

Kinetic study of the nonthermal effect of the esterification of octenyl succinic anhydride modified starch treated by microwave radiation

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ABSTRACT: With cassava starch as a raw material and octenyl succinic anhydride as an esterifying agent, octenyl succinic anhydride modified starch (OSA–starch) was prepared in an aqueous medium and treated by water-bath heating and microwave radiation at a certain temperature, respectively. The reaction kinetics of esterification were studied. The structural analysis and synthesis mechanism of OSA–starch were investigated by means of scanning electron microscopy and Fourier transform infrared spectroscopy. The differences in the esterification reaction kinetics between starches treated with water-bath heating and microwave radiation were observed. Under the condition of water-bath heating, the apparent activation energy of the esterification reaction was 52.22 ± 1.21 kJ/mol, and the pre-exponential factor was $9018.20/\text{min}^{-1}$. Under the condition of microwave radiation, the apparent activation energy of the esterification reaction was 50.13 ± 1.16 kJ/mol, and the pre-exponential factor was $4510.21/\text{min}^{-1}$. We found that microwave radiation could reduce both the activation energy of the reaction and the pre-exponential factor. The lowering effect of the apparent activation energy was greater than that of the pre-exponential factor under the condition of microwave radiation, and this resulted in increased reaction rates. The change in the esterification reaction kinetics was a nonthermal effect of microwave radiation on the esterification of cassava starch. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43909.

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INTRODUCTION

Octenyl succinic anhydride modified starch (OSA–starch) is one of the most important starch derivatives, and it has hydrophilic–lipophilic properties.¹ The modification of starches with octenyl succinic anhydride (OSA) was patented by Caldwell and Wurzburg in 1953.² Then, research on this product attracted more and more attention from researchers.^{3,4} They focused on the optimization of the starch esterification reaction conditions with various starches.^{5–7} In recent years, with the development of microwave technology, researchers have tried to enhance the preparation process of starch with microwave technology,^{8–11} and investigate the thermal and nonthermal effects of starch-modification reactions promoted by microwave heating.^{12–15} Alzbeta *et al.*,¹⁶ Alummoottil *et al.*,¹⁷ and other researchers have also studied the microwave preparation process of starch succinate modification. It has been proven that microwave heating affects the denaturation of starch in two ways.^{18–21} First, microwave heating increases the reactant molecule motion and temperature; this mainly reflects the thermal effects of the microwaves. Second, microwave radiation affects the Lorentz force of ions and weakly polar starch molecules. This results in the particularity of the relative motion between the starch gran-

ules. Such a relative motion is closely related to the microwave frequency, temperature, and modulation scheme; this may be a nonthermal effect of microwave radiation. Therefore, the mechanism of starch modification in a microwave field is quite complex. Generally, to reveal the dynamics effects of a chemical reaction by microwave radiation, the determination of the activation energy and pre-exponential factor is the most basic method. Microwave nonthermal effects and the hypothesis of changes in the activation energy and pre-exponential factor by microwave radiation have been introduced in microwave chemistry.^{22–25} Although researchers have studied the preparation and application of OSA–starch extensively, the investigation of the activation energy, pre-exponential factor, and other kinetic parameters for OSA–starch synthesis by microwave radiation has rarely been reported.²⁶ Currently, the industrial production of OSA–starch mainly uses an aqueous medium, which is endowed with the characteristics of a homogeneous reaction. However, OSA is hydrophobic, and the esterification reaction takes place in a liquid–liquid–solid three-phase reaction system. This reaction occurs under the conditions of alkali catalysis, and a hydrolysis reaction can also occur at the same time. The competitive mechanisms of hydrolysis and esterification exist,

and this directly affects the efficiency of the esterification of OSA. Therefore, the investigation of the reaction kinetics of starch esterification under microwave radiation is significant. It not only provides a theoretical basis for the enhancement of the reaction efficiency of microwave radiation but also provides technical support for the development of a preparation process of high-quality modified starch.

In this study, cassava starch from China Guangxi was used as a raw material, and the reaction kinetics of the esterification reaction in an aqueous medium were studied with the methods of water-bath heating and microwave radiation. The structures of the products were characterized with Fourier transform infrared (FTIR) spectroscopy. The morphology of the products was investigated by scanning electron microscopy (SEM). The effect difference comparison method^{27–29} was used to determine whether a nonthermal effect existed in the starch esterification under microwave radiation, and this might provide the theoretical basis for the microwave synthesis of OSA–starch.

EXPERIMENTAL

Materials

Cassava starch (food grade, 11.46 ± 0.76 wt % moisture) was purchased from Guangxi Hongfeng Starch Co., Ltd. (China). All of the other chemicals used in this investigation were analytical grade. Ethanol and sodium hydroxide (NaOH) were purchased from Guangdong Guanghua Chemical Factory Co., Ltd. (China). OSA was purchased from Hangzhou Zhongxiang Chemical Co., Ltd. (China).

