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Study on physico-chemical properties of dialdehyde yam starch with different aldehyde group contents

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ABSTRACT

Dialdehyde yam starches (DASs) are prepared and characterized. Compared with native starch, viscosity average molecular weight of DASs decreases, and the extent of degradation depends on content of the aldehyde groups. Fourier transform infrared (FT-IR) spectra confirm that the characteristic peak for C=O group at 1732 cm^{-1} is enhanced with the increasing of content of the aldehyde groups. Scanning electron microscopy (SEM) micrographs show that the surface of starch granules becomes wrinkled. X-ray diffraction (XRD) patterns clearly indicate that their crystallinity decreases with the increasing content of the aldehyde groups before they become amorphous at higher oxidation states. The experimental results of thermogravimetric analysis (TGA) show that DASs have poor stability as compared to native starch. With the increase in content of the aldehyde groups, the thermal stability of DAS declines gradually. According to the results of differential scanning calorimetry (DSC), gelatinization temperature (T_o and T_p) of DASs are increased, whereas the gelatinization enthalpy decreased.

1. Introduction

Yam (*Dioscorea opposita* Thunb.) is widely distributed in China and has been used as an important invigorant in traditional Chinese medicine for many years. It has been used for nourishing liver and kidney, promoting production of the body fluids and benefiting the lung and invigorating the kidney and spleen [1]. It was reported that yam contains many chemical components such as mannan, allantoin, dopamine, batatasine, phytic acid, abscisin II, amino-acids, glucoprotein, choline, cholesterol, ergosterol, campesterol, saponins, starch, non-starch polysaccharide and others [2,3]. In the rhizome of yam, starch is the main component making up to 20–60% in the total biomass [4]. However, starch is usually discarded during the isolation and separation of the low molecular weight bioactive ingredients, resulting in the waste of resources and contamination of the environment.

Starch, an important carbohydrate in higher plants, is widely used in the people's everyday life as well as food, pharmacy and other industry. It has been well studied as a biodegradable material by those interested in environmental protection. Many studies have focused on thermoplastic starch (TPS) [5,6]. Unfortunately, TPS exhibits poor mechanical properties and hydrophilicity, which hinders its application [7]. Once the hydroxyl group of starch has been replaced with the aldehyde group, starch shows greater hydrophobicity and the recrystallization of starch is inhibited.

Dialdehyde starches (DAS) from periodate oxidized potato starch [6,8], tapioca starch [9], cornstarch [10,11], pea starch [5] have been produced. However, the authors are not aware of any previous publication on synthesis and characterization of dialdehyde yam starch up to now. It can be used for several industrial applications: as a food additive [12], in paper coatings [13,14], in biomaterials [15], as a wet-strength improver [16,17], and a metal absorbent [11,18–21].

DAS, one of the most valuable form of oxidized starch, is prepared by oxidation of starch with periodic acid which is a selective oxidant and can cleave the C2, C3 bond of anhydroglucose units with the formation of dialdehyde groups [22–24]. The C-2 and C-3 aldehyde groups of the anhydroglucose units in DAS could form inter- and intramolecular hemiacetal and acetal cross-linking in the processing of thermoplastic DAS (TPDAS) [24,25]. DAS with the higher content of the aldehyde groups are more likely to form these crosslinks, contributed to the reinforcement of TPDAS [6]. On the periodate oxidation, the polysaccharide chains in native starch underwent fragmentation and oxidization, resulting in changes in the physicochemical properties such as thermal and crystal properties, particle morphology and so on.

In this study, yam starch was oxidized using various concentrations of periodate in order to investigate the physicochemical properties changes after periodate oxidation, such as average

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molecular weight, formation of aldehyde, morphology, crystalline structure and thermal properties.

2. Experimental

2.1. Materials and chemicals

The Chinese yam (*Dioscorea opposita Thunb.*) flour was provided by Henan Wan Xi Pharmaceutical Company (Tianjin, China). Sodium periodate and other chemicals were purchased from Yuan Li Chemical Company (Tianjin, China).

