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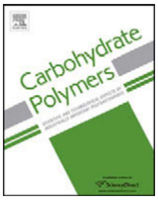

Preparation and properties of oxidized starch with high degree of oxidation

Yu-Rong Zhang, Xiu-Li Wang*, Guo-Ming Zhao, Yu-Zhong Wang*

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, National Engineering Laboratory of Eco-Friendly Polymeric Materials, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610064, China

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ABSTRACT

A highly efficient method for preparing oxidized starches with a high degree of oxidation (DO) was developed, using $CuSO_4$ and H_2O_2 respectively as a catalyst and an oxidant. The effect of different parameters including starch origin, oxidant content, temperature, catalyst content, and reaction time on the DO was investigated systematically. In the present study, only 0.5% of catalyst was added, and the reaction time could be reduced to 1 h, while in the previous study the reaction time of 72 h was necessary to achieve almost the same DO without a catalyst. The structures and properties of oxidized starches were characterized by FT-IR, DSC, TGA, XRD, and transmittance light testing. The oxidation reduced the intrinsic viscosity and thermal stability of the oxidized starches, and could change the crystalline structures into amorphous states when the DO reached 56.3%. When temperature and/or DO increased, the transmittance of suspended solution of oxidized starch increased correspondingly.

1. Introduction

Starch has been widely used in industry for a long time, due to its low cost, biodegradability, and renewability (Fishman, Coffin, Konstance, & Onwulata, 2000; Le Corre, Bras, & Dufresne, 2010). It is composed of amylose, a linear polymer of α-(1-4) glucose units, and amylopectin, a branched polymer of linear α-(1-4) glucose units polymer with periodic branches of α-(1-6) linkages (Serrero et al., 2010). The hydroxyl groups of starch are easily subjected to various types of reactions, such as oxidation, esterfication, etherification, etc. (Zdanowicz, Schmidt, & Spychaj, 2010; Zhang et al., 2007). In particular, the oxidation of starch has been extensively investigated.

Oxidation, as a chemical way of starch modification, is commonly used to obtain modified starches with low viscosity at high solid concentrations. The oxidized starch has been reported to have excellent film-forming properties (Kuakpetoon & Wang, 2001), and its use can improve the strength and printability of paper. In addition, the oxidized starch has also been widely used in industries such as textile, laundry finishing, etc. (Kuakpetoon & Wang, 2001). Hydroxyl groups, primarily at C-2, C-3, and C-6 positions, are transformed to carbonyl and/or carboxyl groups by oxidation (Kuakpetoon & Wang, 2006; Kurakake, Akiyama, Hagiwara, & Komaki, 2009). Therefore, the number of these carboxyl and carbonyl groups of oxidized starch indicates the level of oxidation.

Currently hypochlorite oxidation is the most common method for production of oxidized starches on an industrial scale. The oxidation reaction is usually performed in a mild to moderate alkaline solution in order to favor the yield of carboxyl groups. In commercial conversions, usually sodium or calcium hypochlorite are used as the oxidizing agents (Kuakpetoon & Wang, 2008; Wang & Wang, 2003). Permanganate (Silva et al., 2008; Takizawa, Silva, Konkel, & Demiate, 2004), persulfate and periodate (Zhang et al., 2007) are also investigated as oxidizing agents in the laboratory. Different oxidation procedures directly affect the molecular structure and properties of oxidized starch. Although those oxidations are chemically efficient, they lead to the formation of large amounts of inorganic wastes such as chlorinated products (Sorokin, Kachkarova-Sorokina, Donze, Pinel, & Gallezot, 2004). With environmental concern in a priority, the oxidant hydrogen peroxide, has drawn researchers' great interest because of its low cost and green water decomposition product. Generally, an accessible and inexpensive transition metal catalyst is added so as to speed up the reaction.

Although oxidized starch prepared by hydrogen peroxide has already been investigated (El-Sheikh, Ramadan, & El-Shafie, 2009; Parovuori, Hamunen, Forssell, Autio, & Poutanen, 1995; Wing & Willett, 1997; Zhang, Zhang, Wang, & Wang, 2009; Zhang, Zhang, Wang, Chen, & Wang, 2009), most researchers focus on the preparation of oxidized starch with a low DO, usually below 10%. Dialdehyde starch prepared by sodium periodate has been studied by our group before (Zhang et al., 2010, 2007). However, the cost of oxidant is very high and the decomposed reaction products would pollute the environment. We have also prepared oxidized starch with a high DO using hydrogen peroxide, but the reaction time was

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* Corresponding authors. Tel.: +86 28 85410259; fax: +86 28 85410259.
E-mail addresses: xiuliwang1@163.com (X.-L. Wang), yzwang@scu.edu.cn (Y.-Z. Wang).

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too long (Wang, Zhang, Zhang, & Wang, 2007; Zhang, Zhang, Wang, & Wang, 2009; Zhang, Zhang, Wang, Chen, et al., 2009). For example, when oxidized starch with DO 51.2% was prepared at a 2:1 ratio of oxidant to starch (molar ratio based on the glucose unit in starch molecules) at 35 °C, the reaction time was 72 h.

In this study, Cu (II) ion was added as a catalyst, which had been used to accelerate the reaction before (Achremowicz, Gumul, Bala-Piasek, Tomasik, & Haberko, 2000; Parovuori, Hamunen, Forssell, Autio, & Poutanen, 1995). The effect of the reaction conditions, including starch origin, oxidant content, temperature, catalyst content, and reaction time on DO was well discussed. The thermal transition behavior, thermal stability, XRD, and transmittance of oxidized starch were also investigated.

