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ORIGINAL PAPER

Synthesis of hydroxypropylated debranched pea starch with high substitution degree in an ionic liquid, and its characterization and properties

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Abstract

Hydroxypropylation of debranched pea starch (DPS) has been carried out effectively in an ionic liquid, 1-butyl-3-methylimidazolium chloride, in order to shorten the long time required by starch being normally hydroxypropylated and improve the characteristics of pea starch (PS). As a result, hydroxypropylated debranched pea starch (HDPS) with molar substitution up to 1.34 has been obtained in homogeneous system within 3 h, which was much less than time (18 h) required by normal hydroxypropylation of starch. Based on the synthesis, HDPS was further characterized by infrared spectroscopy, X-ray diffraction, scanning electron microscopy and transflective polarizing microscope, respectively, and some of its properties were also compared with those of PS, DPS and hydroxypropylated pea starch (HPS). The experimental results indicated that the crystalline structure of PS belonged to a C-type; and one of DPS was between B-type and C-type, whereas HDPS structure was almost completely amorphous. The debranching and hydroxypropylation evidently influenced the pasting behavior and thermal properties of PS. The morphology and size of DPS and HDPS particles were remarkably different from those of PS owing to hydroxypropylation and debranching. The peak intensity of –OH groups in DPS and HDPS was evidently weakened by debranching compared with FTIR spectra of PS. The debranching resulted in the reduction in swelling power of DPS, but the hydroxypropylation led to the increase in the swelling power of DPS and HDPS.

Keywords Pea starch · Ionic liquid · Hydroxypropylation · Debranching · Structure · Property

Introduction

Starch, which consists of linear amylose (α -1, 4 glycosidic bonds) and amylopectin (α -1, 6 glycosidic bonds) which is the major macromolecular component and responsible for architecture of the starch granules [1], is one of the cheapest and most cost-effective materials. The physical chararceristics of starch such as retrogradation, viscosity, stability of viscosity and resistant digestibility are influenced by the ratio of amylose to amylopectin and its molecular structure [2, 3]. Starch from various botanical origins differs in the amylose and amylopectin content, chain length distribution and molecular weight. In the direct applications, native starch is limited since they are unstable in changes of temperature, pH and shear forces, especially lacking in functional performances [4]. Several methods, including physical, chemical and enzymatic methods, have been developed to produce the modified starch with the expected characteristics for better applications. The chemical modification, a more common method, which generally includes etherification [5], esterification [6], cross linking, oxidation [7], grafting [8] and so on, is able to lead to the significant variations in gelatinization, retrogradation, swelling power and paste properties. In the enzymatic method, the starch is often modified using α-

Highlights • Ionic liquid could effectively shorten the period of starch hydroxypropylation.
• Crystalline structure of debranched pea starch particles was between B-type and C-type,
• Hydroxypropylation seriously damaged the original structure of debranched pea starch particles.
• Intensity of –OH groups of debranched pea starch and hydroxypropylated debranched pea starch was evidently weakened by debranching.
• Hydroxypropylation of high molar substitution decreased the blue value of starch.

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amylase, β-amylase, glucoamylase and debranching enzyme including isoamylase and pullulanase, which only hydrolyze the α-l, 6-glycosidic bonds in polyglucans [9]. However, they differ in substrate specificity, that is, isoamylase selectively hydrolyzes β-dextrins, whereas pullulanase hydrolyzes pullulan [10]. The increase in debranching degree of starch would give chains more opportunity to align and aggregate to form the perfect crystalline structures, thereby obviously changes the characteristics of starch [11]. For example, debranching of starch using pullulanase is able to significantly enhance the formation and stability of V-complexes [12] Debranched starch has significantly lower viscosity and higher solubility than those of native starch, and its retrogradation increases with an increase of the degree of hydrolysis [13]. In the granular state, however, debranching will only result in a limited change in the amylopectin molecular structure of starch at subgelatinization temperature [14].

Hydroxypropylation is a type of etherification occurred at the hydroxyl groups of the starch. When hydrophilic hydroxypropyl groups are introduced into the molecular chains of starch, they weaken the internal bond structure holding the granule together and prevent water separating from the starch paste through syneresis. Although the hydroxypropylation is capable to alter the functional characteristics of starch, such as improved freeze-thaw stability, reduced gelatinization temperature, high peak viscosity and paste clarity, it has to require very long time to do so, and needs to be achieved in a heterogeneous system [15–17]. In this situation, the hydroxypropylation efficiency becomes very low. However, the appearance of ionic liquids offers a good help for improving the situation. Ionic liquids as almost nonvolatile, nonflammable, thermally stable and reusable green solvents [18] have been used in some reactions. For example, the reported maximum substitution degree of starch esters can reach 2.11, and one of cellulose esters be 2.7 in ionic liquids [19–21]. In these reactions, the main advantages of ionic liquids are effective contact of reactants, rapid reaction and high yield. Based on above information, in this work, we select ionic liquids as a solvent during starch hydroxypropylation to shorten the hydroxypropylaying time. For obtaining the modified pea starch with better properties, the combination of debranching and hydroxypropylation is used for functionality of pea starch to make up the drawbacks of the single modification; that is, the hydroxypropylated debranched pea starch (HDPS) with high degree substitution was prepared using pullulanase as a debranching agent, 1, 2-propylene oxide as an etherification agent, 1-butyl-3-methylimidazolium chloride as a solvent so that HDPS could be well applied for some of special fields. On this basis, HDPS was characterized, and its performances were also determined.

