EFFECTS OF CARBOXYMETHYLATION AND HYDROXYPROPYLATION ON PROPERTIES AND STRUCTURE OF DIFFERENT STARCHES

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The effect of carboxymethylation and hydroxypropylation on the properties and structures of potato starch (PS), tapioca starch (TS), sweet potato starch (SPS), pea starch (Ps), waxy corn starch (WCS) and corn starch (CS) was investigated to produce carboxymethyl starch and hydroxypropyl starch, utilize them properly. The results showed that the increase in swelling capacity of different starches caused by carboxymethylation was greater than that caused by hydroxypropylation. The Blue Values of different starches were less influenced by hydroxypropylation, and significantly more affected by carboxymethylation. The starches were affected differently by carboxymethylation, while PS, TS, Ps and CS had the same behavior after hydroxypropylation. Hydroxypropylation increased the average diameter of PS, SPS, Ps and WCS, but lowered the average diameter of TS and CS. Carboxymethylation altered the crystalline structure of WCS and CS. Hydroxypropylation only changed the crystalline structure of PS. Carboxymethylation led to an increase in the thermal stability of different starches, while hydroxypropylation caused reduction in the thermal stability of starches.

Keywords: starch, carboxymethylation, hydroxypropylation, property, structure

INTRODUCTION

Starch is usually obtained from different plants, such as cereals, potatoes, beans, *etc*.[1] It is not only an important part of the human diet, but also a good additive for improving the quality and structure of foods and non-foods.[2] Starch usually contains 85-90% polysaccharides (amylose and amylopectin), 10-15% moisture and trace non-carbohydrate components.[3] The ratio of amylose to amylopectin in starch depends on the starch source.[4-5] Starches from different sources have a diversity of properties and applications due to the variation in composition and structure. For example, potato starch typically isolated from potatoes has a low pasting temperature, and exhibits high viscosity, easy expansion and high paste clarity; also, it contains a certain number of phosphorous groups. Its crystalline structure belongs to a B-type.[6-7] Tapioca starch is obtained from cassava root processing. Unlike potato starch, it exhibits high stickiness, poor flowability, undesirable gel characteristics.[8-9] Its crystalline structure belongs to an A-type.[10] However, due to its low price, it is commonly used in a wide range of applications, including both foods and non-foods. Pea starch is different from potato starch, tapioca starch, sweet potato starch and corn starch. Due to the high contents of amylose in pea starch, its gelatinization temperature and retrogradation are generally higher than those of the above-mentioned starches,[11-12] but its crystalline structure is a C-type.[13] As a result, pea starch is often mixed with other starches as an auxiliary material to improve the quality of related products. In addition, waxy corn starch is almost entirely amylopectin (free of amylose).[14] Consequently, its properties are very different from those of other starches.

However, native starch exhibits some disadvantages, including low solubility, high viscosity, poor freeze-thaw stability, bad shearing resistance, and so on, which prevents it from being widely used.[15-17] Therefore, it needs to be modified to meet the requirements for specific applications. At present, the modifications of starch include cross-linking,[18] oxidation,[19] esterification,[20] etherification,[21] enzymatic hydrolysis,[22] acidolysis [23] and combinations of these modification processes.[24-25] Among these

modifications, carboxymethylation and hydroxypropylation, which belong under etherification, are often used for the modification of starch. Carboxymethylation can enhance the hydrophilicity, solubility in cold water, transparency and compressibility of starch.[26-27] Carboxymethyl starch is applied in many fields, such as sizing and printing agents in textiles, and excipients in pharmaceuticals.[28] Hydroxypropylation is an important modification method that reduces the retrogradation tendency of starch pastes and gels, and increases the freeze-thaw stability, acid and alkaline resistance of starch.[29]

In this work, six different starches (potato starch, tapioca starch, sweet potato starch, pea starch, waxy corn starch and corn starch) were selected for carboxymethylation and hydroxypropylation, to explore the mechanisms and effects of these modification processes on their properties. Therefore, the physical and chemical properties, and structural variations of these starches and their derivatives were systematically compared.

EXPERIMENTAL

Materials

Potato starch was purchased from Hulunbeier Hesheng Potato Development Co., Ltd. Potato Refined Starch Factory, tapioca starch – from Vietnam Desu Cassava Starch Factory, sweet potato starch – from Lulong County Yidayuan Starch Co., Ltd., pea starch – from Yantai Oriental Protein Technology Co., Ltd., waxy corn starch – from Changchun Dacheng Corn Development Co., Ltd., and corn starch – from Liaoning Ningguan Starch Factory. Anhydrous sodium sulfate and sodium hydroxide were received from Shenyang Huizhong Physical and Chemical Product Factory. Epoxy propane and chloroacetic acid were purchased from Tianjin Damao Chemical Reagent Factory and from Shenyang Economic and Technological Development Zone Reagent Factory, respectively.

Methods

Carboxymethylation of starches

The mass of all dry starch samples was the same. All the starches were subjected to the procedures described below separately. 30 g of dry starch and 13.26 g of NaOH were mixed with 150 mL of 85% (w/w) ethanol solution in a 250 mL three-necked flask. The mixture was stirred well and heated to 35 °C. The starch was alkalized at this temperature for 90 minutes. After that, 17.16 g of chloroacetic acid was added into the mixture, etherification was carried out for 4 h at 50 °C. At the conclusion of the reaction, the mixture was filtered in vacuum. The obtained cake was mixed with 100 mL of 80% (w/w) ethanol. The pH of the suspension was adjusted to neutral with 2 mol/L hydrochloric acid solution. The mixture was filtered again. The obtained cake was washed with 80% (w/w) ethanol until the filtrate was free of chloride ions. After that, a series of operations, such as drying, crushing and sieving, were performed to obtain carboxymethyl starch powder.[30]

The moisture contents of potato starch (PS), tapioca starch (TS), sweet potato starch (SPS), pea starch (Ps), waxy corn starch (WCS) and corn starch (CS) were 14.1%, 11.2%, 10.0%, 12.2%, 10.8% and 13.5%, respectively. The moisture contents of carboxymethyl potato starch (CPS), carboxymethyl tapioca starch (CTS), carboxymethyl sweet potato starch (CSPS), carboxymethyl pea starch (CPs), carboxymethyl waxy corn starch (CWCS) and carboxymethyl corn starch (CCS) were 10.1%, 6.0%, 7.6%, 7.7%, 7.9% and 5.6%, respectively.

