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Short communication

Reaction of octenylsuccinic anhydride with a mixture of granular starch and soluble maltodextrin

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ABSTRACT

The reaction of octenylsuccinic anhydride (OSA) with a mixture of granular waxy maize starch and soluble maltodextrin was investigated. OSA was reacted with a 1:1 (w/w) mixture of the granular starch and maltodextrin at OSA levels of 1.5, 3, 9, and 15% (wt% based on starch weight). After the first 0.5 h of the reaction, degree of substitution (DS) on maltodextrin reached 0.021, 0.030, 0.080, and 0.10 for 1.5, 3, 9, and 15% OSA, respectively, whereas DS for granular starch was only 0.0020, 0.0087, 0.014, and 0.016. At 2 h of the reaction, the bound OS ratio of maltodextrin to granular starch was 10.8 when OSA concentration was 1.5% and the ratio decreased to ca. 5 at higher OSA concentrations. OSA preferred to react with maltodextrin than semi-crystalline granular starch when both existed in the system. OSA reacted with maltodextrin at a much faster rate and to a greater extent than with granular starch, but a significant amount of OSA reacted with granular starch at 3–15% OSA concentrations.

1. Introduction

Octenylsuccinic anhydride (OSA) reaction with starch has been known for decades (Caldwell & Wurzburg, 1953), but interest in it is increasing, as evidenced by the number of published papers in recent years (Sweedman, Tizzotti, Schäfer, & Gilbert, 2013). The product of this reaction, octenylsuccinate (OS) starch, functions as a emulsion stabilizer and has wide food, pharmaceutical, and industrial applications (Trubiano, 1986). The reaction is an esterification reaction normally performed in aqueous solution under alkaline conditions (Trubiano, 1986). OSA reaction has been carried out with granular starch from different botanical sources, including waxy maize (Bai & Shi, 2011; Bhosale & Singhal, 2006; Shogren, Viswanathan, Felker, & Gross, 2000; Zhu, Xie, Song, & Ren, 2011), normal maize (Park, Chung, & Yoo, 2004), high-amylose maize (Zhang, Huang, Luo, Fu, Jiang, & Jane, 2011), potato (Ruan, Chen, Fu, Xu, & He, 2009), rice (He, Song, Ruan, & Chen, 2006; Song, He, Ruan, & Chen, 2006), and amaranth (Bhosale & Singhal, 2006). In general, optimum reaction pH is 7.5 to 8.5 (Bai & Shi, 2011; Bhosale & Singhal, 2006; Song et al., 2006; Zhu, Xie, Song, & Ren, 2011) and optimum temperature is 30–35 °C (Bhosale & Singhal, 2006; Song et al., 2006; Zhu et al., 2011). Degree of substitution (DS) increases with OSA treatment level (Bhosale & Singhal, 2006; Song et al., 2006) and starch concentration (Bai & Shi, 2011; Song et al., 2006; Zhu et al., 2011); however, reaction time may vary from 2 to 24 h depending on the speed of OSA addition, other reaction parameters, and the botanical source of the starch (Bai & Shi, 2011; Bhosale & Singhal, 2006; Song et al., 2006).

Although, OS starch is commonly prepared by reacting granular starch with OSA in an aqueous system and known for decades (Trubiano, 1986), the reaction appears to be unique (Sui, Huber, & BeMiller, 2013) and is not completely understood. Compared with other reagents used to modify starch such as acetic-adipic mixed anhydride, phosphoryl chloride, sodium trimetaphosphate, acetic anhydride, and succinic anhydride, OSA is the least polar and least water-soluble reagent (Sui et al., 2013). The reaction system is suggested to contain both dissolved OSA and small droplets of OSA (Zhang et al., 2011). OSA is believed to be "more soluble in the ordered water in the capillaries of the porous starch granules than in the bulk external water due to an entropy difference that drives OSA molecules into hydrated granules" (Sui et al., 2013). In addition to reacting with hydroxyl groups of starch, OSA may be hydrolyzed in the presence of an alkali (e.g. sodium hydroxide), which is used to increase the nucleophilicity of the hydroxyl groups of starch and enhance their reactions with anhydride moieties (He et al., 2006; Song et al., 2006), In our previous study, we examined OSA reaction with granular waxy maize starch and soluble maltodextrin and found higher reaction efficiency (RE) and a faster rate for soluble maltodextrin (Bai & Shi, 2011). In addition, the substitution pattern on hydroxyl groups appeared to differ between OS maltodextrin and granular OS starch. In this study, instead of examining the reaction of OSA with granular starch and soluble maltodextrin separately, we investigated the reaction of OSA with a mixture