2.2. Starch extraction

The native starch was isolated following the method described by Wang et al. [26]. The yam flour was washed and sieved with a 150 μm mesh sifter. After depositing, the supernatant was removed by suction and the settled starch layer was resuspended in distilled water. After seven or eight cycles of depositing and resuspending repeatedly, the slurry containing starch was centrifuged at 3000 r/min for 20 min. The supernatant was discarded and the upper non-white layer was removed. Ethanol (70%) was added in order to remove the low molecular weight compounds. The white layer was resuspended in distilled water and recentrifuged 3–5 times. The white layer obtained was dried in a convection oven at 50 °C until constant weight. The dried material was milled and sieved with a 75 μm screen to get the starch flour. The yam starch has been investigated for physico-chemical (e.g., amylase content, swelling power, solubility, water-binding capacity, and turbidity), morphological (including shape and size), thermal, and crystalline properties in the previous study [27,28].

2.3. Preparation of dialdehyde yam starch

Dialdehyde yam starch (DAS) was prepared by following the modified method for dialdehyde tapioca starch described by Wongsagona et al. [9]. The dry yam starch of 20.0 g was suspended in 80 mL distilled water in a suitable reaction vessel. Then various quantity of sodium periodate (6.6 g, 13.2 g, 19.8 g, 26.4 g) were added into the suspension and the pH value was adjusted to 3.0 by adding 2% (w/v) hydrochloric acid. Then the mixture was vigorously mechanically stirred and incubated in a water bath at 35 °C for 4 h. At the end of the oxidation, the reaction mixture was filtered and washed five times (5× 200 mL) with distilled water. Next, the product was washed with 50 mL acetone and then dried in a convection oven at 50 °C until constant weight. The dried material was milled and sieved with a 75 μm screen to get the dialdehyde yam starch.

2.4. Determination of content of the aldehyde groups

The aldehyde group content was determined using the rapid quantitative alkali consumption method [29]. Dried DAS (0.15–0.20 g) was suspended in 10 mL of standardized 0.25 mol/L sodium hydroxide in a 125-mL Erlenmeyer flask. The flask was swirled in a water bath at 70 °C for 2 min, and then cooled immediately under running tap water with rapid swirling for 1 min. After that 15 mL of standardized 0.125 mol/L sulfuric acid, 30 mL of distilled water and 1 mL of neutral 0.2% phenolphthalein was added in turn. Titration of the acid solution was carried out using 0.25 mol/L sodium hydroxide. The percentage of dialdehyde units was given by the following equation:

$$\mathrm{Da\%} = \frac{C_1V_1 - 2C_2V_2}{W/161 \times 1000} \times 100\%$$

where C_1, C_2 (mol/L) represent the normality of NaOH and H_2SO_4, respectively. V_1, V_2 (mL) represent the total volume of NaOH and H_2SO_4, respectively. W is the dry weight of the DAS sample, 161 is the average molecular weight of the repeat unit in DAS. The experiments were performed in triplicate.

2.5. Determination of average molecular weight of dialdehyde starch

The determination of average molecular weight (M_w) of dialdehyde starch was based on the measurement of intrinsic viscosity [η]. The measurements were carried out in triplicate at 25.0 ± 0.1 °C with an Ubbelohde viscometer (capillary tube with 0.58 mm in diameter). The samples were dissolved in DMSO, and the concentration of dialdehyde starch was about 1.0 mg/mL. The intrinsic viscosity [η] was determined according to the eguations of Huggins and Kraemer (Eqs. (1) and (2), respectively).

$$\frac{\eta_{sp}}{C} = [\eta] + k_H[\eta]^2C \quad (1)$$

$$\frac{\ln \eta_r}{C} = [\eta] + k_k[\eta]^2C \quad (2)$$

where $\eta_{sp} = \eta_r - 1$, C is the concentration, k_H and k_K are Huggins' and Kraemer' constants, respectively. Average values were considered.

The average molecular weight was calculated according to the Mark-Houwink equation.

$$[\eta] = KM_w{}^{\alpha}$$

where the constants K and α were given elsewhere as 8.5×10^{-3}, mL/g and 0.76, respectively [10,30].