Hydroxypropylation of starches

A 36% (w/w) slurry was prepared by blending 30 g of dry starch with 53.3 g of distilled water in a 250 mL three-necked flask, equipped with a reflux device and a stirrer, and heated to 45 °C in a water bath. 3 g of anhydrous sodium sulfate was added into the slurry. After stirring for 10 minutes, 0.3 g of sodium hydroxide was slowly added into the slurry. The alkalization was conducted for 30 minutes. Then, 3.6 g of propylene oxide was quickly added into the slurry. The hydroxypropylation was carried out for 12 h. At the conclusion of reaction, the pH of the slurry was neutralized with 2 mol/L dilute hydrochloric acid. The operations, such as filtering, washing, drying, crushing and sieving were implemented to obtain hydroxypropyl starch powder.[31] The moisture contents of hydroxypropyl potato starch (HPS), hydroxypropyl tapioca starch (HTS), hydroxypropyl sweet potato starch (HSPS), hydroxypropyl pea starch (HPs), hydroxypropyl waxy corn starch (HWCS) and hydroxypropyl corn starch (HCS) were 8.5%, 7.1%, 8.6%, 9.0%, 11.6% and 8.5%, respectively.

Degree of substitution of carboxymethyl groups

The degree of substitution (DS) of carboxymethyl groups was determined by the acid-base titration method, and the corresponding formula of DS was as follows:[32]

$$w = \frac{(C_1V_1 - C_0V_0)}{m} \times 0.059 \times 100\% \quad (1)$$

$$DS = \frac{162w}{5900 - 58w} \quad (2)$$

where w is the content of carboxymethyl groups (%), m is the mass of sample (g), V_0 and C_0 are the volume of NaOH solution consumed (mL) and the concentration of NaOH solution (mol/L), respectively; V_1 and C_1 are the volume of HCl solution consumed

(mL) and the concentration of HCl solution (mol/L), respectively.

Degree of substitution of hydroxypropyl groups

The degree of substitution of hydroxypropyl groups was evaluated by molar substitution (MS). The molar substitution (MS) of samples was determined by the spectrophotometric method.[33] 0.08 g of the samples weighed accurately was blended with 25 mL of 0.5 mol/L sulfuric acid in a 100 mL volumetric flask. The dispersion was heated in the boiling water bath until it became transparent, then cooled to room temperature and diluted to 100 mL with distilled water. 1 mL of the solution was pipetted and mixed with 8 mL of concentrated sulphuric acid in a 25 mL graduated test tube. After shaking fully, the tube was heated in a boiling water bath for 3 min, and then instantly cooled to 5 °C in an ice water bath. 0.5 mL of ninhydrin was added into the tube. Next, the tube was immediately shaken well and placed in a constant temperature water bath of 25 °C for 100 min. After that, a certain amount of concentrated sulphuric acid was added to the total volume of 25 mL, thoroughly mixed and then allowed to stand still for 5 min. The absorbance was measured by a WFJ 7200 type spectrophotometer (Unico Instrument Co., Ltd., China) at the wavelength of 595 nm. The starch blank was used as the reference. The standard curve was drawn with propylene glycol. The regression equation of the standard curve and the molar substitution degree of hydroxypropyl groups were calculated as follows:

Absorbance = -0.0194 + 0.00812 × propylene glycol concentration (μg/mL) (3)

$$H = F\left(\frac{M_{sample}}{W_{sample}} - \frac{M_{blank}}{w_{blank}}\right) \times 0.7763 \times 100 \quad (4)$$

$$MS = \frac{2.79H}{100 - H} \quad (5)$$

where H is the content of hydroxypropyl groups, MS is the molar substitution degree of hydroxypropyl groups, F is the dilution multiple of samples (F=100), M_{sample} is the propylene glycol content of samples obtained from the standard curve (g), W_{sample} is the mass of samples (g), M_{blank} is the propylene glycol content of the blank samples obtained from the standard curve (g), W_{blank} is the mass of the blank samples (g).

Swelling power and Blue Value

The swelling power of the samples was determined at a concentration of 4% (w/w) and calculated according to the following equations:[34]

$$S = \frac{A}{W} \times 100 \quad (6)$$

$$\text{Swelling power}(\%) = \frac{P \times 100}{m(100 - S)} \quad (7)$$

where A is the mass of dried residue of the supernatant (g), P is the mass of the sediment paste (g), S is the solubility (%), m is the mass of dry samples (g).

The Blue Value is a measure of amylose content in starch. During the measurement of Blue Value, the concentration of samples was chosen to be 0.5 mg/mL and the corresponding calculation formula was as follows:[35]

$$\text{Blue value} = \frac{4 \times \text{absorbance}}{10 \times \text{sample}} \quad (8)$$

where C is the concentration of the sample (mg/L).

Pasting characteristics and size distribution

The gelatinization characteristics of the samples were determined using an MCR102 rheometer (Anton Paar, Austria). The sample was first kept at 50 °C for 1 min, heated from 50 °C to 95 °C at 6 °C/min and kept at 95 °C for 5 min, then cooled from 95 °C to 50 °C at 6 °C/min and held at 50 °C for 2 min. The initial speed of the test was 960 rpm for the first 10 seconds, followed by 160 rpm for the remainder of the test.[36] The mass concentration of the samples was 6.0% (w/w).