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of granular starch and soluble maltodextrin. The experiment was designed to study that in the same reaction system, how OSA was reacted with starch granules, which are partially crystalline and insoluble in water, soluble maltodextrin, which has less steric hindrance compared to starch granules, and water. The hydrolysis of OSA with water in an alkaline solution reflects the amount of the OSA that is not reacted with starch or maltodextrin (i.e. "unreacted OSA").

2. Materials and methods

2.1. Materials

OSA and waxy maize starch (Amoica TF) were obtained from National Starch LLC (Bridgewater, NJ). Maltodextrin (MALTRIN 100) with degree of polymerization (DP_n) ~10 was obtained from Grain Processing Corporation (Muscatine, IA). Other chemicals used in the study were analytical grade.

2.2. OSA reaction

A mixture of granular waxy maize starch (50 g dry weight) and soluble maltodextrin (50 g dry weight) was dispersed in 150 mL water and mixed with an overhead stirrer for 15 min. pH was adjusted to 7.5 by 3% (wt%) NaOH solution. OSA of 1.5, 3, 9, and 15% based on total weight of the mixture of the starch and maltodextrin was added to the slurry, and the pH was controlled at 7.5 during the reaction. Samples were taken during reaction at a time interval of 30 min. Each sample was vacuum-filtered through a filter paper. The maltodextrin fraction in the filtrate was recovered by freeze-drying. The starch cake was washed by distilled water (400 mL) three times and then by methanol (400 mL) three times to remove soluble maltodextrin residue and unreacted OSA. Starch was dried in an oven at 40 °C for 24 h.

In a set of separate experiments, OSA reaction was performed with granular starch alone at concentrations of 3, 9, 15, and 50% (based on starch weight). Sodium sulfate (5% based on starch weight) was added in the reactions of 15 and 50% (based on starch weight) OSA concentration.

2.3. Bound OS content determination

DS and bound OS were determined by Varian 500 NMR system (Palo Alto, CA). Granular OS starch was hydrolyzed by α-amylase for NMR experiments as previously described (Bai, Shi, Herrera, & Prakash, 2011). The freeze-dried maltodextrin (0.2 g) was washed by methanol (1 mL) three times and vacuum-dried. OS starch and maltodextrin products were exchanged with D_2O once, dissolved in D_2O at 10% concentration (wt%), and analyzed by NMR.

2.4. Wide-angle X-ray diffraction

The starch samples were equilibrated to about 20% moisture at 25 °C in a glass enclosure containing water. X-ray diffraction patterns of starches were obtained with an X-ray diffractometer (APD 3520, Philips, Netherlands). The instrument was operated at 35 kV, 20 mA with Cu-Kα radiation, a theta-compensating slit, and a diffracted beam monochromator. Data were recorded between the diffraction angles (2θ) of 2° and 35°.

2.5. Statistical analysis

Experiments were performed in triplicate. Analysis of variance was performed with SAS (version 9.1.3, SAS Institute Inc., Cary, NC). Least significant differences for comparison of means were computed at $P < 0.05$.

3. Results and discussion

OSA reacted significantly more with maltodextrin than granular starch when both existed in the aqueous system (Table 1). At the 1.5% OSA level, the amount of OSA that reacted on maltodextrin was 10.8 times greater than on the granular starch (Fig. 1). As the OSA level increased to 9 and 15%, we still observed more substitution on the maltodextrin, but the ratio of the bound OS in the maltodextrin to that in the waxy maize starch dropped from 10.8 to 4.5 and 5.3, respectively (Fig. 1). It seems that most OSA reacted with soluble maltodextrin initially, but the reaction rate decreased after OS groups were substituted on maltodextrin.