2. Materials and methods

2.1. Materials

Corn starch, pea starch and sweet potato starch containing 11–13% of moisture were obtained from Langfang Starch Company (Technical Grade, Langfang, Heibei, China). Hydrogen peroxide (H_2O_2, 30%) and $CuSO_4{\cdot}5H_2O$ (analytical grade 99.5%) were purchased from KeLong and Chengdu Chemical Reagent Factory respectively (China).

2.2. Oxidation

The oxidation procedure was modified according to the method of Wang et al. (2007), Zhang, Zhang, Wang, and Wang (2009) and Zhang, Zhang, Wang, Chen, et al. (2009). Starch slurry was prepared by adding 10 g starch and 100 ml distilled water into a 250 ml three-neck round bottom flask equipped with a mechanical stirring and heating device. The mixture was heated to 80 °C with modest stirring to gelatinize the starch about 0.5 h. After that, the temperature was decreased to reaction temperatures ranging from 15 to 60 °C. The $CuSO_4{\cdot}5H_2O$ was dissolved in distilled water before being added to the starch. The $CuSO_4$ solution was first added to the starch slurry, followed by the addition of H_2O_2 in half an hour. Molar contents of $CuSO_4$ and H_2O_2 were both based on the glucose unit of starch molecules. When the reaction was completed, the oxidized starch was precipitated in a large amount of ethanol and then separated by centrifuging (Bragd, Besemer, & van Bekkum, 2000). The product was dried for 24 h at 50 °C in the vacuum oven and then at 80 °C for 24 h. Finally it was milled into powder.

2.3. Determining degree of oxidation

The degree of oxidation was expressed as the number of total carboxyl and carbonyl groups per 100 glucose units. In most studies on oxidized starch (Kuakpetoon & Wang, 2001; Wing & Willett, 1997), the contents of carbonyl groups, and carboxyl groups were determined separately by two different analytical methods. The content of carboxyl groups was determined by titrating a sample solution with a standard NaOH solution, while the carbonyl group content was determined by reacting carbonyl groups with hydroxylamine reagent and then back-titrating with an HCl solution. A simpler method was developed to determine the total degree of oxidation of oxidized starch according to the literature (Kuakpetoon & Wang, 2001; Wing & Willett, 1997) with some modifications.

A dry sample (0.1 g) was slurried in distilled water (50 ml) and then 10 ml of 0.1 M NaOH was added. After that, the slurry was heated to a boil to make it completely soluble. The cooled solution was adjusted to a pH value of lower than 7.0 with 10 ml of 0.15 M HCl aqueous solution. Because of the water evaporation in the process of heating, some water was added to keep the solution content the same as before heating. Then, the solution was heated to boil again for 1 min and the mixture was rapidly back-titrated with 0.10 M NaOH to the phenolphthalein end-point. A blank test was performed with nature starch. All samples were tested three times.

$$\mathrm{DO} = \frac{C_{\mathrm{NaOH}}V_{\mathrm{NaOH}} - C_{\mathrm{HCl}}V_{\mathrm{HCl}}}{m/162} \times 100\% \tag{1}$$

$$\mathrm{DO}_S = \mathrm{DO}_T - \mathrm{DO}_B \tag{2}$$

where C_{NaOH} and C_{HCl} represented the concentrations of NaOH and HCl solutions, respectively; V_{NaOH} and V_{HCl} were the volumes of used NaOH and HCl solutions; m was the weight of dry or oxidized starch; DO_S represented the DO of the samples, and DO_B represented the DO of the blank sample.

2.4. Intrinsic viscosity measurement

Intrinsic viscosity was measured with a Ubbelohde capillary viscometer with a capillary diameter of 0.58 mm at 25 ± 0.1 °C. The mixture of 83 vol% dimethyl sulfoxide and 17 vol% water was used as a solvent. 10 mg of dried sample was dissolved in the 25 ml solvent. From the flowing time of the polymer solution (t) and the solvent (t_0), the relative viscosity ($\eta_r = t/t_0$) was obtained. Specific viscosity was calculated from the formula $\eta_{sp} = (t - t_0)/t_0$. Intrinsic viscosity could be obtained by one point method according to the following equation (Abdel-Azim, Atta, Farahat, & Boutros, 1998; Solomon & Ciuta, 1962).

$$\eta = \frac{\sqrt{2(\eta_{sp} - In\eta_r)}}{C}$$

where C represented the concentration of polymer solution (g/ml); η represented the intrinsic viscosity.

2.5. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the native starch and the oxidized starches with different DO were recorded on a Fourier transform infrared spectrometer (Nicolet 6700, Thermo Scientific, MA, USA) in a range of wave numbers from 4000 to 400 cm^{-1}. The samples were kept in a vacuum oven at 60 °C for 72 h to remove the absorbed water before the test. The resolution was 4 cm^{-1} and the scan number 32.

2.6. Thermogravimetric testing (TG)

Thermogravimetric analysis (TGA) of samples (4–5 mg) was carried out by using a NETZSCH thermal analyzer (TG209F1, NETZSCH-Gerätebau GmbH, Selb/Bavaria, Germany) under nitrogen atmosphere at a heating rate of 10 °C/min after the samples were kept in a vacuum oven at 60 °C for 48 h. The range of scanning temperature was from 40 to 500 °C.

2.7. Differential scanning calorimetry testing (DSC)

Thermal properties of the samples were studied by using differential scanning calorimetry (Q200, TA, New Castle, USA) under nitrogen purge. The samples (4–5 mg) were heated from room temperature to 120 °C within 10 min to eliminate any residual water, and then cooled to 20 °C at 10 °C/min. After that the samples were heated up to 200 °C at the same heating rate. An empty capsule was used as a reference.

2.8. Wide angle X-ray scattering (WAXS)

Powder X-ray patterns of oxidized and native cornstarches were obtained using an X-ray diffractometer (X'Pert Pro, Philips, Almelo, Netherlands). The 2θ range was 10–40°. Ni-filtered Cu Kα radiation was used as the X-ray source.