The size distribution of the samples was determined by a Mastersizer 3000 (Malvern Panalytical Ltd., UK). The refractive index of the samples was selected as 1.52. The dispersion medium was compressed air of 0.25 Mpa.[37]

Thermal properties

The thermal properties of the samples were recorded by a Q 50 V 20.10 Build 36 thermogravimetric analyzer (TA Instruments, US), within about 10-700 °C, at a heating rate of 10 °C/min in a nitrogen atmosphere at a flow rate of 60 mL/min.[38]

Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD)

The FTIR and XRD of samples were recorded by an IR Prestige-21 infrared spectrometer (Shimadzu Corporation, Japan), within the range of 4000-400 cm^{-1},[39] and a Bruker D8 Advance X-ray diffractometer (Bruker AXS GmbH, Germany), respectively.[40]

RESULTS AND DISCUSSION

Effect of starch types on DS and MS

The effect of starch types on DS and MS was evaluated by the consumption of chemical reagents under the same other reaction conditions for a reaction, DS of 0.2 for carboxymethyl starches and MS of 0.15 for hydroxypropyl starches. The corresponding results are shown in Table 1. Sodium hydroxide dosage, chloroacetic acid dosage and epoxy propane dosage were defined as the mass percentage ratio of sodium hydroxide, chloroacetic acid and epoxy propane to dry starch. The effect of the type of starch on DS was shown in Table 1. As can be noted from Table 1, when the DS of different carboxymethyl starches was 0.2, their required dosages of sodium

hydroxide and chloroacetic acid were completely different from each other. The carboxymethylation of PS consumed the largest amount of sodium hydroxide and chloroacetic acid, while the carboxymethylation of WCS consumed the smallest amount of sodium hydroxide and chloroacetic acid. It suggested that the reaction activity of various starches was different from each other during carboxymethylation. It should relate to the structure, the ratio of amylose to amylopectin and the impurities in starch. However, when the MS of various hydroxypropyl starches was 0.15, the epoxy propane dosage consumed by the hydroxypropylation of SPS and WCS was different from that consumed by the hydroxypropylation of other starches. The hydroxypropylation of WCS consumed the largest amount of epoxy propane to reach the MS of 0.15. Obviously, the result of hydroxypropylation was not in accordance with that of carboxymethylation.

Effect of carboxymethylation and hydroxypropylation on swelling power and Blue Value of various starches

The effect of carboxymethylation and hydroxypropylation on the swelling power and Blue Value of various starches was investigated and the results are shown in Table 2. The DS of carboxymethyl starches was 0.2, and the MS of hydroxypropyl starches was 0.15. The swelling power of starch was related to its amylopectin contents and structures. High amylopectin contents usually lead to high swelling power. The strong structure of particles could restrain their expansion. As can be seen in Table 2, the swelling power of various starches and their derivatives increased with increasing temperature. The swelling power of tapioca starch at 80 °C was the highest among the starches, while at 70 °C the swelling power of potato starch was the highest. The swelling power of pea starch was the smallest among starches both at 70 °C and at 80 °C. After carboxymethylation and hydroxypropylation of the starches, the swelling power of different carboxymethyl starches and hydroxypropyl starches increased evidently, compared with the corresponding initial starch, but the increase in swelling power caused by carboxymethylation was more pronounced than that caused by hydroxypropylation. The ability of carboxymethylation and hydroxypropylation to improve the swelling of starch granules is well established.[41-42] Interestingly, the swelling power values of different carboxymethyl starches were similar, while those of different hydroxypropyl starches were quite different. Among hydroxypropyl starches, the influence of hydroxypropylation on the swelling power of tapioca starch at 60 °C was higher than that of other native starches. Finally, the sequence of the swelling power of hydroxypropyl starches at 70 °C and 80 °C could be presented as follows: hydroxypropyl tapioca starch > hydroxypropyl pea starch > hydroxypropyl potato starch > hydroxypropyl sweet potato starch > hydroxypropyl waxy corn starch > hydroxypropyl waxy corn starch. The formation of the helical complex between amylose and iodine results in a blue color. Accordingly, the amylose contents can be qualitatively determined. The higher the Blue Value, the higher the amylose contents were.

Table 1
Effect of starch type on DS and MS

Type of starch	Sodium hydroxide dosage, %	Chloroacetic acid dosage, %	Epoxy propane dosage, %
PS	44.2	57.2	12
TS	43.4	52.7	12
SPS	42.5	54.1	13
Ps	38.9	46.4	12
WCS	37.4	40.7	14
CS	40.8	44.2	12

Table 2
Effects of carboxymethylation and hydroxypropylation on swelling power and Blue Value of various starches

Samples	Swelling power, %			Blue Value
	60 °C	70 °C	80 °C	
PS	4.3	10.8	11.9	0.336
TS	4.3	10.2	12.8	0.304
SPS	2.3	5.6	8.8	0.360
Ps	2.7	4.9	8.3	0.472
WCS	2.2	7.2	10.9	0.088
CS	1.9	6.6	8.6	0.376
CPS	15.4	15.7	16.9	0.320
CTS	14.5	15.7	16.7	0.280
CSPS	14.1	15.9	18.6	0.344
CPs	13.6	15.0	15.8	0.448
CWCS	14.9	15.1	16.5	0.056
CCS	14.7	16.0	16.6	0.352
HPS	10.1	11.4	14.6	0.320
HTS	13.7	14.3	15.9	0.282
HSPS	4.9	8.8	11.7	0.328
HPs	7.3	12.2	14.9	0.448
HWCS	5.3	7.4	9.1	0.032
HCS	7.0	8.4	10.9	0.353

From Table 2, the sequence of Blue Values of native starches was as follows: pea starch > corn starch > sweet potato starch > potato starch > tapioca starch > waxy corn starch. It confirms that the amylose contents of pea starch were the highest among these native starches. The amylose content of tapioca starch was also lower than that of other native starches, other than waxy corn starch. This result was in accordance with that of the swelling power. Of course, according to the Blue Value, waxy corn starch was almost free of amylose. Hydroxypropylation had little effect on the Blue Value of different starches, while carboxymethylation had a great effect on it. This suggested that the carboxymethylation was chiefly achieved on amylose, while hydroxypropylation was mainly completed on amylopectin.