2.6. Fourier transforms infrared (FT-IR) spectroscopy

FTIR spectra in the 4000–400 cm^{-1} wavenumber range were recorded with an IR spectrometer (Bruker Vector 22) using potassium bromide (KBr) discs prepared from powdered samples mixed with dry KBr. Samples were prepared by grinding about 1.2 mg dialdehyde starch samples with 150 mg KBr and pressing the mixture into very thin disks.

2.7. Scanning electron microscopy (SEM)

The morphological features of native starch and dialdehyde starches were observed with a scanning electron microscope (ESEM Philips XL-30). The dried samples were mounted on a metal stub and sputtered with gold, and the images were taken at an accelerating voltage of 20 kV. Micrographs were recorded at 500× and 2000× magnifications.

2.8. X-ray diffractometry (XRD)

X-ray diffraction patterns of native starch and dialdehyde starches were analyzed using Rigaku D/max 2500 X-ray powder diffractometer (Rigaku, Tokyo, Japan) with nickel filtered Cu Kα radiation (λ = 1.54056 Å) at a voltage of 40 kV and a current of 150 mA. The scattered radiation was detected in the angular range of 3–50° (2θ), with a scanning speed of 6° (2θ)/min and a step width of 0.02° and step time 0.2 s. The degree of crystallinity of samples was quantitatively estimated following the method of Nara and Komiy [31].

2.9. Thermogravimetric analysis (TGA)

The thermogravimetric measurements were performed with a TG apparatus (Shimadzu TGA-50, Kyoto, Japan). Samples of about

10 mg were heated from 30 to 700 °C at a heating rate of 10 °C /min and a flow rate of 20 mL/min in a nitrogen atmosphere. The experiments were performed in triplicate.

2.10. Differential scanning calorimetry (DSC)

The DSC properties were studied by using a differential scanning calorimeter (NETZSCH, Germany) equipped with a thermal analysis station. Each of starch samples (3.5 mg, dry weight) was loaded into an aluminium pan (Mettler, ME-27331) and distilled water was added with the help of Hamilton microsyringe to achieve a starch–water suspension containing 70% water. These pans were hermetically sealed, equilibrated at room temperature for 1 h and heated from 20 °C to 120 °C at a heating rate of 10 °C/min. The calorimeter was calibrated with an indium standard. Each test was carried out with an empty pan as a reference. The onset temperature (T_o), the peak temperature (T_p), and conclusion temperature (T_c) were, respectively, determined from the first run heating DSC curves. Gelatinization enthalpy (ΔH_g) was evaluated based on the area of the main endothermic peak. Analyses were performed in triplicate.

3. Results and discussion

3.1. Content of the aldehyde groups and yield of DAS

Yam starch was oxidized by sodium periodate to form DAS. The content of the aldehyde groups, which reflect the degree of oxidation, were expressed as the number of carbonyl groups per 100 glucose units. The content of the aldehyde groups of DAS increased with higher ratios of sodium periodate to yam starch. The content of the aldehyde groups of obtained DASs were as follows: 24.75% (DAS 24.75), 49.54% (DAS 49.54), 72.40% (DAS 72.40) and 94.12% (DAS 94.12). The yields of DAS 24.75, DAS 49.54, DAS 72.40 and DAS 94.12 were 92.6%, 84.7%, 78.3%, and 75.4%, respectively. The reason could be that, when the molar ratio of sodium periodate to yam starch increased, the superfluous oxidant degraded the starch and caused some of the DAS to dissolve in the water, resulting in a reduced DAS yield [8]. It is known that the starch has a tendency to hydrolyze at pH lower than 7.0, and this tendency will be accelerated by lower pH and oxidant concentration [10].

