor or solvent method. This fact suggests that microwave irradiation has not any obvious effects on the crystallinity of starch, though it affects the reactivity of starch remarkably.

The results of X-ray diffractometry were confirmed by SEM investigation. SEM photos of native and modified starches are given in Fig. 3a-l. As shown in Fig. 3, the surface of starch was partly damaged after modification as compared to the image of the native starch. But the surface of starch subject to conventional methods such as solvent and Kneading Device as reactor was completely damaged. Thus, modification of starch under microwave irradiation could be occurred not in amorphous region but partial crystalline region (Jyothia et al., 2005).

4.4. Flocculation performance

The flocculation performance can be explained in terms of the transmittance of the supernatant liquid. The higher the transmittance, the better the flocculating agent is. Stated in Table 1 are the comparative studies on the transmittance of supernatant liquid of the modified starch products carried out in 0.1% kaolin suspensions. It is obvious from these results that S-GTDAC, which contains longer alkyl chains, is a better flocculant in kaolin suspension than the other two cationic starches (S-GODAC and S-GDDAC). Cationic starch derivatives can be easily adsorbed to the colloid surface of anionic kaolin suspensions due to electrostatic attraction. Absorbed polymers tend to form loops and extend some distance from the particle surface into the aqueous phase. Their ends also dangle and get adsorbed on the surface of another particle forming a bridge between particles. For effective bridging occur, the length of polymer chains should be long enough to extent from one particle surface to another. Hence, the polymers with longer chains would be more effective than with the shorter chains. As mentioned above, three cationic starches prepared with microwave-assisted method all had better flocculation performance than conventional methods such as wet and Kneading Device as reactor obtained. It may be because non-etherified portion of the starch granule could gelatinize (Staroszczyk et al., 2007). Although modification of starch with microwave irradiation can be achieved in very short time and high reactivity, it had not significant effect on the crystallinity and surface of starch as seen in X-ray and SEM analysis.

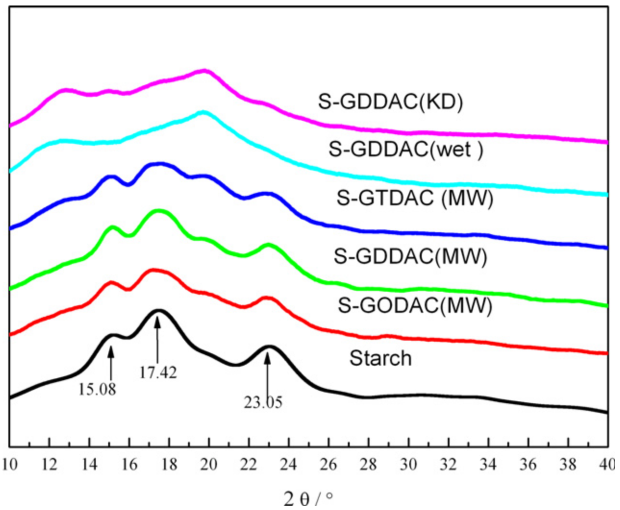


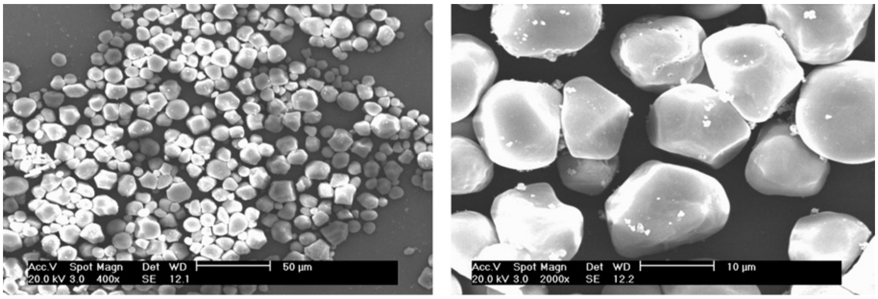
Fig. 2. X-ray of starch and cationic starch derivatives.

Effects of addition dosage, sedimentation time and flocculating time on flocculation performance of S-GTDAC were further investigated in terms of the transmittance of the supernatant liquid using the jar teat method. Fig. 4 showed effects of addition dosage (S-GTDAC) on flocculation performance. Initially the transmittance of the supernatant liquid increased with the increase of addition dosage. As the dosage increased to 0.29 g/L, a maximum of 95.4 reached, then the transmittance value kept constant and even slightly decreased with increasing addition dosage under the experimental conditions. But the transmittance of the supernatant liquid increased with the increase sedimentation time and flocculating time as plotted in Figs. 5 and 6, respectively. At lower dosages, there was insufficient polymer to form adequate bridging links between particles. With excess polymer, there is no longer enough bare particle surface available for attachment of segments and the particles become destabilized, which may involve some steric repulsion. Longer sedimentation time and flocculating time will favor polymer absorbing on the surface of particles and thus bridging them together.

