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Physicochemical properties of granular and non-granular cationic starches prepared under ultra high pressure

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ABSTRACT

Granular and non-granular cationic starches were prepared through the reaction of tapioca and corn starches with 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC) using conventional and ultra high pressure (UHP)-assisted reactions. The cationic starches were characterized with respect to morphology, degree of substitution (DS), FT-IR, ^{13}C NMR, X-ray diffraction pattern, solubility and swelling power, pasting viscosity, and flocculating activity. Non-granular (relative to granular) cationic starches possessed higher DS values. While DS values of non-granular cationic starches were lower for UHP-assisted (relative to conventional) reaction, granular cationic starches did not differ for both reactions. For flocculation activity, granular cationic starches with lower solubility and higher swelling power were higher than non-granular counterparts with reversed patterns in solubility and swelling power, regardless of conventional and UHP-assisted reactions. Overall results suggested that flocculation activity of cationic starches may be directly associated with their swelling powers (relative to DS values).

1. Introduction

Starch is one of the most abundant natural polymers and a common carbohydrate source in staple foods such as corn, wheat, potato, rice, and tapioca. Starch and its chemically and physically modified products have been widely used in industrial applications, due to their low cost and biodegradation. However, the utilization of native starch is limited, due to its cold-water insolubility, uncontrolled consistency of starch pastes and higher tendency to retrogradation and gel formation. Thus, native granular starch is chemically and/or physically modified to improve and extend their physicochemical properties depending on demands of industrial applications (Song, 2010; Wang & Xie, 2010).

Chemically modified starches are commonly prepared by treating native starch granules with reacting reagents that can react with hydroxyl groups on starch molecules. One of the chemically modified starches, cationic starches possess positively charged groups such as amino, imino, ammonium and phosphonium, and are widely used for wastewater purification and non-food products (e.g., papers, textiles and cosmetics). Cationic starches are generally synthesized by reaction of native starch with cationic reacting reagents such as 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC) and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC). Cationic starch derivatives are effective flocculants for negatively charged organic and inorganic colloidal particles over a wide range of pH (Pal, Mal, & Singh, 2005; Wei, Cheng, & Zheng, 2008; Zhang et al., 2012). Most of cationic starches are present in non-granular forms due to the use of excessive NaOH for purpose to enhance their degree of substitution (Wang et al., 2009). However, limited information is available on physicochemical properties of granular-type cationic starch.

UHP or high hydrostatic pressure (HHP) technology is an attractive non-thermal technique as minimal processing technique of food systems, in particular for sterilization, enzyme inactivation, enzyme activity modulation, and bioactive compound extraction (Kim, Kim, & Baik, 2012). More recently, UHP-assisted derivatization of starch granules has been developed using UHP equipment as a reactor. This developed technique has been successfully applied for preparation of chemically modified starches (e.g., acid-thinned starch, starch acetate, phosphorylated cross-linked starch, phosphorylated starch, and hydroxypropylated starch) (Choi, Kim, Park, Kim, & Baik, 2009; Kim, Choi, Kim, & Baik, 2010; Kim, Choi, Kim, & Baik, 2011; Kim, Hwang, Kim, & Baik, 2012; Kim, Kim, et al., 2012; Lee et al., 2006). In acetylation and hydroxypropylation

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reactions, starch reactivities in UHP-assisted (relative to conventional) derivatization were around 25% lower, while reaction time was dramatically reduced at similar reactivity levels (Choi et al., 2009; Kim et al., 2010; Kim et al., 2011; Kim, Kim, et al., 2012). For UHP-assisted $POCl_3$ starch derivatives, significant differences in swelling, gelatinization, and pasting viscosity properties were not observed depending on pressurizing levels (Kim, Hwang, et al., 2012), though influenced by cross-linking reagent addition levels (Hwang, Kim, & Baik, 2009). Nevertheless, UHP-assisted (relative to conventional) cross-linking reaction shortened reaction time, and UHP-assisted $POCl_3$ starch derivatives prepared at pressure ranges of 300–400 MPa revealed similar swelling, gelatinization, and pasting viscosity properties to those of conventional $POCl_3$ starch derivatives (Kim, Hwang, et al., 2012). To date, however, UHP-assisted derivatization is not applied to preparation of cationic starch derivatives, though many studies have been conducted with respect to synthesis of cationic starch derivatives using conventional method (i.e., thermal processing at atmospheric pressure).

Thus, the objectives of this study were to synthesize granular and non-granular forms of cationic starch (tapioca and corn) derivatives using conventional and UHP-assisted derivatization reactions, and characterize their physicochemical properties and flocculating activities for waste water treatment.

2. Materials and methods

2.1. Materials

Tapioca and normal corn starches were purchased from Sing Song Industrial Co. (Seoul, Republic of Korea) and Shin Dong Bang CP Co. (Seoul, Republic of Korea), respectively. Tapioca and normal corn starches were 12.7 and 12.3% (wet basis or w.b.), respectively, for their moisture contents, and 24.6 and 26.5% (dry basis or d.b.), respectively, for their amylose contents. 2,3-Epoxypropyl trimethyl ammonium chloride (ETMAC) (60% solution) as an etherifying agent was purchased from KCI Co. (Ansan, Republic of Korea). Kaolin was obtained from Sigma–Aldrich Co. (St. Louis, MO, USA). Sodium hydroxide and isopropanol were obtained from Daejung Chemical & Metals Co. (Incheon, Republic of Korea).

2.2. Synthesis of conventional non-granular cationic starch

Conventional non-granular cationic starch was synthesized according to Wang et al. (2009). Starch (20 g, d.b.) was dissolved in a mixture of distilled water (90 g) and 10% sodium hydroxide solution (10 g), and stirred at 60 °C for 1 h. ETMAC (45 g) was added to starch solution, and reaction was conducted at 60 °C for 5 h. After completion of reaction, the resultant starch derivatives were precipitated with addition of isopropanol, and recovered by centrifugation (3000 × *g*, 20 min). The recovered cationic starch derivatives were washed three times with isopropanol and dried at 105 °C for 12 h. Dried samples were ground, passed through 60-mesh standard sieve, and stored at room temperature for further analysis.

