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Preparation and thermal stability of carboxymethyl starch/quaternary ammonium salts complexes

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ABSTRACT

Starch complexes were obtained from activated and pregelatinized cassava starch (AS) or carboxymethyl starch (CMS) by using quaternary ammonium salts (QAS). The synthesis of the CMS was carried out by a single or double step carboxymethylation reaction with monochloroacetic acid. Different parameters were assayed to prepare the ionic complexes: CMS or AS as starting materials, anhydroglucose unit/QAS ratio, and length of the alkyl chain of the alkyltrimethylammonium bromide (C_nTAB) salt. The products were characterized by FTIR, ^{1}H and ^{13}C NMR, and the Kjeldhal method. The results indicated a much more favorable complex formation when using CMS, obtaining the highest degree of substitution or complexation (0.72) and reaction efficiency (0.96) when C_{18}TAB was employed. DSC and WAXS experiments evidenced the crystallization of the octadecyl chain introduced in the starch, exhibiting a dependence on sample water content. TGA and TVA analysis showed the stability of the complexes up to ~150 °C and that degradation takes place in at least two stages with the release of the surfactant moiety in a first stage and the degradation of the starch skeleton in a second stage.

1. Introduction

Starch is one of the most important renewable resources because of its biodegradability, easy availability, and low cost. The most commercially important sources of starch are corn, potato, cassava, rice, wheat, and peas. Their applications range is very broad and covers food and non-food areas. Among the latter, their use in paper, oil, pharmaceutical, and plastic industry may be mentioned (Bastioli, 2005; Jie, Wen-ren, Manurung, Ganzeveld, & Heeres, 2004; Pascente, Márquez, Balsamo, & Müller, 2008; Swanson, Westhoff, & Doane, 1988). Native starch may exhibit, however, some drawbacks that restrict its use such as sensitivity to shearing and low pH, thermal resistance, high tendency towards retrogradation, brittleness, and lack of specific functional groups that may interact with different compounds or substances (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006; Averous & Boquillon, 2004; Briassoulis, 2004). Therefore, the chemical modification of this polysaccharide offers an interesting alternative to develop new products, preserving petrochemical resources and providing biodegradation properties with appropriated performance. Chemical modification of starch is generally achieved through derivatization reactions such as esterification, etherification, cross-linking, and grafting (Ortega-Ojeda, 2004; Singh, Kaur, & McCarthy, 2007).

Esterification has been carried out by a variety of pathways using acetic anhydride (Fang, Fowler, Tomkinson, & Hill, 2002; Shogren, 1996), fatty acids and acid chlorides (Aburto, Hamaili, Mouysset-Baziard, Senoq, Alric, & Borredon, 1999; Kapusniak & Siemion, 2007; Sagar & Merrill, 2003), and alkenyl succinic anhydrides (Bhosale & Singhal, 2006; Chi, Xu, Xue, Song, Zang, & Wang, 2007; Jeon, Viswanathan, & Gross, 1999; Jyothi, Rajasekharan, Moorthy, & Sreekumar, 2005; Rivero, Balsamo, & Müller, 2009). On the other hand, starch etherification has been focused on the synthesis of hydroxyalkylated (Bien, Wiege, & Warwel, 2001; Funke & Lindhauer, 2001; Sagar & Merrill, 2003; Tuschhoff, 1987), cationic (Grano, Yli-Kauhaluoma, Suortti, Kaki, & Nurmi, 2000; Heinze, Haack, & Rensing, 2004; Pal, Mal, & Singh, 2005), and carboxymethylated starches (Heinze & Koschella, 2005; Heinze, Pfeiffer, Liebert, & Heinze, 1999; Lazik, Heinze, Pfeiffer, Albrecht, & Mischnick, 2002; Stojanovic, Jeremic, Jovanovic, & Lechner, 2005; Tijsen, Kolk, Stamhuis, & Beenackers, 2001), which up to now have

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been applied almost exclusively in the food and paper industry (Lazik, Heinze, Pfeiffer, Albrecht, & Mischnick, 2002); although, their potential application as corrosion inhibitors has also been recently published (Bello, Ochoa, Balsamo, López-Carrasquero, Coll, Monsalve, & Gónzalez, 2010). One of the problems associated to many chemical modifications is the reduction of the molecular weight that takes place during the reactions when high degrees of substitution are desired; besides, the use of solvents and catalysts such as pyridine in some cases represent a great disadvantage due to environmental restrictions.

The alkylation of polysaccharides other than starch, through the formation of polyelectrolyte/surfactant complexes, has been widely reported. Polyelectrolyte/surfactant interactions were reviewed by Hayakawa and Kwak (1991) in cellulose (CMC)/quaternary ammonium salts complexes, systems in which degrees of complexation of 0.96 were reached; in dilute solution, the surfactant forms micelle-like aggregates adsorbed onto the polyelectrolyte chains (Thalberg, Lindman, & Karlström, 1991). Barck and Stenius (1994) investigated the interactions between CMC and $C_nH_{2n+1}N(CH_3)_3Br$, $n = 10$, 12, 14, and 16, evaluating the effect of polymer charge density, surfactant chain length, and ionic force on CMC/alkyltrimethylammonium bromide (C_nTAB) complex formation; they demonstrated by means of surface tension measurements and phase diagrams that the amount of carboxylate groups in the starting CMC is a determinant parameter and that, in solution, more stable aggregates are formed as the length of the surfactant increases. Tiitu, Laine, Serimaa, and Ikkala (2006) characterized complexes obtained from CMC ($DS = 0.9$) and alkyltrimethyl ammonium chlorides with different alkyl chain lengths; SAXS experiments showed a cylindrical self-assembly in bulk samples and, upon their exposition to moisture, conductivities of ca. 10^{-5} S/cm at room temperature were achieved, which would allow the use of these compounds for antistatic paper coatings.

Taking into account the studies previously mentioned, it was therefore the aim of this work to introduce alkyl chains within the starch molecules through complexation of carboxymethyl starch (CMS) with quaternary ammonium salts (QAS) having different alkyl chain lengths in aqueous medium. Even though the carboxymethylation of starch has been known for a long time, various studies have been recently carried out to optimize reaction conditions, increasing product yield and reaction efficiency (Bhattacharyya, Singhal, & Kulkarni, 1995; Kisung Kwon, Joon Hyuck Auh, Kwan Hwa Park, Chan, & Cheul Jong Ko, 1997; Mollega, Barrios, Feijoo, Contreras, Müller, & López-Carrasquero, submitted; Stojanovic, Jeremic, & Jovanovic, 2000; Tijsen, Kolk, Stamhuis, & Beenackers, 2001), and to the best of our knowledge the preparation of carboxymethyl starch/alkyltrimethylammonium bromide complexes has only been reported in a preliminary study published by us (Balsamo, López-Carrasquero, Contreras, Müller, Laredo, Contó, & Feijoo, 2010). The carboxymethylation of starch results in a modified starch (CMS) due to the introduction of carboxylate groups ($-CH_2COO^-$) that disturb the ordered structure of native starch, reduce the gelatinization temperature, increase solubility in water, and lead to higher storage stability (Hayakawa & Kwak, 1991). In this work we investigate the effect of the amount of carboxylate groups and alkyl chain length of alkyltrimethylammonium bromides (C_nTAB, $n = 12$, 14, 16, and 18) on the final degree of substitution or complexation of CMS/C_nTAB ionic complexes. Due to the fact that the complexes obtained in this study may be potentially used as compatibilizers in polyesters/starch blends, we also investigated their thermal stability, a parameter that may be determinant in the successful processing of this type of blends. It should be mentioned, that this kind of complexes may also find application as protective antistatic films for paper (Tiitu, Laine, Serimaa, & Ikkala, 2006).