2.9. Transmittance of oxidized starch suspension

Transmittance was determined by a UV-vis spectrophotometer (UV-240, Japanese Shimadzu Corporation, Kyoto, Japanese) according to the method of Chang, Park, Shin, Suh, and Kim (2008). The suspension containing 0.2% (w/v) starch (dry weight basis) was kept in separate water baths at 60 °C, 70 °C, and 80 °C respectively for 20 min each, and then those suspensions were stored at 4 °C for 1 d, followed by the transmittance tests of 625 nm.

3. Result and discussion

The starch granule has a highly organized structure and unique thermal properties and functionalities that have permitted its wide uses in food products and industrial applications, but native starch granules cannot disperse in cold water. Therefore, before being modified, they generally are subjected to a gelatinization process that breaks down the inter- and intramolecular bonds of starch molecules in the presence of water and heat, allowing the hydrogen bonding sites to engage more water, which would make the modification easier (Ratnayake & Jackson, 2008, chap. 5). In this paper, all oxidized starches were prepared after gelatinization. The effects of starch origin, oxidant content, temperature, catalyst content, and reaction time on the DO were thoroughly investigated.

3.1. Effect of different starch origins on the degree of oxidation

Different starch origins have different granular sizes, shapes, and molecular structures which can affect how hydrogen peroxide oxidizes starch (Kuakpetoon & Wang, 2001). In this study, we chose cornstarch, pea starch, and sweet potato starch, which have different amylose contents in order to study the effect of starch origins on the reactions. From Fig. 1a, it can be clearly seen that the cornstarch has the highest DO, up to 40.5%, while the DO of pea and sweet potato starch is 21.1% and 34.5% respectively, which indicates that pea starch is not easier to be oxidized than cornstarch and sweet potato starch. Among three kinds of starch origins, pea starch processes the highest content of amylose (29%) as compared to cornstarch (23%) and sweet potato starch (23.7%) (Noda et al., 2009; Orford, Ring, Carroll, Miles, & Morris, 1987), which resulted in the lower DO. In the work of Kuakpetoon and Wang (2008), they also came to the same conclusion that amylopectin was more prone to oxidation than amylose, but the reasons were different. In their work, starch was in an intact granular state during oxidation. The oxidation was more likely to occur near the branching points of amylopectin chains because these branching points were located in the amorphous lamellae, where an easier access could be provided for the oxidizing agent to react with the starch. However, in the current work, the starch has already been gelatinized. The accessibility of hydroxyl groups on starch molecules by the oxidizing agent is not limited by the ordered structure in the granule anymore. Although the total number of free OH-groups was the same for a branched and a linear molecule at a given DP, more amylopectin content was benefit for oxidation. This was due to the fact that the branched chains would lead to increase the space distance between the amylopectin and amylopectin/amylose chains compared with that of amylose and amylose chains, which will make it more facile for hydrogen peroxide to enter and oxide the hydroxyl groups of starch. With the increase of amylopectin content, the oxidative efficiency is enhanced correspondingly. Therefore, to get a higher DO, cornstarch is used in subsequent experiments.

3.2. Effect of molar content of catalyst on the degree of oxidation

Metal ions are often used in the oxidation of starch by hydrogen peroxide to increase the content of functional groups in the modified starch in the same period of time (Parovuori et al., 1995). Fig. 1b shows the effect of varied catalyst contents on the DO. We found that $CuSO_4$ could act as a catalyst and increased the efficiency of oxidation significantly. It is shown that when the $CuSO_4$ content is lower than 0.5% (molar content based on glucose units of starch), the DO increases dramatically. When only 0.02% catalyst is added, the DO increases rapidly from 5.9% to 33.5%, five times higher than that of oxidized starch without catalyst. The result confirms that $CuSO_4$ is an effective catalyst for the oxidative system. In the reaction, Cu^{2+} can help to form hydroxyl radicals, which could oxidize hydroxyl groups in glucose units to carbonyl and/or carboxyl groups. Meanwhile, hydrogen peroxide inevitably decomposes to the oxygen and water (Parovuori et al., 1995). When 0.1% of catalyst is added, the DO significantly increases from 5.9% to 40.5%. However, when its content increases from 0.1% to 0.5%, the increase of DO inconspicuously rises, only from 40.5% to 48.7%. Compared to our previous studies (Wang et al., 2007; Zhang, Zhang, Wang, & Wang, 2009; Zhang, Zhang, Wang, Chen, et al., 2009), when oxidized starch with a DO of 51.2% was prepared under the following conditions: the reaction temperature and time were 35 °C and 72 h, respectively, and the ratio of oxidant content to starch (molar ratio based on glucose unit in starch molecules) was 2:1. In the present study, if only 0.5% of catalyst was added the reaction time could sharply be reduced to 1 h. While the catalyst content is from 0.7% to 1%, the DO reaches a plateau at 46.9%. The results can be explained as follows: when the catalyst is excessive, there will be no sufficient oxidant to be catalyzed and the redundant catalyst cannot show its catalytic performance. However, oxidized starch has good complex properties and heavy metals can be retained by carboxyl functions in the modified starch. The high metal content in modified starch will cause undesirable coloration, which prevents its use where brightness and/or low metal content are required. A low concentration of Cu^{2+} (say 0.02%) has had an obvious catalyst effect, and can produce a white product. Therefore, 0.02% of Cu^{2+} is chosen as a proper dosage.