3.2. Average molecular weight of DAS

The molecular weight of DAS as a function of carbonyl content is shown in Fig. 1. As shown in Fig. 1, the molecular weight of DAS decreases drastically when dialdehyde starch was prepared by using sodium periodate under acidic condition. DAS with the content of the aldehyde groups of 24.75% had an average molecular weight of about 155,000, while that of native yam starch is about 853,000. When the content of the aldehyde groups increased to 94.12% the molecular weight of DAS was below 10,000. Similar observation has been reported for the DAS prepared from corn starch [10] and potato starch [8] and pea starch [5]. The reason for this is that, when $NaIO_4$ cleaved the C2–C3 bonds of the glucose units of yam starch, the oxidation also led to disruption both α-D-(1–4) and α-D-(1–6) glycosidic bonds which causes the average molecular weight of dialdehyde starch to decline drastically [8]. On the other hand, starch is easily degradable at pH higher (such as in the alkaline solution) or lower than 7.0. According to previous reports [5,10], the molecular weight of DAS decreased even under mild oxidizing conditions during the preparation of dialdehyde starch, and the degree of degradation depended on the degree of oxidation (at pH value of 7.0).

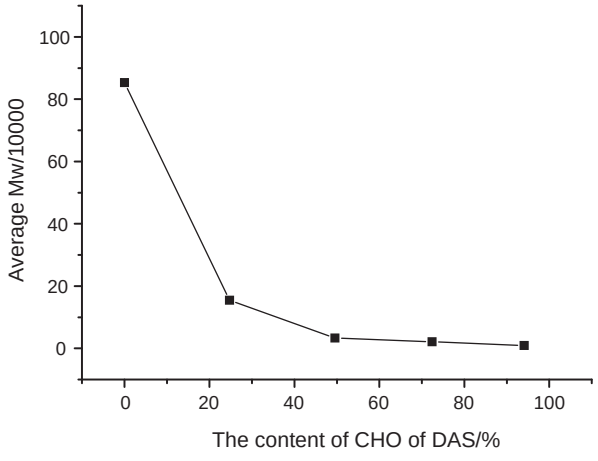

Fig. 1. Relationship between average M_w of dialdehyde yam starch and content of the aldehyde groups.

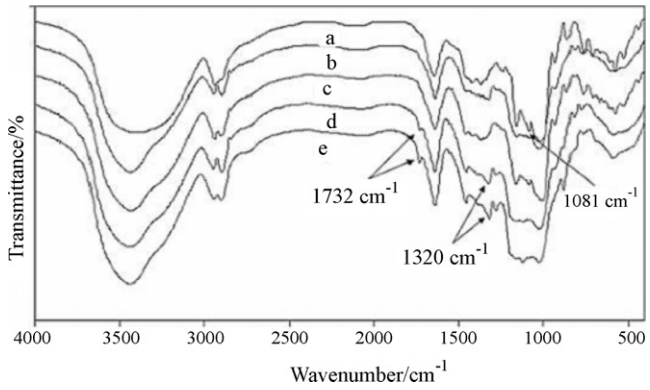

Fig. 2. FT-IR spectra of dialdehyde starch samples: (a) native starch; (b) DAS 24.75; (c) DAS 49.54; (d) DAS 72.40; (e) DAS94.12.

3.3. FT-IR

Fig. 2 shows the effect of content of the aldehyde groups on spectra of DAS. In the spectrums of native yam starch, the broad band between 3600 and 300 cm^{-1} is assigned to O–H stretching and it is due to hydrogen bonding involving the hydroxyl groups on starch molecules. The band at 2933 cm^{-1} is assigned to CH_2 symmetrical stretching vibrations. The band at 1643 and 1430 cm^{-1} is attributed to the scissoring of two O–H bonds of water and CH_2 scissoring vibration, respectively [32]. There are several discernible absorbances at 1159, 1081, 1021 and 930 cm^{-1}, which are attributed to the C–O bond stretching [33]. The bands at 860 and 767 cm^{-1} are due to skeletal stretching vibrations of starch. The DASs of high content of the aldehyde groups show a discernible band at 1732 cm^{-1}, which is the most characteristic band of C=O vibrations in aldehyde groups. This is because hemiacetal formation is formed between oxidized and unoxidized starch residues during the preparation [34], and the amount of residual unoxidized starch is lower for the DAS with the higher content of the aldehyde groups. The band at 2830 cm^{-1} is characteristic of C–H stretches associated with the hydrogen atoms of aldehyde group. The band observed at 780 cm^{-1} can be assigned to the hemiacetal form [11]. With the increasing of content of the aldehyde groups, the characteristic peak for C=O groups at 1320 cm^{-1} (ν_{C-C} in C–CHO) increased, the peaks at 1159, 1081 cm^{-1} are weakened, which is attributed to the C–O bond stretching of C–OH group in the anhydroglucose ring. Similar observation has been reported for DAS of potato [6]. The reason for this may be that the periodate oxidation mainly breaks the C-2 and C-3 bond of the anhydroglucose units, and aldehyde