Materials and methods

Materials

Pea starch was supplied by Yantai Dongfang Protein Science and Technology Co. Ltd. (China). 1-butyl-3-methylimidazolium chloride (BMIMCl) was supplied by CAS Lanzhou Institute of Chemical Physics (China). Pullulanase (2000 U/mL) was supplied by Jining Hemei Biological Engineering Co. Ltd. Other reagents including sodium hydroxide, 1, 2-propylene oxide, potassium iodide and potassium bitartrate were analytical grade.

Preparation of debranched pea starch (DPS)

Pea starch (PS) was debranched according to the method with some modifications [22]. 30 g of PS (dry basis) and 345 g of citric acid- sodium citrate buffer solutions with pH of 4.5 were putted into a 500 mL round-bottom flask to prepare PS slurry with a concentration of 8% (*w/w*). And then starch was gelatinized at 90 °C in the water bath for 60 min. Debranching conditions: debranching temperature 55 °C, pullulanase amount 60 U/g (based on dry starch), debranching time 2 h.

Homogeneous synthesis of hydroxypropylated debranched pea starch (HDPS) in BMIMCl

10 g of 1-butyl-3-methylimidazolium chloride (BMIMCl) was placed into a 100 mL three-necked flask, and heated to 80 °C in an oil bath until it melted completely. 1 g of debranched pea starch was taken and added into ionic liquid, stirring it for completely dissolving debranched pea starch, and heating it to 90 °C. The required sodium hydroxide was added into mixtures, and stirred for 30 min. Afterwards, the required propylene oxide was rapidly added into above solutions in order to do the etherification. After the reaction, the solution was cooled to the ambient temperature. And 30 mL of absolute ethanol was added to separate the crude product. The mixture was centrifuged at 3000 rpm for 15 min, the upper clear liquid was removed. The precipitate was fully mixed with 40 mL of ethanol with a concentration of 95%. Again we centrifuged the mixture, and collected the residue, then dispersed it into absolute ethanol, and filtered it. The collected cake was dried at 50 °C for 48 h in vacuum oven. Finally, hydroxypropylated debranched pea starch was obtained [23, 24].

Determination of debranching degree, molar substitution, blue value and swelling power

We used the dextrose equivalent (DE) values to evaluate the debranching degree of RS, and a DNS (3, 5-dinitrosalicylic acid) colorimetry method to determine the reducing sugar [25]. The molar substitution (MS) of samples was measured

spectrophotometrically after they were reacted with ninhydrin to form a purple color [26]. The blue value was determined according to a previously published procedure [27]. The sample concentration of 4% was selected for determining the swelling power [28].

Determination of numbers of surface hydroxyl groups and pasting characteristics

The surface hydroxyl numbers were determined by a previously published method within the pH of 4.0–9.0 [29]. The pasting characteristics of samples whose concentration was selected as 4% (dry basis) were determined by a MCR102 rheometer (Anton Paar, Austria). The viscosity of the slurries were continuously monitored as they were heated from 50 °C to 95 °C at a rate of 6 °C, held at 95 °C for 5 min, and cooled to 50 °C at a rate of 6 °C and held at 50 °C for 2 min. The initial rotation rate of agitator in 10s was 960 rpm, and then remained at 160 rpm [30].

Infrared spectroscopy, thermal analysis, X-ray diffraction, morphology of particles and energy dispersive spectrum (EDS)

We recorded IR spectra of samples using an IR Prestige-21 infrared spectrometer (Shimadzu Corporation, Japan) within the range of 4000–400 cm^{-1} [31], and carried out the thermal analysis of samples using a TGA Q50 V20.10 Build 36 thermogravimeric analyzer and a DSC Q20 V24.4 Build 116 differential scanning calorimeter (TA Instruments, US) in a nitrogen atmosphere, respectively [32, 33]. XRD patterns were analyzed between 0 and 50° using a X'Pert Pro MPD X-ray diffractometer (PANalytical Co.,Ltd.). Crystallization degree (CD) was calculated from the statistical analysis of the area [34]. The morphology and the energy dispersive spectrum of samples were observed under a XPL-2 transflective polarizing microscope (Nanjing Jiangnan Yongxin Optics Company Limited, China) and a Hitachi S-3400 N scanning electron microscope equipped with an attached energy dispersive spectrometer (Hitachi, Ltd., Japan) [35, 36].

Results and discussion

Effect of etherification time, etherification temperature, amount of 1, 2-propylene oxide and sodium hydroxide on molar substitution of HDPS

The effect of etherification time, etherification temperature, amount of 1, 2-propylene oxide and sodium hydroxide on molar substitution (MS) of HDPS was presented in Fig. 1. The amount of 1, 2-propylene oxide or sodium hydroxide was defined as the percentage ratio of 1, 2-propylene oxide or sodium hydroxide to dry DPS. The homogeneous etherification was completed using DPS as a material, 1, 2-propylene oxide as an etherifying agent, 1-butyl-3-methylimidazolium chloride as a solvent, sodium hydroxide as a catalyst. The etherification

