

THE MODIFICATION OF TAPIOCA STARCH BY ESTERIFICATION TECHNIQUE

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Abstract

Starch is one of the most abundant renewable biopolymer from natural resource. The modified starch exhibits many applications for food and non-food industries. In this study, the native tapioca starch was modified by esterification with maleic anhydride and 4-(dimethylamino) pyridine (DMAP) was used as a catalyst in an aqueous solution. The effects of starch concentration, molar ratio of starch to maleic anhydride, and reaction time on the degree of substitution (DS) and reaction efficiency (RE) were investigated. The modified starch was characterized by attenuated total reflectance-fourier transform infrared spectra (ATR-FTIR), thermal gravimetric analysis (TGA) and proton nuclear magnetic resonance spectroscopy (¹H – NMR). The peak of ester group of modified starch at 1713 cm⁻¹ was shown in ATR-FTIR spectrum and the intensity was correlated with the content of DS. TGA thermograms confirmed that the thermal stability of native tapioca starch was changed when the native starch was modified. Moreover, the vinyl proton of maleic anhydride was found by ¹H – NMR spectrum from the modified starch at 6.4 ppm. This confirmed that the modification of the native tapioca starch by esterification with maleic anhydride was achieved.

Keywords: Esterification, maleic anhydride, modification, starch

Introduction

Starch is a natural, renewable, low cost, and biodegradable polymer produced by many plants as a resource of stored energy (Le, *et al.*, 2010). It is common carbohydrate in the

human diet. Starch is found in plant roots, stalks, crop seeds, and staple crops such as corn, potato, rice, wheat, and tapioca (Buléon, *et al.*, 1998). Starch is a hydrophilic

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macromolecule, and the polysaccharides were composed of two different molecules, amylose as the α -(1 $\rightarrow$ 4) linear links and amylopectin as the α -(1 $\rightarrow$ 6) branched links (Sweedman *et al.*, 2013). The hydrophilic nature of starch severely limits the application of starch – based materials. Native starch has some disadvantages such as poor mechanical properties, limited solubility in water, and limited applications for industrial. Starch is commercialized both as native and modified starch. The latter refers to starch that has been chemically modified aiming to give them specific properties (Tupa *et al.*, 2013). In recent years, many types of chemically modified starch have been prepared by acid hydrolysis, oxidation, esterification and cross-linking (Jayakody and Hoover, 2002). The chemical modifications of starch including esterification are effective methods to improve the properties of starch (Chi *et al.*, 2008). Modified starch can be used in wide range of applications. In food industry, the starch acetate can be used as an additive, thickener, stabilizer, emulsifier, flavored toppings and sauces (Chowdary and Radha, 2011). Non-food industry uses the starch as adhesives for the papermaking process and the production of corrugated boards, binders for the pharmaceutical industry, laundering of clothes, as additives to adjust the viscosity of drilling fluids used in petroleum extraction, as substitutes for talcum powder and other beauty, health products, degradable plastics in the field of packaging, etc (Mose and Maranga, 2011). Esterification of starch by replacement of hydroxyl groups with ester groups improves the native starch to be more hydrophobic so it reduces the water sorption. Consequently, this results in materials with better mechanical property retention in aqueous environment (Cyras *et al.*, 2006).

Normally, most commercial modified starch is produced by reaction of starch in aqueous medium with anhydrides and sodium hydroxide (NaOH) at pH 7–9 by preparation of acetylated waxy, normal, and high-amylose corn starches in aqueous solution with 20% (w/w) NaOH as a catalyst, and compared the properties of three acetylated corn starches by use of scanning electron microscope (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and pasting properties

(Luo and Shi, 2012). Some procedures developed treatment time on acid-alcohol consisting of methanol, ethanol, and 2-propanol at 45°C for 1 h. The modified starches were ultimately achieved to be homogeneous. The starch treatment by acid-alcohol showed that the degree of polymerization gradually decreased as the carbon number of the alcohol increased (Yiu *et al.*, 2008). Moreover, esterification with anhydrides by using pyridine as a catalyst was reported. However, the conditions used were at high temperature and high ratio of starch to pyridine. The high cost, manipulation difficulties of the catalyst, toxic solvent has limited the commercial development of this technology (Bhandari and Singhal, 2002).