Preparation of OSA–Starch

Appropriate amounts of cassava starch and distilled water were added to a two-necked flask, and the mass fraction of the starch slurry was adjusted to 40% w/w. The starch slurry was stirred with a magnetic stirrer. Then, the pH of the suspension was adjusted to 9.0 with a 1 mol/L NaOH solution. The suspension was alkalized for 20 min to obtain the alkalized starch emulsion. Herein, two alkalized starch emulsions were prepared. One alkalized starch emulsion was treated by water-bath heating to prepare OSA–starch, and the other was treated by microwave radiation to prepare the OSA–starch.

The typical preparation of the OSA–starch treated by water-bath heating was performed as follows. The two-necked flask with an alkalized starch emulsion was placed into a thermostat heating magnetic stirrer (DF-101S, Gongyi, China) and continuously stirred. Water-bath heating was used to maintain the appropriate temperature. Thermostatic water was used as a cooling medium in the water-bath heating system. The cooling media were used to maintain a constant temperature in the starch emulsion throughout the course of the esterification reaction. The pH of the starch slurry was maintained at 9.0 with a 1 mol/L NaOH solution. Then, 3% (relative to the mass ratio of dry starch) OSA was rapidly added (diluted four times relative to volume with absolute alcohol) to the alkalized starch slurry, and the reaction was started. The reaction mixture (8–10 mL) was drawn from a two-necked flask with a pipette at reaction times of 10, 20, 30, 40, 50, and 60 min, respectively. This reaction mixture was rapidly injected into a 70% v/v ethanol aqueous

solution with a volume of 50 mL, and the pH of the starch slurry was adjusted to 6.5 with a 1 mol/L HCl solution. The mixture was filtered, and the esterification reaction was terminated. The filter cake was washed twice with distilled water and twice with 70% v/v ethanol aqueous solution. Then, the solid was put into a vacuum oven (BPZ-6090Lc, Shanghai, China) at 45 °C and dried for 24 h. The OSA–starch samples with different reaction times were obtained after shattering and passed through a 100-mesh sieve.

The typical preparation of OSA–starch treated by microwave radiation was performed as follows. The two-necked flask with the alkalized starch emulsion was placed into a microwave oven (NJL07-3, Nanjing, China) and stirred continuously. The microwave radiation (microwave power = 50 W, frequency = 2455 MHz) was used to maintain an appropriate temperature. The silicone oil (it did not absorb microwave radiation) was used as a cooling medium in the microwave radiation system. The silicone oil was used to maintain constant temperature in the starch emulsion throughout the course of the esterification reaction. Other preparation processes were the same as those used for the preparation of OSA–starch treated by water-bath heating.

Determination of the Degree of Substitution (DS)

DS is the average number of hydroxyl groups substituted per glucose unit. DS of OSA–starch was determined according to the method reported by Ali *et al.*³⁰ The following equation was used to calculate DS:

$$DS = \frac{0.162AM/W}{1 - 0.210AM/W} \quad (1)$$

where A is the titration volume of a standard NaOH solution (mL), M is the molarity of a standard NaOH solution, and W is the dry weight of octenyl succinic starch ester (g).

Characterization Methods

Surface Morphology Analysis. A small amount of the powder sample was fixed onto the metal sample stage with a double-sided conductive adhesive. After the sample stage was sprayed with gold *in vacuo*, it was placed in an SEM instrument (S-3400N, Hitachi, Japan). The morphology and size of the sample were observed (accelerating voltage = 10 kV, magnification = 5000×).

FTIR Analysis. A 5-mg sample of the powder and 70 mg of KBr were mixed and pressed into a 0.205-mm disk. The IR spectrum of the KBr-disc-formed sample was scanned with an FTIR spectrometer (IRAffinity-1, Shimadzu, Japan). The scanning number was 17 s^{-1} , and the scanning scope was 400–4000 cm^{-1} .

Data Analysis

Excel and Origin 8.0 were used to analyze the experimental data.

RESULTS AND DISCUSSION

Esterification Reaction Mechanism of Cassava Starch

OSA–starch was synthesized in an aqueous slurry system. First, cassava starch was immersed in an alkaline solution, and the swelling of starch granules was promoted. NaOH penetrated the

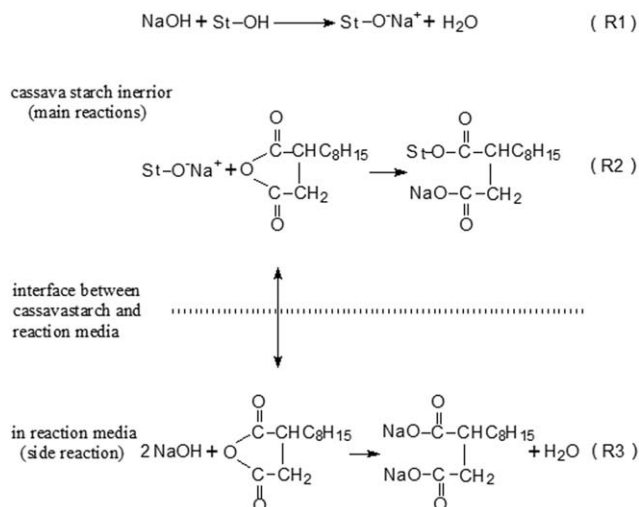


Figure 1. Chemical reactions during OSA modification.