We used 3% OSA and reacted it with (i) waxy maize starch, (ii) soluble maltodextrin, and (iii) a mixture of the starch and maltodextrin. After reaction, granular starch remained crystalline and still existed as compact granules as reflected by easy filtration, while the maltodextrin fraction was clear in water indicating that their solubility did not change probably because the DS was low after reacting with 3% OSA. It is interesting to compare the reaction results (Table 1). The RE was almost 100% when 3% OSA was reacted with maltodextrin (Table 1) and DS was 0.024, whereas RE was ca. 80% for the granular starch with DS of 0.019. In comparison, when 3% OSA was reacted with a mixture of the granular starch and maltodextrin (1/1, w/w) for 2 h, the total RE was 84.4% (Table 1).

Table 1
Characterization of octenylsuccinate (OS) starch or maltodextrin when prepared in a mixture of waxy maize starch and maltodextrin (1/1, w/w) as well as starch or maltodextrin only.

OSA level (%)	Reaction time (h)	Degree of substitution	%OS	% Reacted based on total OSA	Degree of substitution	%OS	% Reacted based on total OSA
		Mixed reaction system					
		Starch fraction			Maltodextrin fraction		
1.5	0.5	0.0020	0.26	8.7	0.021	2.7	89.3
	1.5	0.0018	0.24	8.0	0.021	2.6	86.3
3.0	0.5	0.0087 ± 0.0004^{c}	1.1 ± 0.06^{b}	18.5 ± 0.9^{c}	0.030 ± 0.004^{a}	3.7 ± 0.50^{a}	61.9 ± 8.3^{a}
	1.0	0.0080 ± 0.0003^{b}	1.0 ± 0.03^{b}	16.7 ± 0.3^{b}	0.034 ± 0.001^{a}	4.2 ± 0.07^{a}	67.9 ± 2.5^{a}
	2.0	0.0072 ± 0.0002^{a}	0.9 ± 0.02^{a}	15.4 ± 0.5^{a}	0.033 ± 0.001^{a}	4.1 ± 0.01^{a}	69.0 ± 1.4^{a}
		Starch only*			Maltodextrin only*		
3.0	0.5	0.014 ± 0.001^{a}	1.75 ± 0.01^{a}	n/a	0.023	2.92	n/a
	1.0	0.019 ± 0.001^{b}	2.39 ± 0.01^{b}	n/a	0.023	2.95	n/a
	1.5	0.019 ± 0.001^{b}	2.42 ± 0.01^{b}	n/a	0.024	2.99	n/a
	2.0	0.019 ± 0.001^{b}	2.37 ± 0.01^{b}	n/a	n/a	n/a	n/a

Numbers in the same column followed by a letter in common are not significantly different at $P < 0.05$.

* Data from Bai and Shi (2011) are incorporated here for comparison.

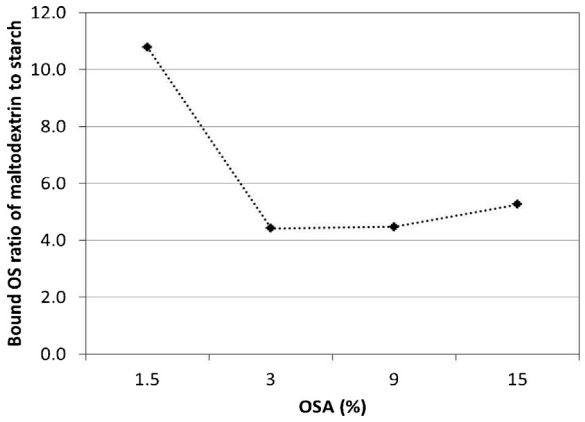

Fig. 1. Ratio of octenylsuccinic anhydride (OSA) reacted on maltodextrin to waxy maize starch at different levels of OSA.

