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Cationization of field pea starch in salt-free aqueous suspension

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ABSTRACT

Industrial production of cationic starches involves excessive amounts of costly and environmentally toxic salts (~60%, starch dry weight basis) as swelling inhibitors. The present study investigated the preparation of cationic field pea starch using the reagent, 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC), substituting a commonly used salt, sodium sulfate, with natural sugars such as sucrose or glucose under alkaline conditions. The effects of sugar type and concentration on the degree of substitution were studied. At a concentration of 20% of the weight of starch solids both sucrose and glucose effectively prevented starch granule swelling. Under reaction conditions similar to those used in industrial processing, cationization of pea starch in the presence of sodium sulfate resulted in a degree of substitution and reaction efficiency approximately twice as high as sucrose and four times as high as glucose. For this reason, sucrose was investigated further as a more suitable alternative to sodium sulfate than glucose in the salt-free preparation of cationic starch. Optimization of reaction conditions such as temperature, pH, swelling inhibitor and cationic reagent concentrations using sucrose as the swelling inhibitor resulted in a cationic starch with a degree of substitution of 0.07, comparable to the 0.06 that was obtained using sodium sulfate. These results indicate that sucrose may be a viable alternative to sodium sulfate in the production of cationic pea starch.

1. Introduction

Cationic starch that bears positive ionic charges on its etherized amine groups is widely used as an additive in the paper, textile, cosmetic and other industries. In the paper industry, cationic starches with tertiary amino and quaternary ammonium groups are commonly used to bind cellulose fibers, to remove interfering substances in the wet-end, to improve retention of fines, for surface sizing, and as coating binders (Solarek, 1986). Such cationic starch is prepared by the reaction of starch with cationic reagents, such as 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) and 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) under alkaline conditions using dry (e.g. extrusion cooking and spray-heat treatment) (Hellwig, Bischoff, & Rubo, 1992; Khalil & Farag, 1998; Radosta et al., 2004; Wilpiszewska & Spychaj, 2008; Xie, Yu, Liu, & Chen, 2006) or wet processes (e.g. native starch suspension in water or organic solvent and gelatinized starch paste) (Carr & Bagby, 1981; Kweon, Bhirud, & Sosulski, 1996; Lim, Liang, & Seib, 1992; Radosta et al., 2004; Wang et al., 2009). The functional properties of cationic starches depend strongly on starch botanical origin, modification method and medium, type and distribution of cationic groups, and degree of substitution (DS) (Butrim, Butrim, Bil'dyukevich, Yurkshtovich, & Kaputskii, 2008; Haack, Heinze, Oelmeyer, & Kulicke, 2002; Liu, Corke, & Ramsden, 1999; Manelius, Buleon, Nurmi, & Bertoft, 2000; Radosta et al., 2004; Yook, Sosulski, & Bhirud, 1994). In general, in dry cationization process, the cationic reagent reacts on the surface of starch granule with limited penetration inside the granule. Compared to the dry process, the wet process avoids residual salts, reagents and by-products in the starch ether with advantage of producing a uniform product and is the main process used industrially (Rutenberg & Solarek, 1984). The effects of reaction conditions, such as starch concentration, cationic reagent molar ratio, temperature, pH and reaction duration, on DS and reaction efficiency in aqueous cationization processes, as well as characterization of cationic starch properties, have been extensively investigated and reported in numerous publications. For example, cationic starch is typically prepared in aqueous suspension at a starch concentration of 30–45% using a swelling inhibitor, such as sodium chloride (Butrim et al., 2008), sodium sulfate (Carr & Bagby, 1981; Yook et al., 1994), calcium chloride (Lim et al., 1992) or organic solvent (Kweon et al., 1996; Kweon, Sosulski, & Bhirud, 1997; Wang et al., 2009), although cationic starch can be prepared in aqueous phase at a low starch concentration (<20%) without using a swelling inhibitor (Kuo & Lai, 2007), which may impact its dispersion properties (Carr & Bagby, 1981). The use of large amounts of salts and solvents during the cationization process result in challenges to waste disposal, salt removal and solvent recovery (Rutenberg & Solarek, 1984; Villwock & BeMiller,

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2005) though CHPTAC and EPTMAC are also not without their own negative environmental impact on aquatic ecosystems (NPCAWH (Finland), 2008). The use of sodium sulfate is particularly troublesome because sulfate in the waste water may be converted to hydrogen sulfite by bacteria under anaerobic conditions and further converted into sulfuric acid resulting in environmental pollution (Villwock & BeMiller, 2005). Therefore, producing cationic starch without the use of sodium sulfate in particular would be both more environmentally friendly and economical for the starch and paper industries.