interior of the granules, and the alkalinized reaction occurred with the hydroxyl groups of C2, C3, and C6 in the anhydroglucose unit of starch. Then, the activity center of the esterification reaction, starch alkoxide (StO^-), was produced. It further came into contact with OSA or its sodium salt under alkaline conditions, and nucleophilic substitution reactions occurred (Figure 1).^{31,32}

The esterification rate (R2) depended on the diffusion rate of the permeation of NaOH and OSA into the interior of the cassava starch granules (R1). The structure of the granules became more loose when the crystalline regions of cassava starch granules were destroyed; this improved the esterification rate. However, NaOH and OSA were retained in the reaction medium, and the side reaction (R3) occurred; when the crystalline regions of cassava starch granules were difficult to destroy, this resulted in much more byproducts.

Because the esterification of cassava starch was complex, two assumptions were made during the examination of the aqueous medium synthesis of the OSA–starch under the conditions of both water-bath heating and microwave radiation:

1. The distribution of NaOH and OSA in the reaction system was uniform.
2. OSA only occurred the main reaction during the preparation process and without the participation of other side reactions.

The following discussion focuses on the esterification kinetics of cassava starch at different temperatures under water-bath heating and microwave radiation conditions. The comparison and analysis of the esterification kinetics of cassava starch in two different reaction system were carried out.

Esterification Reaction Kinetics of Cassava Starch

The esterification process of cassava starch were reflected by the quantity of substituted hydroxyl on average per anhydroglucose unit; this is known as DS. As shown in Figure 2, the curves of DS with esterification time are given under the water-bath heating and microwave radiation conditions.

As shown in curve a of Figure 2(W), we found that DS increased with increasing esterification time when the reaction system was controlled at 30°C by water-bath heating. The increase in DS was rapid within 0–40 min; this indicated that the reaction rate was faster at this stage. The increase in DS was

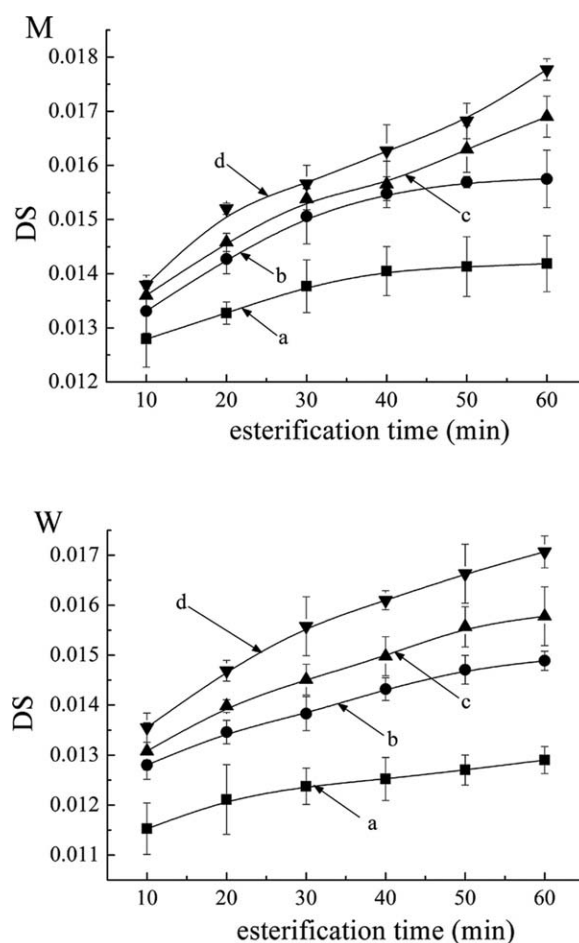


Figure 2. Curves of the DS with the esterification time with (W) water-bath heating and (M) microwave radiation: (a) 30, (b) 35, (c) 40, and (d) 45°C.