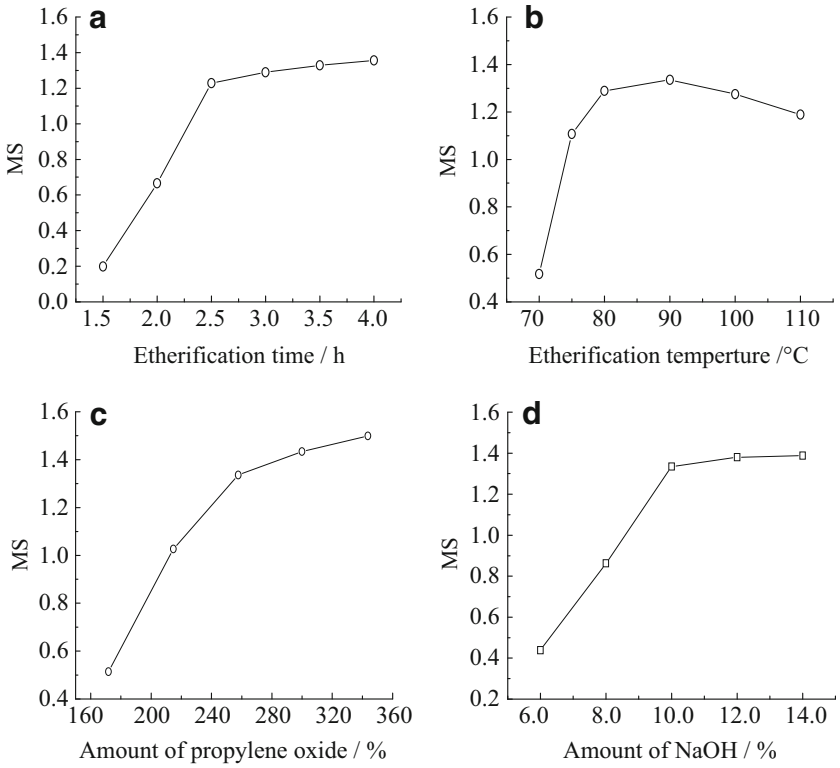


Fig. 1 Effect of etherification time (**a**), etherification temperatue (**b**), amount of propylene oxide (**c**) and sodium hydroxide (**d**) on MS of HDPS

Table 1 Effect of debranching and hydroxypropylation on blue value and swelling power of PS,DPS.HPS and HDPS

Samples	Blue value	Swelling power/ %
PS	0.504 ±0.004^{c}	15.4±0.3^{b}
DPS(DE = 0.21)	0.776±0050^{d}	7.9±0.2^{a}
HPS (MS = 1.40)	0.320±0030^{a}	26.1±0.5^{d}
HDPS(DE = 0.21,MS = 1.34)	0.406±0040^{b}	17.8±0.4^{c}

Data are means of triplicate analyses with standard deviation. Means in the same line with different superscripts were significantly different at the 5% level

time ranged from 1.5 h to 4.0 h to examine the etherification time effects (Fig. 1a). Fixed conditions for the variable of etherification time was as follows: etherification temperature 80 °C, amount of sodium hydroxide 10%, amount of propylene oxide 257.7%. When the etherification time was less than 2.5 h, the MS of HDPS increased quickly as increasing the etherification time. The increase became slow after etherification time of more than 3 h. And at the etherification time of 3 h, MS of HDPS could reach 1.29. Nevertheless, the general etherification of starch in other solvent without ionic liquid had to require at least 16 h, and MS of obtained products was very low under a certain conditions [37, 38]. It suggested that ionic liquid was able to very effectively improve the etherification of DPS, evidently shortened reaction time, and distinctly increased MS of products. Therefore, the suitable etherification time was selected as 3 h.

The etherification temperature ranged from 70 °C to 110 °C to examine the etherification temperature effects (Fig.1b). Fixed conditions for the variable of etherification temperature was as follows: etherification time 3 h, amount of sodium hydroxide 10%, amount of propylene oxide 257.7%. The MS of HDPS rose as increasing the etherification temperature when the etherification temperature was less than 90 °C. It might relate to more starch being dissolved by ionic liquid at high temperature. However, the MS of HDPS dropped off slightly with increasing the etherification temperature after the etherification temperature of more than 90 °C. Therefore, the etherification temperature of 90 °C was suitable.

The amount of 1, 2-propylene oxide ranged from 2.0 to 4.0 to examine the effects of propylene oxide amount (Fig.1c). Fixed conditions for the variable of propylene oxide amount was as follows: etherification temperature 90 °C, etherification time 3 h, amount of sodium hydroxide 10%. When the amount of propylene oxide was less than 257.7%, The MS of HDPS increased quickly with the increase in propylene oxide. The increase in MS became small after propylene oxide amount of more than 257.7%. Therefore, the amount of propylene oxide was selected as. 257.7%.

The amount of NaOH as a catalyst ranged from 6 to 14% to examine the effects of NaOH amount (Fig.1d).