Effect of carboxymethylation and hydroxypropylation on pasting properties of various starches

The effect of carboxymethylation and hydroxypropylation on the gelatinization properties of various starches was examined and the obtained results are listed in Table 3. According to Table 3, the pasting temperature of CS was the highest among these native starches, while the pasting temperature of PS was the lowest. The peak viscosity, trough viscosity, breakdown and final viscosity of PS were greater than those of other native starches. The breakdown of Ps and the setback of WCS were the smallest among these native starches. It suggested that Ps had strong shear resistance, and WCS had poor retrogradation, compared with other native starches. The carboxymethylation reduced the peak viscosity, trough viscosity, final viscosity, breakdown and setback of carboxymethyl starches, except for the breakdown of CPs. The hydroxypropylation decreased the peak viscosity of HPS and HPs, but enhanced the peak viscosity of HTS, HSPS, HWCS and HCS. The hydroxypropylation could weaken the retrogradation of PS, TS, SPS, Ps and WCS, but increase the retrogradation of CS. The result was similar to that reported previously.[43] The hydroxypropylation could improve the shear resistance of PS, but decrease the shear resistance of TS, SPS, Ps, WCS and CS. Obviously, the effect of hydroxypropylation on the gelatinization properties of various starches was different from that of carboxymethylation. Also, the hydroxypropylation had a different effect on the pasting characteristic parameters of various starches.

Table 3
Effect of carboxymethylation and hydroxypropylation on pasting properties of various starches

Samples	PT, °C	PV, cP	TV, cP	FV, cP	BD, cP	SB, cP
PS	65.9	2579.0	1016.0	1656.0	1563.0	640.0
TS	66.1	1932.0	724.9	1429.0	1207.0	704.1
SPS	72.5	1496.0	995.1	1645	500.8	649.9
Ps	69.1	501.6	499.2	761.1	2.4	261.9
WCS	69.5	417.0	137.3	208.5	279.7	71.2
CS	74.2	1004.0	744.3	1186.0	259.9	441.7
CPS	-	1118.0	541.5	840.1	576.6	298.6
CTS	-	810.2	429.2	636.7	381.0	207.5
CSPS	-	656.5	407.9	589.0	248.6	181.1
CPs	-	300.9	248.6	403.8	52.3	155.2
CWCS	-	183.1	111.0	178.3	72.1	67.3
CCS	-	289.9	173.8	266.3	116.1	92.5
HPS	61.3	999.0	877.9	1383.0	133.5	505.1
HTS	59.2	2211.0	863.1	1349.0	1348.0	485.9
HSPS	66.2	1584.0	756.9	1155.0	827.0	398.1
HPs	64.5	189.7	148.2	253.8	41.5	105.6
HWCS	64.9	441.9	86.3	141.5	355.6	55.2
HCS	65.7	1009.0	500.8	1360.0	508.2	859.2

Note: pasting temperature (PT), peak viscosity (PV), trough viscosity (TV), breakdown (BD=PV-TV), final viscosity (FV), and setback (SB=FV-TV)

Effect of carboxymethylation and hydroxypropylation on size distribution of various starches

The effect of carboxymethylation and hydroxypropylation on the size distribution of various starches is shown in Table 4. According to the data, the particle size distributions of CS, PS, TS and SPS were narrow, while those of Ps and WCS were wider. TS, SPS and CS had more small particles than the other starches, while Ps and WCS had more large particles. The sequence of Dv (10) was the following: PS > Ps > WCS > CS > TS > SPS. The sequence of Dv (50) was: WCS > PS > Ps > SPS > TS > CS. The sequence of Dv (90) was: WCS > Ps > PS > SPS > TS > CS. After carboxymethylation of various starches, the Dv (10), Dv (50) and Dv (90) of CTS and CPs decreased, while the Dv (10), Dv (50) and Dv (90) of CPS, CSPS, CWCS and CCS increased. The variation in Dv (10), Dv (50) and Dv (90) of CCS was much greater than that of other carboxymethyl starches. The carboxymethylation could reduce the particle size of TS and Ps, but increased the particle size of PS, SPS, WCS and CS. After hydroxypropylation of various starches, the Dv (10), Dv (50) and Dv (90) of HPS, HSPS and HPs enhanced, but the Dv (10), Dv (50) and Dv (90) of HTS and HCS lowered. The Dv (10) and Dv (50) of HWCS decreased, while its Dv (90) rose. The variation in Dv (90) of HPS was much greater than that of other hydroxypropyl starches. Also, the variation in Dv (90) of HWCS, HPS and HPs was greater than their change in Dv (10) and Dv (50). This suggested that the hydroxypropylation was mainly achieved on the large particles of WCS, PS and Ps. Obviously, the effect of carboxymethylation on the particle size of various starches was different from that of hydroxypropylation. Moreover, the carboxymethylation and hydroxypropylation had different effects on the particle size of various starches. Both processes decreased the average diameter of TS, but increased the average diameter of PS, SPS and WCS. The hydroxypropylation increased the average diameter of Ps, whereas the carboxymethylation lowered the average diameter of Ps. The carboxymethylation enhanced the average diameter of CS, while the hydroxypropylation reduced the average diameter of CS. The increase in the average diameter of starch caused by carboxymethylation was consistent with the findings reported in the literature.[44]

Table 4
Effect of carboxymethylation and hydroxypropylation on size distribution of various starches