3.3. Effect of reaction temperature on the degree of oxidation

Fig. 1c displays the effect of reaction temperature on the DO. When reaction temperature increases from 15 to 55 °C, DO increases from 25.4% to 53.8%, but when reaction temperature continues to increase from 55 to 60 °C, DO drops to 48.3%, which is the combined result of several factors. For example, an increase of temperature would result in the enhanced activity of hydrogen peroxide as well as the swelling of the starch gels. However, when temperature is higher than 55 °C it causes the decomposition of oxidant, resulting in the drop of DO.

3.4. Effect of reaction time on the degree of oxidation

As shown in Fig. 1d, the DO increases with the increase of the reaction time. A significant increase in DO appears in the reaction time ranging from 5 to 60 min, corresponding to 22.1–40.5%, while from 60 to 660 min the DO increases only from 40.5% to 51.8%. At the beginning, the oxidant concentration is higher and the oxidation is easier. As the reaction was conducted, the oxidant was consumed, resulting in decreasing reaction efficiency. Therefore 60 min is the optimal reaction time.

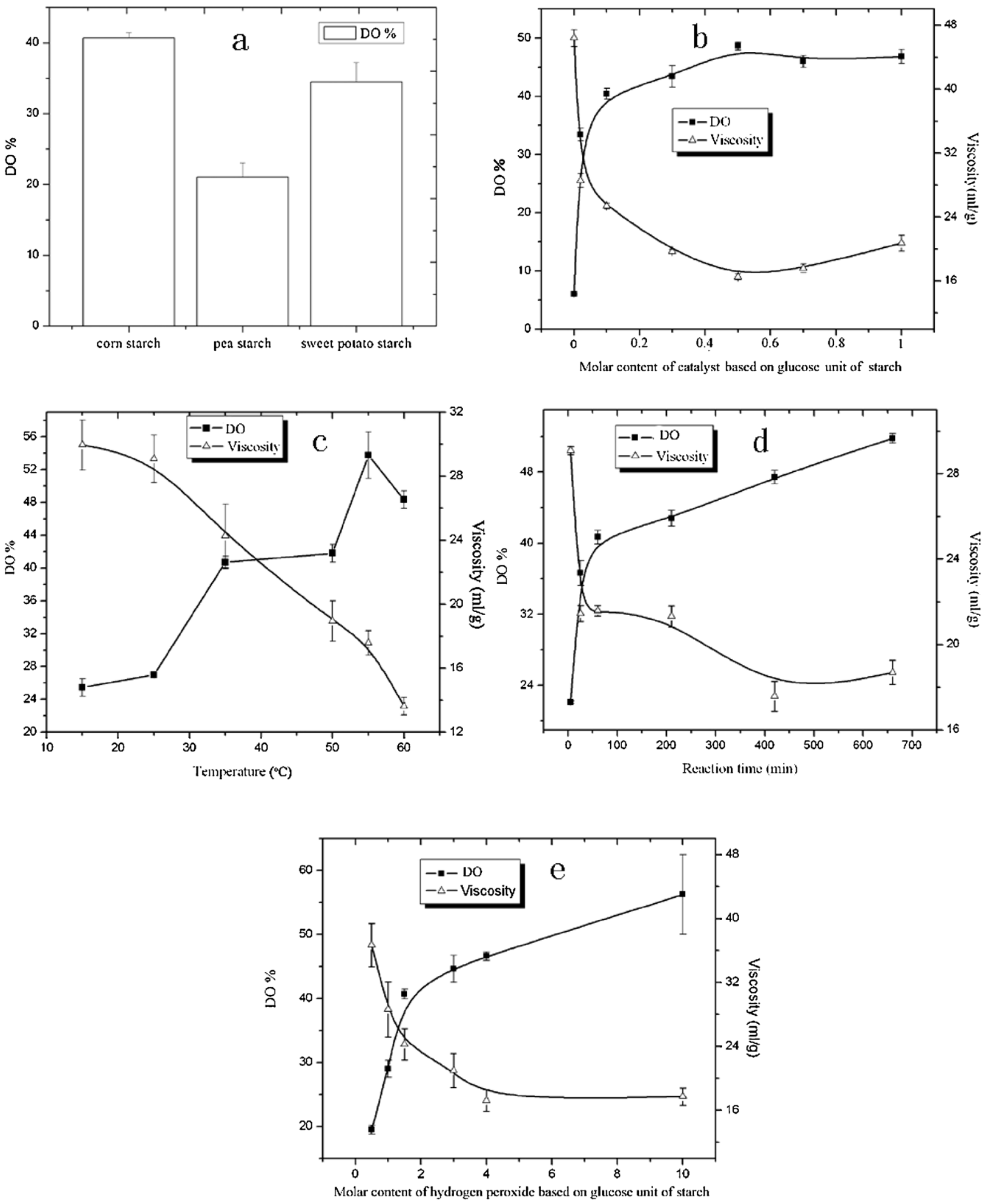
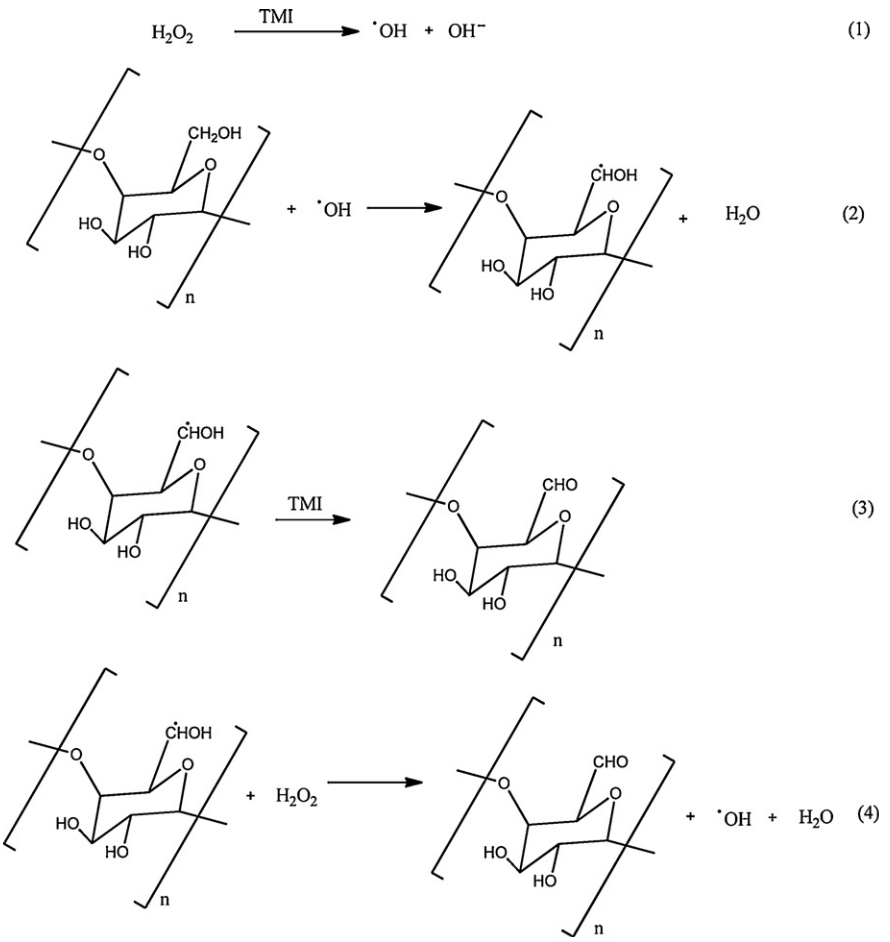