2. Materials and methods

2.1. Synthesis of modified starches

2.1.1. Materials

Cassava starch was kindly supplied by Agroindustriales Mandioca S.A., Venezuela (30% amylose). Alkyltrimethylammonium bromide surfactants ($RN^+Me_3Br^-$) with $R = C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, and $C_{18}H_{37}$ were purchased from Aldrich Chemicals and used as received. Other chemicals and reagents were of analytical grade and employed without further purification. Water used in the preparation of CMS and complexes was distilled and deionized before use.

2.1.2. Preparation of AS and CMS precursors

Cassava starch was activated and pregelatinized (AS) by a drop wise addition of a 10% w/v NaOH aqueous solution to a 10% w/v aqueous dispersion of cassava starch in a glass reactor. Then, the slurry was heated at 60 °C for 2 h under agitation. A fraction of the product was precipitated and washed in ethanol, and it was finally dried under vacuum at 50 °C for 48 h. Starch carboxymethylation (CMS) was carried out from the remaining fraction, following the procedure previously described by Mollega et al. (submitted); the temperature was reduced down to 50 °C and a 10% w/v aqueous solution of monochloroacetic acid (MCAA) was added to this mixture; a molar NaOH:AGU:MCAA ratio of 2:1:1 was used, where AGU refers to the starch anhydroglucose unit. The reaction was carried out for 3 h. After the reaction, the CMS was precipitated by adding ethanol. It should be mentioned that due to the reaction conditions, the resulting product is the CMS sodium salt. Then, it was washed with ethanol and dried under vacuum at 50 °C for 48 h.

The degree of substitution of CMS, DS_{CMS}, which is defined as the average number of hydroxyl groups substituted per anhydroglucose (AGU) unit, was determined by an acid–base back titration (Stojanovic, Jeremic, & Jovanovic, 2000); all measurements were done in duplicate. In addition, we prepared another CMS with a higher DS_{CMS} using a multistep carboxymethylation (Heinze & Koschella, 2005; Lazik, Heinze, Pfeiffer, Albrecht, & Mischnick, 2002). In this case, the synthesized CMS in a first step was subjected again to an additional carboxymethylation reaction similar to that described above. The success of the carboxymethylations was corroborated by the appearance of the respective signals by FTIR, ^{13}C NMR, and DEPT 135 (Lazik, Heinze, Pfeiffer, Albrecht, & Mischnick, 2002; Mollega et al., submitted). FTIR (cm^{-1}): 1606 (υ_{as} $-CH_2-COO^-$) and 1417 (υ_s $-CH_2-COO^-$). ^{13}C NMR (in D_2O at 70 °C) (ppm): 70.3, 71.6 ($-O-CH_2-COO^-$); 97.6 (C1 due to C2 substitution), 178.1, 180.0 ($-CH_2-COO^-$). The degrees of substitution were of 0.24 ± 0.04 ($CMS_{0.24}$) and 0.30 ± 0.01 ($CMS_{0.30}$).

2.1.3. Preparation of AS/C_nTAB and CMS/C_nTAB Ionic complexes

Ionic complexes from AS and CMS were prepared as described in Fig. 1, where the different reaction parameters are illustrated. A 4% w/v aqueous solution of CMS sodium salt was slowly added to a 4% w/v aqueous solution of surfactant under magnetic stirring. Quaternary ammonium salts (QAS) with different alkyl chain lengths were used: dodecyl, tetradecyl, hexadecyl, and octadecyl trimethylammonium bromide (C_{12}TAB, C_{14}TAB, C_{16}TAB, and C_{18}TAB), being the C_{12}TAB solution added at a temperature of 25 °C, while for the other compounds the process was carried out at 50 °C. Upon completion of surfactant addition, the reaction mixture was cooled down to room temperature and the precipitated product was isolated and washed with water at 40 °C several times. In order to ensure that no free surfactant remained in the products, the bromide AgBr test was performed. Finally, the products were dried under vacuum at 50 °C for 24 h. When AS was the starting material, only a molar ratio AGU:QAS 1:0.75 was employed.

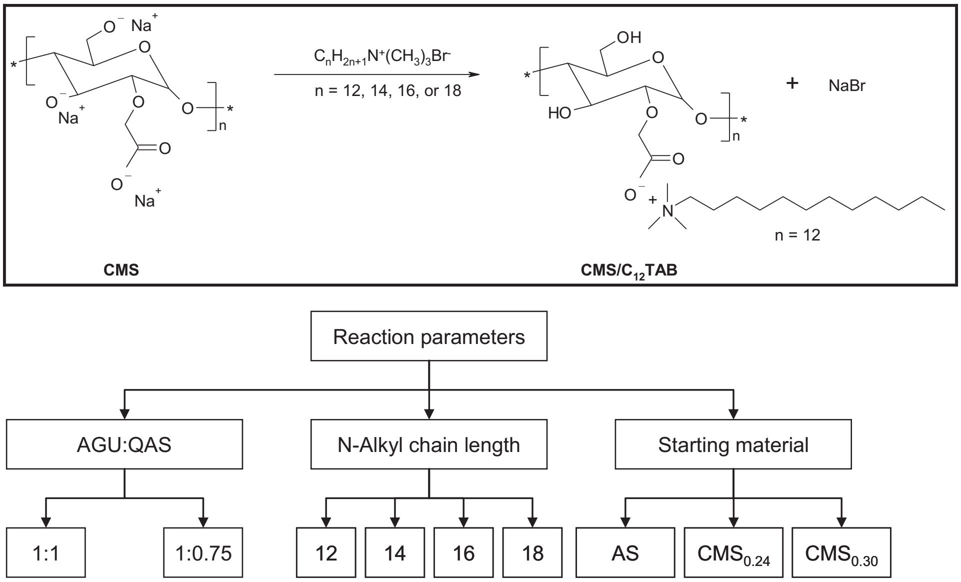

Fig. 1. Schematic representation of the preparation of CMS/C_nTAB ionic complexes, indicating the parameters that were varied.

2.2. Structural characterization

FTIR spectra were recorded from KBr discs using a Nicolet Magna IR 550 spectrometer with a resolution of 4 cm^{-1} and 64 scans, and a wavenumber range between 400 cm^{-1} and 4000 cm^{-1}. The data were analyzed by using the OMNIC Utility version 3.0. ^{13}C NMR, ^{1}H NMR, and DEPT-135 spectra were collected on a Bruker AVANCE-500 at room temperature, using DMSO-d_6 as solvent or D_2O at 70 °C for AS, after the samples were maintained under agitation for 24 h. Nitrogen content was estimated by the Kjeldhal method.