Samples	D[4,3], μm	Dv(10), μm	Dv(50), μm	Dv(90), μm
PS	36.6	22.0	34.8	54.0
TS	16.9	9.1	15.8	26.5
SPS	18.2	9.0	17.1	29.3
Ps	44.1	16.9	33.0	86.5
WCS	50.9	12.2	39.1	104.0
CS	16.7	9.3	15.6	25.7
CPS	38.9	23.3	36.8	57.6
CTS	14.5	8.0	13.9	22.5
CSPS	20.3	9.4	18.7	33.9
CPs	30.0	16.3	27.7	47.6
CWCS	129.0	16.6	84.9	310.0
CCS	148.0	34.1	116.0	309.0
HPS	86.3	24.7	49.8	213.0
HTS	14.2	7.8	13.7	22.0
HSPS	19.0	9.3	17.8	30.8
HPs	62.8	17.2	33.8	151.0
HWCS	54.1	8.1	16.2	174.0
HCS	15.5	9.2	14.7	23.1

Note: Dx (10), Dx (50) and Dx (90) represent the average particle diameters at cumulative volume fraction of 10%, 50%, 90%, respectively. D[4,3] represents the mean diameter of volume

Fourier transform infrared spectroscopy (FTIR) of carboxymethyl starches and hydroxypropyl starches

FTIR spectra of carboxymethyl starches and hydroxypropyl starches are shown in Figure 1. As may be noted, the spectra of different starches look similar, except for the absorption peak intensity. In the FTIR spectrum of CS and SPS, the peak intensity of –OH groups at 3380 cm^{-1} is obviously stronger than that of other starches. The peaks of –OH groups of the PS and Ps are wider and flatter than those of other starches. It might relate to the structure of starch particles. The stretching vibration peak at 2931 cm^{-1} belongs to C-H bonds. The absorption peaks at 1160 cm^{-1}, 1082 cm^{-1}, 1004 cm^{-1} were assigned to the asymmetric stretching vibrations of C-O-C, C-O and C-C bonds. After carboxymethylation of various starches, a new peak at about 1740 cm^{-1} appeared on the FTIR spectra of all carboxymethyl starches, and was assigned to the stretching vibration of C=O bonds. It confirmed that the carboxyl groups have been successfully introduced into the molecular chains of starches. This result is consistent with that reported previously.[45] After the hydroxypropylation of various starches, no new peaks appeared in the FTIR spectra of all hydroxypropyl starches. In addition, after the carboxymethylation and hydroxypropylation of starches, the absorption peaks of C-O-C, C-O and C-C bonds also did not change. It indicates that the carboxymethylation and hydroxypropylation did not destroy the backbone of glucose units.

XRD analysis

The XRD patterns of carboxymethyl starches and hydroxypropyl starches are shown in Figure 2. The X-ray diffraction pattern reflects the "fingerprint" of the crystalline structure of starches. The hydrogen bonds were responsible for the formation of the crystalline structure of starch molecules and kept the stability of the crystal structure. As noted in Figure 2, the diffraction peaks of PS appeared at diffraction angles of 11.4°, 15.1°, 17.1°, 19.6°, 22.3°, 24. 0°, 26.4°, 31.6° and 34°, respectively, indicating that the crystalline structure of PS was a B-type. This result was consistent with that reported earlier.[46] After the carboxymethylation and hydroxypropylation of PS, the diffraction peaks of CPS only appeared at 15.1°, 17.1°, 19.6°, 22.3° and 24.0°, respectively, while the diffraction peaks of HPS were only at 15.1°, 17.3°, 19.8°, 23.1°, 31.9° and 34.2°, respectively. It indicated that the crystalline structure of CPS was still a B-type, while the crystalline structure of HPS was a C-type.