low within 40–60 min; this indicated that the reaction rate slowly increased at this stage. Subsequently, the reaction system temperature increased to 35, 40, and 45 °C by water-bath heating. As shown in curves b–d in Figure 2(W), DS increased with increasing temperature. This indicated that elevated temperatures could accelerate the reaction rate to some extent. Herein, the different trends of the increase in DS between 40–60 min and 0–40 min, as reflected by curves a–d, were observed; this could be explained by the different starch granules involved in the esterification [see Figure 5(a–g), shown later]. The esterification might have occurred on the surface of the cassava starch granules or amorphous regions within 0–40 min. The effective collision of OSA and starch molecules occurred more frequently, the reaction rate was faster, and DS increased rapidly. The crystalline regions of cassava starch granules might have been damaged to some extent within 40–60 min, and this might have resulted in OSA permeating into the cassava starch crystalline region and reacting with the reactive hydroxyl groups in the crystalline regions of cassava starch.³³ However, such a permeation process of OSA in the cassava starch crystalline region was more difficult than that in the surface of cassava starch granules or amorphous regions. Therefore, the effective collision of OSA and reactive hydroxyls in the crystalline region of cassava starch did not occur frequently; this resulted in a slow increase in DS. As shown by curves a–d in Figure 2(M), the increase in DS within 0–60 min increased substantially with increasing esterification time when the temperature was controlled by microwave radiation. The DS obtained at the corresponding time point was larger when the temperature of the reaction system was elevated. The microwave radiation increased the temperature of the reaction system and continuously accelerated the reaction rate; this might have resulted from the fact that the surface of starch granules became more rough and developed holes or caves in the microwave field [see Figure 5(a'–g'), shown later].³⁴ Such a special structure of starch granules made OSA diffuse easily into the amorphous region and the crystalline region of cassava starch. Thus, DS of esterification continuously increased within 0–60 min, and this was especially reflected by the DS at higher temperatures of 40 or 45 °C [see curves c and d in Figure 2(M)].

Because the anhydroglucose unit in the starch molecules contained three hydroxyl groups,³⁵ the maximum DS was 3. Herein, the kinetics relationship of the remaining hydroxyl number (3 – DS) per anhydroglucose unit and the esterification time are shown in Figure 3.

As shown in curves a–d in Figure 3(W,M), each line had a good linear fit relationship. This indicated that the dependency relationship of $\ln(3 - \text{DS})$ for the esterification time of OSA–starch synthesis in aqueous medium could be represented by the pseudo-first-order kinetic equation in both the water-bath heating system and the microwave radiation system^{36,37}:

$$\ln(3 - \text{DS}) = -kt + C \quad (2)$$

where t is the esterification time (min), k is the reaction rate constant (min^{-1}), and C is a constant.

The esterification rate constants were obtained from Figure 3 in the water-bath heating system and the microwave radiation system (see Table I).

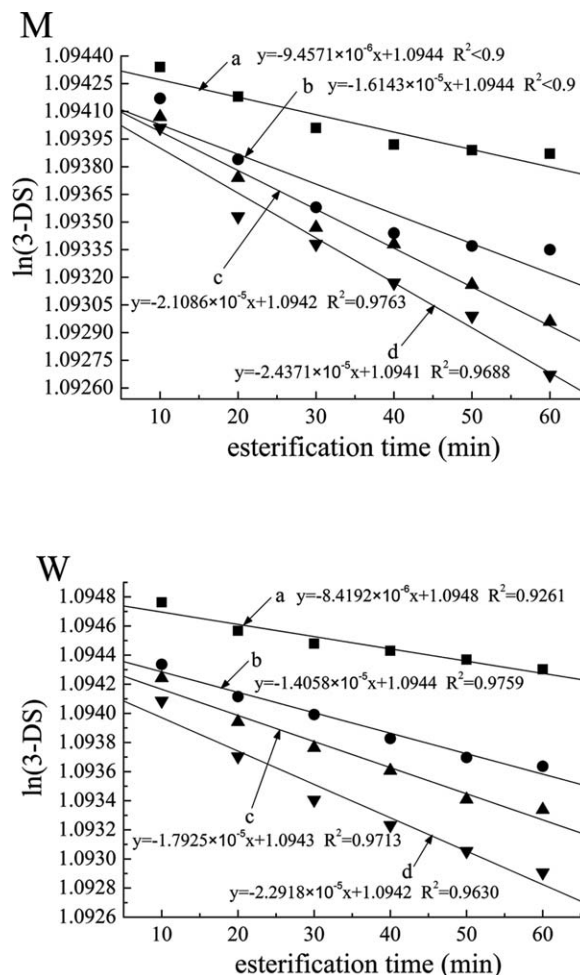


Figure 3. Kinetic curves of the starch esterification reaction with (W) water-bath heating and (M) microwave radiation: (a) 30, (b) 35, (c) 40, and (d) 45 °C.

Table I suggests that the water-bath heating rate constant and the microwave radiation rate constant both increased as the temperature increased in the range 30–45 °C. The relationship between $\ln k$ of cassava starch and $1/T$ (where T is the temperature) is shown in Figure 4.