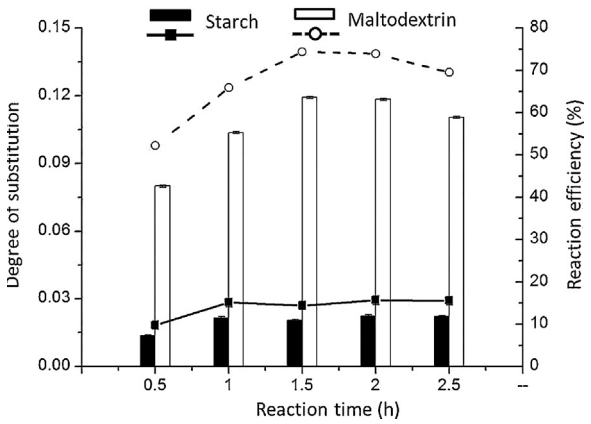

Fig. 2. Degree of substitution (bar graph) and reaction efficiency (line graph) of 9% octenylsuccinic anhydride modification on the mixture of waxy maize starch and maltodextrin.

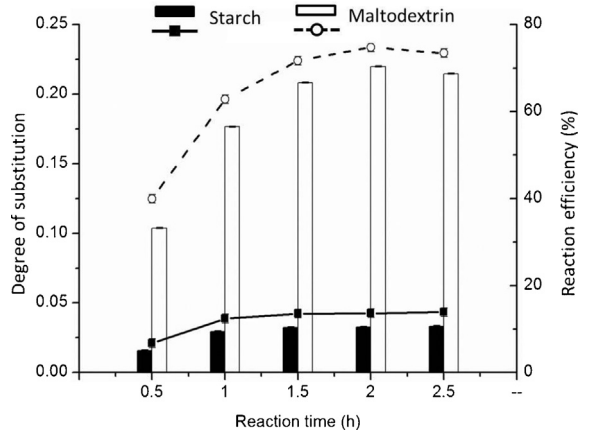

Fig. 3. Degree of substitution (bar graph) and reaction efficiency (line graph) of 15% octenylsuccinic anhydride modification on the mixture of waxy maize starch and maltodextrin.

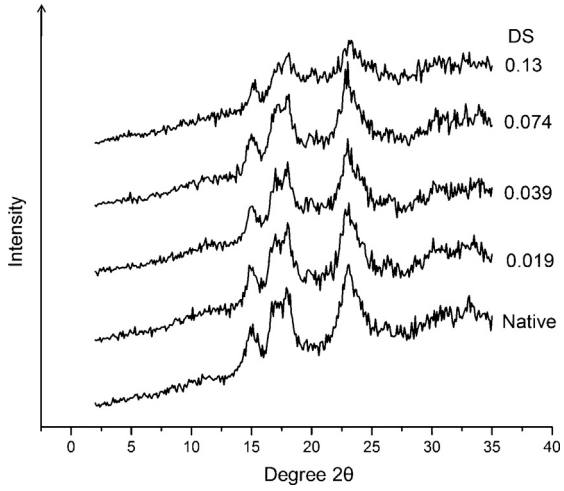

Fig. 4. Wide-angle X-ray diffraction patterns of native waxy maize starch and octenylsuccinate starches of degree of substitution (DS) 0.019, 0.039, 0.074, and 0.13.

Among the total OSA reacted, 69.0% reacted on the maltodextrin, resulting in 4.1% OS on the maltodextrin, In contrast, only 15.4% reacted on the granular starch (Table 1). DS of maltodextrin fraction was 0.033, which was more than 4 times higher than the granular starch fraction.