2.3. Synthesis of UHP-assisted non-granular cationic starch

Starch (20 g, d.b.) was dissolved in a mixture of distilled water (90 g) and 10% sodium hydroxide solution (10 g), and stirred at 60 °C for 1 h. ETMAC (45 g) was added to starch solution. The reaction mixture was immediately transferred into a retortable pouch and hermetically sealed using a heat sealer. It was pressurized in UHP unit (Ilshin Autoclave, Daejeon, Republic of Korea) using distilled water as a pressure medium. During pressurization, the UHP unit was maintained at room temperature (25 °C). The UHP treatments were conducted at 500 MPa for 15 min. After UHP treatment, the resultant starch derivatives were post-treated as previously mentioned in Section 2.2.

2.4. Synthesis of conventional granular cationic starch

ETMAC (38.27 g) was dissolved in distilled water (41.316 g), and then starch (20 g, d.b.) was slowly added to a reaction medium under continuous stirring. The pH of a reaction mixture was adjusted to 11.0 using 25% (w/v) sodium hydroxide solution. Reaction was conducted at 25 °C for 18 h under continuous stirring, after which the resultant starch derivatives were recovered by centrifugation (3000 × *g*, 20 min). The recovered starch derivatives were washed three times with isopropanol, dried at 105 °C, ground, passed through 60-mesh standard sieve, and stored at room temperature for further analysis.

2.5. Synthesis of UHP-assisted granular cationic starch

ETMAC (38.27 g) was dissolved in distilled water (41.316 g), and then starch (20 g, d.b.) was slowly added to a reaction medium under continuous stirring. The pH of a reaction mixture was adjusted to 11.0 using 25% (w/v) sodium hydroxide solution. The reaction mixture was immediately transferred into a retortable pouch and hermetically sealed using a heat sealer. It was pressurized in UHP unit (Ilshin Autoclave, Daejeon, Republic of Korea) using distilled water as a pressure medium. During pressurization, the UHP unit was maintained at room temperature (25 °C). The UHP treatments were conducted at 500 MPa for 15 min. After UHP treatment, the resultant starch derivatives were post-treated as previously mentioned in Section 2.4.

2.6. Scanning electron microscopy (SEM)

Morphological characteristics of native and cationic starches were viewed using scanning electron microscopy (TM3000, Hitachi, Tokyo, Japan). The starch samples were dusted onto a conductive double glued carbon tape on a cylindrical aluminum tray, and coated to 20 nm thickness using a sputtering coater with gold-palladium (60:40). All specimens were observed at an accelerating voltage of 15 kV.

2.7. Nitrogen content and degree of substitution (DS)

The nitrogen content of native and cationic starches was determined by a semi-micro Kjeldahl method. Degree of substitution (DS) was calculated as following:

$$\mathrm{DS} = \frac{162 \times N\%}{14 \times 100 - (151.5 \times N\%)}$$

where 14 is the molecular weight of nitrogen, 162 is the molecular weight of an anhydrous glucose unit (AGU) of starch, and 151.5 is the molecular weight of ETMAC.

2.8. FT-IR spectroscopy

FT-IR analysis of ETMAC, and native and cationic starches was conducted using Spectrum One System (Perkin-Elmer, Waltham, MA, USA). The starch samples were mixed with potassium bromide (KBr), and pelleted. The spectra were examined with a resolution of 4 cm^{-1} and a wavelength range of 400–4000 cm^{-1}.

2.9. ^{13}C nuclear magnetic resonance (NMR) spectroscopy

NMR spectra of native and cationic starches were recorded on a 300 MHz nuclear magnetic resonance spectrometer (JNM-AL300,

JEOL, Nieuw-Vennep, Netherlands). After samples were dissolved in D_2O at 80 °C, the analysis was conducted at 25 °C.

2.10. X-ray diffraction

X-ray diffraction (XRD) patterns of native and cationic starches were determined using an X-ray diffractometer (D8 Advance, Bruker, Grossbottwar, Germany) operated in a transmission mode with a Ni filter Cu-Kα radiation at 40 kV and 300 mA. The X-ray source has a wavelength of 1.54056 Å, and XRD data were collected at scanning angle 2θ from 4° to 40°. Relative crystallinity was defined as the percent (%) ratio of sum of crystalline peak areas to that of the total diffractogram (including crystalline and amorphous peak areas) (Lee et al., 2006).

2.11. Swelling power and solubility

Swelling power and solubility of native and cationic starches were investigated according to the method outlined by Koo et al. (2005). Starch samples (0.5 g, d.b.) were suspended in distilled water (30 ml) and heated in a shaking water bath at 30, 50, 70 and 90 °C for 30 min. After heating, the tubes centrifuged at 3000 × *g* for 60 min and precipitates were separated from the supernatant and weighed. The supernatant was dried at 105 °C and weighed to determine starch solubility. Solubility and swelling power were calculated as following:

$$\text{Solubilty}\ \ (\%) = \frac{\text{soluble material weight}\ \ (\text{g, d.b.})\ \ \text{in supernatent}}{\text{Starch sample weight}\ \ (\text{g, d.b.})} \times 100$$

$$\text{Swelling power}\ \ (\%) = \frac{\text{Precipitate weight}\ \ (\text{g, wetbasis}) \times 100}{\text{Starch sample weight}\ \ (\text{g, d.b.}) \times (100 - \text{solubility})}$$

2.12. Rapid Visco Analyzer (RVA)

Pasting viscosity properties of native and cationic starches were determined using a Rapid Visco Analyzer (RVA-3D, Newport Scientific Pty. Ltd., NSW, Australia). Starch samples (1.0 g, d.b.) were directly weighed into an RVA canister, followed by the addition of distilled water (25 ml). Starch suspensions were analyzed under continuous shear (160 rpm) beginning with an initial hold at 50 °C (1 min), linear heating to 95 °C at a heating rate of 12 °C/min, an intermediate hold at 95 °C (2.5 min), linear cooling to 50 °C at a cooling rate of 12 °C/min, and a final hold at 50 °C (2 min).