Figure 4 shows that $\ln k$ and $1/T$ exhibited a better linear fitting relationship under water-bath heating and microwave radiation; this indicated that the relationship of $\ln k$ and $1/T$ could be expressed by the Arrhenius equation³⁸:

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (3)$$

Table I. Water-Bath Heating Rate Constant (k_W) and Microwave Radiation Rate Constant (k_M) Values at Different Temperatures

	Temperature (°C)			
Rate constant	30	35	40	45
$k_W \times 10^5$ (min)	0.842	1.406	1.794	2.292
$k_M \times 10^5$ (min)	0.946	1.614	2.109	2.437

or

$$k = Ae^{-E_a/RT} \quad (4)$$

where k is the reaction rate constant (min^{-1}), E_a is the apparent activation energy (J/mol), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and A is the pre-exponential factor. As shown in the slopes and intercepts in Figure 4 and in the results of the duplicate experimental verification, the apparent activation energy in the water-bath heating system was $52.22 \pm 1.21 \text{ kJ/mol}$, and the apparent activation energy in the microwave radiation system was $50.13 \pm 1.16 \text{ kJ/mol}$. The pre-exponential factors were 9018.20 and 4510.21 min^{-1} , respectively.

Analysis of the Nonthermal Effect of Microwave Radiation

In a microwave reaction system, the temperature of the reaction system was measured and monitored with a temperature sensor device for optical fibers. In combination with mechanical agitation, the microwave reaction system could provide uniform microwave radiation in a wide range of sample viscosities. Typically, the microwave power was 50 W. Therefore, the microwave thermal effect was not obvious under such low microwave power irradiation, and this might have provided a better base for the investigation of the nonthermal effects of microwave radiation. Dimethyl silicone oil, which does not absorb microwaves, was used in this study. The constant temperature of the esterification reaction system was maintained by the continuously circulating silicone oil bath. On the basis of the relationship between the DS and esterification time in Figure 2, we concluded that the effects of water-bath heating and microwave radiation were different. The DSs of the samples treated by microwave radiation at different time points were higher than those treated by water-bath heating. The results of the significant differences in the DSs are shown in Table II.

As shown by the test results of the DSs in Table II, significant differences in the DSs existed above a 95% confidence level when the temperatures of the esterification reaction were controlled by water-bath heating and microwave radiation. Moreover, as shown by the esterification reaction kinetics data in Figure 3 and Table I, we found that the rate constants were different when the same initial and final temperatures were controlled by water-bath heating and microwave radiation. The microwave radiation rate constant was greater than the water-bath heating rate constant. Therefore, because the same initial temperature and the same final temperature were controlled in the water-bath heating system and microwave radiation system, respectively, we concluded that the nonthermal effect was present in the esterification of cassava starch.

Equation (4) shows that two factors, the apparent activation energy and the pre-exponential factor, mainly influenced the reaction rate constants at a certain temperature. The results of the significant differences in the apparent activation energy are shown in Table III.

As shown by the test results for the apparent activation energy in Table III, the significant differences in the apparent activation energy values were observed above the 90% confidence level when the temperatures of the esterification reaction were controlled by water-bath heating and microwave radiation, respec-

tively. Compared with water-bath heating, microwave radiation decreased the apparent activation energy by 2.09 kJ/mol ; it reached the energy degree necessary to destruct the molecular interaction of the starch chain. Microwave radiation decreased the apparent activation energy, perhaps because microwave radiation could change the morphology of starch granules and the structure of the molecular chains.^{13,15} This further resulted in an increasing proportion of reactive hydroxyl groups in the starch molecule. The efficient collision between the OSA and starch molecules was enhanced; this increased the rate of esterification further. Additionally, the alternating electromagnetic field generated by microwave radiation made the weakly polar starch molecules and OSA trend in the same direction of the electric field, and this led to an anisotropy collision of the reaction mixture.^{39,40} This decreased the pre-exponential factor in the microwave radiation system to some extent (approximately half of the pre-exponential factor in the water-bath heating system), and this reduced the rate of the reaction to a certain extent. However, the apparent activation energy was in the index position, and the effect of the apparent activation energy was more pronounced. Therefore, the reaction rate increased overall under microwave radiation. Similar observations were also reported by Fumitaka *et al.*,⁴¹ Jelena *et al.*,⁴² and Borivoj *et al.*⁴³ Therefore, on the basis of the significant differences in the DS and apparent activation energy mentioned previously, microwave radiation promoted the esterification reaction by nonthermal effects.

Analysis of the Structural Changes by SEM

Figure 5 shows SEM images of the native cassava starch granules and OSA–starch granules treated at 40°C by water-bath heating and microwave radiation.

As shown in Figure 5(a–g), the depressions or holes on the surface of the starch granules gradually increased with increasing reaction time at 40°C in the water-bath heating system. In particular, more obvious holes or wrinkles were observed on the surface of the starch granules between 50 and 60 min; this made OSA permeate easily into the inner starch granules and react with the reactive hydroxyl groups in the crystalline regions of starch. Similarly, Figure 5(a'–g') shows the granular morphology of synthesized OSA–starch under microwave radiation. The depressions or holes on the surface of the starch granules also gradually increased with increasing reaction time; this was similar to the observations shown in Figure 5(a–g). However, the surfaces of the starch granules were rougher under microwave radiation than those of the starch treated by water-bath heating at each same time point. In particular, the starch granules changed to irregular flat spherical granules at 60 min [Figure 5(g')]. More surface depressions, holes, and wrinkles were observed; this indicated that the surface of starch granules in the microwave field was destroyed more significantly than that in the water-bath heating. Therefore, OSA efficiently permeated into the internal crystalline region of the granules, reacted with the reactive hydroxyl groups in starch, and continuously increased DS. These observations were in agreement with the relationship between the DS and esterification time, as reflected by curve c in Figure 2(M).