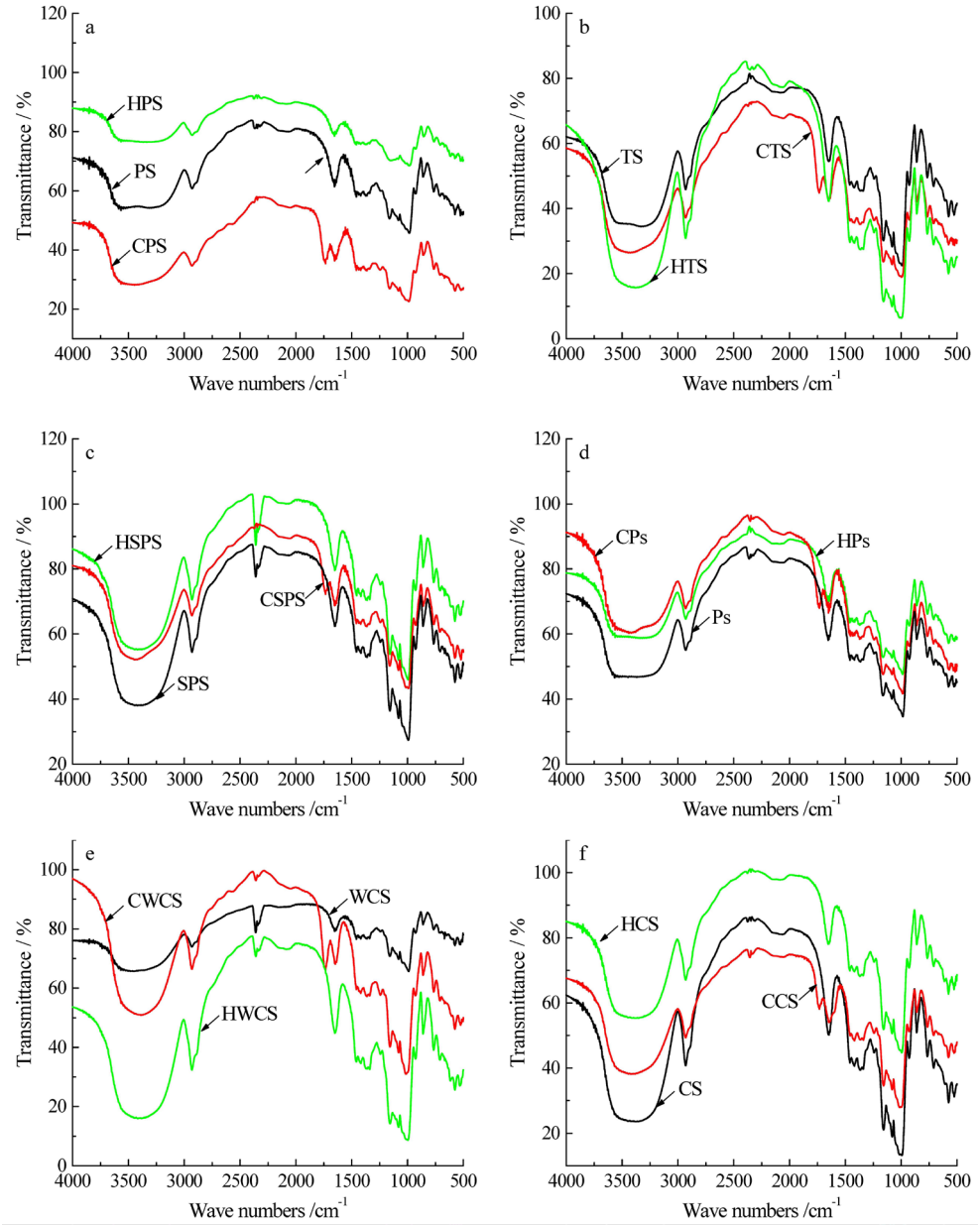

Figure 1: FTIR spectra of native starches, carboxymethyl starches and hydroxypropyl starches
(a: PS and its derivatives, b: TS and its derivatives, c: SPS and its derivatives, d: Ps and its derivatives, e: WCS and its derivatives, f: CS and its derivatives)

The diffraction peaks of TS, HTS and CTS appeared at diffraction angles of 11.4°, 15.3°, 17.1°, 18.0°, 23.1°, 26.7°, 30.6 ° and 33.6°, respectively, indicating that the crystalline structure of TS, HTS and CTS was a A-type. The carboxymethylation and hydroxypropylation did not change the crystalline structure type of TS. The result was consistent with that reported previously, when the substitution degree was low.[47-48]

The diffraction peaks of SPS appeared at diffraction angles of 11.3°, 15.1°, 17.3°, 23.1°, 26.3°, 30.4°, 33.7° and 38.2°, separately, indicating that the crystalline structure of SPS was a C-type. The diffraction peaks of HSPS appeared at diffraction angles of 11.3°, 15.1°, 17.3°, 23.1°, 31.9°, 33.7° and 38.2°, respectively. The diffraction peaks of CSPS appeared at diffraction angles of 11.3°, 15.1°, 17.3°, 23.1° and 26.3°, respectively. It indicated that the basic diffraction peaks of HSPS and CSPS were not changed, except for the peak intensity, confirming that the carboxymethylation and hydroxypropylation did not change the structure

type of SPS.

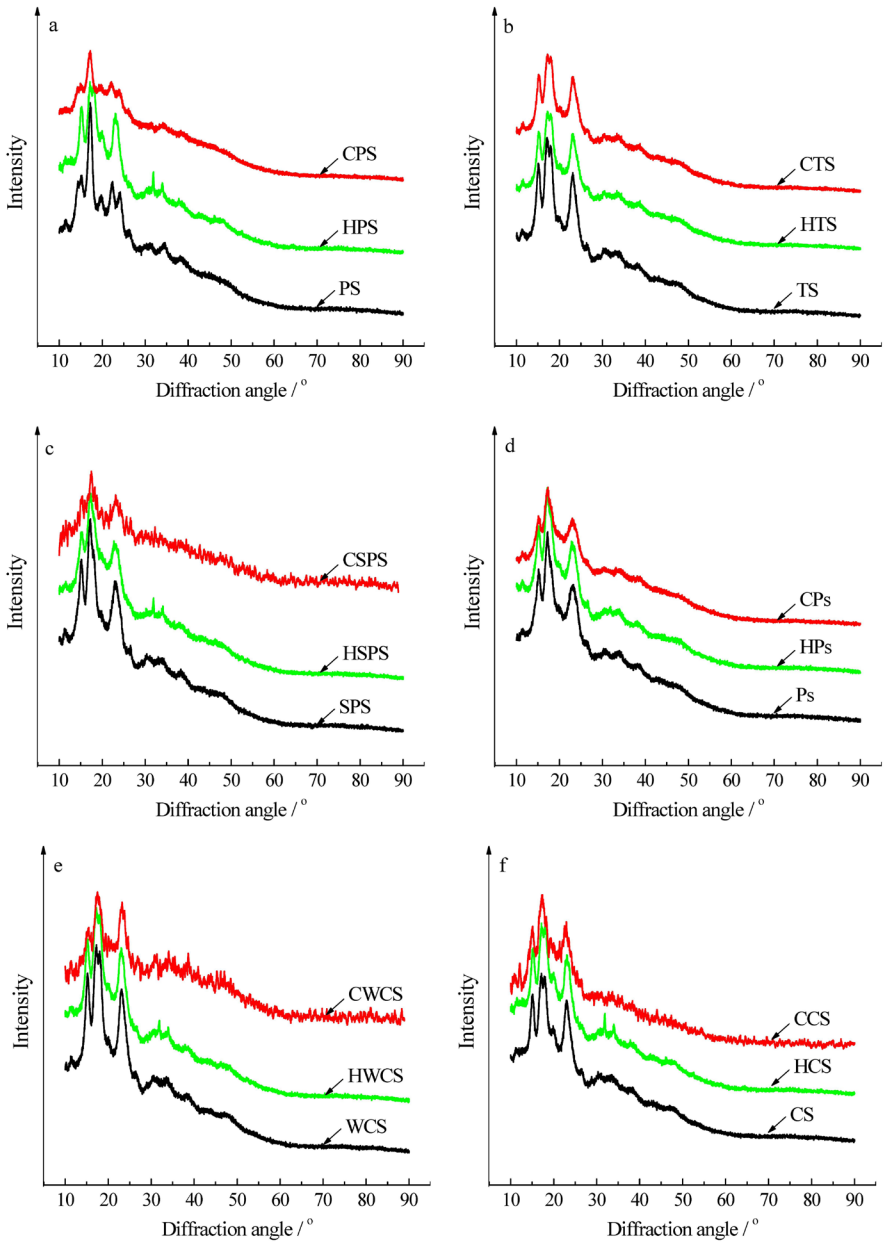

Figure 2: X-ray diffractograms of native starches, carboxymethyl starches and hydroxypropyl starches (a: PS and its derivatives, b: TS and its derivatives, c: SPS and its derivatives, d: Ps and its derivatives, e: WCS and its derivatives, f: CS and its derivatives)

