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Effect of octenylsuccinylation on physicochemical, thermal, morphological and stability of octenyl succinic anhydride (OSA) modified sago starch

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Sago starch (*Metroxylon sagu*) and gelose 80 starches were esterified with octenyl succinic anhydride (OSA) and effect of the reaction was evaluated in terms of physicochemical properties. The degree of substitution (DS) of 0.0120 was obtained for OSA sago starch and 0.0145 for OSA gelose 80 starch. The amylose content of OSA starches (OSA sago starch: 25.27%; OSA gelose 80: 70.70%) was found to decrease significantly ($p < 0.05$) compared to native starches (Sago starch: 30.18%; Gelose 80: 78.47%). FTIR spectroscopy showed two new peaks on OSA starches spectrum at 1720 cm^{-1} and 1566 cm^{-1} due to C=O and RCOO-, respectively. The particle size of both OSA starches significantly ($p < 0.05$) increased (OSA sago starch = 29.89 μm, OSA gelose 80 = 20.37 μm) due to structural disorder that happens after modification. The surface tension for OSA sago starch was found to be 58.40 mN/m while OSA gelose 80 was 54.87 mN/m. The gelatinisation temperature and enthalpy for OSA sago starch and gelose 80 starch ranged from 67.56 °C to 79.83 °C (enthalpy: 10.25 J/g) and 65.69 °C to 95.26 °C (enthalpy: 7.45 J/g), respectively with reduction pattern was observed for both starches. The morphology of starch granule examined by scanning electron microscopy (SEM) showed some rough surface and a few changes in shape of OSA starches. To confirm the success of the esterification on the sago starch, the physicochemical properties of OSA commercial starch was used as a comparison.

1. Introduction

The usage of native starch in daily life was widespread; however the deficiency in their properties such as inability to produce stable starch and gels, loss of viscosity and insolubility in cold water, have restrict the use of starch in industrial application. The shortcoming of native starch can be overcome by starch modification. In general, starch modification can be achieved in different ways which include derivatization (grafting of starch, esterification, etherification), decomposition (oxidation of starch, acid or enzymatic hydrolysis) and the use of heat or moisture via physical treatment (Singh, Kaur, & McCarthy, 2007). The sago starch was obtained from sago palm (*Metroxylon* spp.*),* which accumulate in the stem of the palm and belongs to the *Palmae* family. It has been widely distributed in South East Asia and become one of the important food sources to the people in rural areas (Maaruf, Che Man, Asbi, Junainah, & Kennedy, 2001). With the annual production of approximately 51,000 tonnes of dry starch, it make Malaysia as one of the leading in the production and largest exporter of sago starch in the world (Othman, Hassan, & Hashim, 2015; Yunus, Md Jahim, Anuar, Abdullah, & Kofli, 2014). Sago starch was known as it is relatively cheap and abundant, some other important properties of sago starch such as easy to gelatinise, high viscosity, easily moulded and low gel synerisis has been reported earlier (Ahmad, Williams, Doublier, Durand, & Buleon, 1999). In order to meet industrial demand and enhance the functional properties, modification via physical or chemical can be carried out on sago starch.

A starch that has been altered chemically or physically with the aim to improve their properties and tailor to specific application in the industry was known as modified starches. Some common chemical modification reactions include esterification, cross-linked and etherification. Chemical modification will introduce newly functional group in the native starches with the aim to improve their physicochemical properties. The native sago starch has less affinity for hydrophobic substances due to its properties that are naturally hydrophilic. Thus, modification of sago starch via

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esterification with octenyl succinic anhydride (OSA) can introduce hydrophobic group. The esterification of starch with dicarboxylic acids was first patented by Caldwell and Wurzburg in 1953 and the product was known as starch sodium octenyl succinate (SSOS) (Magnusson & Nilsson, 2011). The availability of hydroxyl groups at carbon 2, 3 and 6 make native starch become reactive for substitution reaction. The esterification of native starch with OSA in aqueous slurry system will produce starch with amphiphilic properties and confer surface active properties (Song, Chen, Ruan, He, & Xu, 2006). Starch modified with OSA has received attention as it has been approved for food use by Food and Drug Administration (FDA) with the amount limit to 3% of OSA.