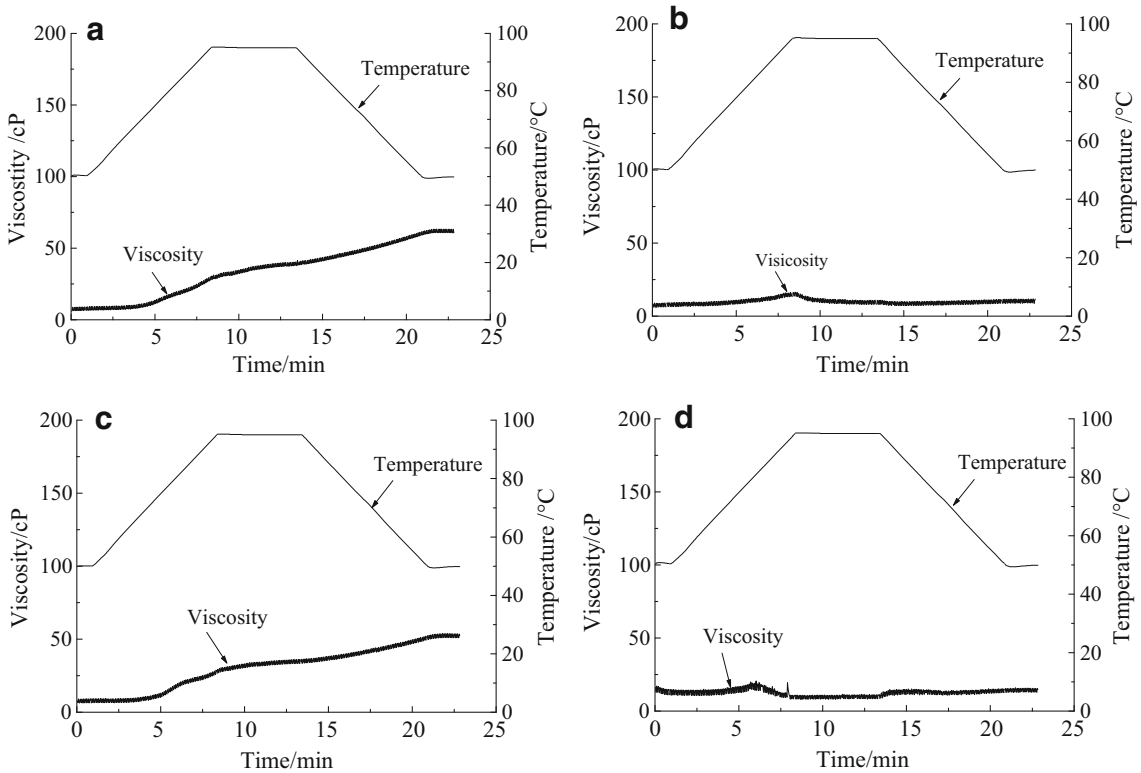


Fig. 2 Pasting characteristics of PS (**a**), DPS (**b**), HPS (**c**), and HDPS (**d**)

Table 2 Characteristic parameters of pasting properties of PS, DPS, HPS and HDPS

Samples	Pasting temperature/ °C	Peak viscosity/ cP	Trough viscosity /cP	Final viscosity/ cP	Breakdown /cP	Setback /cP
PS	70.8	40.31	37.80	60.69	2.51	22.89
DPS(DE = 0.21)	79.6	16.45	7.13	11.71	9.32	4.58
HPS(MS = 1.40)	70.0	36.24	33.48	52.34	2.76	18.86
HDPS(DE = 0.21,MS = 1.34)	73.0	20.62	8.00	14.65	12.62	6.65

Fixed conditions for the variable of NaOH amount was as follows: etherification temperature 90 °C, etherification time 3 h, amount of propylene oxide 257.7%. When the amount of sodium hydroxide was lower than 10%, the MS of HDPS increased quickly as increasing NaOH amount, while the MS of HDPS changed little after NaOH amount of higher than 10%. Therefore, NaOH amount of 10% was suitable.

Effects of debranching and hydroxypropylation on blue value and swelling power

The blue value and swelling power of pea starch (PS), debranched pea starch (DPS), hydroxypropylated pea starch (HPS) and HDPS were presented in Table 1. The blue value is used to measure the content of amylose in starch. The greater the blue value, the higher is the content of amylose. As shown in Table 1, obviously, the blue value of PS was influenced by the debranching and hydroxypropylation. The variation in the blue value caused by the debranching was more than that by the hydroxypropylation. The debranching evidently enhanced DPS blue value, whereas the hydroxypropylation reduced the blue value. It proved that the debranching was very successful, and the introduction of the hydroxypropyl groups could affect the interaction between HPS, HDPS and iodine molecules. In addition, the debranching resulted in the reduction in the swelling power of DPS, whereas the hydroxypropylation did the increase in the swelling power of the DPS and HDPS. Clearly, the effect of debranching on swelling power was different from one of hydroxypropylation.

Effect of debranching and hydroxypropylation on pasting properties

The pasting characteristics of PS, DPS, HPS and HDPS were presented in Fig. 2. The pasting characteristics of DPS, HPS and HDPS were obviously different from those of PS (Fig.2). In other words, the debranching and hydroxypropylation influenced evidently the pasting behavior of PS. The debranching distinctly lowered the viscosity of DPS. The specific characteristic parameters of pasting behavior of PS, DPS, HPS and HDPS were listed in Table 2.

As shown in Table 2, the pasting temperature of DPS was obviously higher than one of native PS due to debranching. Compared with pasting temperature of PS, the variation in pasting temperature of HPS was small. The debranching and hydroxypropylation led to reduction in the setback value, but increased the breakdown value of PS. Consequently, the breakdown value decreased in order of PS, HPS, HDPS and DPS, and the setback value increased in order of PS, HPS, DPS and HDPS. Similarly, we could draw that the final viscosity of PS and HPS was greater than their peak viscosity, whereas the final viscosity of DPS and HDPS was less than their peak viscosity.

FTIR analysis

The FTIR spectra of PS, DPS and HDPS were presented in Fig. 3. As shown in Fig.3, the FTIR spectroscopy of DPS and HDPS were distinctly different from one of PS. Compared with the –OH group peak intensity at wave number of 3428 cm^{-1} in FTIR spectra of PS,

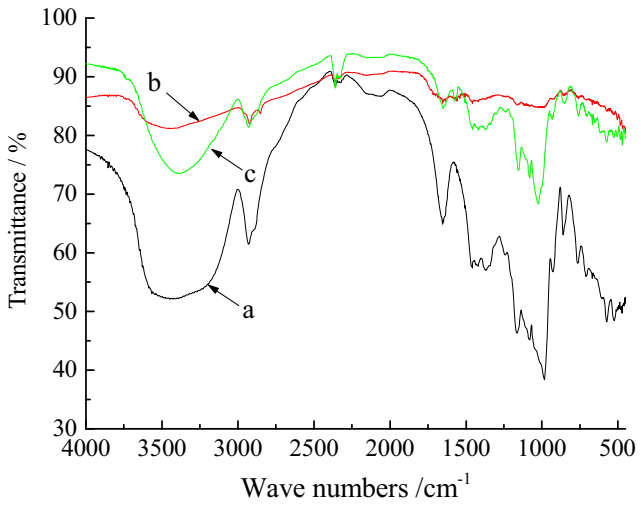


Fig. 3 FTIR spectroscopy of PS (**a**), DPS (**b**), HDPS (**c**)