Considerable research has been undertaken regarding the inhibitory effect of sugars on starch swelling and gelatinization in the starch–sugar–water system (Ahmad & Williams, 1999; Baek, Yoo, & Lim, 2004; Hester, Briant, & Personius, 1956; Hoover & Senanayake, 1996; Savage & Osman, 1978; Wootton & Bamunuarachchi, 1980), but there are very few reports in relation to starch cationization. Cationic field pea starch has shown unique functional properties, such as rapid granule dispersion at low pasting temperatures and reduction in realignment of starch molecules during cooling and subsequent storage, which are highly desirable qualities in relation to its industrial applications (Kweon, Sosulski, & Han, 1997; Yook et al., 1994). Thus, field pea starch was used in the present study to prepare cationic pea starch with CHPTAC in a salt-free aqueous suspension using either sucrose or glucose as a swelling inhibitor. The effects of reaction conditions in the presence of sucrose on DS of cationic field pea starch were investigated to optimize the cationization process using sugars.

2. Materials and methods

2.1. Materials

Field pea starch (ACCU-GEL) was supplied by Parrheim Foods, Winnipeg, MB, Canada. It contained 34% amylose, 8.25% moisture and 0.045% nitrogen. Quat 188, an aqueous solution of 3-chloro-2-hydroxypropyltrimethyl ammonium chloride (CHPTAC) containing 65% (w/w) active amine was provided by Dow Chemical Company (Midland, MI, USA). Anhydrous sodium sulfate, sodium hydroxide, hydrochloride, glucose and sucrose were of analytical grade.

2.2. Aqueous starch cationization

Starch was slurried in glucose, sucrose or sodium sulfate solution in a three-neck flask equipped with a head stirrer in a constant-temperature water bath at 40 °C or 50 °C. The pH of the starch slurry was adjusted to either 11 or 12 by slowly adding 3 M NaOH solution. A certain amount of CHPTAC was added based on the active amine/starch molar ratio. The reaction mixture containing 30% or 40% starch solids in aqueous phase (w/w) was stirred for up to 24 h. The concentration of swelling inhibitor used was 20, 40 or 60% of starch solids. After reaction, the mixture was neutralized with 3 M HCl, centrifuged and water-washed five times in a 400-mL centrifuge bottle. Finally, the starch derivative was filtered and washed with 95% ethanol and dried in a forced-air oven at 40 °C overnight.

2.3. Viscosity measurement

The viscosity of the reaction mixture (30% starch solids, active amine/starch molar ratio of 0.1, pH 11) with various concentrations of sucrose or glucose (0–60% of starch solids) was determined using a rotational rheometer equipped with a Peltier heating system and a CC23/Pr measuring system (Paar Physica UDS 200, Anton Paar USA Inc., Ashland, VA). All tests were performed at a shear rate of 32.1/s and 50 °C with sample volume of 11.5 mL in duplicate.

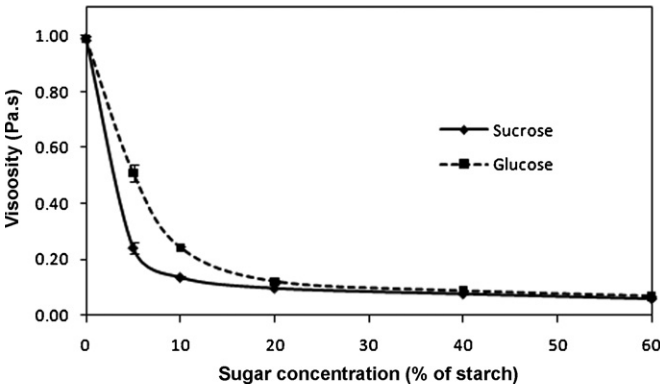

Fig. 1. Viscosity as a function of sugar concentration in the reaction mixture of field pea starch. The measurment was conducted in aqueous suspension at 30% starch solids (w/w), 0–60% glucose or sucrose (starch solids basis), active amine/starch molar ratio of 0.10, pH 11, shear rate of 32.1/s, 50 °C.