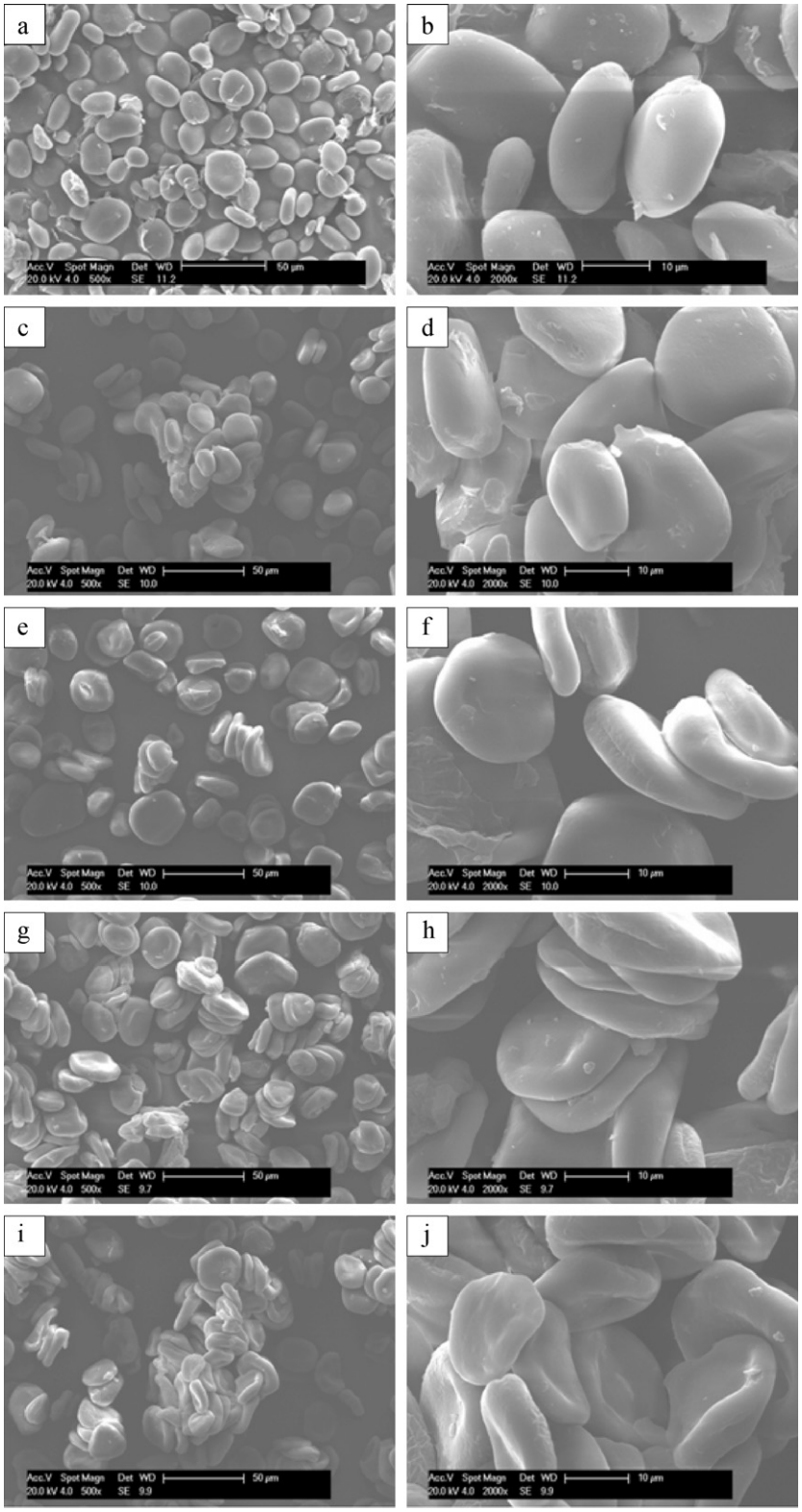

Fig. 3. SEM images of dialdehyde starch samples: (a and b) native starch; (c and d) DAS 24.75; (e and f) DAS 49.54; (g and h) DAS 72.40; (I and j) DAS94.12.

groups are formed and take the place of C–OH groups at C-2 and C-3.