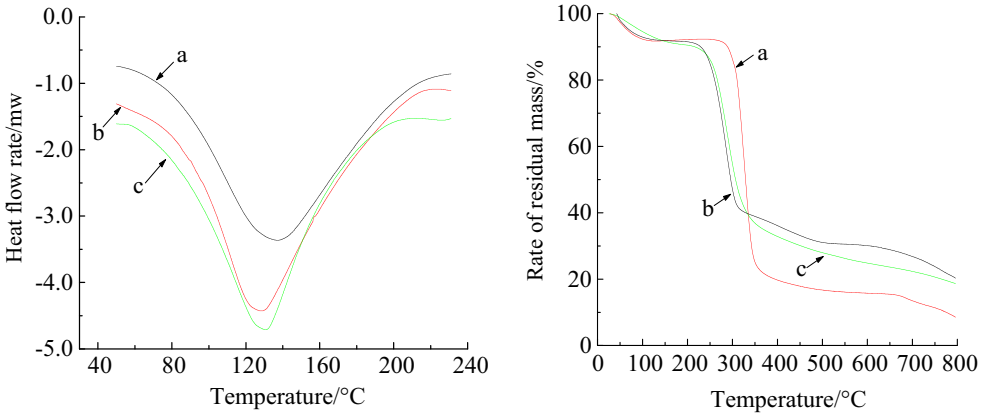


Fig. 4 The DSC (left) and TGA (right) curves of PS (**a**), DPS (**b**), HDPS (**c**)

the intensity of –OH groups of DPS and HDPS was evidently weakened by debranching. The appeared situation might be ascribed to the reduction in free –OH groups caused by the increase in hydrogen bonds between DPS molecular chains although the intensity of –OH groups of HDPS was slightly strengthened by the introduction of hydroxypropyl groups, compared with that of DPS. The intensity of peak at wave number of 2923 cm^{-1} in FTIR spectra of DPS and HDPS, which was assigned to C-H bond stretching vibration [39], was also reduced by debranching. Apparently, the increase in the linear chains in DPS and HDPS resulted in their structure being different from one of PS. The small absorption peak at the wave number of 1655 cm^{-1} in FTIR spectrum of DPS, which belonged to water molecules absorbed in the amorphous region, further proved above analyzed results. The absorption peak at wave number of 1171 cm^{-1} attributed to the stretching vibration of the C–O–C bonds [40].

Effect of debranching and hydroxypropylation on thermal properties

The DSC and TGA curves of PS, DPS (DE = 0.21) and HDPS (DE = 0.21, MS = 1.34) were showed in Fig.4. The debranching and hydroxypropylation remarkably influenced the thermal properties of PS (Fig.4). In TGA curves, the dehydration and decomposition as two separate processes could be observed clearly during the thermal degradation of samples [41]. The first step occurred below about 100 °C, which was mainly related to the free water in samples; the PS second stage in which the mass of samples dropped down dramatically started at about 290 °C, and ended at about 350 °C. However, the second stage of DPS and HDPS started at about 220–240 °C, and ended at about 310 °C. After the rapid decomposition of DPS and HDPS, the slopes of their curves became steeper than that of PS, suggesting that the distribution of molecular chains of DPS and HDPS was wider than that of PS. In DSC curves, debranching and hydroxypropylation made the DSC curves of DPS and HDPS to move to the left. After the modification of PS, the endothermic peaks of its derivatives were strengthened. The above results confirmed that the debranching and hydroxypropylation changed the thermal stability and melting process of PS. According to DSC and TGA curves, the relevant thermodynamic parameters calculated were listed in Table 3 to further analyze the thermal behavior of PS, DPS and HDPS.

According to Table 3, the onset decomposition temperature, end decomposition temperature and rate of

Table 3 DSC and TGA thermodynamic data of PS, DPS and HDPS

Samples	PS	DPS(DE = 0.21)	HDPS (DE = 0.21, MS = 1.34)
Onset temperature / °C	79.0	88.7	83.4
Peak temperature / °C	137.0	128.3	130.7
End temperature / °C	203.0	191.2	178.0
Melting enthalpy /J.g^{-1}	237.7	228.8	283.8
Onset decomposition temperature /°C	294.8	242.6	228.3
End decomposition temperature /°C	344.3	318.5	307.4
Rate of mass loss /%	65.5	43.8	47.1

Table 4 Effect of debranching and hydroxypropylation on the numbers of surface hydroxyl groups

Samples	Numbers of surface hydroxyl groups / g^{-1}
PS	0.286×10^{20}
DPS(DE = 0.21)	2.15×10^{20}
HPS (MS = 1.40)	1.44×10^{20}
HDPS (DE = 0.21, MS = 1.34)	3.29×10^{20}

mass loss of DPS and HDPS were less than those of PS. Both onset decomposition temperature and end decomposition temperature increased in order of HDPS, DPS, PS; meanwhile the rate of mass loss increased in order of DPS, HDPS, PS. It suggested that the debranching enhanced the thermal stability of PS, but obviously reduced the onset decomposition temperature, end decomposition temperature and rate of mass loss of DPS. This result was identical to one obtained from reference [42]. The influence of hydroxypropylation on the onset decomposition temperature and end decomposition temperature of DPS was same as debranching. However, the effect of hydroxypropylation on rate of mass loss was different from debranching, that is, the hydroxypropylation increased the rate of mass loss of HDPS. The effect of debranching on the thermal stability of PS was more than that of hydroxypropylation. The onset temperature increased in order of PS, HDPS, DPS; the peak temperature and end temperature rose in order of HDPS, DPS, PS, and the melting enthalpy went up in order of DPS, PS and HDPS. Debranching enhanced the onset temperature of DPS, but decreased the peak temperature, end temperature and melting enthalpy of DPS. The hydroxypropylation reduced the onset temperature, peak temperature and end temperature, but enhanced the melting enthalpy. In a word, the above results should be ascribed to the alteration in the structure, linear chain content and interaction between molecular chains.