WAXS experiments were performed in an automatic Panalytical X'pert-pro diffractometer equipped with a fast acquisition data device, X'Celerator, with Cu Kα, Ni-filtered radiation (λ = 1.54178 Å). The spectra were recorded at different temperatures from 25 °C to 60 °C in an Anton Paar TTK 450 variable temperature attachment. The angular range explored was $4° < 2\theta < 40°$.

2.3. Thermal characterization

The study of the crystallization and melting of the alkyl chains for $CMS_{0.30}/C_{18}$TAB (1:1) and C_{18}TAB was carried out by means of differential scanning calorimetry (DSC) in a Perkin-Elmer DSC-7. Samples (10.0 ± 0.1 mg) were encapsulated in aluminum pans and high purity dry nitrogen was used as inert atmosphere. For calibration, indium and strontium were employed. Samples were cooled down to 0 °C at a rate of 10 °C/min after they were held at 130 °C for 3 min to erase the previous thermal history; then, they were heated at 10 °C/min from 0 °C up to 130 °C.

Themogravimetric analyses (TGA) were performed in a Perkin-Elmer TGA-7 thermobalance using 10 mg samples, which were heated from 25 °C up to 500 °C at a rate of 10 °C/min under an ultra pure nitrogen atmosphere.

Thermal volatilization analyses (TVA) were carried out in a home-made equipment coupled to a vacuum line; 100 mg of sample were heated from room temperature up to 290 °C during 30 min under a moderate primary vacuum. Gases or non-condensing fractions were collected in a gas cell equipped with NaCl windows (A) at liquid nitrogen temperature and volatile fractions condensing at room temperature were collected in the so-called cold ring (B). The different fractions were then analyzed by FTIR, and ^{1}H NMR spectra were taken when needed.

2.4. Water absorption measurements

Water uptake at 25 °C was estimated after the samples were equilibrated for 18 days in a controlled moisture environment with a saturated K_2SO_4 solution (water activity: 0.936 ± 0.006 at 25 °C). Then, the samples were evaluated in a moisture analyzer AND MS-70 (sensitivity of ±0.001%) by heating from 21 °C up to 120 °C; at this temperature no change was observed in the sample weight.

3. Results and discussion

3.1. Preparation and characterization of AS/C_nTAB and CMS/C_nTAB ionic complexes

As it was described in the experimental part, in a first stage, we synthesized CMS precursors in aqueous medium obtaining degrees of substitution, DS_{CMS}, of 0.24 and 0.30. These DS_{CMS} are typically obtained under the conditions (medium, temperature, and reagents ratio) that we used to carry out the carboxymethylation reactions. Even though it is possible to reach higher DS_{CMS}, employing organic media, it has been demonstrated that the products do not exhibit suitable rheological and water solubility properties (Heinze, Haack, & Rensing, 2004; Mollega et al., submitted). On the other hand, the use of water as reaction medium results very attractive from environmental and cost points of view.

The formation of a complex between the AS or CMS polyelectrolyte and C_nTAB surfactant was qualitatively evident from the immediate precipitation that took place when the drop wise addition of AS or CMS to the surfactant solution began. Depending on the surfactant employed, the appearance of the final product was different; thus, a white powder was observed when C_{16}TAB and C_{18}TAB were used, while a gelatinous product was obtained in the other cases. In addition, it is important to point out that all complexes prepared in this work were soluble in DMSO at room temperature, contrasting with the insolubility of the CMS precursors in this solvent.

Fig. 2 compares the FTIR spectra of AS/C_{18}TAB and $CMS_{0.30}/C_n$TAB (n = 12 and 18), which are representative of the whole series, with those of $CMS_{0.30}$ and C_{18}TAB. From the spectra, the typical bands of AS and CMS are observed; the absorptions at 575 cm^{-1}, 765 cm^{-1}, and 862 cm^{-1} are due to the

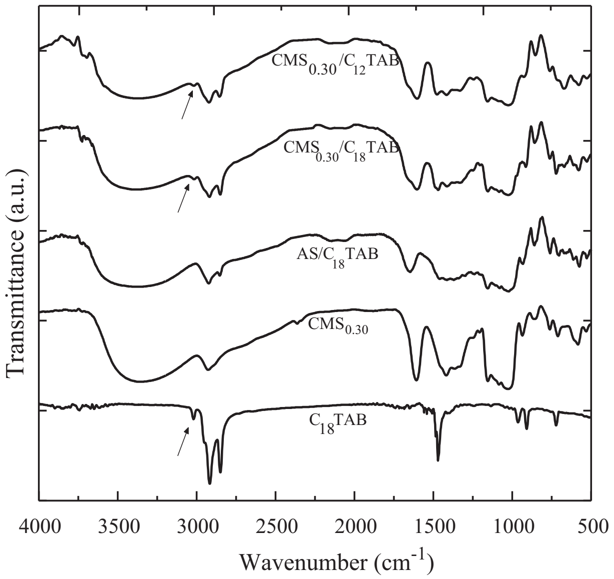

Fig. 2. FTIR spectra of $CMS_{0.30}/C_nTAB$ ($n = 12, 18$), $AS/C_{18}TAB$ (1:0.75), $CMS_{0.30}$, and $C_{18}TAB$.

C–C stretching and C–H bending vibrations of the glycosidic ring. In the fingerprint region between 900 cm^{-1} and 1500 cm^{-1}, the bands located at 930 cm^{-1}, 1014 cm^{-1}, 1082 cm^{-1}, and 1159 cm^{-1} correspond to –C–O–C– bonds in the anhydroglucose unit (Fang, Fowler, Sayers, & Williams, 2004). The band at 1648 cm^{-1} originates from tightly bound water present in starch (Hatakeyama & Hatakeyama, 2004; Kakurakova & Wilson, 2001). The complexes exhibit a new band at 2854 cm^{-1}, which is due to the stretching of C–H bonds present in the alkyl fragment of the surfactant (Pretsch, Bühlmann, & Affolter, 2000); nevertheless, this signal is less intense in $AS/C_{18}TAB$, indicating that the alkoxide groups of the activated and pregelatinized starch are not enough reactive to extensively form ionic bonds with the cationic fraction of the QAS in comparison with the carboxylate groups of CMS; in fact, the signal at ~1605 cm^{-1}, typical of the carboxylate symmetric stretching vibration, could only be clearly observed in the spectra of the complexes obtained from CMS. Those bands observed at 3018 cm^{-1} and 716 cm^{-1} also corroborate the formation of ionic complexes; the first one (indicated by arrows), observed again only in the CMS/C_nTAB complexes due to their higher degree of complexation, corresponds to the stretching of the quaternary ammonium group (Nakanishi & Solomon, 1977), while the weak signal appearing at 716 cm^{-1} is due to the methylene rocking vibrations of the alkyl chain.