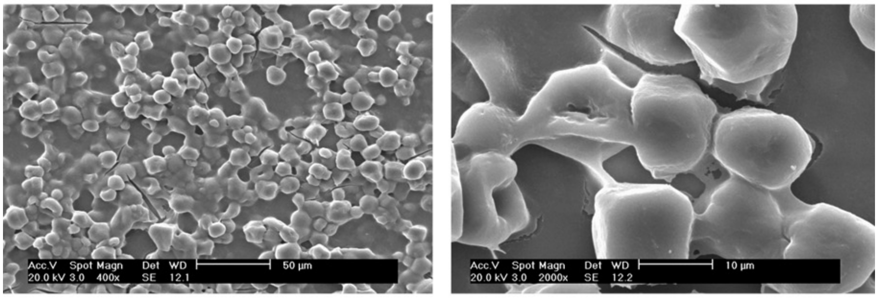
In Fig. 7, an attempt has been made to compare the flocculation efficiency of S-GTDAC with commercial available flocculant (MP-584). It is obvious that S-GTDAC is a better flocculant maintaining a high and almost constant transmittance over a wide range of polymer dosage than MP-584. In addition, flocculating efficiency of the S-GTDAC to the paper-making wastewater was investigated as shown in Fig. 8. As shown in Fig. 8, the transmittance of the supernatant liquid was sharply increased when the polymer dosage increased from 0.5 to 1.5 g/L. After this point, the transmittance of the supernatant liquid was slowly increased with the increase of polymer dosage. It was obvious that S-GTDAC can be used as a potentially efficient flocculant to treat wastewater. Further research to fully investigate other flocculation properties such as turbidity is under way in our lab.

5. Conclusions

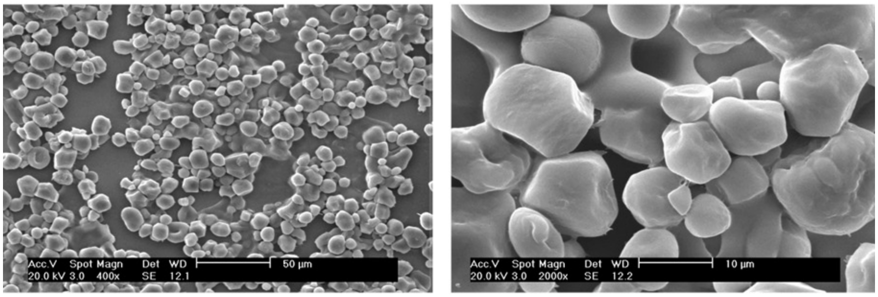
A series of cationic starch derivatives grafted cationic moiety with different chain length were synthesized. These polymers were characterized for the flocculation performance in terms of the transmittance of the supernatant liquid in Kaolin suspension. It was found that starch derivatives obtained with microwave-assisted method had better flocculation efficiency than conventional ones such as Kneading Device as reactor and wet conditions. As for S-GDDAC, the transmittance of the supernatant liquid was 92.7 for microwave irradiation, 77.6 for Kneading