3.4. SEM

SEM micrographs of native starch and DAS with different content of the aldehyde groups are shown in Fig. 3a–j. Studies reveal that the granules of native yam starch (Fig. 3a and b) present oval or elliptical shapes with smooth surface, and their sizes range from 6 to 18 μm in width and 15 to 26 μm in height. This observation is consistent with previous reports on shapes of starches from Chinese yam [27]. After oxidization by periodate, the particles (Fig. 3c–j) appear obviously diverse. The sample of DAS 24.75 (Fig. 3c and d) has a slightly distortion with some wrinkles. As the content of the

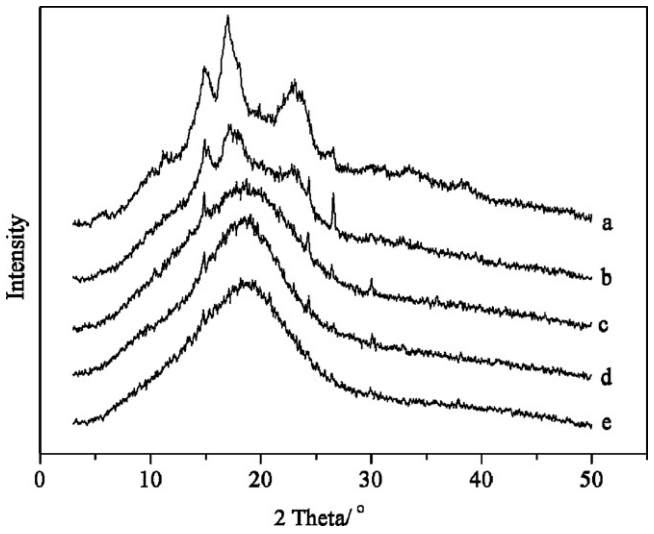

Fig. 4. X-ray diffraction spectra of dialdehyde starch samples: (a) native starch; (b) DAS 24.75; (c) DAS 49.54; (d) DAS 72.40; (e) DAS94.12.

aldehyde groups of DAS increased, the surface of starch granules (Fig. 3e–j) obviously sinks due to oxidated corrosion. As observed, the sample of DAS 94.12 (Fig. 3i–j) does not present a ring form, which is unlike previous reports on DAS (with content of the aldehyde groups of 93.05%) of potato starch [6]. Clearly, the cleavage of glucoside rings leads to an altered uneven surface, creating pit on the particles. Also notable was that the particles were conglomerated closely, and the granules became bigger in contrast to the original. The agglomeration could be due to a strong depolymerization and oxidation of the surface, which leads to higher interactions between the granules. The observation also corroborates previous investigations on DAS of cornstarch [11].

3.5. XRD

The diffraction patterns of native starch and DAS with different content of the aldehyde groups are presented in Fig. 4a–e. The crystal characterizations of starch granules were often carried out using X-ray diffraction patterns, which had been classified as A, B or C pattern. It can be seen that the native yam starch (Fig. 4a) has a typical C-type crystalline structure, a mixture of A and B types, with four strong diffraction peaks at around 2θ of 5.6°, 14.8°, 17.0° and 23.1°. The sample of DAS 24.75 (Fig. 4b) also has three strong diffraction peaks at the same diffraction angles as native starch, while its intensity is decreased. When the content of the aldehyde groups of DAS exceeds 49.54%, the samples of DAS show no crystal peak of starch (Fig. 4c–e). The crystallinity levels of native starch and DAS are shown in Fig. 5. As observed, the degrees of crystallinity decrease from 27.18% to 3.24% with the increase in content of the aldehyde groups. It implies that periodate oxidation could destroy the crystalline regions of starch granules. Similar observation has been reported for DAS prepared from potato starch [6,8] and pea starch [5]. According to current models of starch granule, the crystallinity of starch granules arises from parallel radial packing of double helices in amylopectin molecules, while amylose molecules are in an amorphous state [35,36]. As a result, parallel double amylopectin molecules of starch can be oxidized to form amorphous DAS, while amylose molecules in side of starch granules can be degraded [6,9]. Therefore, the molecular weight of dialdehyde starch declines drastically, and the surface of starch granules becomes obviously depressed (Fig. 3e–j).