2.13. Flocculating activity

Flocculating activity of kaolin was determined using previously reported methods (Shogren, 2009; Xie, Feng, Cao, Xia, & Lu, 2007). Kaolin (0.5 g) was suspended in 50 ml distilled water and mixed for 5 min using a magnetic bar. Flocculants (native and cationic starches, 10–100 ppm) were added and mixed at 300 rpm for 2 min, followed by 180 rpm for 5 min. Then the flocs were allowed to settle down for 1–10 min. After settling, the transmittance of the supernatant was measured by UV-1200 spectrophotometer (Labentech, Incheon, Republic of Korea).

2.14. Statistical analysis

The conventional and UHP-assisted cationization reactions were replicated twice for each treatment. DS values and all measured starch properties were determined at least twice for each experimental replicate. Also, experimental data were analyzed using Analysis of Variance (ANOVA), and expressed as mean ± standard deviation. Significant differences among experimental means were assessed by a Duncan's multiple range test ($\alpha < 0.05$). All statistical computations and analyses were conducted using SAS version 8.02 for Windows (SAS Institute, Inc., Cary, NC, USA).

3. Results and discussion

3.1. Scanning electron microscopy

Morphological characteristics of native and cationic starches (tapioca and normal corn) were viewed using SEM and shown in Fig. 1. As generally known (Swinkels, 1985), native tapioca starch was truncated and polygonal in a granular shape, and native corn starch was round and polygonal in a granular shape. Cationic tapioca and corn starches subjected to conventional and UHP-assisted reactions following preparation of reaction mixtures (starch, catalyst, ETMAC) at 60 °C no longer showed their respective granular structures, and revealed irregular, continuous matrix structures, typically observed for retrograded starches (Kim et al., 2013). The noted cationic starches were referred to as non-granular cationic starches. The observed morphologies of cationic starches was due to thermal alkaline starch gelatinization during reaction and preparation of reaction mixtures at 60 °C near which tapioca and corn starches began to gelatinize (Choi et al., 2009; Swinkels, 1985). Further, higher pH of the reaction mixtures facilitated alkaline gelatinization (at 60 °C) of starches through inter-repulsion of anionic alkoxide ions (generated by ionization of hydroxyl groups) on starch molecules (Gray & BeMiller, 2005). In contrast, cationic starches subjected to conventional and UHP-assisted reactions following preparation of the reaction mixtures at 25 °C still maintained their granular structure, though the reaction mixture possessed the same alkalinity to that for preparation of non-granular cationic starches. Also, they exhibited similar morphologies observed for their native starches. These cationic starches, which were prepared at 25 °C, were referred to as granular cationic starches. Overall, the observed morphological differences between granular and non-granular cationic starches resulted from different reaction temperatures (60 °C and 25 °C for non-granular and granular cationic starches, respectively).

3.2. Nitrogen content and degree of substitution

Nitrogen contents of cationic starches prepared via conventional and UHP-assisted reactions of tapioca and normal corn starches with ETMAC at different temperatures and pressures were measured by the semi-micro Kjeldahl method (Table 1). Their DS values were calculated from their net nitrogen (determined by subtraction of nitrogen contents of native starches from those of their cationic starches) contents, and depicted in Table 1. All cationic tapioca and corn starches revealed higher nitrogen contents and corresponding DS values than their respective native starches. Within reaction systems, the non-granular (relative to granular) forms in cationic tapioca and corn starches showed much higher nitrogen contents and DS values. These results were due to enhanced accessibility of ETMAC to starch molecules, resulting from gelatinization (or rupture) of starch granules. The noted phenomena were also observed for the report of Xu, Miladinov, and Hanna (2004), who prepared highly substituted starch acetates through acetylation reaction accompanying gelatinization (or rupture) of starch granule by heating.

For granular cationic tapioca and corn starches, nitrogen contents and DS values did not differ for both reactions (Table 1), though greatest difference in reaction time between both conventional (18 h) and UHP-assisted (15 min) reactions. This result may be due to bulky structure of ETMAC which made penetration of ETMAC into starch granule interior and matrix difficult. Thus, UHP-assisted (relative to conventional) reaction appeared to be more

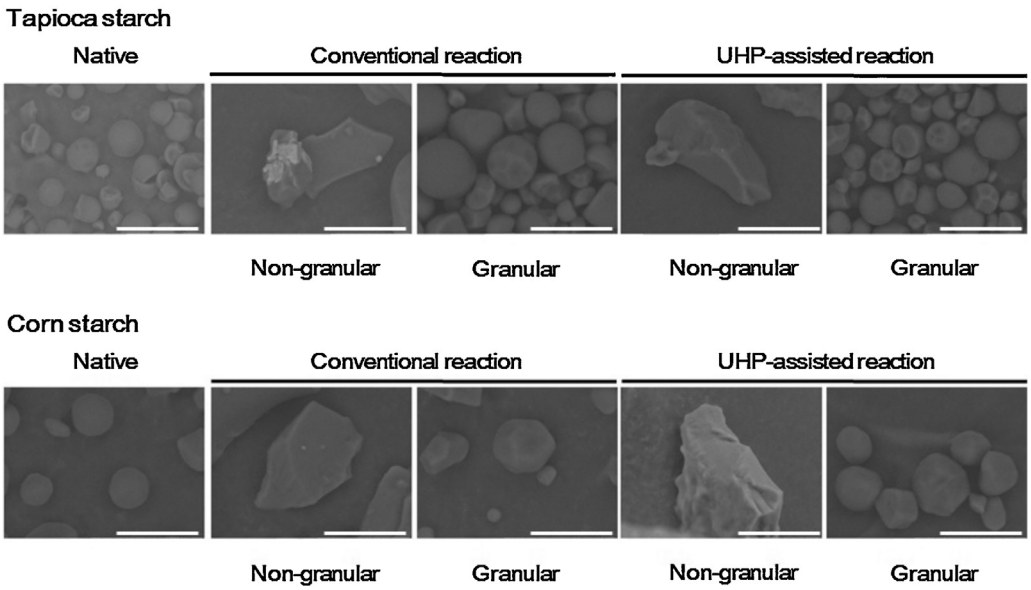

Fig. 1. Scanning electron microscopy (SEM) images of native and cationic starches. Tapioca (a) and corn (b) starches (scale bar = 30 μm).