A more detailed structural analysis was carried out by ^{13}C NMR and DEPT 135 for $CMA_{0.30}/C_{12}TAB$ (1:0.75), which may be considered representative of the whole ionic complexes series. Nevertheless, it should be mentioned that from the ^{13}C NMR spectrum shown in Fig. 3, only the signals corresponding to the surfactant fragment could be clearly appreciated when the spectra were taken in DMSO-d_6 at room temperature. This difficulty to perform NMR analysis from starch derivates has been previously reported when the product is not subjected to an additional chemical treatment, and may be attributed to a restricted mobility of the starch backbone, as well as to the conformation of the complex in solution, orienting their hydrophobic moieties towards the solvent; similar results have been published for systems such as poly(itaconic acid)/QAS or poly(methyl monoitaconate)/QAS (Báez, Jiménez, Laredo, García, Martínez, & López-Carrasquero, 2007). In spite of this limitation, the combined analysis of the ^{13}C NMR spectra together with DEPT 135 allowed us to confirm the presence of the alkyl chain within the starch molecule, as it is indicated in the spectrum, where the signals were assigned to the different carbons of the complex.

The average degree of substitution, DS, of the complexes was calculated from the w/w nitrogen percentage (%N) obtained by means of the Kjeldhal method (Heinze, Haack, & Rensing, 2004) using Eq. (1):

$$DS = \frac{M_{AGU(X)} \times \%N}{1401 - [(M_S - 1) \times \%N]} \tag{1}$$

where DS indicates the experimental amount of quaternary ammonium cations complexed per carboxymethylated anhydroglucose unit (AGU_{CMS}) or anhydroglucose unit (AGU_{AS}), whose molecular weights $M_{AGU(X)}$ are 220 g/mol or 162 g/mol, respectively. M_S is the molecular weight of the substituent introduced in the AGU unit: $C_{12}TA^+$ (228 g/mol), $C_{14}TA^+$ (256 g/mol), $C_{16}TA^+$ (284 g/mol), and $C_{18}TA^+$ (312 g/mol). 1401 is the nitrogen atomic mass multiplied by 100.

Table 1 lists the results obtained in all cases as well as the reaction efficiency, RE, which is given by the relationship between experimental and expected complex degree of substitution, as it is shown in Eq. (2) after taking into account only the carboxymethylated units:

$$RE = \frac{DS}{DS_T} \tag{2}$$

When using CMS as precursor, the molar amount of surfactant is in excess with respect to the amount of carboxymethylated units; therefore, DS_T corresponds to the degree of complexation as if all the CMS carboxylate groups were substituted with ammonium quaternary cations ($CnTA^+$). The calculations were performed according to Eqs. (3) and (4), assuming that no complexation takes place in any alkoxide group and that only one substituent is introduced per modified AGU:

$$DS_T = \frac{M_{AGU(X)} \times \%N_T}{1401 - [(M_S - 1) \times \%N_T]} \tag{3}$$

$$\%N_T = \left(\frac{M_N}{M_{Complex}}\right) \times 100 X_{Complex} \tag{4}$$

$$X_{Complex} = \frac{M_{Complex} \times DS_{CMS}}{[M_{Complex} \times DS_{CMS}] + [M_{AGU} \times (1 - DS_{CMS})]} \tag{5}$$

where M_N is the atomic mass of nitrogen (14.01 g/mol), $M_{Complex}$ is the molecular weight of the complexed anhydroglucose unit (AGU_{COON}) (448, 476, 504, and 532 g/mol for $C_{12}TA^+$, $C_{14}TA^+$, $C_{16}TA^+$, and $C_{18}TA^+$, respectively), and $X_{Complex}$ is the weight fraction of complexed AGU_{COON}. M_{AGU} corresponds to the molecular weight of the non-modified starch anhydroglucose unit (162 g/mol), and DS_{CMS} is the degree of substitution of the carboxymethylated starch (CMS).

From Table 1 it is possible to observe that, under the assumption that only carboxymethylated anhydroglucose units (AGU_{CMS}) can be substituted, reaction efficiencies higher than 1 are obtained in almost all cases. It might be speculated that some non-bonded surfactant may have remained in the product as impurity; however, as we will demonstrate below by WAXS, this was not the case, demonstrating that the complex formation is also taking place in some of the unmodified AGU units. Nevertheless, when the efficiency of the reaction with activated starch (AS) is analyzed, a maximum RE value of 0.07 is obtained, thus evidencing the easier complexation through the alkoxide groups of the AGU units in CMS than in AS. These results may be explained, on the one hand, by the lower steric hindrance that the carboxylate groups have to form the complex with the surfactant because they are located slightly farther from the starch backbone than the alkoxide groups; and on the other hand, by the improved solubility of CMS in water, which causes an

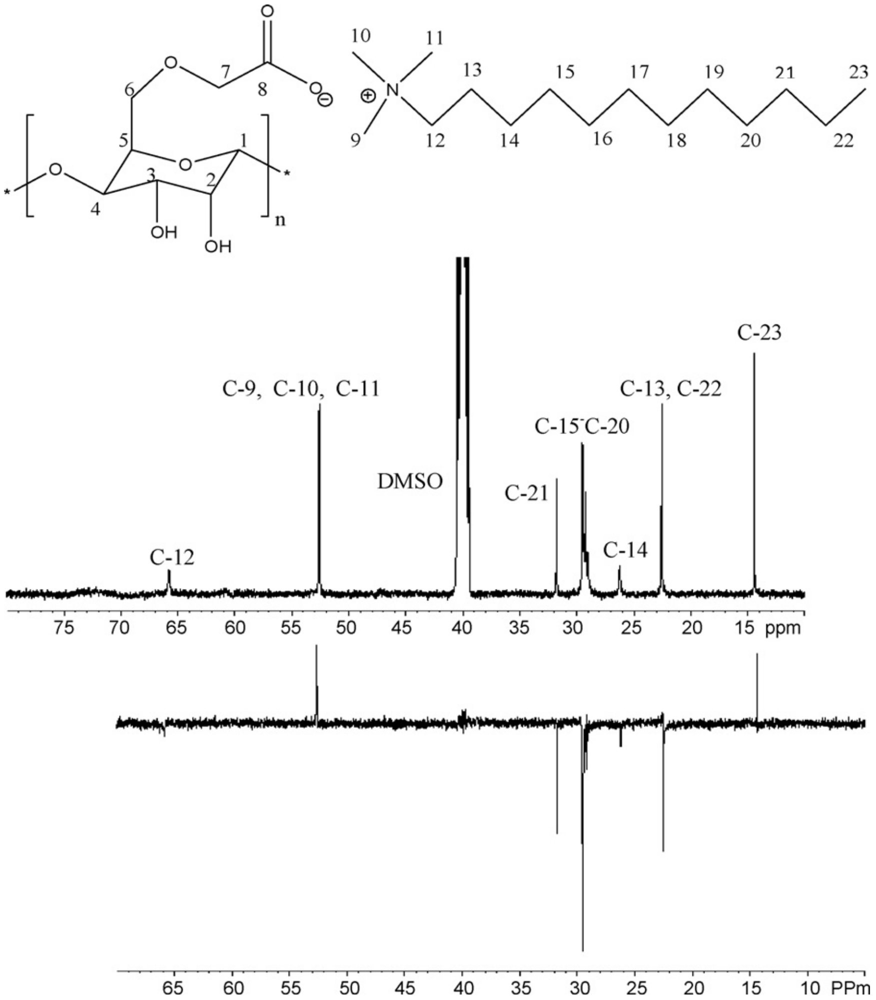

Fig. 3. ^{13}C RMN and DEPT135 spectra with signal assignments for $CMS_{0.30}/C_{12}TAB$ (1:0.75) in DMSO-d$_6$ at 25 °C.