The objective of this study was to produce modified starch by an aqueous solution method with simple and inexpensive process with less amount of waste solvent and gas. The methodology was based on the use of 4-(dimethylamino)pyridine (DMAP) as a catalyst for ring-opening reaction of maleic anhydride (MA) and esterification of polysaccharides. The modified starch from this process was characterized by ATR-FTIR, TGA, and ^1H -NMR.

Materials and Methods

Materials

Tapioca starch, maleic anhydride, and 4-(dimethylamino) pyridine were purchased from Bangkok Inter Food Co., Ltd. (Thailand), Merck (Thailand), and Sigma-Aldrich (Thailand), respectively. These were loaded in an oven at 40°C for 24 h to eliminate moisture before use. All chemical substances were AR grade.

Synthesis of Modified Starch by Esterification Reaction

Esterification was carried out by taking the accurate amount of starch and deionized water (DI water) in a 250 ml three necks round bottom flask fitted with a magnetic stirrer. The first neck was fitted with the thermometer pocket. The second neck was fitted with reflux condenser to prevent the loss of anhydride and the third neck was fitted with a septum bottom. Then the solution was heated to 120°C under

continuous agitation in an oil bath. When the solution achieved the target temperature, 4-(dimethylamino) pyridine solution in DI water was dropped to the third neck. The solution was mixed for 10 min. Then maleic anhydride solution in DI water was dropped. The reaction time was varied from 7-24 h. After reaching the reaction time, the reaction vessel was cooled to room temperature. Starch maleate was isolated from the reaction solution of 4-(dimethylamino) pyridine by rotary evaporation and precipitated in absolute acetone. The product was washed 2-3 times successively with acetone to remove the traces of 4-(dimethylamino) pyridine and maleic anhydride from the product. It was then dried in a vacuum oven at 50°C for 8 h.

The process parameters including starch concentration, starch/maleic anhydride ratio, and reaction time were varied and optimized for getting the modified starch form tapioca starch.

Determination of the Degree of Substitution (DS)

Degree of substitution (DS) of a maleated starch is defined as the number of hydroxyl (OH) groups substituted per anhydroglucose unit of the starch polymer. The anhydroglucose unit possesses three reactive hydroxyl groups so the maximum DS value is 3. Maleated starch were determined by heterogeneous saponification and back titration with HCl. Approximately 0.11 g of dry modified starch was weighed accurately and transferred to 100 mL erlenmeyer flask to which 10 mL of ethyl alcohol (75%) was added. Afterwards, 10 ml of 0.5 M aqueous sodium hydroxide solution was added. The erlenmeyer flask was agitated, warmed to 50°C and stirred for 30 min. Erlenmeyer flask was finally cooled at room temperature for 30 min. At the end of this time, the excess NaOH present in the flasks was back titrated with 0.5 M aqueous hydrochloric acid solution, using phenolphthalein as the end-point indicator. A blank determination (native tapioca starch) was carried through the complete procedure. NaOH and HCl solutions were standardized using previously dried standard potassium hydrogen phthalate and standard sodium hydroxide solution, respectively.

The degree of substitution (DS) was calculated by (Tupa *et al.*, 2013):

$$W_{MA}(\%) = \frac{98C(V_B - V_S)}{1000 \times 2W} \times 100$$

where W_{MA} is the content of maleic anhydride substituted, %; W is the mass of the sample, g; 98 is the molecular weight of the maleic anhydride, g/mol; C is the concentration of aqueous hydrochloric acid solution, mol/L; V_B is the consumed volume of aqueous hydrochloric acid solution by blank sample, mL; V_S is the consumed volume of aqueous hydrochloric acid solution by modified starch sample, mL.

$$DS = \frac{162W_{MA}(\%)}{98 \times (100 - W_{MA}(\%))}$$

where 162 is the molecular weight of anhydroglucose units.