efficient for preparation of granular cationic starches. In contrast, for non-granular cationic tapioca and corn starches, the reactivities (determined by DS values) of conventional reaction were 1.7–2.5 times higher than those of UHP-assisted reaction (Table 1). Similar patterns that starch reactivity was reduced in UHP-assisted (relative to conventional) reaction were observed for other reactions (e.g., acetylation, hydroxypropylation) (Choi et al., 2009; Kim et al., 2010; Kim et al., 2011; Kim, Hwang, et al., 2012). These noted phenomena may result from differences in reaction time between conventional (18 h) and UHP-assisted (15 min) reactions. While UHP-assisted reaction time was 1.4% of convention reaction time, DS values of UHP-assisted non-granular cationic starches were achieved to be 58.7% (for tapioca starch) and 40% (for corn starch) of those of conventional non-granular cationic starches. Thus, UHP-assisted cationization reaction may be an efficient way of synthesizing non-granular cationic starch, because similar or higher DS values of UHP-assisted (relative to conventional) non-granular cationic starches were anticipated to be achieved through extension of reaction time in UHP-assisted reaction.

3.3. FT-IR spectroscopy

FT-IR spectra of native and cationic starches (tapioca and corn) were depicted in Fig. 2A and B. Native tapioca and corn starches exhibited the broad bands at 3400 cm^{-1} and 2923 cm^{-1}, resulting from stretching vibration of both O—H bond and C—H bonds, respectively. Also, the bands at 1156, 1066, 1011 cm^{-1} were attributed to stretching vibration of the C—O bonds in the anhydrous glucose unit (AGU). On the other hand, all cationic starches prepared by both conventional and UHP-assisted reactions exhibited the bands observed in the spectra of native starches as well as an additional band at 1480 cm^{-1} assigned to the stretching vibration of C—N bond (Wang et al., 2009; Wang & Xie, 2010). These spectrum patterns provided obvious evidence that cationic moiety of ETMAC was substituted onto the starch backbone.

3.4. ^{13}C NMR spectroscopy

To further confirm successful reaction of tapioca and corn starches with ETMAC, native and cationic starches were analyzed with ^{13}C NMR, and their spectra were shown in Fig. 2C and D. Native tapioca and corn starches exhibited major peaks in the chemical shift ranges of 60–100 ppm, resulting from carbons of the unreacted AGU. The peaks observed at 100.0, 78, and 62 ppm corresponded to C_1, C_4, and C_6 of AGU within starch, respectively (Heinze, Haack, & Rensing, 2004; Wang et al., 2009). Moreover, the overlapping peaks at 72–75 ppm were due to C_2, C_3 and C_5 of AGU within starch. After conventional and UHP-assisted cationization reactions, additional peaks at 55, 66, and 69 corresponding to C_{10}, C_8, and C_9, respectively, were observed. Further, original peaks observed for native starches were split and/or tailed (Fig. 2C and D). Compared to NMR spectra of native starches, consequently, emerging peaks of cationic starches provided obvious evidence that substitution reaction of starch backbone with ETMAC successfully occurred.

Table 1
Mean[a] values for nitrogen content, degree of substitution (DS), and relative crystallinity of native and cationic starches.

Starch source	Starch form	Reaction	Nitrogen content (%)	DS	Relative crystallinity (%)
Tapioca	Granular	Native	0.09 ± 0.03^{e}	0.00 ± 0.00^{e}	10.59 ± 0.64^{a}
	Granular	Conventional	1.81 ± 0.11^{c}	0.26 ± 0.02^{c}	8.31 ± 1.17^{ab}
	Granular	UHP-assisted	1.56 ± 0.13^{d}	0.22 ± 0.02^{d}	8.64 ± 0.31^{b}
	Non-granular	Conventional	5.40 ± 0.00^{a}	1.50 ± 0.00^{a}	–
	Non-granular	UHP-assisted	4.18 ± 0.04^{b}	0.88 ± 0.02^{b}	–
Corn	Granular	Native	0.12 ± 0.00^{d}	0.00 ± 0.00^{d}	9.64 ± 0.33^{a}
	Granular	Conventional	1.71 ± 0.12^{c}	0.24 ± 0.02^{c}	7.62 ± 0.01^{c}
	Granular	UHP-assisted	1.65 ± 0.23^{c}	0.23 ± 0.04^{c}	8.28 ± 0.83^{ab}
	Non-granular	Conventional	4.58 ± 0.27^{a}	1.05 ± 0.12^{a}	–
	Non-granular	UHP-assisted	2.62 ± 0.03^{b}	0.42 ± 0.01^{b}	–

[a] Mean values of three measurements; values sharing the same lowercase letters within columns of a given starch source are not significantly different ($\alpha < 0.05$).