Fig. 1. Effect of different reaction parameters on DO.

3.5. *Effect of the content of oxidant on reaction*

The reaction mechanism of starch oxidized by hydrogen peroxide is very complex and has been reported to be a radical chain reaction (see Scheme 1). In the presence of metal catalyst, hydrogen peroxide is rapidly decomposed, forming hydroxyl radical (HO•). This highly reactive free radical oxidizes the glucose unit by subtracting hydrogen from a C–H group on the sugar ring, forming a radical (R•CHOH) that further reacts with metal ion or hydrogen peroxide yielding a carbonyl groups (Sangseethong, Termvejsayanon, & Sriroth, 2010a). Fig. 1e shows effect of oxidant content on the DO of the starches. When oxidant increases from 0.5 to 10 (molar content based on glucose unit in starch molecules), the DO increases from 19.5% to 56.3% accordantly. The DO increases



Scheme 1. Proposed oxidative mechanism when hydrogen peroxide and transition metal ion (TMI) were used as oxidant and catalyst respectively.

more rapidly from 19.5% to 40.5% when the molar content of the hydrogen peroxide is below 1.5. However, while the oxidant content increases from 1.5 to 10, DO increases only from 40.5% to 56.3%. Those results can be explained as follows: at constant catalyst content, when the oxidant content increases from 0.5 to 1.5, the amount of catalyst is enough. However, while its content is kept on increasing, catalyst cannot be sufficient to react with hydrogen peroxide forming hydroxyl radical (HO•), which leads to the lower reaction efficiency. At the same time, hydrogen peroxide is prone to decompose at high concentration. The results indicate that 1.5 of oxidant (molar content based on glucose unit) is an appropriate content.

3.6. *Effect of degree of oxidation on the intrinsic viscosity of oxidized starch*

The intrinsic viscosity of oxidized starches was measured by one point method, in which only one concentration is needed to be determined. If the concentration of the solution is low enough, intermolecular interaction between polymers can be neglected (Abdel-Azim et al., 1998; Solomon & Ciuta, 1962). The depolymerized extent of starch during oxidation depends on the content of catalyst and oxidant, reaction time, and temperature. Fig. 1b–e all show that when DO increases the intrinsic viscosity decreases. Those results are in agreement with earlier reports (Saĭnchez-Rivera, Garcıĭa-Suaĭrez, Velaĭzquez del Valle, Gutierrez-Meraz, & Bello-Peĭrez, 2005; Wang et al., 2007; Zhang, Zhang, Wang, & Wang, 2009). The decrease in viscosity is caused by the partial cleavage of the glucosidic linkages during the extensive oxidation, resulting in a decrease in molecular weight of starch molecules (Kuakpetoon & Wang, 2001). When starch is oxidized by hydrogen peroxide, not only hydroxyl groups are oxidized to carbonyl and carboxyl groups, but also carbohydrate chains are cleaved. The reduction rate of viscosity is faster at the beginning and slower later when catalyst content (at 0.1% molar content), reaction time

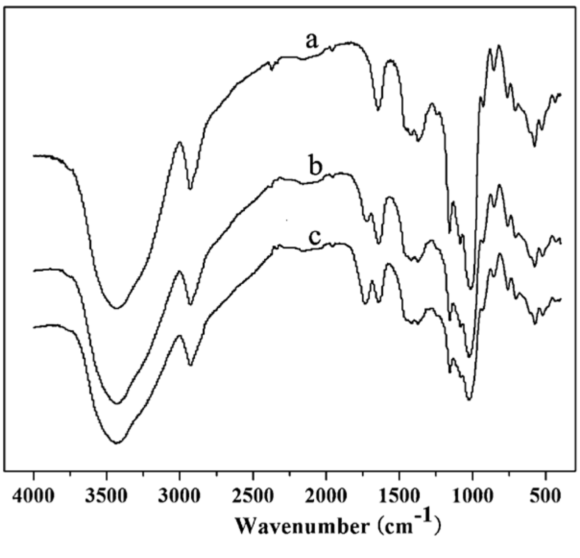


Fig. 2. IR curves of the native starch and the oxidized starches with different DO.