The reaction rate of OSA modification on maltodextrin appeared different from granular starch. After the first 0.5 h of the reaction, DS on maltodextrin reached 0.021, 0.030, 0.080, and 0.10 for 1.5, 3, 9, and 15% (wt% based on starch weight) OSA, respectively, whereas DS for granular starch was only 0.0020, 0.0087, 0.014, and 0.016 (Table 1, Figs. 2 and 3). These results indicate that OSA reacted much faster on maltodextrin than granular starch. At high OSA concentrations of 9 and 15% (wt% based on starch weight), interesting results were observed. At 9% OSA (Fig. 2), the DS of the maltodextrin continued to increase from 0.5 h to 1.5 h, remained constant from 1.5 to 2.0 h, and decreased from 2.0 h to 2.5 h. The reaction stopped after 1.5 h was probably because of the increase in hydrophobicity after OS substitution. In contrast, the DS of the granular starch increased from 0.5 h to 1.0 h, then remained constant up to 2.5 h (Fig. 2). A similar trend was observed for 15% (wt% based on starch weight) OSA concentration (Fig. 3). These results suggest that the OSA reaction rate was fast at the early stage of the reaction for both granular starch and soluble maltodextrin, but it slowed as the reaction progressed. Reaction rate on granular starch decreased much faster than maltodextrin. The fast decrease in reaction rate was probably due to the steric hindrance in granular starch for OSA to react as well as the increase in starch hydrophobicity after OS substitution. Granular starch appeared to have much less available space for OS substitution than maltodextrin.

OSA reaction was performed on granular starch alone, and the granular structure change was investigated by wide-angle X-ray diffraction. Native waxy maize starch showed an A-type crystalline pattern. At DS of 0.019 and 0.039, crystalline pattern of OS starch appeared to be the same as native starch (Fig. 4). As DS reached 0.074, the crystalline pattern started to lose definition, and peak broadening was observed (Fig. 4). These results suggest that at low level of OSA modification, OS substitutions occurred primarily at the amorphous region. For granular waxy maize starch without starch swelling, the maximum DS was about 0.088 (Bai & Shi, 2011), reflecting limited reaction space in the amorphous regions.

Therefore, the difference in OSA reaction on granular starch and maltodextrin was due to that the granular starch was partially crystalline, whereas maltodextrin was soluble in water. OSA reacted preferably with granular starch at the amorphous region and granular surface (Huang, Fu, He, Luo, Yu, & Li, 2010; Shogren, Viswanathan, Felker, & Gross, 2000; Song et al., 2006). The crystalline region of granular starch was tightly packed and was not readily accessible for starch modification (Richardson, Nilsson, Cohen, Momcilovic, Brinkmalm, & Gorton, 2003). In contrast, maltodextrin, which was completely amorphous and soluble in water, had all the molecules available, or, in other words, had more sites

for reaction; therefore, it appeared to have a faster reaction rate than granular starch.

When both maltodextrin and granular starch existed in one reaction system, OSA preferably reacted with maltodextrin and granular starch in its amorphous region, but the reaction was more profound in maltodextrin. For example, in the 3% OSA reaction, DS of the maltodextrin fraction in the mixture of starch and maltodextrin was higher than that of maltodextrin alone (Table 1). The bound OS in the maltodextrin fraction in the mixed reaction was greater than 3%. This is because that when a mixture of granular starch and maltodextrin was used, the percentage of OSA based on the weight of the maltodextrin fraction was 6%. As the reaction progressed, OSA reaction on maltodextrin and starch slowed; however, due to a much lower reaction rate on granular starch, OSA reacted with maltodextrin, which had more sites available for reaction, until no available OSA in the system. However, significant amount of OSA still reacted with granular starch at 3–15% OSA in the mixture of granular starch and maltodextrin (Table 1, Figs. 2 and 3), indicating the some OSA molecules were driven into the hydrated granules as suggested by Sui et al. (2013).

4. Conclusions

In an aqueous system mixed with the granular starch and maltodextrin, OSA preferably reacted with the soluble maltodextrin at OSA concentration of 1.5–15% (wt%, based on starch weight), but a significant amount of OSA reacted with granular starch at 3–15% OSA concentration. The initial reaction rate of maltodextrin with OSA was much faster than that of the granular starch. OSA preferably reacted with granular starch in its amorphous region and with soluble maltodextrin.

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