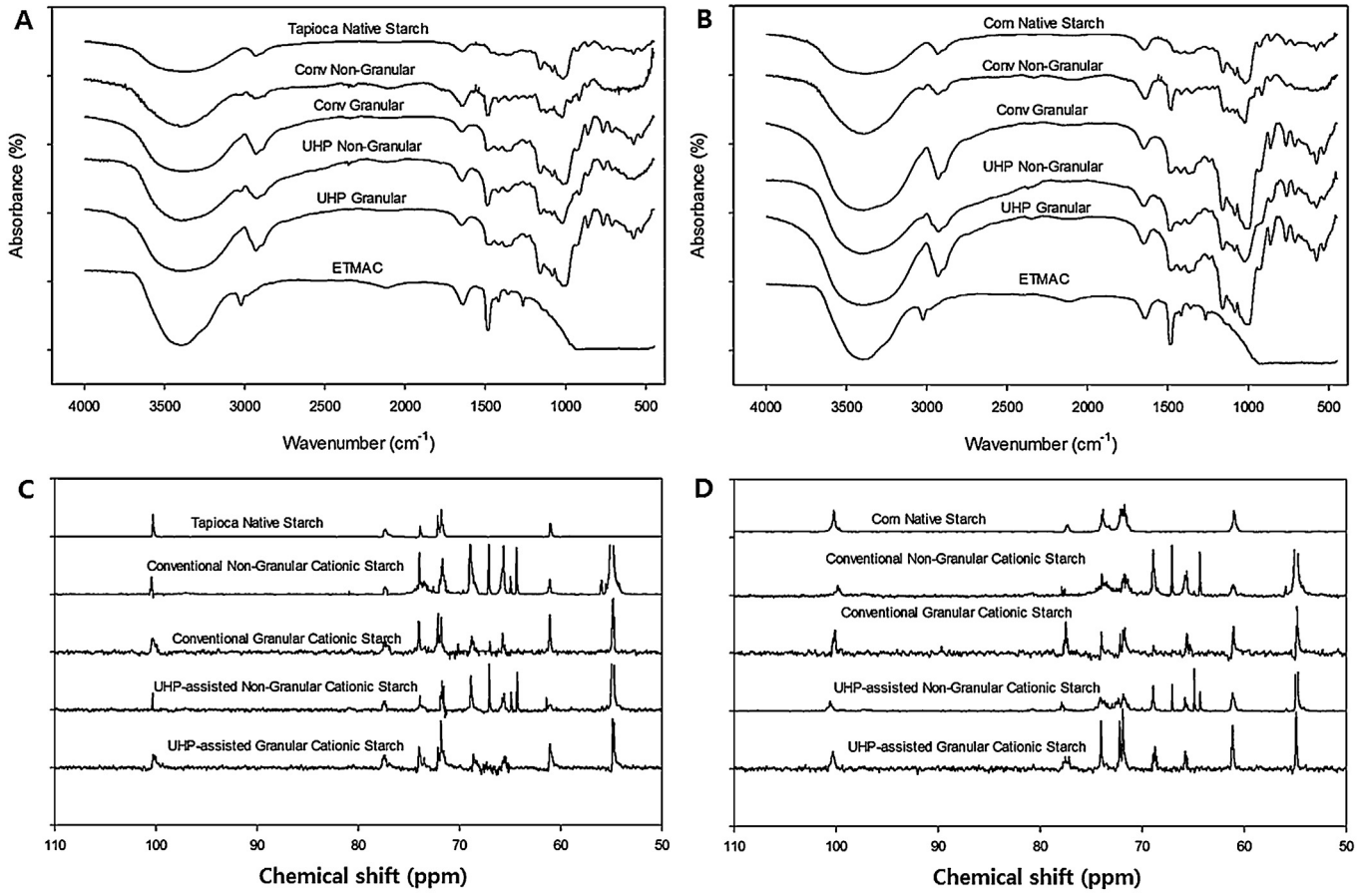

Fig. 2. Fourier transformed infrared (FTIR) (A and B) and nuclear magnetic resonance (NMR) (C and D) spectra of native and cationic starches, and ETMAC. Tapioca (A and C) and corn (B and D) starches.

3.5. X-ray diffraction

The crystal packing arrangement of conventional and UHP-assisted cationic starches (tapioca and corn) are investigated with powder X-ray diffractometer and shown in Fig. 3. Native corn and tapioca starches showed typical A-type and C-type crystal packing arrangements, respectively (Zobel, 1988). Granular cationic tapioca and corn starches subjected to conventional and UHP-assisted reactions exhibited similar crystal packing arrangements to those of their respective native starches, although peak intensities of crystalline regions in XRD diffractograms were somewhat reduced (Fig. 3). In non-granular cationic tapioca and corn starches, however, XRD patterns were broader without crystalline peaks, indicating a typical amorphous structure (Cheetham & Tao, 1998; Flores, Famá, Rojas, Goyanes, & Gerschenson, 2007; Wang & Xie, 2010). These results were supported by SEM observation of non-granular cationic starches (Fig. 1). Also, the noted findings may be due to alkaline-induced gelatinization of non-granular cationic starches, resulting from preparation of the reaction mixture at 60 °C prior to conventional and UHP-assisted reactions.

Relative crystallinity of native and cationic starch (tapioca and corn) granules was listed in Table 1. Relative crystallinities of native tapioca and corn starch granules were 10.59% and 9.64%, respectively. However, relative crystallinities of granular cationic tapioca and corn starches subjected to conventional and UHP-assisted reactions were slightly reduced than those of their respective native starches (Table 1). These results were explained by mild alkaline treatment during long reaction time (18 h) and UHP treatment, which may slightly alter the crystalline structure of native starch granules. It has been reported that the starch crystalline structure greatly decreased with UHP treatment at 500 MPa for 20 min (Hibi, Matsumoto, & Hagiwara, 1993). In this study, however, UHP-assisted cationization reactions were conducted at 500 MPa for 15 min. Also, the concentrations of starch granules in the reaction mixtures were over 20% (w/v). An increase of starch concentration in a starch–water suspension was reported to enhance resistance of starch granules against UHP (Kim, Kim, et al., 2012). Consequently, UHP-assisted cationization reaction applied to this study may minimize destruction of crystal structures within starch granules.

3.6. Solubility and swelling power

The solubility and swelling power of native and cationic starches (tapioca and corn) were depicted in Fig. 4. The solubility and swelling power of native tapioca and corn starches dramatically increased over 50 °C and were further enhanced with increasing temperature, comparable with results of others (Hwang et al., 2009; Kim & Huber, 2010). However, cationic tapioca and corn starches, regardless of starch forms and reaction types, exhibited similar solubilities and swelling powers across temperature ranges of 30–90 °C (Fig. 4), implying that those of cationic starches were not influenced by temperature. These results may be due to enhanced repulsion of positive charges on cationic starch molecules. Also, non-granular cationic starches exhibited higher solubilities than granular counterparts, and solubilities of cationic starches increased with increasing their DS values. These phenomena were consistent with those generally reported for substituted starches (Choi et al., 2009; Kim et al.,

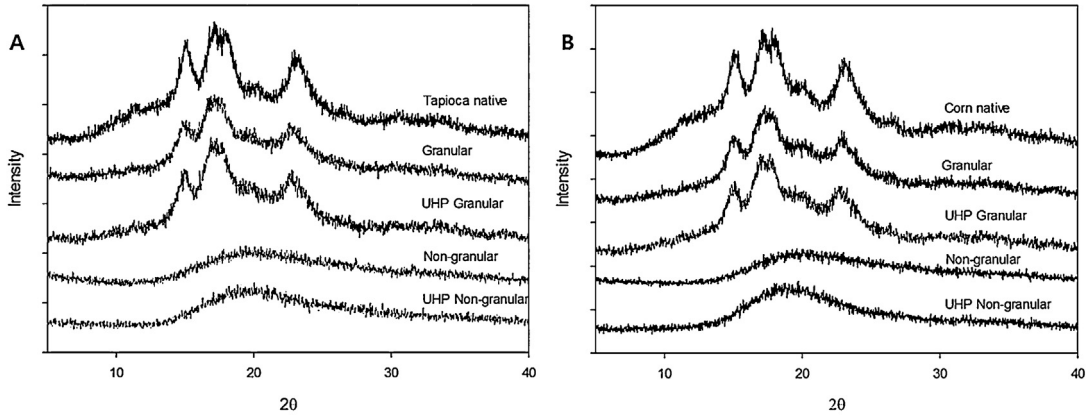

Fig. 3. X-ray diffraction patterns of native and cationic starches. Tapioca (A) and corn (B) starches.