Table II. Comparison of the DS Values of the Products from Water-Bath Heating and Microwave Radiation

Temperature (°C)	Heating method	Esterification reaction time (min)					
		10	20	30	40	50	60
30	Water-bath heating	0.01153 (0.00051) ^a	0.01211 (0.00070) ^a	0.01237 (0.00036) ^a	0.01252 (0.00043) ^a	0.01270 (0.00030) ^a	0.01290 (0.00027) ^a
	Microwave radiation	0.01279 (0.00052) ^b	0.01327 (0.00021) ^a	0.01377 (0.00049) ^b	0.01405 (0.00045) ^b	0.01413 (0.00055) ^b	0.01418 (0.00052) ^b
35	Water-bath heating	0.01280 (0.00010) ^a	0.01346 (0.00024) ^b	0.01383 (0.00034) ^b	0.01432 (0.00023) ^b	0.01471 (0.00029) ^b	0.01489 (0.00019) ^b
	Microwave radiation	0.01331 (0.00041) ^a	0.01427 (0.00027) ^c	0.01506 (0.00051) ^c	0.01548 (0.00013) ^c	0.01569 (0.00010) ^c	0.01575 (0.00053) ^b
40	Water-bath heating	0.01308 (0.00057) ^a	0.01398 (0.00013) ^a	0.01451 (0.00031) ^a	0.01498 (0.00039) ^a	0.01557 (0.00040) ^a	0.01578 (0.00059) ^a
	Microwave radiation	0.01360 (0.00028) ^a	0.01458 (0.00017) ^b	0.01538 (0.00020) ^b	0.01565 (0.00043) ^a	0.01630 (0.00043) ^a	0.01690 (0.00037) ^b
45	Water-bath heating	0.01355 (0.00029) ^a	0.01469 (0.00021) ^b	0.01558 (0.00059) ^b	0.01610 (0.00019) ^b	0.01663 (0.00059) ^b	0.01707 (0.00032) ^b
	Microwave radiation	0.01379 (0.00018) ^a	0.01520 (0.00010) ^c	0.01566 (0.00034) ^b	0.01627 (0.00048) ^b	0.01682 (0.00033) ^b	0.01777 (0.00020) ^c

All values shown are means (with the standard deviations in parentheses) for three samples. Within each column, the means followed by different superscripts letters (a-c) are significantly different ($p < 0.05$).

Table III. Comparison of the Apparent Activation Energies of the Products from Water-Bath Heating and Microwave Radiation

Heating method	Apparent activation energy (kJ/mol)
Water-bath heating	52.22 (1.21) ^a
Microwave radiation	50.13 (1.16) ^b

All values shown are means (with the standard deviations in parentheses) for three repeats. Means followed by different superscript letters (a and b) are significantly different ($p < 0.10$).

Analysis of the Structural Changes by FTIR Spectroscopy

Succinylation led to the substitution of hydroxyl groups in the starch molecules with carbonyl groups of OSA. The introduction of carbonyl groups was confirmed by FTIR spectroscopy. Figure 6 shows the IR spectra of OSA–starch at different reaction times.

As shown in curve a of Figure 6(W), the strong and broad absorption peak at $3570\text{--}3100\text{ cm}^{-1}$ in the IR curve of native cassava starch was the stretching vibration absorption peak of —OH . The absorption peak at 2931 cm^{-1} belonged to the stretching starch vibration absorption peak of —CH_2 .⁴⁴ The strong and wide peak at $1157\text{--}995\text{ cm}^{-1}$ was the stretching vibration absorption peak of C—O—C in starch.^{45,46} A comparison of curves b–g in Figure 6(W) and curve a in Figure 6(W) showed that the stretching vibration absorption peak of —CH_2 at 2931 cm^{-1} , and the stretching vibration absorption peak of C—O—C at $1157\text{--}995\text{ cm}^{-1}$ remained. However, the stretching vibration absorption peaks of —OH at $3570\text{--}3100\text{ cm}^{-1}$ changed to a narrowing peak with increasing the DS and reaction time; this was similar to the reports of Wang *et al.*⁴⁷ and Lei *et al.*⁴⁸ This might have been because the —OH in native starch esterified with OSA, the number of hydroxyl groups decreased, and the hydroxyl absorption peak narrowed. Compared with the spectrum of native cassava starch [curve a in Figure 6(W)], and the spectra of OSA–starch [curves b–g in Figure 6(W)] showed new peaks at 1716 and 1570 cm^{-1} . The new peak located at 1716 cm^{-1} corresponded to the characteristic IR stretching vibrations of C=O ; this suggested the formation of ester carbonyl groups.^{5,49} The other new peak that