2.4. Differential scanning calorimetry

The gelatinization temperatures of starch in the reaction mixture (30% starch solids, active amine/starch molar ratio of 0.1, pH 11) without or with addition of glucose or sucrose (20% of starch solids) was determined using a differential scanning calorimeter (DSC) (DSC Q100, TA Instruments-Waters LLC, New Castle, DE, USA). Thoroughly mixed sample (10–15 mg) was weighed into an aluminum DSC pan after the reaction mixture was prepared. The pan was hermetically sealed and equilibrated at ambient temperature for 0.5–1 h before loading to DSC cell. Indium was used as a calibration standard, and a sealed, empty aluminum pan was used as reference. Samples were heated from 5 °C to 140 °C at 10 °C/min. All samples were prepared twice and then run in DSC in duplicate at least. Gelatinization temperatures (onset T_o and peak T_p) were calculated using a thermal analysis software (Universal Analysis 2000, Version 4.5A, TA Instruments-Waters LLC).

2.5. Nitrogen analysis and degree of substitution

Total nitrogen content of cationic starch was determined by the Dumas combustion method (Rutherford, McCarthy, Arendt, & Figueiredo, 2008) using a Costech ECS 4010 Elemental Combustion System (Costech Analytical Technologies Inc., Valencia, CA, USA). The DS of cationic starch was calculated from the nitrogen increase using the formula $DS = 162\ (\%N)/[1400 - 117(\%N)]$. Reaction efficiency (RE) was calculated from the equation $\%\ RE = DS/(\text{active amine/starch molar ratio}) \times 100$. All analyses were run in duplicate.

2.6. Statistical analysis

Experiments were performed in duplicate at least. Significant differences among means (Tukey's test) were analyzed using the SAS System for Windows, Version 9.1.2 (SAS Institute Inc., Cary, NC, USA) at $P < 0.05$. Mean values are reported in figures with error bars of ±1 standard deviation.

3. Results and discussion

3.1. Effect of inhibitor

As shown in Fig. 1, levels of glucose or sucrose up to 20% (starch solids basis) in the reaction mixture greatly reduced the viscosity of the starch slurry under alkaline conditions and elevated temperature. At sugar concentrations below 20%, sucrose reduced the viscosity more than glucose. However, the viscosity was quite stable beyond the addition level of 20%. These results indicated that

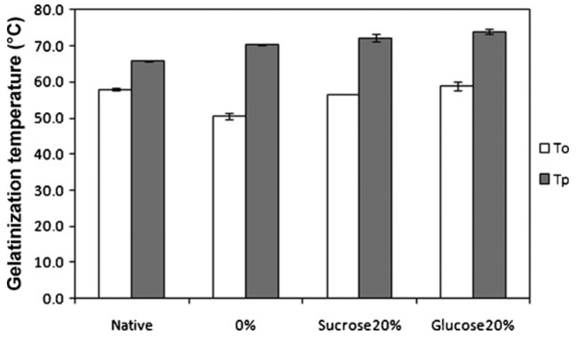

Fig. 2. Gelatinization temperatures of field pea starch in the reaction mixture. Native: starch in water at neutral pH; 0%: starch in a reaction mixture of 30% starch solids (w/w) and active amine/starch molar ratio of 0.10 at pH 11; 20% glucose and 20% sucrose: starch in a reaction mixture of 30% starch solids (w/w), 20% sugar, and active amine/starch molar ratio of 0.10 at pH 11.

both glucose and sucrose effectively inhibited starch swelling during cationization. Compared to the gelatinization temperatures (T_o 58.0 °C and T_p 65.8 °C) of native starch (starch slurried in water at neutral pH), the T_o (50.6 °C) of the starch in the reaction mixture (pH 11) without addition of sugar was significantly reduced, whereas the T_p (70.3 °C) was significantly increased (Fig. 2), indicating that chemical gelatinization occurred at high pH. When glucose was added to the reaction mixture at a level of 20%, the T_o and T_p of the starch increased to 56.6 °C and 72.3 °C, respectively. When the same amount of sucrose was added, instead of glucose, the T_o and T_p increased to 58.8 °C and 73.9 °C, respectively (Fig. 2). These results confirmed that field pea starch started to gelatinize during cationization approximately at pH 11 and 50 °C without using a swelling inhibitor. Addition of 20% glucose or sucrose to the reaction mixture significantly prevented starch gelatinization under alkaline conditions.