Reaction efficiency (RE) was calculated by:

$$RE = \frac{DS}{n(MAH) \div n(AGU)} \times 100\%$$

where $n(MAH)$ is the molar quantity of maleic anhydride, $n(AGU)$ is the molar quantity of anhydroglucose units in starch.

Characterization of Modified Starches

Attenuated total reflectance-Fourier transform infrared spectra of dried modified starches were acquired using a Bruker FTIR spectrometer (Tensor 27) with Opus 7.0 software. Spectra were collected with 32 scans in the range of 4000 to 700 cm^{-1} with a resolution of 4 cm^{-1} .

Thermo gravimetric analysis of dried modified starch was conducted in a Pyris Diamound, Perkin Elmer instrument. Modified starch (5 mg) was loaded into an aluminum oxide pan. Experiments were tested from 50 to 850°C with 10°C/min of heating rate and 100 ml/min of nitrogen gas flow.

Proton nuclear magnetic resonance spectra of dried modified starches were carried out on a Varian Mercury-400 NMR Spectrometer operating at 400 MHz for ^1H -NMR. Native starches as well as modified

starches were dissolved in dimethyl sulphoxide (DMSO)-d6 at 50°C to obtain clear solutions. The analysis for starch and modified starch was carried out at 25°C.

Results and Discussion

Effects of Preparation Conditions on DS and RE of Modified Starch

The Effects of Reaction Time on DS and RE

The effect of reaction time on DS and RE at reaction temperature 120°C, starch/maleic

anhydride ratio of 1:2, and 2% starch concentration was shown in Figure 1. From Figure 1, DS of modified starches increased from 0.42-0.59 and RE (%) increased from 23-32% with increasing reaction from 7 to 8 h. This could be due to the increased rate and time of collisions of maleic anhydride with starch through the formation of maleyl-4-(dimethylamino) pyridinium intermediate (Bhandari *et al.*, 2002). At higher reaction times (more than 8 h) DS and RE were decreased. This may be attributed to the increasing trend of side reactions such as a hydrolysis (Choi *et al.*, 2002).