2010; Kim et al., 2011). On the other hand, swelling powers of cationic starches did not follow the patterns observed in solubilities of cationic starches. Granular cationic starches revealed higher swelling powers than non-granular counterparts, though granular (relative to non-granular) cationic starches possessed lower DS values. These findings were due to the fact that granular cationic starches maintaining their granularities may have greater capacity to absorb and hold water within swollen starch granules. In contrast, non-granular cationic starches did not form three dimensional networks to hold water due to cationic bulky substituents on starch molecules, resulting in lower swelling powers. For granular cationic starches, UHP-assisted cationic starches revealed lower swelling powers than conventional ones, though both cationic starches possessed similar DS values. These results were compatible with those in UHP-assisted acetylation and hydroxypropylation reactions (Choi et al., 2009; Kim et al., 2010; Kim et al., 2011).

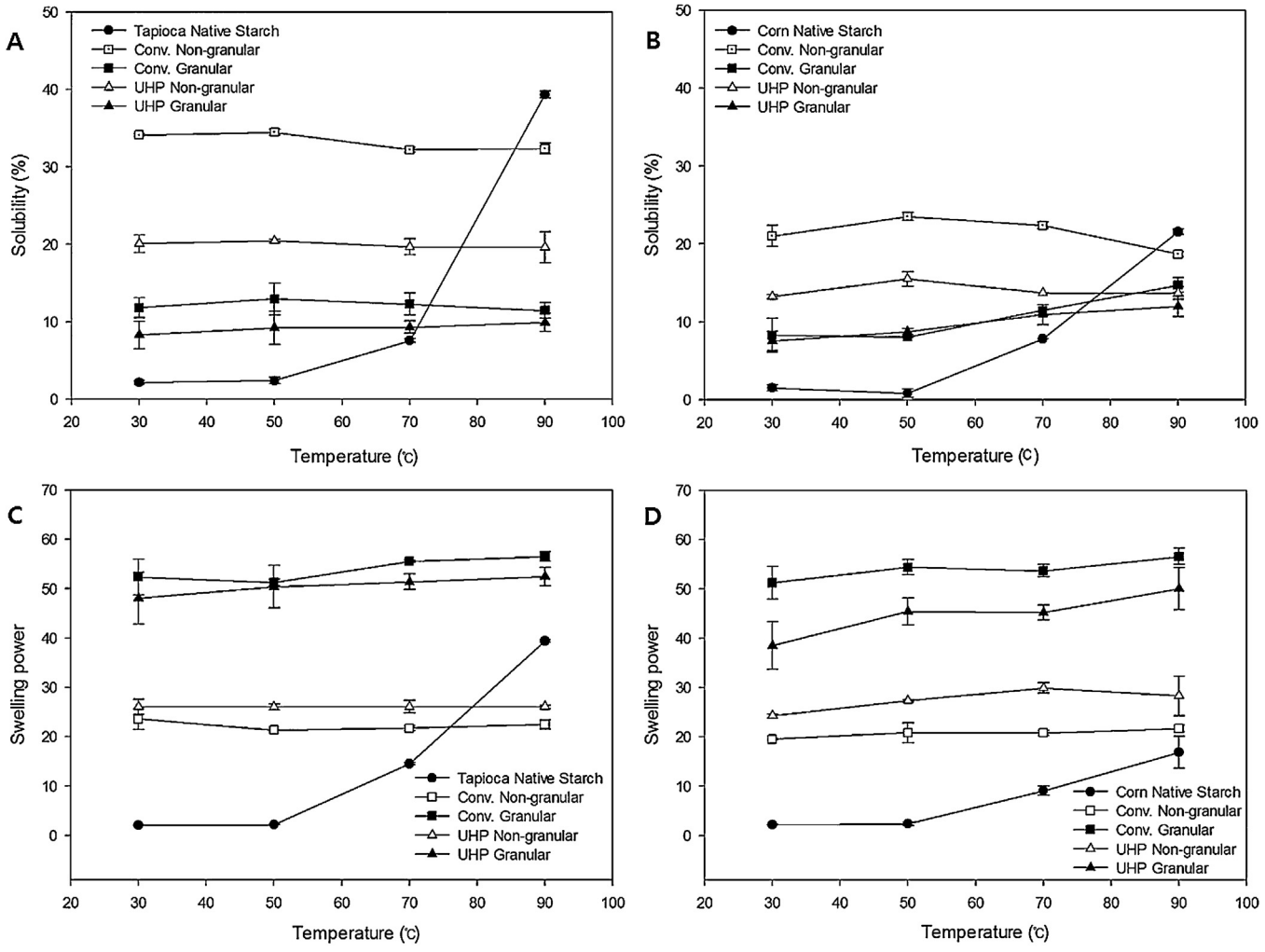

Fig. 4. Solubility (A and B) and swelling power (C and D) of native and cationic starches. Tapioca (A and C) and corn (B ad D) starches.