When glucose and sucrose were used as swelling inhibitors during cationization of field pea starch, their effect on DS and reaction efficiency (RE) was compared with that of sodium sulfate under the same reaction conditions. As shown in Fig. 3, the DS and the RE increased as a function of reaction time, but sodium sulfate was nearly twice as efficient as sucrose and nearly four times more efficient than glucose in the cationic conversion process. One of the possible reasons is that sucrose or glucose, being a smaller molecule than starch, shows a higher affinity to the cationic reagent, resulting in a lower availability of cationic reagent for the reaction with starch. The DS and the RE of the cationic starch also were affected by the concentration of sucrose used (Fig. 4). An increase in sucrose concentration decreased the DS and the RE. This suggested that a higher sucrose content in the reaction mixture was more restrictive in granule swelling and more preventive in the access of the cationic reagent to the granule interior.

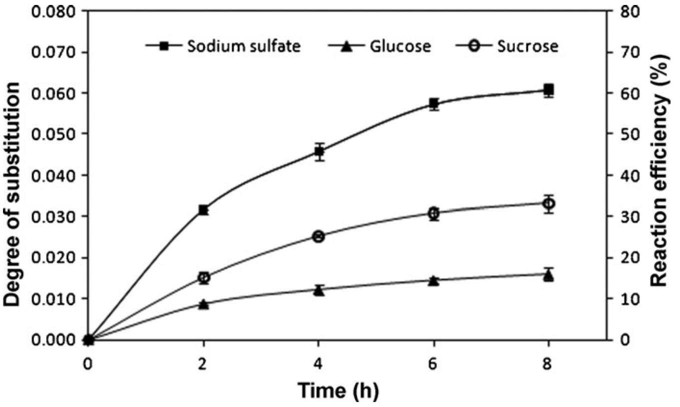

Fig. 3. Degree of substitution as a function of reaction time in the cationization of field pea starch using different swelling inhibitors. The reaction was conducted in aqueous suspension at 30% starch solids (w/w), 60% swelling inhibitor (starch solids basis), active amine/starch molar ratio of 0.10, pH 11, 40 °C, 0–8 h.

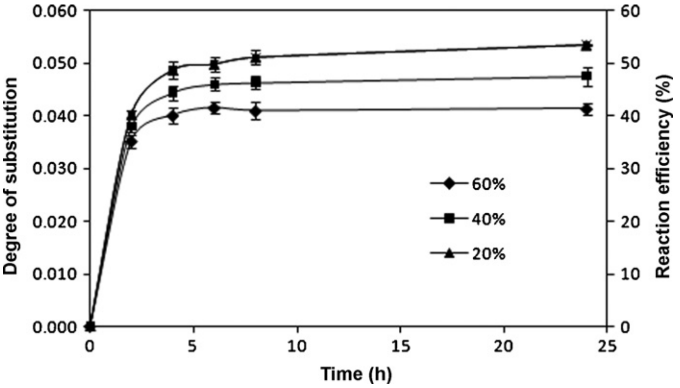

Fig. 4. Degree of substitution as a function of reaction time in the cationization of field pea starch using sucrose as the swelling inhibitor at different concentrations. The reaction was conducted in aqueous suspension at 30% starch solids (w/w), 20–60% sucrose (starch solids basis), active amine/starch molar ratio of 0.10, pH 12, 40 °C, 0–24 h.