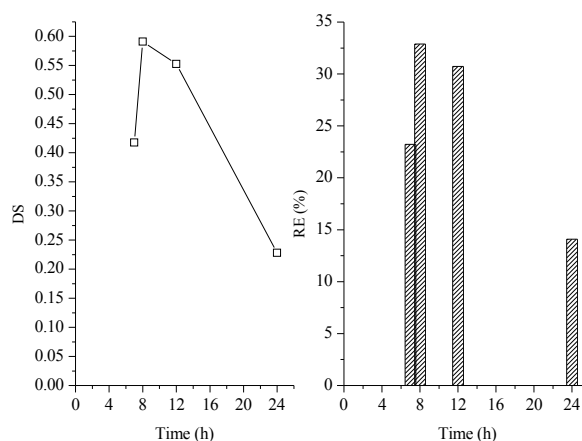


Figure 1. DS and RE of modified starch prepared at various reaction times

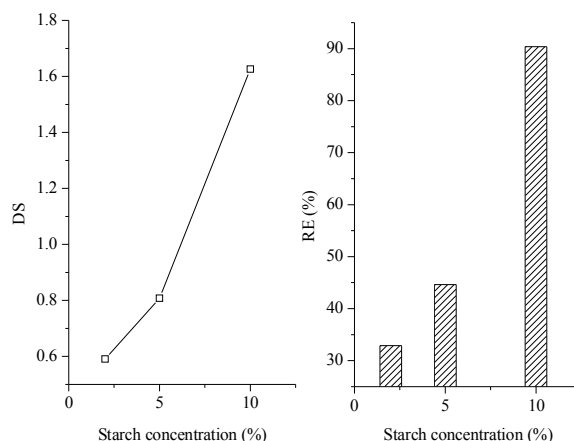


Figure 2. DS and RE of modified starch prepared by various starch concentrations

The Effect of Starch Concentrations on DS and RE

The effect of starch concentrations on DS and RE at the reaction temperature 120°C, starch/maleic anhydride ratio 1:2, and reaction time 8 h was investigated. The experiments were performed in the starch concentration range of 2-10%. As shown in Figure 2, DS and RE increase with increasing starch concentrations. This is because the increase in the starch concentration led to more probability for the reaction to occur (Witono *et al.*, 2012).¹⁴ As a result, increasing level of DS and RE were observed. Nevertheless, 10% starch concentration was not chosen for further

use due to its high viscous and inhomogeneous mixture.

The Effect of Starch/Maleic Anhydride Ratio on DS and RE

Figure 3 showed the effect of starch/maleic anhydride ratio on DS and RE at the reaction temperature 120°C, 5% starch concentration, and reaction time 8 h. The starch/maleic anhydride ratio has studied in 3 ratios (1:0.5, 1:1, and 1:2). It can be seen that as the starch/maleic anhydride ratio increases there is an increase in the DS. On the other hand, a decrease in the RE was observed. At higher maleic anhydride, many reactions may

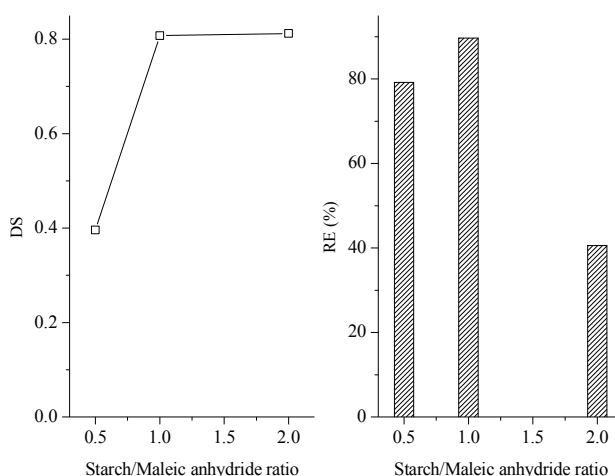


Figure 3. DS and RE of modified starch prepared by various starch/maleic anhydride ratios

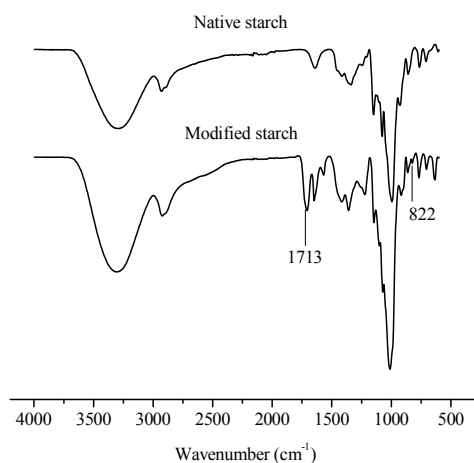


Figure 4. Infrared spectra of native starch and modified starch

compete due to limited reaction sites on the starch molecules for the esterification. Therefore, certain amount of maleic anhydride was reacted to the starch (Shi and He, 2012; Tupa *et al.*, 2013). The appropriate conditions for the modification of starch and maleic anhydride were found to be at 5% starch concentration, starch/maleic anhydride ratio at 1:1, and temperature 120°C for 8 h

Characterization of Modified Starch

Characterization by Attenuated Total Reflectance-Fourier Transform Infrared Spectra (ATR-FTIR)