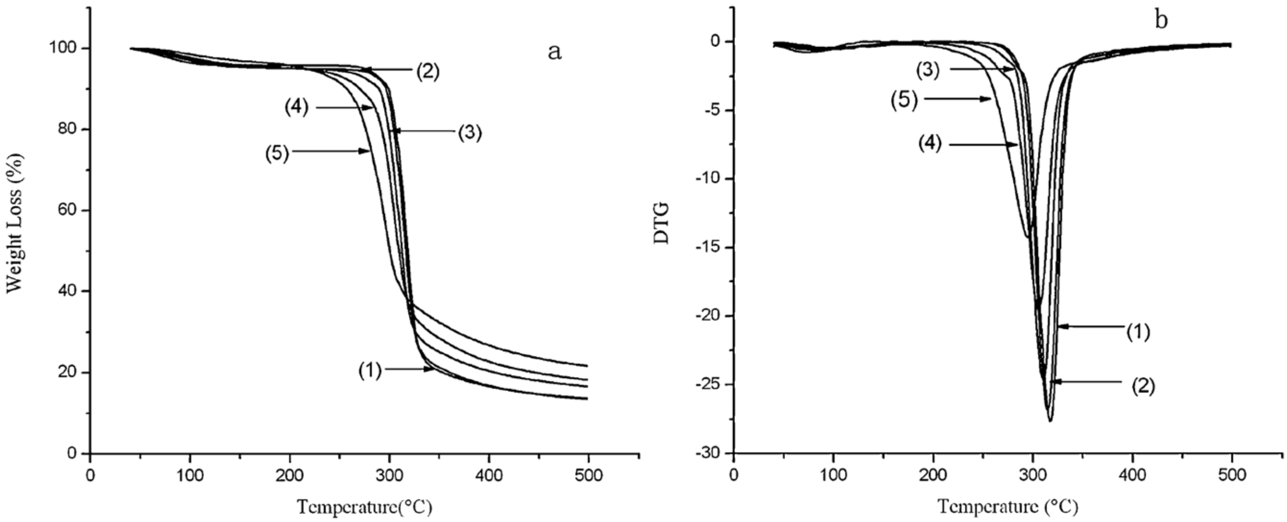


Fig. 3. Thermogravimetric and DTG curves of the native starch and the oxidized starches with different DO.

(at 60 min), or oxidant content (at 1.5 molar content) increased respectively. The reason is that hydrogen peroxide rapidly depolymerized amylopectin at the beginning of the reaction, which is proved by the observation of a rapid decrease in viscosity (Whistler & Schweiger, 1959). Observed from Fig. 1c, when temperature rises from 15 to 60 °C, the reduction rate of viscosity is almost the same with the increase ratio of DO. It can be proposed that the amount of hydroxyl groups at C1 and/or C2 react with hydrogen peroxide is in a certain ratio to the amount of those at C3. This ratio is almost kept constant when temperature increased from 15 to 60 °C. But when catalyst content (lower than 0.1% molar content), reaction time (shorter than 60 min), or oxidant content (lower than 1.5 molar content) increased, the hydrogen peroxide preferentially oxidizes hydroxyl groups at C2 and/or C3 of glucose units to carbonyl and/or carboxyl groups. The presence of oxidation at C2 or C3 will weaken the bond at the C1 position accompanied by the opening monomeric rings and depolymerization of starch chains via β-elimination (Sangseethong et al., 2010a). This also gives a hint there why DO increased faster in the beginning of the reaction. When the catalyst content (higher than 0.1%), reaction time (longer than 60 min) or oxidant content (higher than 1.5 molar content) continued to increase, hydrogen peroxide mainly oxidized the hydroxyl groups at C1 of anhydroglucose units, which made the reduction rate of viscosity more modest.

3.7. *Infrared spectroscopy*

Oxidation leads to the change of hydroxyl groups into carbonyl and carboxyl groups in the starch molecules. The introduction of carbonyl groups could be confirmed by FT-IR spectroscopy. The FTIR spectra of native and oxidized starches with different degrees of oxidation are shown in Fig. 2. The spectra a–c show that native and oxidized starches have similar profiles. In the fundamental region, the absorption peaks at 3426.7 cm^{-1} and 2927.7 cm^{-1} are from the –OH and –CH_2 stretching vibration of the glucose unit. The absorption at 1642.7 cm^{-1} is a typical band residing in the spectra of starch and its derivative, which is attributed to an H_2O bending vibration (Luo, Huang, Fu, Zhang, & Yu, 2009; Wang et al., 2007); numbers of hydroxyl groups in starch molecules lead to the absorption of water. Compared with native starch (a), a new absorption band at 1735.6 cm^{-1} can be seen in spectrum b (DO = 40.5%) and c (DO = 56.3%), and it is assigned to the C=O stretching vibration (Hui, Qi-he, Ming-liang, Qiong, & Guo-qing, 2009; Kweon, Choi, Kim, & Lim, 2001; Para, 2004). Moreover, with an increasing DO, we observed the enhanced absorption at 1735.6 cm^{-1} in curve (c), which suggested that more carbonyl and/or carboxyl groups were formed. The results indicate that native starch was successfully oxidized by hydrogen peroxide, and hydroxyl groups were changed to carbonyl and/or carboxyl groups.