Table 1
Degree of substitution or complexation and reaction efficiency calculated from the nitrogen content estimated by the Kjeldhal method.

Complex	AGU:QAS	*N* (w.-%)	DS[a]	RE (%)[a]	DS*[b]	RE* (%)[b]
$AS/C_{12}TAB$	1:0.75	0.4	–	–	0.06	8
$CMS_{0.24}/C_{12}TAB$	1:0.75	1.4	0.28	95	0.23	30
$CMS_{0.24}/C_{12}TAB$	1:1	1.4	0.28	95	0.23	30
$CMS_{0.30}/C_{12}TAB$	1:0.75	1.6	0.34	92	0.28	37
$CMS_{0.30}/C_{12}TAB$	1:1	1.9	0.43	118	0.35	47
$AS/C_{14}TAB$	1:0.75	0.5	–	–	0.07	9
$CMS_{0.24}/C_{14}TAB$	1:0.75	1.1	0.22	72	0.17	23
$CMS_{0.24}/C_{14}TAB$	1:1	1.3	0.27	89	0.21	29
$CMS_{0.30}/C_{14}TAB$	1:0.75	1.8	0.42	115	0.34	46
$CMS_{0.30}/C_{14}TAB$	1:1	2.0	0.49	135	0.40	54
$AS/C_{16}TAB$	1:0.75	0.4	–	–	0.06	8
$CMS_{0.24}/C_{16}TAB$	1:0.75	1.3	0.28	92	0.22	30
$CMS_{0.24}/C_{16}TAB$	1:1	1.6	0.37	124	0.30	40
$CMS_{0.30}/C_{16}TAB$	1:0.75	1.8	0.45	121	0.36	48
$CMS_{0.30}/C_{16}TAB$	1:1	2.1	0.57	156	0.47	63
$AS/C_{18}TAB$	1:0.75	0.3	–	–	0.04	5
$CMS_{0.24}/C_{18}TAB$	1:0.75	2.0	0.57	189	0.45	60
$CMS_{0.24}/C_{18}TAB$	1:1	1.6	0.39	130	0.31	42
$CMS_{0.30}/C_{18}TAB$	1:0.75	2.2	0.68	184	0.55	74
$CMS_{0.30}/C_{18}TAB$	1:1	2.5	0.89	241	0.72	96

[a] Values obtained after considering that only the AGU_{CMS} units are active for the complexation.

[b] Values obtained taking into account that both AGU_{CMS} and AGU_{AS} are active.

expansion of the CMS molecules and, consequently, a higher accessibility of the surfactant molecules to the polyelectrolyte anions. Besides, rheological measurements that have been carried out in caboxymethylated starches (CMS) (Balsamo, López-Carrasquero, Contreras, Müller, Laredo, Contó, & Feijoo, 2010) have shown that, regardless of the conditions employed for the carboxymethylation, a reduction of the molecular weight takes place, a fact that could make easier the contact between the surfactant micelles and the anions of the starch polyelectrolyte. Considering that the surfactant is also able to form a complex with the alkoxide groups of the CMS molecules, we recalculated the degree of complexation and reaction efficiency taking into account all anhydroglucose units and not only the carboxymethylated ones. Thus, $M_{AGU(X)}$ in Eqs. (1) and (3) was taken as the molecular weight of the average anhydroglucose unit calculated as follows:

$$M_{AGU(X)} = (DS_{CMS} \times 58) + 162 \tag{6}$$

The recalculated values are also shown in Table 1 with a star, where it may be appreciated that depending on the case, RE* varies between 29% and 96%.

As might be expected, a higher degree of carboxymethylation leads to higher DS* and RE* due to the aforementioned reasons. Regarding the effect of the different molar ratios employed for the preparation of the complexes, AGU:QAS (1:0.75) and (1:1), it may be observed, in general, that as the dose of QAS increased, DS* was higher, the difference being greater when $CMS_{0.30}$ was used, as explained before. It is noteworthy that the use of CMS as starting material leads to degrees of substitution between 0.17 and 0.72, which are much higher than the DS* reached by other authors when reacting starch with different long alkyl chain modifying agents. For example, optimum values of 0.025–0.040 have been reported, when reacting starch with dodecenyl succinic anhydride (DDSA) (Chi, Xu, Xue, Song, Zang, & Wang, 2007; Rivero, Balsamo, & Müller, 2009), and values in the range 0.10–0.29 when acyl chlorides with different carbon chain lengths were used (Fang, Fowler, Sayers, & Williams, 2004). In Table 1, a trend may be observed as DS* and RE* increased with the alkyl chain length; these results are contrary to those obtained by other authors using different modifying agents, but are in agreement with the previous works by Thalberg, Lindman, and Karlström, 1991 and Tiitu, Laine, Serimaa, and Ikkala (2006) due to the ionic nature of the modifying agent. Tiitu et al. demonstrated that as the chain length of the surfactant decreases, the interactions between polysaccharide-type polyelectrolytes (hyaluronan, carboxymethyl cellulose) and quaternary ammonium salts are weaker due to the formation of smaller surfactant micelles. The concentration of the surfactants used in our work is considerably higher than the critical micellar concentration (cmc); therefore, they build micelles, whose aggregation number, Ns, increases with the alkyl chain length (Rafati, Gharibi, Iloukhani, & Safdari, 2003). Considering that the behavior of this kind of systems is driven by both electrostatic and hydrophobic interactions, that the micelles formed from longer C_nTAB molecules have a higher surface density charge (Hansson, 1996), and that the CMS solutions are in the semi-dilute regime where the polymer chains are extended, stronger interactions with the polyelectrolyte are expected as the alkyl chain length increases, leading to higher DS*. Simultaneously, longer C_nTAB molecules lead to increased hydrophobic interactions between the surfactant chains.