The mechanism by which sodium sulfate acts as a swelling/gelatinization inhibitor differs from that of sugar (Chinachoti, White, Lo, & Stengle, 1991). The inhibitory effect of sodium sulfate has been attributed to its ionic nature caused by its moderate lyotropic property and Donnan potential effect (Chinachoti et al., 1991; Villwock & BeMiller, 2005; Wootton & Bamunuarachchi, 1980), which allows limited granule swelling. This restricted swelling promotes the reaction of starch with the modifying reagent by gradually opening up more molecular regions without unrestricted swelling, resulting in a higher RE (Villwock & BeMiller, 2005). The inhibitory effects of sugars on starch swelling and gelatinization in the starch–sugar–water system have been explained by a number of proposed mechanisms based on sugar–water and sugar–starch interactions. These include the ability of sugars to reduce water availability, increased free volume of sugar–water cosolvent, antiplasticization properties relative to water, stabilization of the granular structure due to sugar–starch interaction (Chiotelli, Rolee, & Le Meste, 2000; Elgadir et al., 2009; Hansen, Setser, & Paukstelis, 1989), the molecular size and conformation changes of starch (Wootton & Bamunuarachchi, 1980), and changes in hydrodynamic volume and lower translational and rotational mobility (Sharma, Oberoi, Sogi, & Gill, 2009). The inhibitory effect on starch swelling and gelatinization varies among sugars. In general, disaccharides have a greater effect than do monosaccharides (Baek et al., 2004; Savage & Osman, 1978; Sharma et al., 2009; Slade & Levine, 1987). The higher DS achieved with sucrose than with glucose in the present study may be related to a greater ability of sucrose to stabilize the water structure surrounding starch molecules due to its having more equatorial hydroxyl groups than does glucose, as discussed in earlier work (Ahmad & Williams, 1999; Hoover & Senanayake, 1996). Research (Villwock & BeMiller, 2005) has already indicated that starch swelling is correlated with RE and a limited degree of swelling is necessary for reaction to occur. Addition of sugar at too high a level may completely inhibit starch granule swelling and thus reduce the DS and the RE.

3.2. Effect of starch concentration in the presence of sucrose

Starch concentration in the presence of sucrose affected the DS. As shown in Fig. 5, a starch concentration of 40% (w/w) resulted in a higher DS at both active amine/starch molar ratios in the pres-

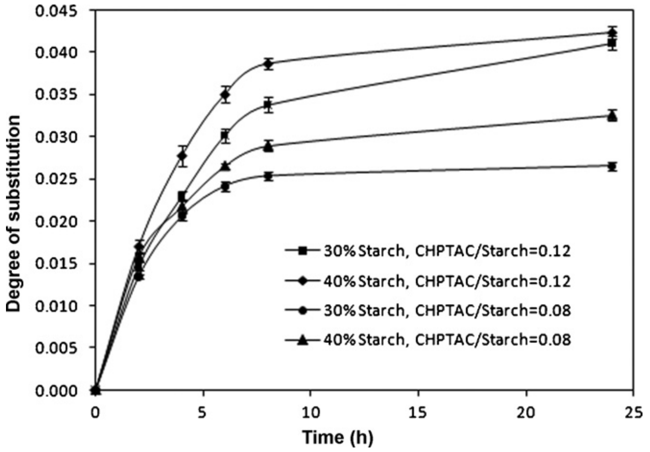

Fig. 5. Degree of substitution as a function of reaction time in the cationization of field pea starch at different starch concentrations. The reaction was conducted in aqueous suspension at 30% or 40% starch solids (w/w), 60% sucrose (starch solids basis), active amine/starch molar ratio of 0.08 or 0.12, pH 11, 40 °C, 0–24 h.

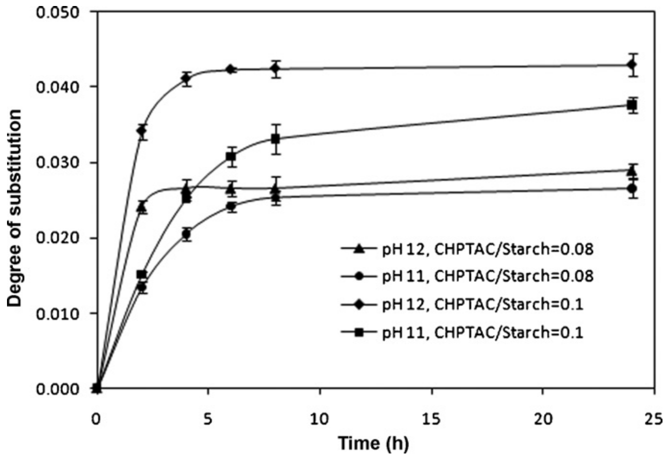

Fig. 6. Degree of substitution as a function of reaction time in the cationization of field pea starch at different pHs. The reaction was conducted in aqueous suspension at 30% starch solids (w/w), 60% sucrose (starch solids basis), active amine/starch molar ratio of 0.08 or 0.10, pH 11 or 12, 40 °C, 0–24 h.