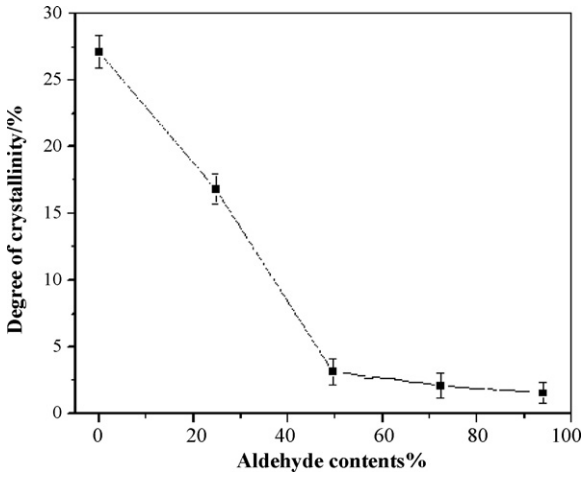

Fig. 5. Relationship between degree of crystallinity and content of the aldehyde groups of dialdehyde yam starch.

3.6. TGA

The TG and DTG curves for native starch and DAS with different content of the aldehyde groups are shown in Figs. 6 and 7. The native starch (Figs. 6a and 7a) and DAS 24.75 (Figs. 6b and 7b) shows a two-stage weight loss bellow 700 °C, the first one corresponding to the loss of water around 60–130 °C and the other one corresponding to its decomposition. The derivatogram of native starch indicates that maximum decomposition occurs at the range of 273–360 °C, while DAS 24.75 appears between 210 and 425 °C. The other three DASs (Figs. 6c–e and 7c–e) show three-stage weight loss, the first minor one corresponding to the loss of water and the other two (double peaks) corresponding to its decomposition. With the increase in content of the aldehyde groups there is a shifting of peak maximum (double peaks) towards lower temperatures. It was found that the DASs have poor stability as compared to native starch. The higher the content of the aldehyde groups, the lower the initial thermal decomposition temperature. DAS94.12 (Figs. 6e and 7e) showed the poorest thermal stability among the five samples. This observation also corroborates previous investigations on DAS prepared from cornstarch [10] and pea starch [5]. This can be attributed to the decreasing average molecular weight of the DAS and the poor thermal stability of the aldehyde group [10].

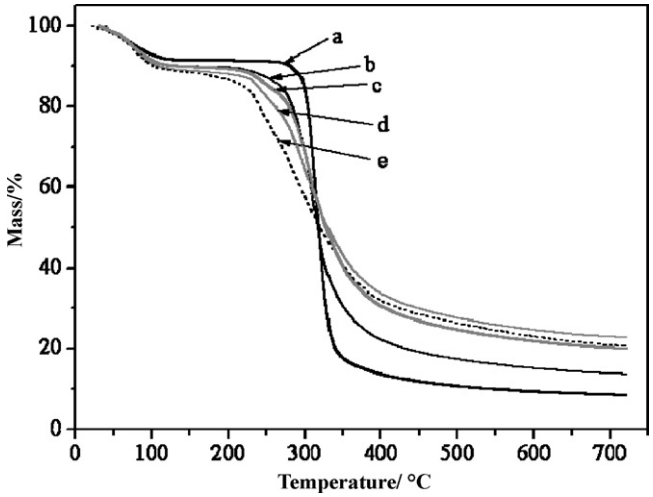

Fig. 6. TG curves of dialdehyde starch samples: (a) native starch; (b) DAS 24.75; (c) DAS 49.54; (d) DAS 72.40; (e) DAS94.12.