The effect of debranched and hydroxypropylation on numbers of surface hydroxyl groups

The effect of debranched and hydroxypropylation on the surface hydroxyl numbers of PS was presented in Table 3. As shown in Table 4, the surface hydroxyl numbers increased in order of PS, HPS, DPS, HDPS, that is, debranching and hydroxypropylation enhanced the surface hydroxyl numbers of PS. It possible that the functionality altered the basic structure of native PS granules, as a result, the more hydroxyl groups from the inner of the granules were further released by the destruction. Of course, the inferences would be also further confirmed by the subsequent measurement of SEM and XRD.

X-ray diffraction analysis

The obtained XRD patterns of PS, DPS (DE = 0.21) and HDPS(DE = 0.21, MS = 1.34) were presented in Fig. 5. According to Fig. 5, the strong diffraction peaks for PS showed at diffraction angle of 15.1°, 17.1°, 23.2°, respectively, and the weak peak appeared at diffraction angle of 5.6°. It proved that the crystalline structure of PS was assigned to a C-type. This result was accordance with that concluded by literature [43]. For DPS diffractograms, the strong diffraction peaks were only at diffraction angle of 17.1° and 22.4°, respectively, whereas the weak diffraction peaks were at diffraction angle of 19.3 ° and 26.6°. Obviously, the crystalline structure of DPS particles did not belong to any of A-type, B-type or C -type, but was between B-type and C-type, and here defined as a CB-type. It proved that the debranching completely changed the structure of PS particles. The small strong diffraction peak of HDPS appeared at diffraction angle of 31.8 ° and 45.6 °, separately. Within the range of diffraction angle from 5° to 30°, however, no one of its crystalline peaks appeared.

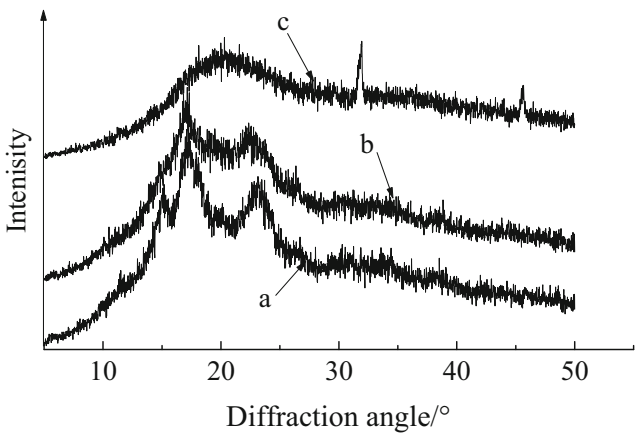


Fig. 5 XRD patterns of PS (**a**), DPS (**b**) and HDPS (**c**)

The crystalline structure of HDPS was almost close to amorphous one, which could be ascribed to starch dissolving in ionic liquids during hydroxypropylation. Finally, according to the XRD patterns, the calculated crystallinity degree of PS, DPS and HDPS were 24.45%, 19.46%, 2.28%, respectively. Obviously, the crystallinity degree of PS and DPS were more than that of HDPS. It revealed that the debranching and hydroxypropylation disrupted the crystalline region of PS.

Particle morphology and EDS analysis

The polarizing microscope photos, SEM and EDS of PS, DPS (DE = 0.21) and HDPS (DE = 0.21, MS = 1.34) were presented in Figs. 6, 7 and 8, respectively. After debranching and further hydroxypropylation of PS, the particle morphology and size of DPS and HDPS were remarkably different from those of PS (Figs. 6 and 7). The most of PS particles were elliptical, although spherical and irregularly shaped granules were also found, and their size ranged about from 5 μm to 25 μm. The surfaces of most of PS granules were not smooth enough due to the existence of some wrinkles, which was accord with the result concluded by reference [44]. There was Maltese cross on each of PS particles. On DPS and HDPS granules, however, no polarizing cross existed. DPS grains were irregular, and its size was more than PS one. The PS surface was smooth, but the HDPS surface became very rough. Many very tiny fragments and tiny pores could be observed on HDPS granules. These results proved that the debranching and hydroxypropylation seriously damaged the original structure of PS particles, but the destroying manner was different from each other.

From Fig.8, on PS granule surface, the contents of carbon and oxygen atoms were 69.57%, 30.43%, separately. Similarly, on DPS and HDPS granule surface, the contents of carbon and oxygen atoms were 75.80%, 21.86%, 78.55%, 20.43%, respectively. The increase in carbon atoms of HDPS confirmed the introduction of hydroxypropyl groups into HDPS molecules. The increase in carbon atoms of DPS suggested that the more alcohol hydroxyl groups at C5 in molecular chains were exposed to the surface, compared to PS. These results were consistent with those obtained from the surface hydroxyl numbers.