ence of 60% sucrose (starch solids basis), compared to the DS value obtained at a starch concentration of 30%. Research (Bendoraitiene, Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2006) has pointed out that DS and RE decrease when the amount of available water is twice or thrice as high as that required to hydrate starch, dissolve the catalyst, diffuse the cationic reagent, and facilitate the swelling of the starch granule during the cationization process. The optimum starch/water ratio for an aqueous-alcoholic starch cationization process was approximately 1:1 (Kweon, Sosulski, & Bhirud, 1997). At a lower concentration of starch, both the dilution effect of water/liquid and any side reactions which may occur would lead to a lower DS (Khalil, Farag, & Hashem, 1993). Differences in DS such as those caused by starch concentration in the presence of sucrose were not seen in the cationization of starch at a concentration of 35–45% in aqueous suspension when sodium sulfate was used as the swelling inhibitor (Carr & Bagby, 1981) or at 24–42% when sodium chloride was used (Butrim et al., 2008).

3.3. *Effect of pH in the presence of sucrose*

Results for cationization of field pea starch at 30% starch solids (w/w), 60% sucrose (starch solids basis), and pH 11 and 12 are presented in Fig. 6. Use of a pH of 12 greatly accelerated the cationization rate during the first 2 h with the maximum DS achieved within 2–6 h, compared to 8–10 h at pH 11. Similar DSs (0.027–0.029 at 24 h) were achieved at pH 11 and 12 at an active amine/starch molar ratio of 0.08, whereas the maximum DS achieved was substantially greater at pH 12 (DS 0.043 at 24 h) than at pH 11 (DS 0.038 at 24 h) at an active amine/starch molar ratio of 0.1. This suggests that a higher concentration of alkali does not contribute significantly to a higher DS when the amount of available cationic reagent is more limited in the reaction mixture. Too high a concentration of alkaline accelerates the side reactions of cationization, such as hydrolytic and de-etherification reactions (Heinze, Haack, & Rensing, 2004; Kavaliauskaite, Klimaviciute, & Zemaitaitis, 2008; Khalil et al., 1993). Thus, as a reaction catalyst, the alkali concentration needs to be kept at the optimum level during cationization.

3.4. *Effect of temperature in the presence of sucrose*

A temperature between 40 °C and 50 °C is effective for cationization of corn and barley starches (Kweon et al., 1996; Kweon, Sosulski, & Bhirud, 1997). Fig. 7 shows the effect of reaction temperature on the DS and the RE of cationic field pea starch. Increasing the temperature from 40 °C to 50 °C increased DS and RE at pH 11 and at pH 12, moreso at pH 12 and at shorter reaction times. As indicated by others (Kuo & Lai, 2009; Mentzer, 1984), a temperature increase not only accelerated the cationic substitution, but also increased the rate of starch granule swelling, which in turn facilitated the diffusion of cationic reagent into the interior of the starch granule and thereby enlarged the effective area for cationization. In the present study, cationization at 50 °C and pH 11 for 24 h in the presence of 20% of sucrose with active amine/starch molar ratio of 0.05, the DS and the RE of cationic starch were 0.032 and 65%, respectively. However, at 50 °C and pH 12, the DS and the RE were 0.025 and 50%, respectively. High reaction temperature and high pH with the presence of a low concentration of sugar may cause extensive starch swelling and gelatinization, solubilization of starch molecules, complicated starch recovery from the final washings (Butrim et al., 2008), and also facilitatation of the de-etherification reaction (Wang et al., 2009), resulting in lower DS and RE. However, cationic groups in starch are distributed more uniformly at higher reaction temperatures (Butrim et al., 2008) and at longer reaction times (more than 5 h) as revealed by confocal scanning microscopy (Kuo & Lai, 2007, 2009).