3.8. *Thermal stability of oxidized starch*

TGA tests were performed for native and oxidized starches with different DO_S; as shown in Fig. 3, the weight loss and the degradation of products are monitored as a function of temperature. $T_{5\%}$, the temperature corresponding to 5% weight loss, was obtained from Fig. 3a and listed in Table 1. T_{max}, which is the temperature at the maximum rate of weight loss, is determined from derivative thermogravimetry (DTG) curves. DTG curves of native and oxidized starches varied with DO_S are shown in Fig. 3b and the values of T_{max} are listed in Table 1. Compared with $T_{5\%}$ of native starch at 275.9 °C, $T_{5\%}$ of the oxidized starches dramatically decrease to as low as 210.2 °C. However, $T_{5\%}$ of the oxidized starches do not vary significantly with the DO although it increases from 5.9% to 56.3%. T_{max} decreased from 317.2 to 294.7 °C with the increase of DO. Compared with native starch, there is a reduction in thermal stability with the increase of the DO of the samples. The reason might be that the oxidation leads to the depolymerization of molecular chains, which causes the molecular weight decrease with the increase of DO. So the thermal stability was decreased when the DO increased. Usually the thermal processing temperature can be lower than 210 °C ($T_{5\%}$ of oxidized starch) and this indicates that the obtained oxidized starch can be thermally processed into products.

3.9. *Thermal transition behavior of oxidized starch*

When starch is used as a thermoplastic, plasticizers such as glycerol and water are usually added due to its the lack of

Table 1
Thermogravimetric parameters of the native starch and the oxidized starches with different DO.

	$T_{5\%}$ (°C)	T_{max} (°C)
Native starch	275.9	317.2
Oxidized starch 5.9%	210.9	314.5
Oxidized starch 19.5%	211.0	310.1
Oxidized starch 40.5%	210.2	305.6
Oxidized starch 56.3%	217.7	294.7

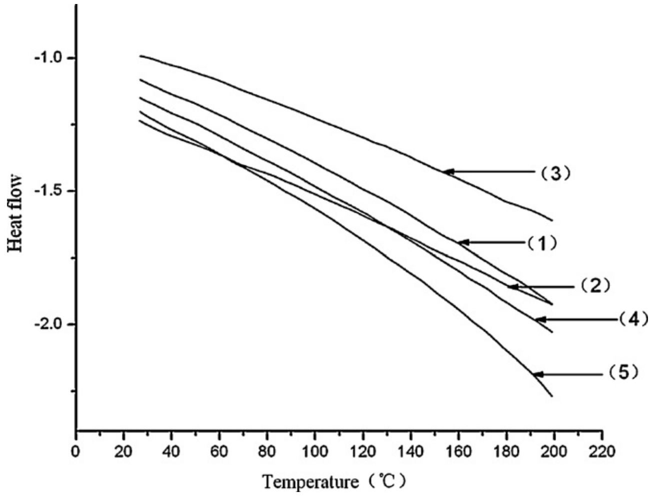


Fig. 4. DSC curves of the native starch and the oxidized starches with different DO.

thermoplasticity. If the glass transition temperature can be found for the obtained oxidized starch, this indicate that it has some thermoplasticity and can be used alone as a material without the addition of a plasticizer. When hydroxyl groups are changed to carbonyl groups, the hydrogen bonds between the hydroxyl groups and carbonyl groups are not as strong as that between hydroxyl groups. So when the carbonyl content is high enough, a glass transition is expected. We determined the glass transition of the native and oxidized starches with different DO$_S$ from the DSC measurement. As depicted in Fig. 4, no glass transition is found in the oxidized starches from 20 to 200 °C, although the DO increases from 5.9% to 56.3%, just like native starch. Even though the oxidation changes the hydroxyl groups to carbonyl groups, which weakens the hydrogen bonds between molecules, there are so many intra- and intermolecular hydrogen bonds in starch which restrain the movement of molecules leading to no glass transition in the oxidized starch. So oxidized starch is not thermoplastic, which means that its thermoplastic processing can only be accomplished by adding plasticizers, just as we studied before (Zhang, Zhang, Wang, & Wang, 2009; Zhang, Zhang, Wang, Chen, et al., 2009).

3.10. X-ray diffraction of oxidized starch

The crystal type of starch is divided into A, B and C. Native starch commonly exists in a granular structure with about 15–45% crystallinity, which belongs to type A (Ma, Jian, Chang, & Yu, 2008). The X-ray diffractograms of the two oxidized, gelatinized starch, and native corn starches are depicted in Fig. 5. The native corn starch has sharp peaks in curve 1 at 15.3°, 17.2°, 18.1°, and 23.3°, which represents the typical pattern of type A corn starch (Ma et al., 2008). Although the crystal structure of gelatinized starch was completely destroyed when it was in gel, the retrogradation would happen when it was dried because most of the hydrogen bonds between starch molecules were restored. We tested the crystallinity of gelatinized starch before (Zhang, Zhang, Wang, & Wang, 2009). The intensity of peaks of gelatinized starch at 15.3°, 17.2°, 18.1°, and 23.3° are much lower than those of the native starch, which means that the gelatinization lower the degree of crystallinity, as shown in Fig. 5 (curve 2). However, when the starch is oxidized, the crystalline structure is changed. The carboxyl and/or carbonyl groups play an important role in stabilizing the linear amylose molecules and minimizing retrogradation. For oxidized starch with a DO of 40.5% (O$_S$ 40.5%), as described in Fig. 5 (curve 3), the intense peaks appeared at 2θ values of 17.1° and 20.0°, respectively. However, the other peaks disappear, meaning that the original crystal structure of the native starch is subjected to a great change: a portion of original crystalline structure is destroyed during the reaction and a new crystal structure is formed. No peak is found from the diffraction pattern when the DO reaches 56.3% and the peaks of native starch completely disappear, exhibiting an amorphous phase.