Conclusions

HDPS could be synthesized well in an ionic liquid, that is, 1-butyl-3- methylimidazolium chloride, and its MS could be 1.34. The crystalline structure of PS was a C-type, and DPS

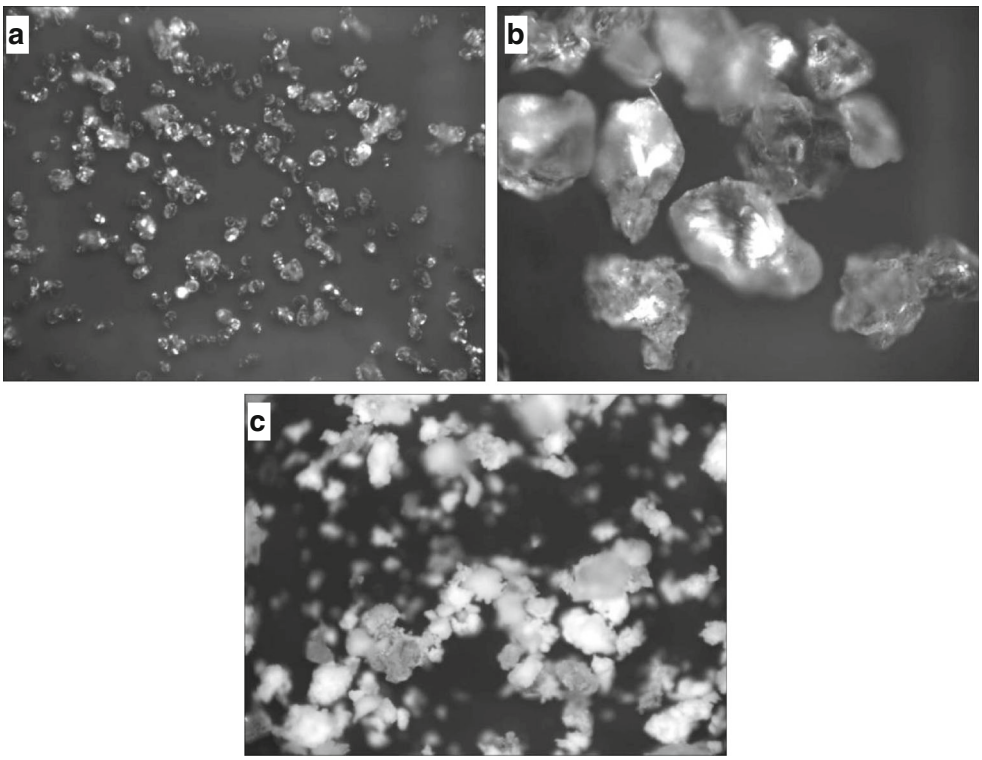
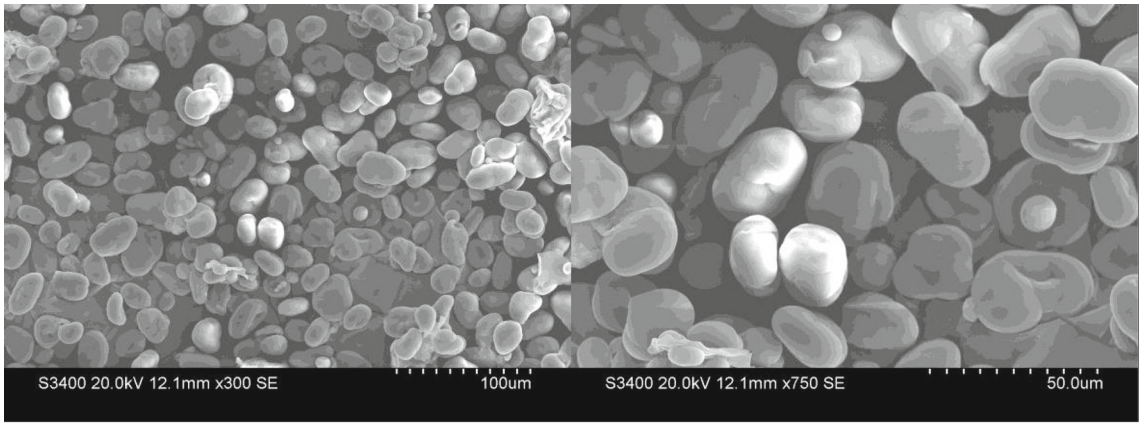


Fig. 6 Polarizing microscope photos of PS (**a**), DPS (**b**) and HDPS (**c**) (×312.5)



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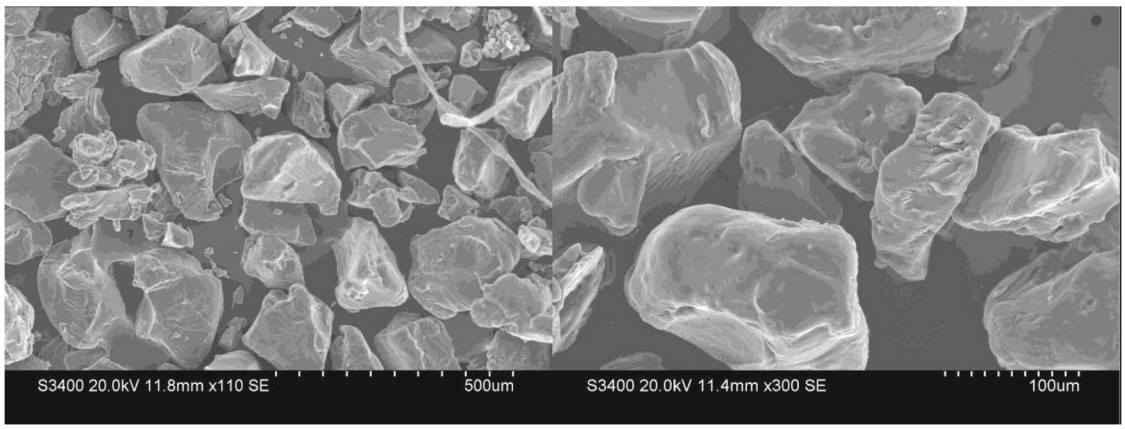