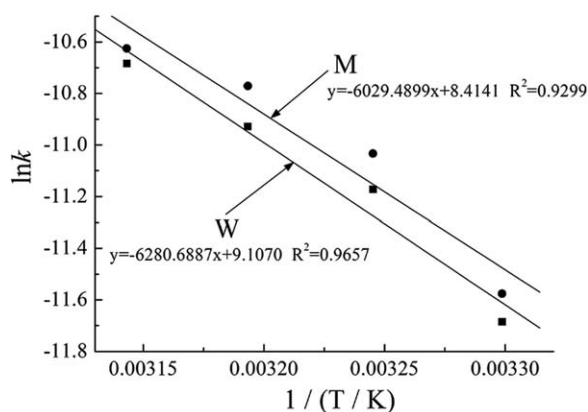


Figure 4. Relationship between $\ln k$ and $1/T$ with (W) water-bath heating and (M) microwave radiation.

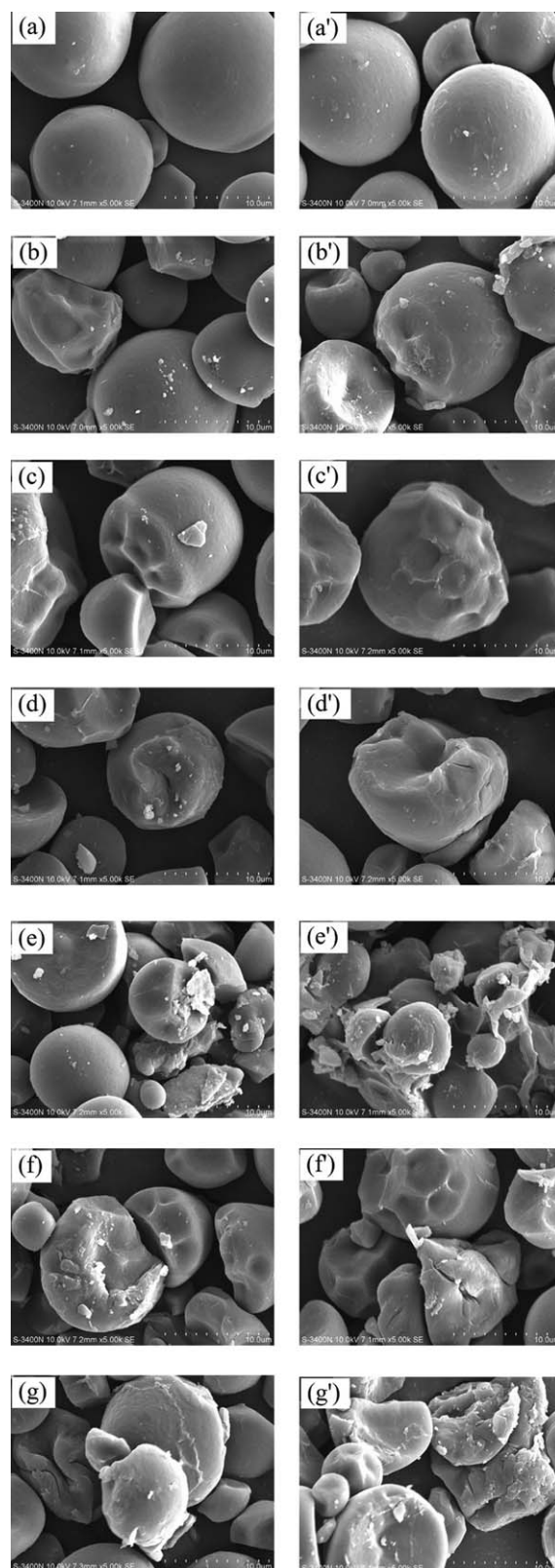


Figure 5. SEM images of (a,a') native starch; OSA–starches during water-bath heating at 40°C after (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, and (g) 60 min; and OSA–starches during microwave radiation at 40°C after (b') 10, (c') 20, (d') 30, (e') 40, (f') 50, and (g') 60 min.