ATR-FTIR spectra of native starch and modified starch were shown in Figure 4. Native starch shows characteristic bands of polysaccharide consisting of a broad band between 3700 and 3000 cm^{-1} assigned to the stretching of hydrogen bonded O-H groups (Garg and Jana, 2011), a band in the region of 2800-3000 cm^{-1} attributed to C-H stretching modes (Diop *et al.*, 2011), and a band at 1639 cm^{-1} assigned to the O-H bending vibration of water molecules adsorbed in the amorphous regions of starch granules (Kizil *et al.*, 2002). The region around 1500-1200 cm^{-1} shows highly overlapped bands, among which vibrations typical of C-O-H bending, CH_2 twisting, CH_2 bending and C-O-C stretch (Cael *et al.*, 1975). Native starch spectrum shows the presence of bands at 1149 and 928 cm^{-1} which

could be assigned to the C-O bond stretching, and the α -1,4 glucosidic bond vibration, respectively (Garg and Jana, 2011). The absorption bands shown in native starch spectrum at low wave numbers are attributed to skeletal mode vibrations of the C-H and CH_2 deformation (859 cm^{-1}), and C-C stretching (763 cm^{-1}) (Kizil *et al.*, 2002). In comparison, maleic anhydride esterified starch not only contains all of the above characteristic absorption peaks, but also contains a C=O absorption peak at neighboring 1713 cm^{-1} (Zuo *et al.*, 2013). Moreover, there was a butyl absorption peak at 822 cm^{-1} , which was formed in the starch by ring opening and esterification of maleic anhydride. The esterification reaction of starch and maleic anhydride should show C=C in the modified starch. However, C=C was not observed from this result because it may overlap with the O-H bending vibration peak (1639 cm^{-1}) (Zuo *et al.*, 2013).

Characterization by Proton Nuclear Magnetic Resonance Spectra (^1H -NMR)

Native starch and modified starch were analyzed by ^1H -NMR spectrometer. The ^1H -NMR spectra of native starch and modified starch were shown in Figure 5. The chemical shifts of the protons of amylose and amylopectin in starch were assigned at 3.62–3.74 ppm corresponding to proton at H-3, H-5, and H-6. The chemical shifts of the protons at 2.98–3.28 ppm were corresponding to proton

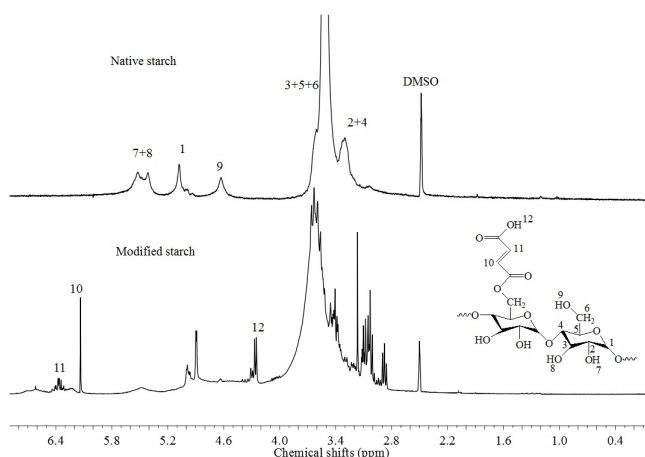


Figure 5. ^1H -NMR spectra of native starch and modified starch

at H-2 and H-4 (Tizzotti *et al.*, 2011; Sweedman *et al.*, 2013). The chemical shifts of H-1, OH-7, OH-8, and OH-9 were 5.09, 5.41, 5.53, and 4.63 ppm, respectively (Chi *et al.*, 2008). Compared to the native starch, the ^1H -NMR spectra of modified starches shows the protons of vinyl groups of maleic anhydride appeared at 6.14–6.35 ppm and proton of hydroxyl group of maleic anhydride appeared at 4.27 ppm.