Table 1
The DSC data of dialdehyde yam starch with different aldehyde group contents.

Samples	T_o (°C)[a]	T_p (°C)[b]	T_c (°C)[c]	ΔH_g (J/g)[d]
Native starch	70.11 ± 0.52	77.23 ± 0.74	84.30 ± 0.76	10.54 ± 0.35
DAS 24.75	72.34 ± 0.71	77.85 ± 0.64	85.12 ± 0.65	9.78 ± 0.41
DAS 49.54	73.97 ± 0.64	78.67 ± 0.69	84.30 ± 0.57	9.12 ± 0.39
DAS 72.40	75.03 ± 0.61	79.32 ± 0.58	83.58 ± 0.59	8.51 ± 0.37
DAS 94.12	75.84 ± 0.59	80.59 ± 0.67	85.25 ± 0.71	8.02 ± 0.35

[a] T_o: onset temperature.
[b] T_p: peak temperature.
[c] T_c: conclusion temperature. Values are means ± *SD* (n = 3).
[d] ΔH_g: gelatinization enthalpy.

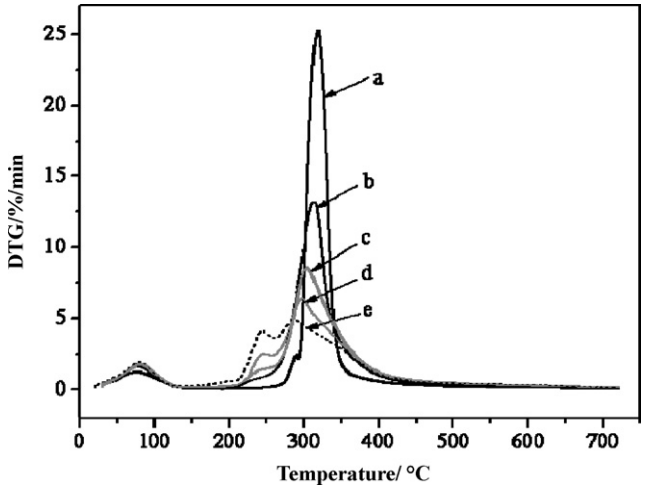

Fig. 7. DTG curves of dialdehyde starch samples: (a) native starch; (b) DAS 24.75; (c) DAS 49.54; (d) DAS 72.40; (e) DAS94.12.

3.7. DSC

Starch gelatinization is a process that involves the uncoiling of double helices and melting of the starch crystallites in the starch crystalline region. The temperatures and enthalpy values associated with gelatinization of native starch and DASs are presented in Table 1. It was found that transition temperatures (T_o, T_p, and T_c) and gelatinization enthalpies (ΔH_g) of native starch and DASs with different content of the aldehyde groups differ significantly. With the increasing of content of the aldehyde groups, the gelatinization temperature (T_o and T_p) increased. This observation is consistent with previous report on DAS of tapioca starch [9]. It is probably due to the formation of hemiacetal crosslinking within aldehyde groups in DAS molecules, increasing the stability of the starch molecules [9]. As observed, the gelatinization enthalpy (ΔH_g) of DAS decreased with the increase in content of the aldehyde groups, and the ΔH_g of DAS was positively related to the degree of crystallinity. This is because the crystallinity of DAS decreased in relation to native starch according to the X-ray diffraction results [37].

4. Conclusions

Dialdehyde starches (DASs) are prepared by the oxidation of yam starch using sodium periodate as an oxidant. Compared with yam starch, DAS has a decreased molecular weight, and the extent of degradation depends on content of the aldehyde groups. The crystallinity of DAS decreased with increasing content of the aldehyde groups before they became amorphous at higher oxidation states. As a result, the surface of starch granules becomes wrinkled, and the granules of DAS with higher content of the aldehyde groups are conglomerated closely. The DASs have poor stability as compared to native starch. With the increase in content of the aldehyde groups, the thermal stability of DAS declines gradually, and the gelatinization temperature (T_o and T_p) increased. The presence of aldehyde groups causes hemiacetal linkages, which contributes to the increasing of gelatinization temperature of DAS.

Acknowledgements

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