As we mentioned before, there may remain a level of uncertainty with respect to the purity of the complexes that have been prepared. Therefore, we took a sample of the system in which the highest DS* was obtained, $CMS_{0.30}/C_{18}$TAB (1:1), and it was investigated by differential scanning calorimetry and wide angle X-ray diffraction. Previous studies on the crystallization of polyelectrolyte/QAS ionic complexes have shown that the alkyl chains of the surfactants are able to crystallize when they reach a minimum length, which changes depending on the system that is being investigated (Báez, Jiménez, Laredo, García, Martínez, & López-Carrasquero, 2007; López-Carrasquero et al., 2006); nevertheless, their transitions appear at temperatures that are markedly depressed compared with the free surfactant. The DSC heating scans obtained for $CMS_{0.30}/C_{18}$TAB (1:1) and C_{18}TAB as reference (results not shown here) demonstrated that complexes with shorter alkyl chains did not show any crystallization under the conditions explored. $CMS_{0.30}/C_{18}$TAB (1:1) exhibits a bimodal endotherm between 53 °C and 58 °C, which corresponds to the melting of crystals formed by the methylene sequences of the C_{18}^{+}TAB bonded to the active groups of CMS; the marked depression, compared with the neat surfactant (at ~110.0 °C), indicates the highly disturbed crystallization of these sequences. These results are in agreement with the melting temperatures reported in other polyelectrolyte/QAS complexes such as poly(itaconic acid)/C_{18}TAB (López-Carrasquero et al., 2006). The reason for the bimodality is not clear; however, it should be remembered that the starch is composed by linear (amylose) and branched (amylopectine) fractions with which the surfactant may interact. The absence of an endotherm at about 110 °C in the complexes indicates that there is not free surfactant in the sample.

Fig. 4 shows the diffractograms recorded at different temperatures for $CMS_{0.30}/C_{18}$TAB (1:1) and its precursor $CMS_{0.30}$. As expected, the $CMS_{0.30}$ does not show any crystalline order due to the destructuration process during the chemical modification and the impossibility to retrograde after the carboxylate groups have been introduced in the starch molecule. On the contrary, the diffractogram of the complex recorded at 25 °C shows a low intensity reflection at 21.42°, which corresponds to an interplanar spacing of 4.15 Å, characteristic of the orthorhombic unit cell of paraffins with cell constants $a = 25.9$ Å, $b = 7.249$ Å, and $c = 5.629$ Å. This Bragg reflection indicates the crystallization of the grafted chains and the width of the curve is due to the formation of imperfect crystals. A second reflection, considerably less intense, at 24.5° would be expected, and it is observed in curves (b) and (f) as a small bump on the high angle tail of the amorphous halo of the modified starch. Once the complex was heated up to 60 °C, the reflection at 21.42° disappears (curve c), indicating the melting of the grafted paraffinic chains (in agreement with the DSC curve), demonstrating that no rests of free surfactant remain in the product, since free surfactant melts at about 110 °C. The diffractogram recorded immediately after the sample was cooled down to 25 °C does not show any crystalline reflection (curve d); this result disagrees with the presence of a melting endotherm observed by DSC. Nevertheless, it could be demonstrated that the discrepancy is due to the conditions under which the sample was crystallized. The DSC curves were taken from a sample encapsulated in a hermetic pan where moisture cannot leave out, whereas WAXS heating experiments were performed in open atmosphere. Therefore, we carried out WAXS experiments after the sample remained under ambient conditions (23 °C, 80% humidity) for 24 and 50 h and the results are shown in curves (e) and (f). The reflection at 21.49° appears again and increases in intensity with the duration of exposition to atmospheric conditions (the sample moisture content reached 14%). This demonstrates that moisture present in the atmosphere is sufficient to induce a plasticizing effect on starch, and it promotes the slow crystallization of the alkyl chains inserted in the starch molecules (Aburto, Hamaili, Mouysset-Baziard, Senoq, Alric, & Borredon, 1999). The reflection in curve (f) is much narrower than in curve (b) indicating a larger lamellar thickness.

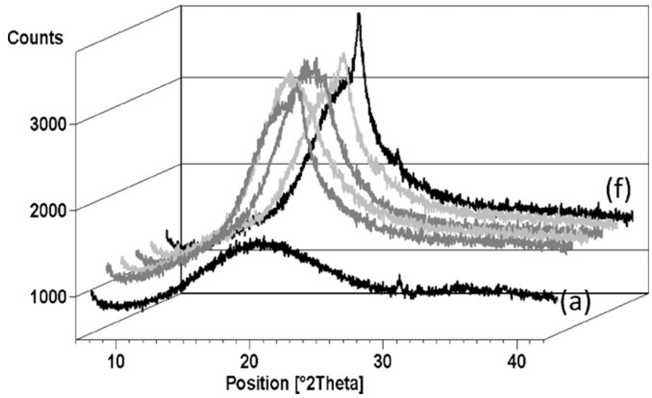

Fig. 4. WAXS diffractograms, from front to back: (a) of $CMA_{0.30}$ at 25 °C; of $CMS_{0.30}/C_{18}$TAB (1:1) at (b) 25 °C, (c) 60 °C, (d) 25 °C immediately after cooling, (e) after 24 h at 25 °C, and (f) after 50 h at 25 °C.

In order to evaluate the ability of the complexes to absorb moisture, the samples were equilibrated as indicated in the experimental part, using K_2SO_4, which has a water activity of 0.936 at 25 °C (Bell & Labuza, 2000). A comparison of the results obtained for native starch, CMS, and CMS/C_nTAB in Fig. 5 allows us to differentiate the effects that influence water absorption in this kind of materials. When compared with native starch, it is clear that the introduction of carboxylate groups leads to a highly hydrophilic starch, as has been previously reported (Fig. 5a), exhibiting an increase of about 20% of moisture absorption when the DS_{CMS} varied from 0.24 to 0.30; i.e., when DS_{CMS} increased 25%. The introduction of the alkyl chains through complexation leads to a reduction of water absorption of up to 50% in comparison with

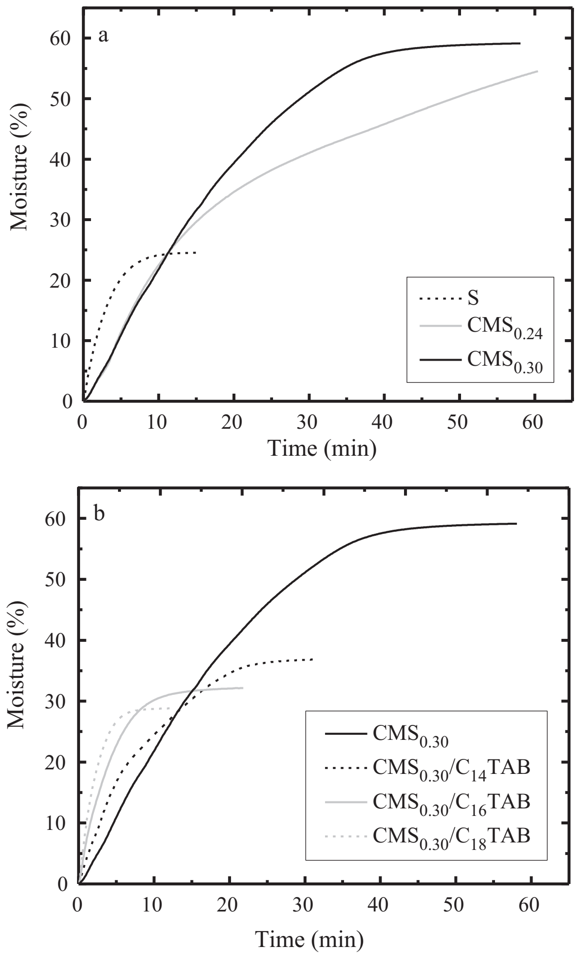

Fig. 5. Curves of percentage of moisture as a function of time during heating for (a) CMS and AS (b) complexes CMS$_{0.30}$/C$_n$TAB (1:1) (n = 14, 16, 18). The measurements were carried out up to 120 °C.

the corresponding CMS precursor in the case of CMS/C$_{18}$TAB (see Fig. 5b), the complex that showed the highest DS*. Nevertheless, it must be pointed out that from these results it is evident that the introduction of the alkyl chains does not lead to more hydrophobic starches than native starch. This indicates that, in spite of the fact that the alkyl chains are hydrophobic moieties, their bulkiness causes a structural reorganization, as a result of the steric hindrance, which facilitates water percolation within the modified starch, with the consequent increase in water absorption; however, as the surfactant changes from C$_{14}$TAB$^+$ to C$_{18}$TAB$^+$ the bulkiness and the hydrophobic behavior of the alkyl chains compete in such way that CMS/C$_{18}$TAB behaves similarly to native starch with respect to water absorption. A more detailed study on the moisture sorption kinetics of these materials in the presence of different water activities has been published by Cova et al. (2010).