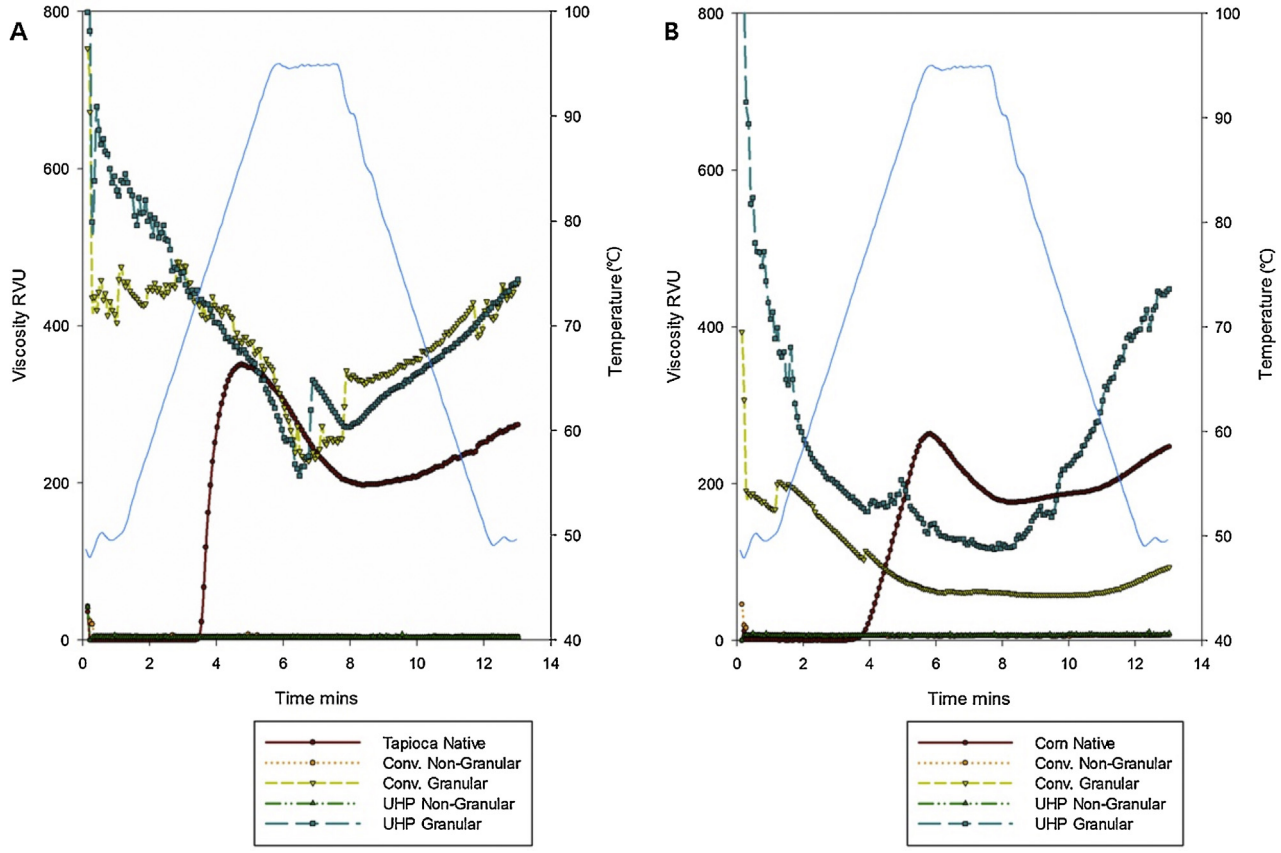

Fig. 5. Pasting viscosity profiles of native and cationic starches. Tapioca (A) and corn (B) starches.

The noted phenomena were likely due to the different reaction patterns between conventional and UHP-assisted reaction and the retrogradation (following partial gelatinization) of cationic starch granules by UHP treatment, as suggested by others (Choi et al., 2009; Kim et al., 2010; Kim et al., 2011). For non-granular cationic starches, however, the trends in swelling powers observed for granular cationic starches were reversed, though conventional cationic starches possessed higher DS values than UHP-assisted cationic starches. These phenomena might be the results of that UHP forced partial formation of weak junction zones among non-substituted regions of cationic starch molecules.

3.7. Rapid Visco Analyzer (RVA)

The pasting viscosity profiles of native and cationic starches were analyzed using a Rapid Visco Analyzer (RVA) and shown in Fig. 5. Native tapioca and corn starches exhibited typical RVA pasting viscosity profiles, while different patterns in pasting viscosity profiles were observed for cationic starches. For granular cationic starches, the greatest peak viscosities appeared at an initial stage holding at 50 °C for 1 min, and then greater breakdown viscosities were generated with further increasing temperature (Fig. 5). As temperature decreased, pasting viscosities increased. While the patterns developing pasting viscosities depending on temperatures were similar to those of native starches, the greater deviations in pasting viscosity levels between native and cationic starches were present. The similar trend in pasting viscosity was observed for anionic wheat starch granules substituted with a propylene oxide analog (POA) (Kim & Huber, 2010). Although the molecular backbone of POA was very similar to that of ETMAC, a trimethyl ammonium group of ETMAC was replaced to sulfonic acid, providing anionic charge to POA-derivatized starch granules. Consequently, the phenomena observed in this study were due to cationic, bulky substituents on starch molecules of cationic starches which resulted in arrival at maximum swelling of starch granules. On the other hand, non-granular cationic starches failed to develop their viscosities using RVA (Fig. 5). RVA is an equipment to measure viscosity generating frictions among swollen starch granules, ruptured starch granule fragments, and interaction of leached starch molecules. However, non-granular cationic starches did not contain starch granules and also minimized interaction of starch molecules due to cationic, bulky substituents on starch molecules. Thus, the sensitivity of RVA appeared to be too low to detect viscosity of non-granular cationic starches.