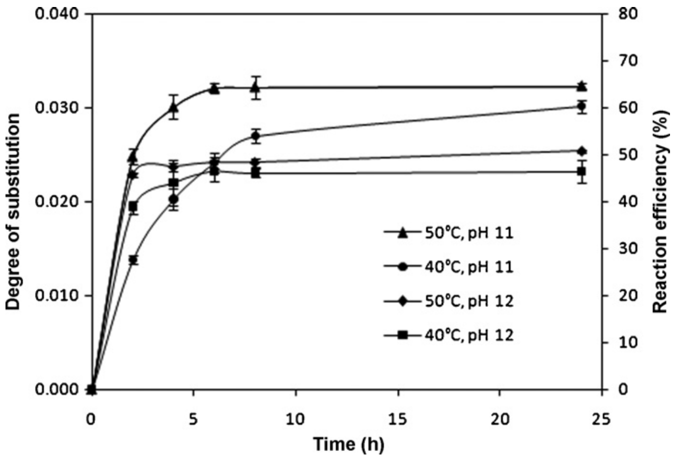

Fig. 7. Degree of substitution as a function of reaction time in the cationization of field pea starch at different temperatures. The reaction was conducted in aqueous suspension at 30% starch solids (w/w), 20% sucrose (starch solids basis), active amine/starch molar ratio of 0.05, pH 11 or 12, 40 or 50 °C, 0–24 h.

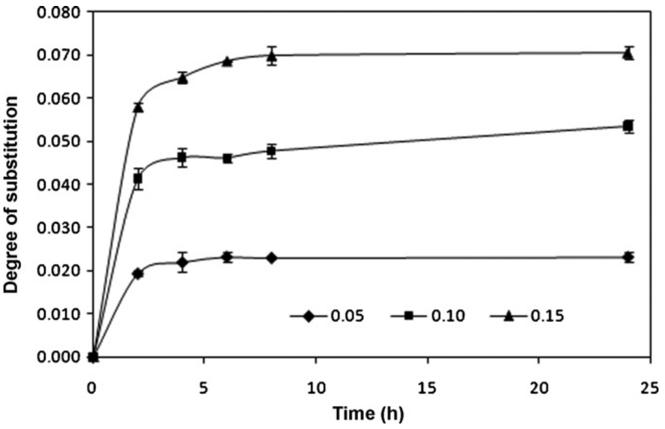

Fig. 8. Degree of substitution as a function of reaction time in the cationization of field pea starch at different molar ratios of active amine/starch. The reaction was conducted in aqueous suspension at 30% starch solids (w/w), 20% sucrose (starch solids basis), active amine/starch molar ratio of 0.05, 0.10 or 0.15, pH 12, 40 °C, 0–24 h.

3.5. Effect of active amine/starch molar ratio in the presence of sucrose

The effect of the molar ratio of active amine/starch over the range of 0.05–0.15 is shown in Fig. 8. The DS of starch increased proportionally from 0.023 to 0.070 with an increase in the molar ratio of active amine/starch from 0.05 to 0.15 at 8 h of reaction, whereas the RE was constant at approximate 47%. A high active amine/starch molar ratio would require additional alkali use, which caused technical problems due to starch swelling and thickening of the reaction slurry, presenting difficulties in recovery of the end product (cationic starch). A high active amine/starch molar ratio also may reduce RE due to the saturation of binding sites by cationic reagent (Kweon et al., 1996; Kweon, Sosulski, & Bhirud, 1997). The cationization reaction occurred rapidly initially, with the maximum DS achieved at approximately 8 h. Cationic starch with a DS of 0.02–0.04, which is commonly used in the wet-end in the paper industry (Xie et al., 2006), was obtained in 2 h at an active amine/starch molar ratio of 0.05–0.10, pH 12, 40 °C. Thus, the DS of cationic starch can be controlled under the appropriate reaction conditions by adjusting the active amine/starch molar ratio using sugar as the swelling inhibitor, as was the case with the aqueous-alcoholic cationization process (Kweon et al., 1996; Kweon, Sosulski, & Bhirud, 1997).

4. Conclusions

Both sucrose and glucose were effective at preventing granule swelling. Under conditions similar to those used in industrial production of cationic starch, the use of sucrose resulted in a degree of substitution and reaction efficiency twice as high as glucose and was chosen for further study to optimize the reaction conditions. The cationic field pea starch obtained with sucrose as a swelling inhibitor under optimized conditions had a degree of substitution of 0.07, comparable to the 0.06 obtained when sodium sulfate was used as the swelling inhibitor. For this reason, sucrose has potential to be used as a possible alternative to sodium sulfate in the production of cationic field pea starch. Furthermore, the new approach of using sugars seems to be suitable for the production of cationic starch with low DS. Substitution of sucrose for sodium sulfate also allows a three times lower concentration of swelling inhibitor (60% sodium sulfate vs. 20% sucrose) to be used which would be less costly as well as contribute to reducing the environmental impact of the industrial process.

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