The study on esterification of various starches with OSA has been reported earlier in scientific literature such as waxy maize and amaranth starch (Bhosale & Singhal, 2006), early *Indica* rice starch (Song et al., 2006), potato starch (Han, Zhu, & Zhang, 2011; Hui, Qi-he, Ming-liang, Qiong, & Guo-qing, 2009; Wang, Su, & Wang, 2010; Won et al., 2016), barley starch (Nilsson & Bergenståhl, 2007), sugary maize soluble starch and waxy maize starch (Miao et al., 2014), plantain starch (Bello-Flores, Nuñez-Santiago, Martín-Gonzalez, BeMiller, & Bello-Pérez, 2014), waxy rice starch (Chen, Yin, Chen, Xiong, & Zhao, 2014) and cassava starch (Bao Zhang, Mei, Chen, & Chen, 2017). There a few common factors that were being optimize for the preparation of OSA starch for instance OSA concentration, pH, temperature, reaction time and starch concentration. The preparation condition of each starch was varied depending on the starch type and their botanical origin. An attractive newly properties have been obtained after esterification has expanded the usability of the starch. The improved properties such as low gelatinization temperature, decreased synerisis, improved paste clarity (Bhosale & Singhal, 2007); low pasting temperature, reduce retrogradation and increase viscosity (Tukomane & Varavinit, 2008); and better freeze-thaw stability (Song, Zhu, Li, & Zhu, 2010) has been described earlier. The OSA modified starch has been apply to encapsulate nutritional supplement of CoQ_{10} (Cheuk et al., 2015), carrier agent to produce spray-dried propolis powder (Da Silva et al., 2013) and bioactive food component (Wang et al., 2011), surfactant for the formulation of lavandin essential oil in O/W emulsion (Varona, Martín, & Cocero, 2009), stabilizer in O/W emulsion (Yusoff & Murray, 2011) and milk protein (Liu et al., 2017), fat replacer in cookies (Dapčević Hadnađev, Hadnađev, Pojić, Rakita, & Krstonošić, 2015) and muffin (Chung, Lee, Han, & Lim, 2010), and also as emulsifier (Williams et al., 2017).

A majority of earlier studies on starch esterification by OSA were focused on the common type of starch. However, the report on preparation and physicochemical properties of OSA sago starch was still scarce. When sago starch was modified by OSA, the internal hydrogen bonding was weakened and starch will start to gelatinize at lower temperature. Retrogradation was retarded as formation of starch paste ordered structure was prevented by the presence of bulky succinyl group. The amphiphilic character of OSA sago starch makes it able to form a strong film at the oil-water interface. The starch becomes more water-soluble which results in high viscosity than native starch. Our previous work has determine the optimum condition for the preparation of OSA sago starch via response surface methodology (RSM) (Zainal Abiddin, Yusoff, & Ahmad, 2015). To add-on, the goal of the present study is to determine the effect of each factor on the preparation of OSA sago starch. After the optimum OSA sago starch was obtained, the starch was characterized in term of amylose content, thermal activity, surface tension, morphology and also particle size of the starch granules. The addition of hydrophobic group into the naturally hydrophilic sago starch extends the usage of this starch in industrial application. The OSA sago starch could be used as an effective emulsifier and stabilizer in the production of oil-in-water (O/W) emulsion. The OSA starch has been known to form a strong film at the interface of O/W emulsion and also can prevent coalescence (Abdollahzadeh, Mehranian, & Vahabzadeh, 2008). The experiments were carried out using sago starch and gelose 80 starch that has been made hydrophobic using the obtained optimum condition in the laboratory, and OSA commercial starch that was obtained from National Starch. The results will focus on the comparison in physicochemical properties of native starch and esterified starch as well as between the three different types of starch used in this study.

2. Materials and methods

2.1. Materials

Food grade sago starch was purchased from Nee See Ngeng & Sons Sago Industries Sdn Bhd (Sarawak, Malaysia). Gelose 80 is unmodified high amylose maize starch that contains approximately 80% of amylose and was donated by Ingredion (Bridgewater, New Jersey). Octenyl succinate anhydride commercial starch was a gift of N-Starch Sdn Bhd (Shah Alam, Malaysia) and was used without any further treatment. Octenyl succinic anhydride (OSA) was obtained from Dixie Chemical Company, Pasadena, Texas, USA. Sodium hydroxide, hydrochloric acid, acetone and dimethyl sulfoxide were of analytical grade and purchased from Sigma-Aldrich.

2.2. Preparation of OSA starches

Sago and gelose 80 starches were subjected to esterification using OSA by treating with the optimum condition obtained through response surface methodology (RSM). The optimum condition for the preparation of OSA starches was at 5.00% OSA concentration, pH 7.20 and reaction time of 9.65 h. Preparation of OSA starches and determination of degree of substitution (DS) were based on study from Bhosale and Singhal (2006) and has been reported in our earlier work (Zainal Abiddin et al., 2015). The DS was calculated as follows:

$$\text{OSA substitution}(\%) = \frac{\left(V_{blank} - V_{sample}\right) \times 0.1 \times N \times 100}{W}$$

Where V_{blank} = the volume of HCl required for blank titration; V_{sample} = volume of HCl required to titrate the sample; W = weight (g) of the sample; N = normality of HCl solution.

$$\text{DS} = \frac{162 \times \text{OSA substitution}(\%)}{21000 - [209 \times \text{OSA substitution}(\%)]}$$

Where 162 = molecular weight of the glucose unit; 21000 = 100 × molecular weight of octenyl succinyl group; 209 = molecular weight of octenyl succinyl group minus molecular weight of hydrogen.

In term of DS, the OSA gelose 80 was analyzed as a comparison with OSA sago starch. The difference in physicochemical properties was analyzed between native and modified starch also with other OSA starch in this study.

2.3. Determination of physico-chemical properties

2.3.1. Morphological properties

The morphological characteristics of native and OSA starches were observed through scanning electron microscope (Leo Supra 50VP Field Emission SEM, Carl Zeiss SMT, Germany). The starch samples were air-dried in an oven at 40 °C and make sure to be completely dry before imaging to avoid any interference of