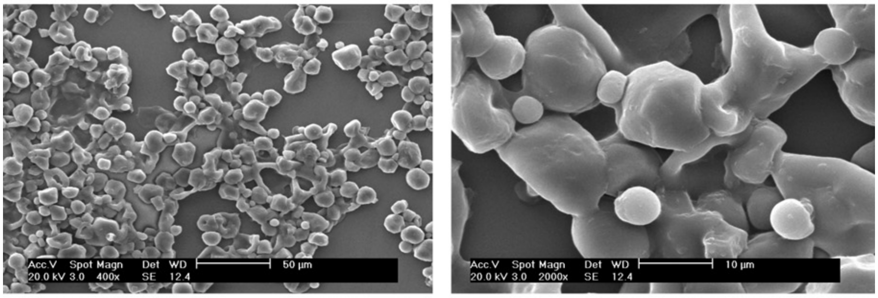
(a) starch×400 **(b) starch×2000**



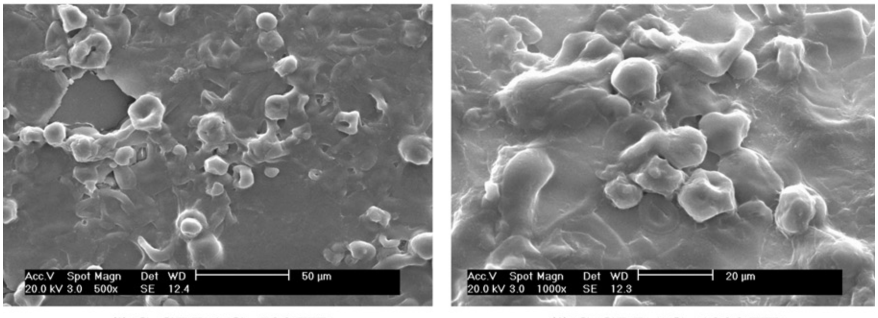
(c) S-GODAC×400 MW **(d) S-GODAC×2000 MW**



(e) S-GDDAC×400 MW **(f) S-GDDAC×2000 MW**

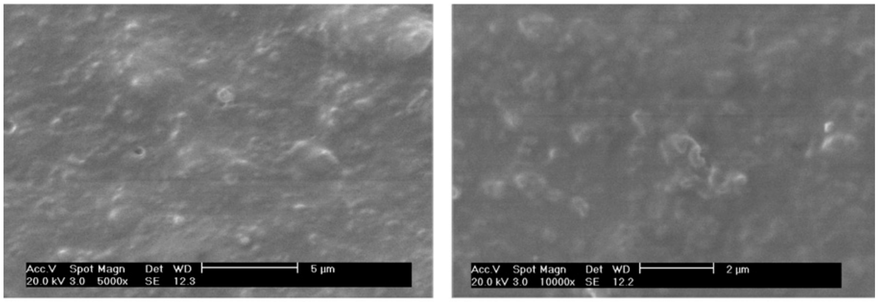


(g) S-GTDAC×400 MW **(h) S-GTDAC×2000 MW**



(i) S-GDDAC×500 KD **(j) S-GDDAC×1000 KD**

Fig. 3. SEM photos of starch and modified starch.



(k) S-GDDAC×5000 WET **(l) S-GDDAC×10000 WET**

Fig. 3 (*continued*)

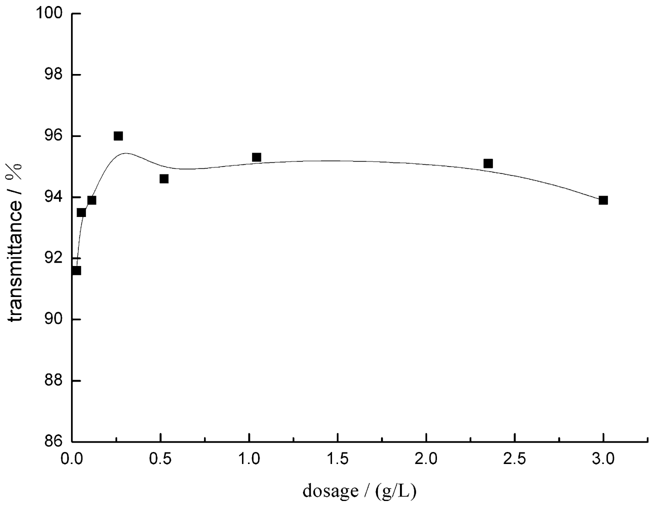


Fig. 4. effects of dosages for S-GTDAC on flocculating efficiency.

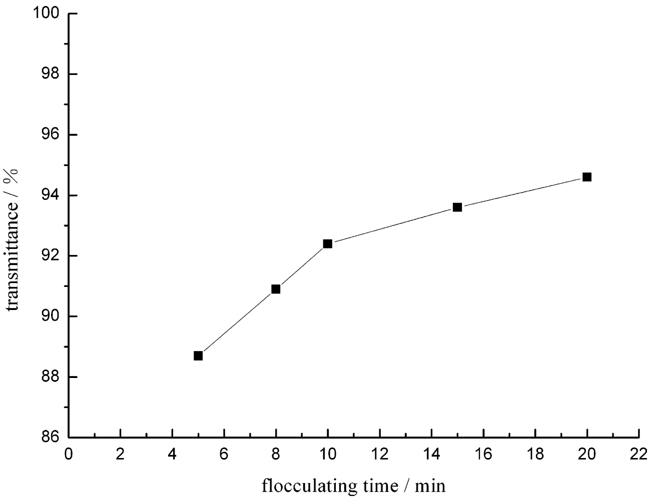


Fig. 6. Effects flocculating time on flocculating efficiency.