The diffraction peaks of Ps appeared at diffraction angles of 11.4°, 15.3°, 17.3°, 23.1°, 26.3°, 30.6°, 33.9°, 39.5°, separately, indicating that the crystalline structure of Ps was still a C-type. After the carboxymethylation and hydroxypropylation of Ps, the characteristic diffraction peaks of HPs and CPs did not change, but their secondary diffraction peaks changed. It indicated that the carboxymethylation and hydroxypropylation also did not change the structure type of Ps.

The diffraction peaks of WCS appeared at diffraction angles of 11.4°, 15.1°, 17.1°, 18.0°, 23.1°, 26.2° and 30.8°, indicating that the crystalline structure of WCS was an A-type. The diffraction peaks of HWCS appeared at diffraction angles of 11.4°, 15.1°, 17.1°, 18.0°, 23.1°, 31.9° and 34.0°. The characteristic peaks of HWCS were the same as those of WCS, except for the different peak intensity, indicating that the hydroxypropylation did not influence the crystalline structure type of WCS. However, after

the carboxymethylation of WCS, the diffraction peaks of CWCS appeared at diffraction angles of 11.4°, 15.2°, 17.5°, 23.2°, 31.1°, 34.3° and 38.7°, respectively. Obviously, the crystalline structure of CWCS belonged to a C-type, that is, the carboxymethylation changed the crystalline structure type of WCS. Of course, both carboxymethylation and hydroxypropylation weakened the intensity of diffraction peaks of WCS.

The diffraction peaks of CS appeared at diffraction angles of 11.4°, 15.1°, 17.0°, 18.0°, 23.0°, 26.6°, 30.6° and 33.4°, indicating that the crystalline structure of CS was an A-type, which was same as that of WCS. The diffraction peaks of HCS appeared at diffraction angles of 11.4°, 15.1°, 17.0°, 18.0°, 19.9°, 31.7° and 34.2°. Except for the diffraction angles of 19.9°, 31.7° and 34.2°, the positions of the remaining peaks of HCS were the same as those of CS. The hydroxypropylation also did not influence the crystalline structure type of CS. However, the diffraction peaks of CCS only appeared at diffraction angles of 10.9°, 12.0°, 15.1°, 17.3° and 23.2°, respectively, while other peaks disappeared. The crystalline structure of CCS belonged to a C-type.

In a word, the carboxymethylation and hydroxypropylation influenced differently the crystalline structure of starches, depending on their type.

TG analysis

The TGA curves of carboxymethyl starches and hydroxypropyl starches are shown in Figure 3. According to Figure 3, the carboxymethylation had a great influence on the TGA curves of different starches and shifted them to the left. It suggested that the initial decomposition temperature of native starches was apparently reduced by carboxymethylation. The hydroxypropylation had a small impact on the TGA curves of different starches, compared with carboxymethylation, and only slightly moved the TGA curves of PS, Ps and CS to the right. The rapid decomposition stages of carboxymethyl starches were obviously shorter and slower than those of native starches and hydroxypropyl starches. The rapid decomposition stages of hydroxypropyl starches were longer than those of native starches. It confirmed that the carboxymethylation enhanced the thermal stability of starches. This result was in accordance with other reports in the literature.[49] However, the hydroxypropylation lowered their thermal stability, and this finding was contrary to that regarding hydroxypropyl cellulose reported in the literature.[50-51] In order to accurately analyze the TGA of different starches and their derivatives, their key thermodynamic parameters were calculated according to their corresponding curves, and the results could be seen in Table 5.

Table 5
Effect of carboxymethylation and hydroxypropylation on TGA thermodynamic parameters of various starches

Samples	Onset decomposition temperature, °C	End decomposition temperature, °C	Mass loss, %
PS	312.5	341.8	46.3
TS	313.7	347.6	53.0
SPS	311.1	348.9	56.6
Ps	306.0	355.1	51.6
WCS	314.9	351.5	53.8
CS	304.7	342.6	49.0
CPS	282.2	338.2	37.0
CTS	279.8	340.1	39.1
CSPS	265.8	333.7	40.5
CPs	268.4	336.3	39.8
CWCS	281.0	331.3	22.5
CCS	258.1	338.2	34.9
HPS	308.7	361.5	65.8
HTS	307.4	355.1	62.8
HSPS	308.3	353.9	66.1
HPs	301.2	364.0	62.7
HWCS	303.6	358.9	65.9
HCS	302.2	361.5	63.8