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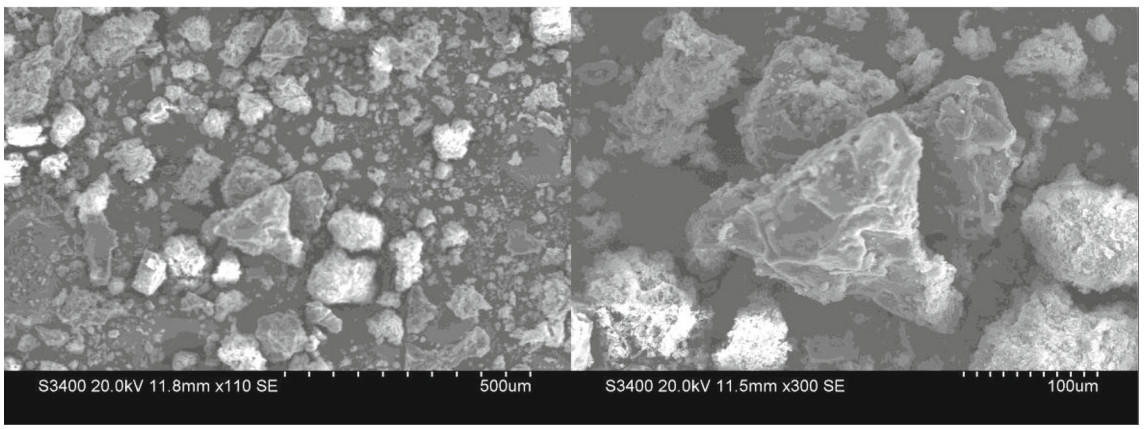

c

Fig. 7 SEM of PS (**a**), DPS (**b**) and HDPS (**c**)

was between B-type and C-type, whereas HDPS was almost completely amorphous. The debranching cut down the viscosity of DPS. The debranching and hydroxypropylation led to the reduction in the setback value, but the increase in the breakdown value of PS. The onset decomposition temperature, end decomposition temperature and rate of mass loss of DPS and HDPS were less than those of PS. Debranching and hydroxypropylation destroyed the crystalline regions of PS, but the manner of destroying these regions was different each other. Debranching obviously increased blue value of DPS, but the hydroxypropylation decreased one of HPS and HDPS. The debranching reduced the swelling power of DPS, but

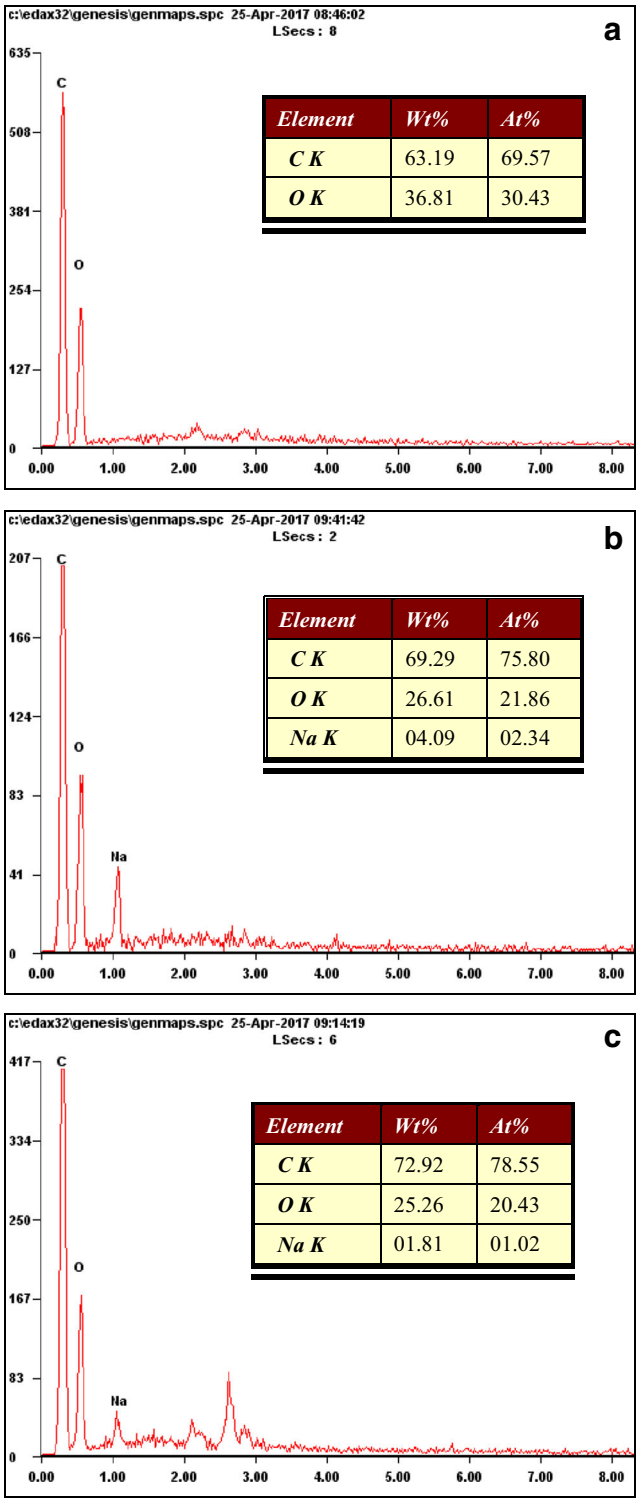

Fig. 8 EDS of PS (**a**), DPS (**b**) and HDPS (**c**)

hydroxypropylation raised the swelling power of DPS and HDPS. PS, DPS and HDPS particles remarkably differed in their morphology and size. Compared to FTIR spectra of PS, the intensity of –OH groups in DPS and HDPS was evidently weakened by debranching.

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Compliance with ethical standards

Conflict of interest All authors of this manuscript have directly participated in planning, execution, and analysis of this study,and have given approval to the final version of the manuscript. All the authors declare no conflict of interest.

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