Characterization by Thermogravimetric Analysis (TGA)

TGA and DTG curves of native tapioca starch and modified starch were shown in

Figures 6 and 7, respectively. One can observe that native starch showed two stages of weight loss. The first stage of weight loss was observed from 50 to 130°C due to the dehydration. The second stage of weight loss was from 280 to 400°C due to thermal decomposition of native starch. The decomposition of native starch is a result of the inter-intramolecular dehydration reactions of the starch molecules (Barud *et al.*, 2007). The

maximum decomposition temperature ($T_{\max}$) of native tapioca starch was found at 323°C as shown in DTG curve. On the other hand, TGA curve from modified starch shows three

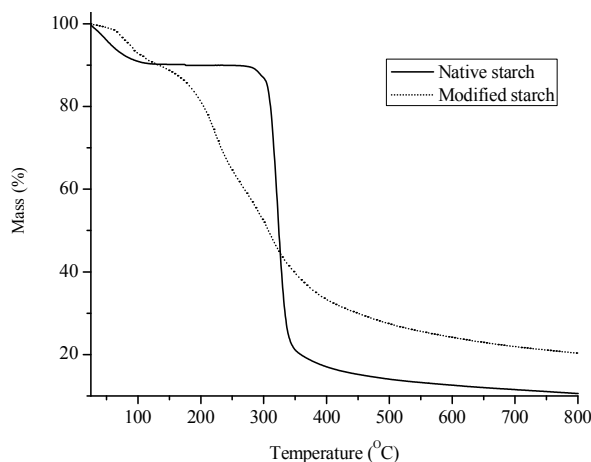


Figure 6. TGA curves of native starch and modified starch

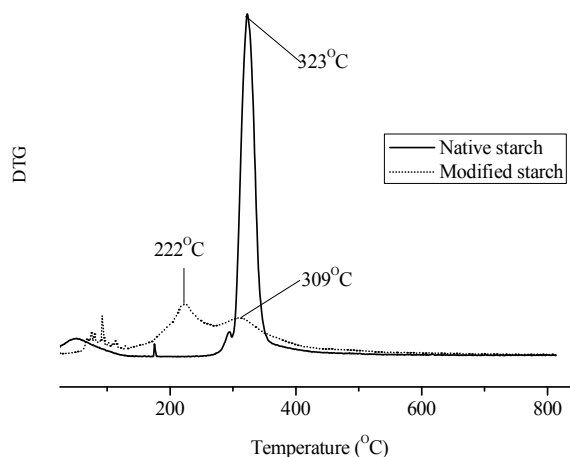


Figure 7. DTG curves of native starch and modified starch

stages of weight loss. The first stage from 50 to 130°C corresponds to the dehydration. The second stage from 130 to 280°C was assigned to thermal decomposition of maleic anhydride (Zuo *et al.*, 2013). The maximum decomposition temperature of modified starch was found at 222°C from DTG data. The third stage from 280 to 400°C was assigned to thermal decomposition of starch molecules. The maximum decomposition temperature at the third stage of modified starch was at 309°C. This indicates that the thermal stability of native tapioca starch was changed when the native starch was modified. This implied that the native tapioca starch has been successfully modified by maleic anhydride.

Conclusions

In this research, the native tapioca starch was successfully modified by esterification with maleic anhydride and 4-(dimethylamino) pyridine (DMAP) was used as a catalyst in an aqueous solution. The optimum condition for preparation of modified starch was at 120°C of reaction temperature and 8 h of reaction time, 5% of starch concentration, 1:1 of starch/maleic anhydride ratio. The maximum degree of substitution and reaction efficiency can be obtained at 1.63 and 90.39%, respectively. ATR-FTIR was used to confirm the esterification reaction by appearance of ester group at 1713 cm⁻¹. ¹H-NMR of modified starch showed the new peaks at 4.27 and 6.12–6.35 ppm indicating the hydroxyl and vinyl protons of maleic anhydride, respectively. The thermal stability of modified starch was lower than the native tapioca starch.

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