3.2. Thermal stability of the ionic complexes

In order to investigate the thermal stability of the ionic complexes and analyze the structure of the volatile fragments and solid rests generated throughout the different weight loss steps, thermogravimetric (TGA) and thermal volatilization experiments (TVA) were combined. TGA experiments were performed in the whole series of ionic complexes; since all of them exhibited a similar behavior, only the detailed analysis of AS/C$_{18}$TAB and CMS/C$_{18}$TAB is shown. TGA curves and their derivatives, presented in Fig. 6, indicate that the CMS/C$_{18}$TAB complexes are stable up to about 150 °C and that after this temperature they exhibit at least two decomposition stages.

Below 150 °C, a little weight loss is observed, which is related to the loss of adsorbed and bound hydration water (López-Carrasquero et al., 2006). The first significant stage of weight loss takes place approximately between 150 °C and 300 °C, and it is mainly attributed to the release of the alkyl chains coming from the surfactant moieties. The percentage of weight loss for all complexes in this first stage increases by increasing the chain length, similar to the results reported for other complex systems (López-Carrasquero et al., 2006). Likewise, all ionic complexes obtained from CMS$_{0.30}$ exhibit a larger weight loss than those prepared from CMS$_{0.24}$, a fact that is explained by the higher DS* because, on the one hand, there is a higher amount of alkyl groups, and on the other hand, the precursor CMS$_{0.30}$, prepared from a second carboxymethylation step carried out onto CMS$_{0.24}$, has already experienced certain degradation showing molecular weight reduction, which is the consequence of the subsequent thermal treatments during the reactions. In fact, as it was previously mentioned, rheological measurements (Balsamo et al., 2010) demonstrated such reduction of the molecular weight.

The second decomposition stage shows a minimum in the range 300–350 °C, ant it corresponds to the degradation of the starch matrix. TGA and DTGA traces of AS/C$_{18}$TAB indicate that they are stable up to about 250 °C with an apparent decomposition minimum at ~350 °C. These results suggest a higher thermal stability of AS/C$_n$TAB than CMS/C$_n$TAB, probably due to the reduction of the molecular weight that has taken place during the carboxymethylation. Besides, even though AS/C$_n$TAB complexes seem to have only

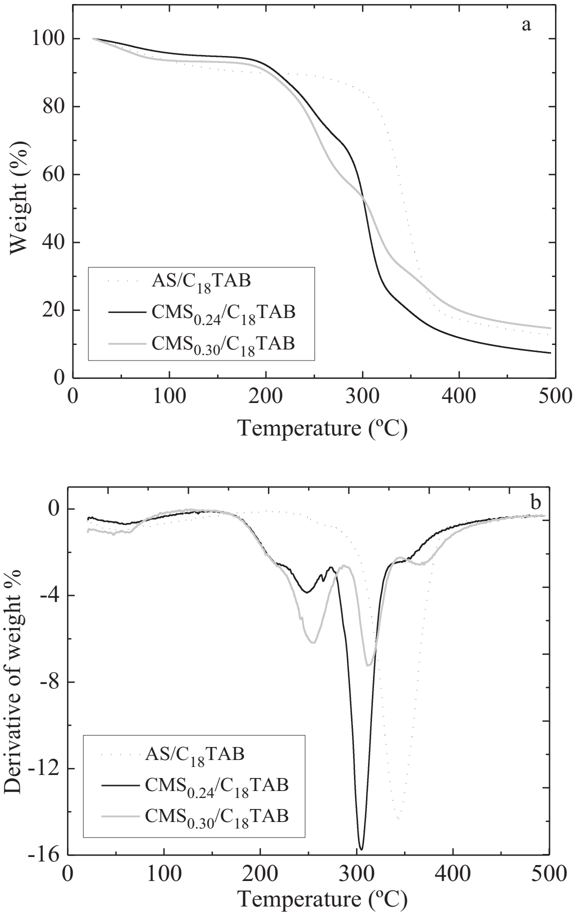

Fig. 6. (a) TGA and (b) DGTA traces as a function of temperature for AS/C$_{18}$TAB and CMS/C$_{18}$TAB (0.75:1) complexes.

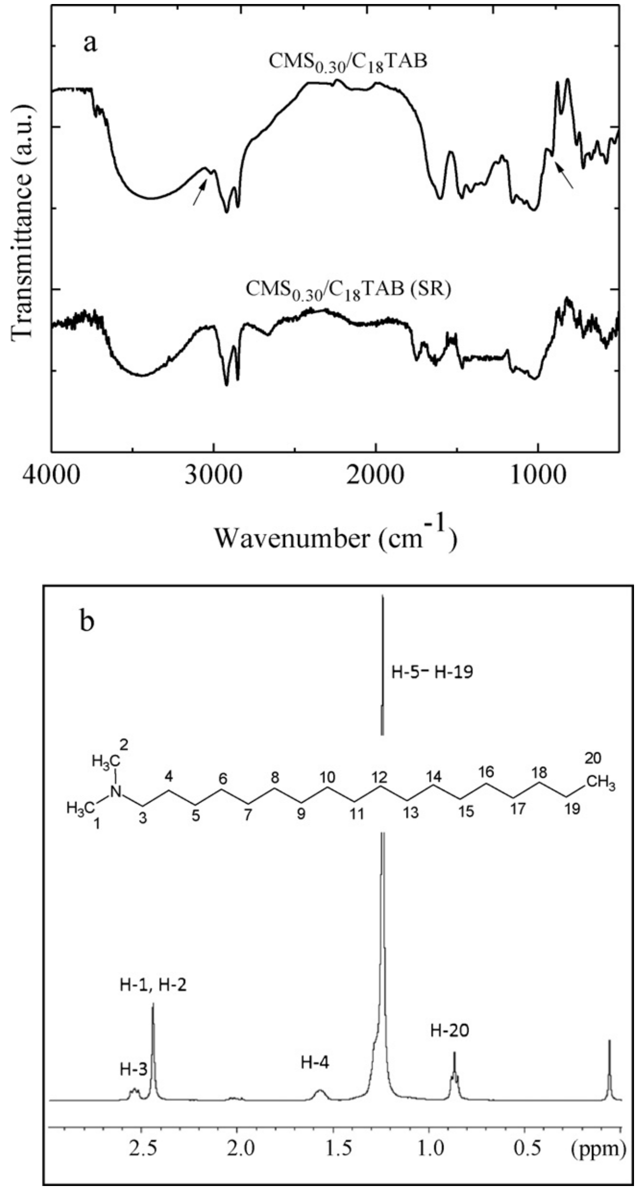

Fig. 7. (a) FTIR spectra of $CMS_{0.30}/C_{18}TAB$ (1:1) and solid residues (SR) after the samples were heated up to 280 °C. (b) ^1H NMR spectrum of the $CMS_{0.30}/C_{18}TAB$ (1:1) cold ring condensate ($CHCl_3$ d1 at 25 °C).

one degradation stage, it may be pointed out that the their low *DS* might make difficult the observation of the first stage.