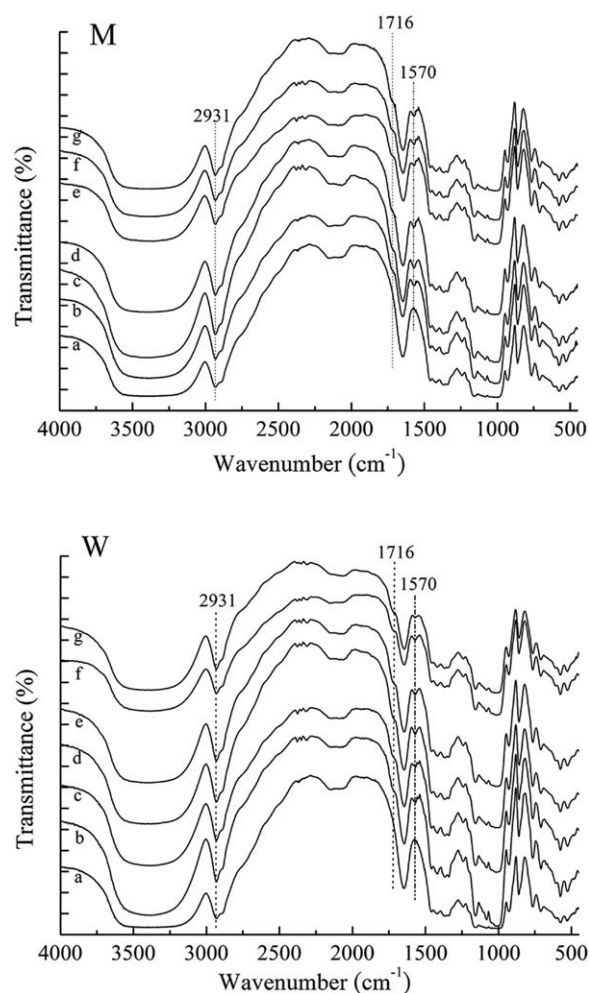


Figure 6. FTIR spectra of OSA-starch at different reaction times with (W) water-bath heating and (M) microwave radiation at 40 °C: (a) native starch, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 50 min, and (g) 60 min.

appeared at 1570 cm^{-1} was ascribed to the asymmetric stretching vibrations of carboxylate (RCOO^-).^{50,51} These observations proved that the esterification between OSA and starch indeed occurred. The absorption peak transmittances of RCOO^- were 31.1, 25.9, 22.8, 22.2, 18.7, and 18.5%, respectively; this indicated that the absorption peak intensity of RCOO^- increased with increasing reaction time. This observation was in agreement with the relationship between the DS and esterification time reflected by curve c in Figure 2(W).⁵² The changes in curves a–g in Figure 6(M) and Figure 6(W) were similar, and the stretching vibration absorption peaks of $-\text{OH}$ in native starch at 3570–3100 cm^{-1} narrowed with increasing reaction time. The absorption peak at 2931 cm^{-1} belonged to the stretching starch vibration absorption peak of $-\text{CH}_2$. The strong and wide peak at 1157–995 cm^{-1} was the stretching vibration absorption peak of $\text{C}-\text{O}-\text{C}$ in starch. The new absorption peaks at 1716 and 1570 cm^{-1} were observed. The absorption peak transmittances of RCOO^- were 23.8, 22.8, 20.9, 19.0, 18.2, and 17.8%, respectively; this also indicated that the absorption peak intensity of RCOO^- increased with increasing reaction time. This was in agreement with the relationship

between the DS and esterification time reflected by curve c in Figure 2(M). The difference between curves b–g in Figure 6(M) and Figure 6(W) was the absorption peak intensity of RCOO^- at 1570 cm^{-1} . During the IR experiments, the sample was selected with the same number, and they were pressed into a sheet with the same thickness. Therefore, the difference of the absorption peak transmittance (although the numerical difference was not obvious) was mainly due to the short reaction time (only 10, 20, 30, 40, 50, and 60 min). Water-bath heating and microwave radiation caused the absorption peak transmittances of RCOO^- to exhibit regular changes; this proved that microwave radiation could produce different esterification effects compared with water-bath heating. The peak intensity of RCOO^- in OSA-starch treated by the microwave radiation system was greater than that treated by the water-bath heating system; this was in agreement with the change relationship of the DS and esterification time reflected in the water-bath heating system and microwave radiation system in Figure 2(M,W). This further suggested that microwave radiation not only maintained the reaction temperature but also provided nonthermal effects.

CONCLUSIONS

The heterogeneous nucleophilic substitution reaction of OSA and cassava starch was achieved; this produced OSA-starch in the aqueous medium. The esterification reaction system was treated by water-bath heating and microwave radiation to maintain a certain temperature. The DS showed an increasing trend with increasing esterification time. The dependency relationship between $\ln(3 - \text{DS})$ of the remaining hydroxyl number per anhydroglucose unit of cassava starch and the esterification time could be represented by the pseudo-first-order kinetic equation. The relationship between $\ln k$ and $1/T$ could be expressed by the Arrhenius equation. The differences in the esterification reaction kinetics of water-bath heating and microwave radiation were observed. Under the condition of water-bath heating, the apparent activation energy was 52.22 ± 1.21 kJ/mol, and the pre-exponential factor was $9018.20/\text{min}^{-1}$. The apparent activation energy was 50.13 ± 1.16 kJ/mol, and the pre-exponential factor was $4510.21/\text{min}^{-1}$ under the condition of microwave radiation. We found that microwave radiation reduced both the activation energy and pre-exponential factor. The lowering effect of the apparent activation energy was greater than that of the pre-exponential factor under the condition of microwave radiation; this resulted in increased reaction rates. The change in the esterification reaction kinetics was a nonthermal effect of microwave radiation on the esterification of cassava starch.

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