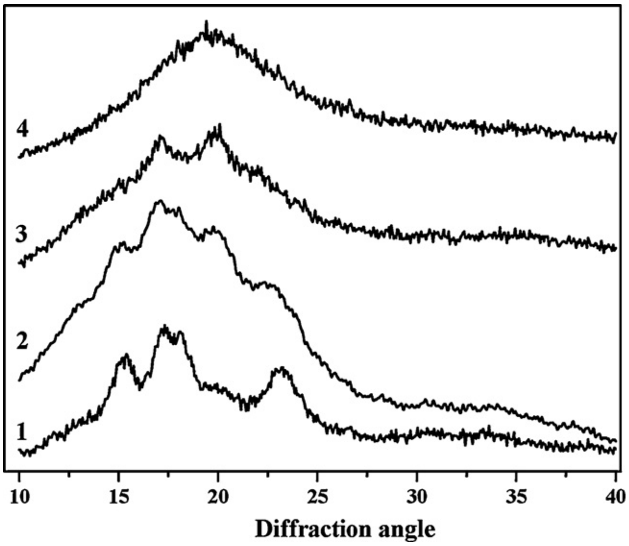


Fig. 5. Wide-angle X-ray diffraction patterns of native cornstarch and the oxidized starches.

However, our results are different from those reported by Carolina, Wang, and Luis (2008). They found that there were no XRD pattern changes for the oxidized starches with different oxidation levels. The main reason might be that the starch granules did not destroy through gelatinization and the reactions mainly happen in the amorphous lamellae. In our study, starch was gelatinized before reaction to free all the hydroxyl groups in the amylose and amylopectin chain. When starch is oxidized by hydrogen peroxide, the molecular chain depolymerizes with the increase of oxidation and the type of crystal structure is changed (Li & Vasanthan, 2003). The DO of oxidized starch they prepared is too low and the oxidation did not penetrate into the starch granular to change the crystal structure. It is very interesting to find that oxidized starch with low and high DO has different impacts on the type and degree of crystallization.

3.11. Transmittance of oxidized starch suspension

Transmittance of the suspension of the oxidized starch with different DO$_S$ and native cornstarch are shown in Table 2. The transmittance increases greatly as the degree of oxidation and/or heating temperature increases. Native starch does not increase its transmittance very significantly, only from 2.44% to 3.22%, when the temperature increases from 60 to 80 °C. However, as the temperature increases from 60 to 70 °C, the transmittance of the oxidized starch with DO$_S$ of 5.9% and 40.5% markedly increases, from 12.68% to 35.20% and from 28.98% to 61.87%, respectively. When the temperature continues to increase, the increase of transmittance is

Table 2
Transmittances of suspensions of the oxidized starches and the native starch respectively in different temperature.

	60 °C	70 °C	80 °C
Native starch	2.44 ± 0.059	3.00 ± 0.055	3.22 ± 0.067
Oxidized starch 5.9%	12.68 ± 0.449	35.20 ± 2.183	41.40 ± 1.734
Oxidized starch 40.5%	28.98 ± 3.693	61.87 ± 2.453	75.04 ± 0.622
Oxidized starch 56.3%	69.80 ± 2.740	70.22 ± 1.572	75.57 ± 0.622

not obvious. For oxidized starch with a DO of 56.3%, although the transmittance increases with the rise of temperature, the change is small. The reason might be that the oxidized starch with a DO of 56.3% is almost gelatinized at 60 °C and the increase of temperature has no obvious influence on it. This can be ascribed to the fact that the oxidized starch is more prone to gelatinize, making the starch paste more transparent (Chang et al., 2008). Furthermore, the molecular weight of oxidized starch dropped correspondingly with the increase of DO and its crystal structure is destroyed, which makes the oxidized starch easier to gelatinize and harder to retrograde. However, there were many cases where oxidation caused a decrease in molecular weight of starch but resulted in an increase in gelatinization temperature (Sangseethong, Termvejsayanon, & Sriroth, 2010b). There are two reasons for their elevated gelatinization temperatures. The first one is, when starch is heated in an aqueous environment below the gelatinization temperature, annealing will make crystallization more perfect which cause an increase in the gelatinization temperature. The other possible reason is that the oxidation mainly leads to the depolymerization of the molecular chain in the amorphous region which acts to destabilize the crystal lamella. Once the amorphous regions are degraded, their destabilizing effect on the crystal domains is destroyed. Therefore, the gelatinization of the resulting starch appears at a higher temperature (Sangseethong et al., 2010b). These two reasons can be generalized as follows: the crystal degree of the product increases when oxidation is performed, which is the most important reason for the elevation of gelatinization temperature. But in our case, the situation is different. The crystallinity of the oxidized starches decreases with the increase of DO, which has been confirmed by their wide-angle X-ray diffraction (Fig. 5). Starch is gelatinized before the reaction in order to destroy the crystal structure to form a uniform gel. All of the hydroxyl groups in the former amorphous and crystal regions can equally react with hydrogen peroxide. After starch was oxidized to a high degree, the crystal structure could not totally form back again when the product was dried. The other reason is that the stronger electrostatic repulsion between starch molecules when the DO increase is caused by negative charges on the carboxyl groups, leading to easier transmittance for light through the solution (Boruch, 1985).

4. Conclusions

The preparation parameters of oxidized starch, including starch origin, temperature, catalyst content, and reaction time were investigated. The results showed that $CuSO_4$ was an effective catalyst for the oxidation of starch by hydrogen peroxide. It was found that the molecular weight of starch was decreased during the oxidization process. Besides this, the thermal stability of oxidized starch was also lowered. However, it would not affect the thermal processing of oxidized starch. DSC results showed that the oxidized starch did not have a glass transition temperature although the DO was as high as 56.3%. XRD analysis showed that the crystal structure was destroyed by oxidation. The light transmittance increased greatly as the degree of oxidation increased along with the heating temperature. In short, a fast way to prepare oxidized starch with a high DO value was successfully established. The obtained oxidized starch had potential applications in the food industry, paper, textile, laundry finishing, plastics, and so on.

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