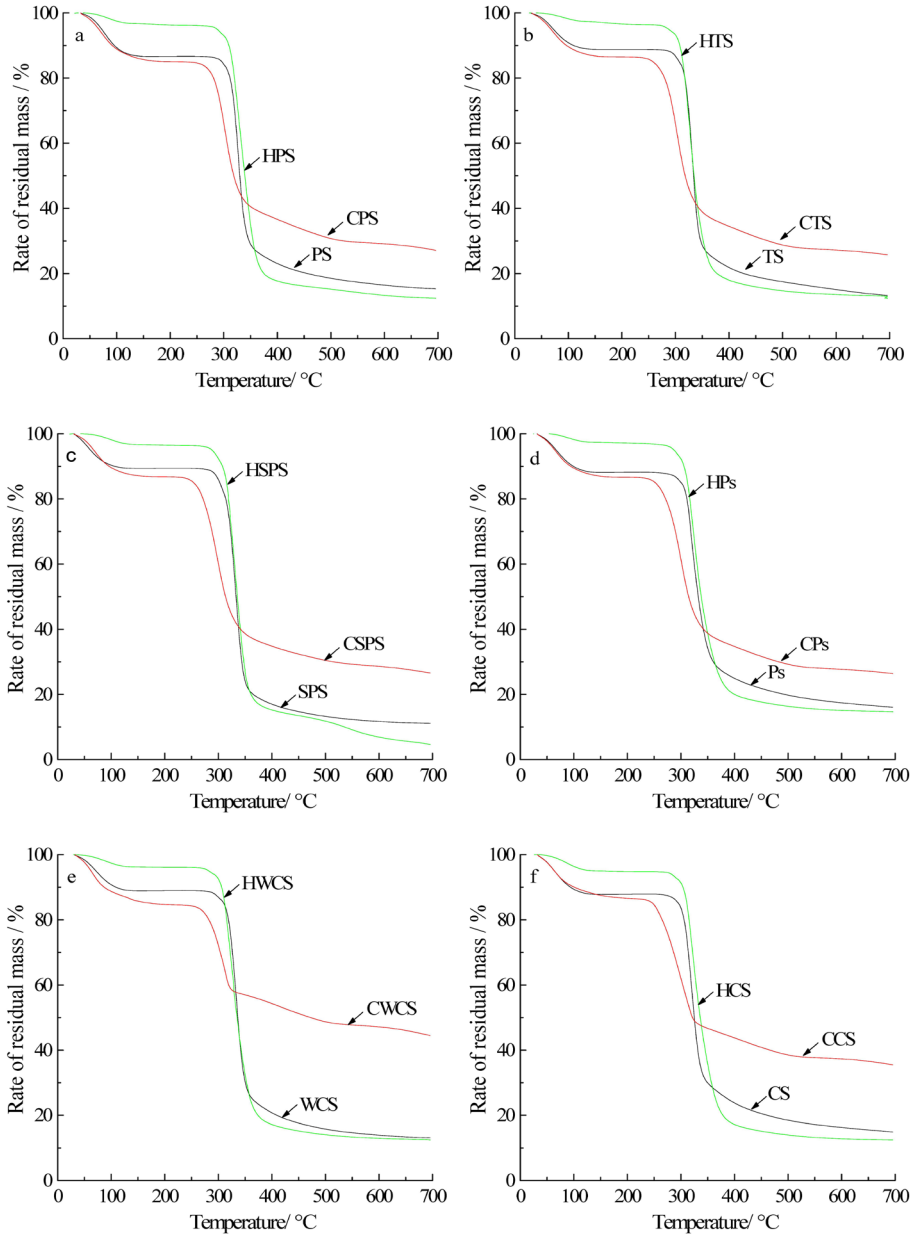

Figure 3: TGA curves of native starches, carboxymethyl starches and hydroxypropyl starches
(a: PS and its derivatives, b: TS and its derivatives, c: SPS and its derivatives, d: Ps and its derivatives, e: WCS and its derivatives, f: CS and its derivatives)

As may be noted in Table 5, the initial decomposition temperature of the starches was different. The initial decomposition temperature of WCS was the highest, while that of CS was the lowest. The sequence of onset decomposition temperature was as follows: WCS > TS > PS > SPS > Ps > CS. It should relate to the content of amylopectin, length of chains and degree of hydrogen bonding between molecular chains in starches. However, the order of the end decomposition temperature of different starches did not follow the same sequence as that of the onset decomposition temperature. Thus, according to their end decomposition temperature the starches could be ordered as follows: Ps >WCS > SPS > TS > CS > PS.

At the same time, the sequence of the mass loss rate was also not consistent with the order of the onset decomposition temperature and end decomposition temperature. The order of the mass loss rate was: SPS > WCS > TS > Ps > CS > PS, that is, the sequence of thermal stability was: SPS

< WCS< TS < Ps < CS < PS. After the hydroxypropylation of starches, their onset decomposition temperature decreased, but their end decomposition temperature and mass loss rate increased. Interestingly, the onset decomposition temperatures of HPS, HTS and HSPS were similar to each other, and the onset decomposition temperatures of HPs, HWCS and HCS were close to each other. After the carboxymethylation of starches, their onset decomposition temperatures, end decomposition temperature and mass loss rate were obviously reduced. The onset decomposition temperature of CS and end decomposition temperature of WCS were reduced the most by carboxymethylation, while the onset decomposition temperature and end decomposition temperature of PS were lowered the least by carboxymethylation. The thermal stability of WCS was increased the most by carboxymethylation, whereas the thermal stability of PS was enhanced the least by carboxymethylation. In a word, the carboxymethylation could improve the thermal stability of different starches, while the hydroxypropylation did the reverse.

CONCLUSION

Carboxymethylation influenced differently PS, TS, SPS, Ps, WCS and CS, while upon hydroxypropylation, PS, TS, Ps and CS showed the same behavior. The swelling power and Blue Value of the starches were greatly influenced by carboxymethylation, and less by hydroxypropylation. Carboxymethylation affected the gelatinization properties of various starches in a different way from that of hydroxypropylation. Hydroxypropylation could weaken the retrogradation of PS, TS, SPS, Ps and WCS, but increase the retrogradation of CS. The influence of carboxymethylation on the average diameter of PS, SPS, WCS and CS was entirely different in the case of TS and Ps. The hydroxypropylation was mainly completed on the large particles of WCS, PS and Ps. The stretching vibration of C=O bonds of carboxymethyl starches appeared at the wavenumbers of around 1740 cm^{-1}. The carboxymethylation altered the crystalline structure of WCS and CS, while the hydroxypropylation changed the crystalline structure of PS. The carboxymethylation could increase the thermal stability of starches, while the hydroxypropylation had the opposite effect on the thermal stability.

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