The FTIR spectrum of the solid products remaining (SR) after a controlled heating of $CMS/C_{18}TAB$ in the TGA up to 280 °C is compared with its precursor in Fig. 7(a). The small signal located at ~3020 cm^{-1} (ν_{st} $NR4^+$, see arrow) disappears, indicating the structural destruction of the substituted quaternary ammonium cation; nevertheless, the spectrum shows the absorption attributed to the stretching of the alkyl chain (ν_{st} C–H at ~2850 cm^{-1}). This fact evidences that after heating, some alkyl remains may be present in the solid. On the other hand, a good agreement was observed when the weight loss values measured by TGA in the first stage of the degradation were compared with the percentage of surfactant moiety determined by nitrogen content, confirming that during the first stage complex destruction and release of the surfactant moiety occurs. The FTIR spectrum of Fig. 7(a) also shows absorptions that are typical of carbonyl compounds (1749 cm^{-1} and 1645 cm^{-1}), which are produced upon degrading the starch matrix. Indeed, for different kind of starches the appearance of these absorptions has been reported (Marques, Lima, Bianco, Laurindo, Borsali, Le Meins, & Soldi, 2006). The lack of the weak absorption at 920 cm^{-1} (see arrow), attributed to the stretching of the α-(1-4) glycosidic bond, suggests that depolymerization occurs during the degradation process; this process and dehydration have been considered as the two main reactions associated with the degradation mechanism of polysaccharides (Marques, Lima, Bianco, Laurindo, Borsali, Le Meins, & Soldi, 2006; Richards, 1987; Soares & Soldi, 2005).

For TVA analysis the samples were heated up to temperatures between 210 °C and 290 °C (first stage of degradation) in a vacuum line. A condensate appeared in the cold ring at ~170 °C for $CMS_{0.30}/C_{16}TAB$ (1:1) and $CMS_{0.30}/C_{18}TAB$ (1:1) and at ~190 °C for $CMS_{0.30}/C_{12}TAB$ (1:1) and $CMS_{0.30}/C_{14}TAB$ (1:1). FTIR and ^1H NMR spectra of the substances forming the cold ring showed that it is mainly constituted by the N,N-dimethyl-*n*-alkyl amine derivative of the corresponding surfactant, as it is shown in the ^1H NMR spectrum of Fig. 7(b), where the characteristic signals of N,N-dimethyloctadecyl amine are clearly observed. These results are in agreement with those reported for the thermal degradation of systems formed from clays modified with QSA (Leszczyńska, Njuguna, Pielichowski, & Banerjee, 2007). It is also noticeable that the degradation of the $CMS_{0.30}$ precursor did not produce any condensate in the cold ring. While the degradation process of the surfactants begins at temperatures of about 230 °C (results not shown here), the complexes showed their degradation onset at 170–190 °C; this fact strongly suggests that the ionic bond formed between the quaternary cation and the bromine ion is more stable than the one formed between the carboxylate group and the quaternary cation.

A preliminary study of the volatiles and gases evolved during the first step of the degradation process that do not condense at room temperature was carried out. These products were spectroscopically analyzed after they were collected at N_2(l) temperature in a gas cell equipped with NaCl windows (A). The FTIR spectra of the gaseous mixture recovered after the degradation of $CMS_{0.30}/C_{18}TAB$ (1:1) and $CMS_{0.30}$ showed the presence of an intense signal at 3420 cm^{-1} for $CMS_{0.30}$, suggesting the formation of water, possibly by condensation and dehydration of the AGU hydroxyl groups (Marques, Lima, Bianco, Laurindo, Borsali, Le Meins, & Soldi, 2006; Soares & Soldi, 2005; Zhang, Golding, & Burgar, 2002). The formation of CO_2 (2359 cm^{-1} and 669 cm^{-1}) and CO (2170 cm^{-1} and 2120 cm^{-1}) was also evident from the CMS spectrum, which results from decarboxylation reactions of the carboxylate groups and from the thermal scission of the starch backbone (Marques, Lima, Bianco, Laurindo, Borsali, Le Meins, & Soldi, 2006; Soares & Soldi, 2005). Signals at 1717 cm^{-1} and 1647 cm^{-1} (C=O) and 1006 cm^{-1} (C–O–C) indicated the formation of carbonyl compounds as well as low molecular weight fractions resulting from the degradation of $CMS_{0.30}$. $CMS_{0.30}/C_{18}TAB$, on the other hand, showed intense stretching C–H bands between 2967 cm^{-1} and 2873 cm^{-1}, which were attributed to alkyl volatile fractions of the *n*-alkyl chain. Bands at 2775 cm^{-1} and 1740 cm^{-1} were also present due to low molecular weight amine fragments and carbonyl compounds, which are not detected in $CMS_{0.30}$. Similar results were obtained for the other complexes, indicating that in the complexes there is a higher fraction of carbonylic products released upon scission of the anhydroglucose ring than in the CMS precursors, which becomes also evident from the increase of the band at 1055 cm^{-1} (υ_{st} C–O–C) in the complexes in comparison with $CMS_{0.30}$.

4. Conclusions

In this study it was shown that it is possible to prepare ionic complexes from carboxymethyl starch (CMS) and alkyltrimethylammonium bromide surfactants (C_nTAB), whose formation is much more favorable than when using activated and pregelatinized starch (AS). The lower steric hindrance that the carboxylate groups have to form the complex, in comparison with the alkoxide groups, and the improved solubility of CMS in water, lead to relative high degrees of complexation and efficiencies, especially with longer C_nTAB molecules.

DSC and WAXS experiments demonstrated that only the *n*-alkyl chains of the surfactant moiety in the CMS/C_{18}TAB/CMA complexes are able to crystallize in paraffinic phases and the crystallization kinetics depends on sample water content. Regarding complexes moisture absorption, it was shown that they are much more hydrophobic than their corresponding CMS precursors, but when compared with unmodified starches the behavior is governed by a balance between alkyl chain hydrophobicity and bulkiness.

The complexes are stable up to temperatures of about 150 °C and after this temperature they exhibit at least two decomposition stages, which involve the destruction of the substituted quaternary ammonium cation and the release of the surfactant moiety, together with the degradation of the starch skeleton with the consequent release of CO_2 and CO.

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