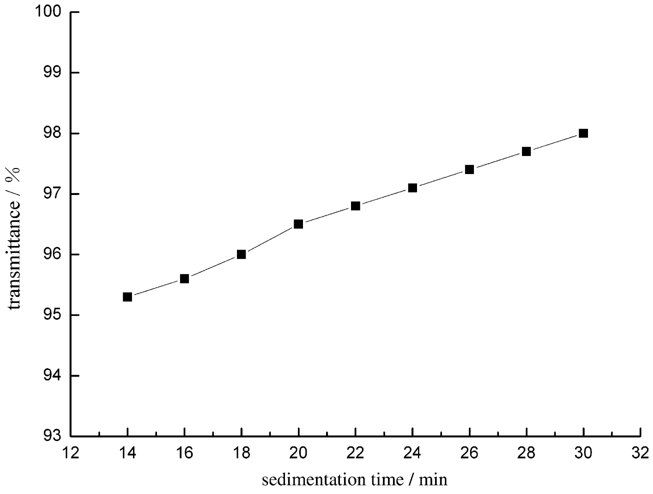


Fig. 5. Effects sedimentation time on flocculating efficiency.

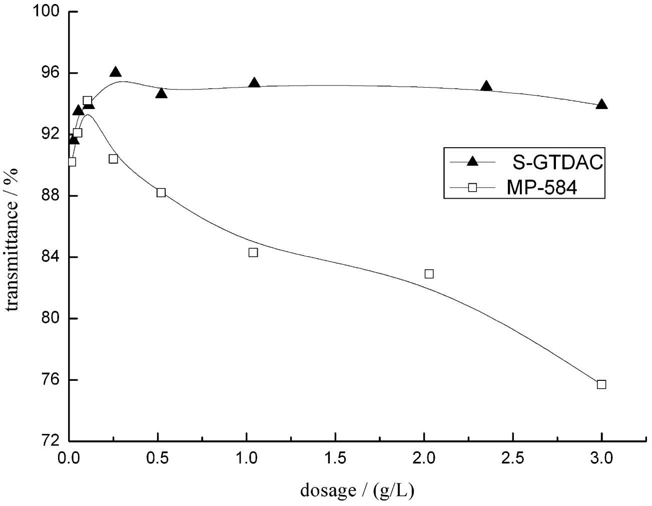


Fig. 7. Jar test results in Kaolin suspension with addition of S-GTDAC and commercial flocculant.

Device as reactor and 58.3 for wet (solvent) condition, respectively. Compared to the two conventional methods, microwave irradiation has not any obvious effects on the crystallinity of starch, though it affects the reactivity of starch remarkably. Among three cationic starches obtained with microwave irradiation, S-GTDAC with longer chains had the best performance, which was superior to the commercially available flocculant (MP-584). The transmittance of the supernatant liquid in Kaolin suspension for S-GTDAC reached 93.9, higher than other two (90.4 for S-GODAC and 92.7 for S-GDDAC). Also, the flocculation performance for S-GTDAC was increased with the increase of sedimentation and flocculating time. Finally, these cationic starches can find use as a potential flocculating agent for the treatment of wastewater.

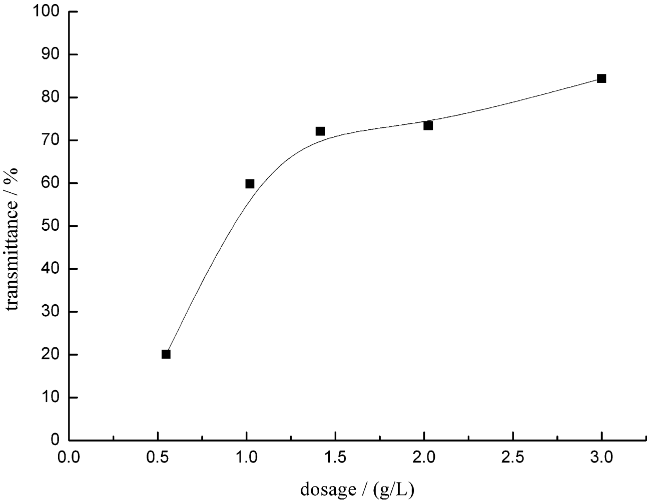


Fig. 8. Flocculating efficiency of the S-GTDAC to the paper-making wastewater.

Acknowledgment

This work was financially supported by Tianjin Natural Science Foundation (Project. 043602611).

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