3.8. Flocculating activity

The flocculating activity of native and cationic starches were determined by UV-spectrophotometer and depicted in Figs. 6 and 7. To determine an addition dosage of cationic starches achieving maximum flocculating activity, the tests were conducted at three addition levels (10, 50 and 100 ppm) of cationic starches. In general, cationic starches revealed better flocculating activities than native starches. Flocculating activities of cationic starches increased with increasing their concentration, and in all cationic starches, maximum flocculating activities were obtained at 100 ppm. At maximum flocculating activity (100 ppm), granular cationic starches subjected to conventional and UHP-assisted reactions exhibited higher flocculating activities than non-granular counterparts, though their DS values were opposite (Table 1). These observed patterns were consistent with those of swelling powers of granular (relative to non-granular) cationic starches. Within the limited volume of aqueous kaolin-cationic starch suspension, the swollen cationic starch granules accounted for most volume

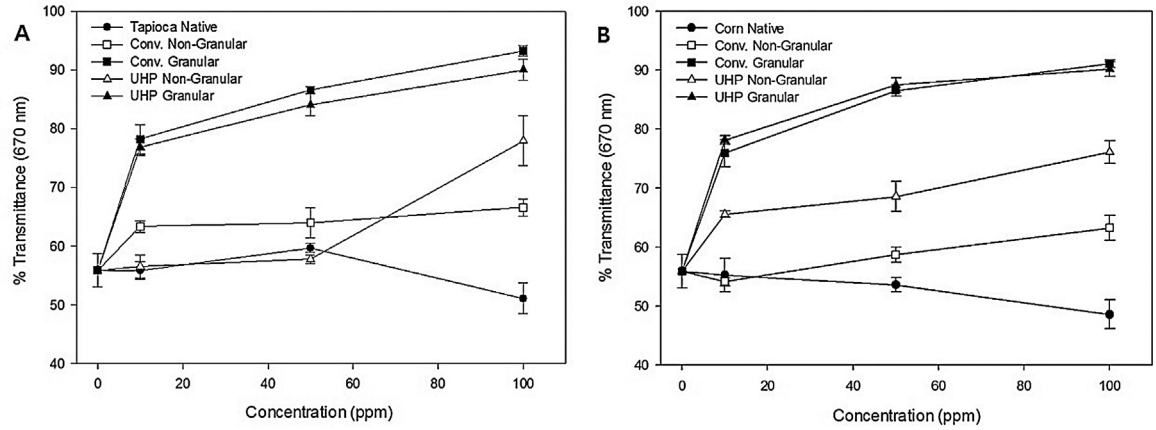

Fig. 6. Effects of concentrations of native and cationic starches on flocculation of kaolin in water (measured by light transmittance after settling for 2 min). Tapioca (A) and corn (B) starches.

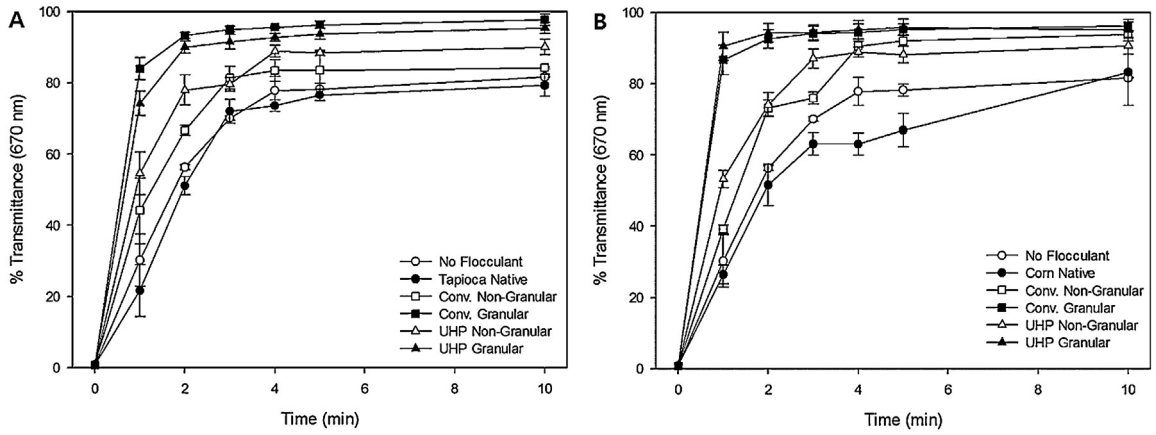

Fig. 7. Influences of settling time on flocculation of kaolin in water (measured by light transmittance at starch concentration of 100 ppm). Tapioca (A) and corn (B) starches.

of the suspension, which reduced relative volume of continuous phase containing kaolin. Consequently, the contact among kaolin particles within reduced continuous phase was likely enhanced, facilitating their flocculation. In contrast, non-granular cationic starches with higher solubility and lower swelling power (Fig. 4) may be present among kaolin particles, which could interrupt their flocculation. Further, the noted suggestion was also explained by non-granular cationic starches. UHP-assisted non-granular cationic starches exhibited slightly (but significantly) higher swelling powers than conventional cationic starches (Fig. 4). These patterns were compatible with flocculation activities of UHP-assisted (relative to conventional) non-granular cationic starches (Fig. 6). Overall results implied that flocculating activities of cationic starches may result from their swelling powers.

To investigate the effect of cationic starches on settling time of kaolin, kaolin suspensions including 100 ppm cationic starches were held for 1–10 min, and the transmittance of the supernatant were measured (Fig. 7). Flocculation activities followed the patterns observed for tests that assessed the effects of cationic starch addition levels. As anticipated, granular cationic starches achieved maximum flocculation activities within 2 min settling time. In contrast, non-granular cationic starches reached the highest transmittance around 4 min (Fig. 7). Similar to the previous results, regardless of conventional and UHP-assisted reaction, granular cationic starches showed better flocculating activity than non-granular cationic starches.

4. Conclusions

Cationic starches in granular and non-granular forms were prepared via conventional and UHP-assisted reactions. DS values of granular cationic starches (tapioca and corn) did not differ for conventional and UHP-assisted reactions, although conventional reaction required longer reaction time than UHP-assisted reaction. This finding suggested that UHP-assisted reaction was an efficient way of preparing cationic starches which maintained their granular forms. In the cases of non-granular cationic starches, however, their DS values may be enhanced mainly with increasing the reaction time relative to UHP treatment. FT-IR and ^{13}C NMR spectra confirmed that ETMAC was successfully incorporated onto hydroxyl groups of starch molecules during UHP-assisted reaction. Regarding characterization of cationic starches, general results observed for modified starches substituted with cationic or anionic, bulky reagents were obtained. Nevertheless, flocculation activities were much higher for granular (relative to non-granular) cationic starches with higher swelling powers. Thus, the swelling power was the most crucial factor to determine flocculation activity of cationic starches than their DS values. Considering DS value (which revealed relatively lower significance for flocculation activity of cationic starches) and reaction time, furthermore, UHP-assisted (relative to conventional) cationization reaction may be more efficient way of preparing cationic starches.

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