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Thermal decomposition chemistry of starch studied by ^{13}C high-resolution solid-state NMR spectroscopy[☆]

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Abstract

The chemical structure and thermal reaction pathway of four native and modified starch samples after being heated up to 600 °C have been examined by ^{13}C high-resolution solid-state NMR spectroscopy. Chemical reactions for the samples started around 300 °C to generate ether and ethylene segments via thermal condensation and dehydration mechanisms. Heating at increased temperatures generated substituted phenol/benzene and furan structures with methylene or ether linkages between these aromatic rings. Varied thermal reactivity was observed for starch samples around 300 °C due to their difference in molecular weight, pH or structural modification. However, the reaction pathway was similar. Above 400 °C, the starch structure was destroyed and the product appeared structurally similar to thermally cross-linked/decomposed phenolic/furfuryl alcohol resins, thereafter, the thermal reaction of the systems followed a similar pathway as these resins. No significant difference of chemical structures was obtained for the four samples after heating above 350 °C and identical carbon structures were generated at 600 °C. © 2002 Published by Elsevier Science Ltd.

Keywords: Starch; Thermal decomposition chemistry; High-resolution solid-state NMR

1. Introduction

Starch is one of the main polymers present in nature, its structure and properties have been investigated extensively in the last century and the use of starch has been applied in many fields [1,2]. Increasing environmental concerns in recent years have led to biodegradable materials replacing petro-chemical polymers in many applications. Starch has shown advantages and superior characteristics over other natural and synthetic biodegradable plastics, especially because of the low cost of raw materials [3–5]. Its applications have been extended from traditional food, paper and textile industries to packaging, controlled drug delivery and many other areas in either its native or modified forms.

The chemical structures and material properties of various native and modified starches have been examined and reported previously [6–11]. Their thermal decomposition characteristics were also studied by thermal analytical techniques such as DSC, TGA and DMTA [12–17]. Along with temperature increases, solid-state reactions of starch start with combination of phase transitions such as melting, evaporation and sublimation as well as chemical condensation, decomposition and finally carbonization at very high temperatures. Thermal analysis techniques are normally applied to monitor the mass loss and the endothermic or exothermic nature of any physico-chemical changes involved in thermal processes. These provide valuable insights when assessing the chemistry of the thermal decomposition. The examination of the chemical structure changes that occur at increased temperatures and the thermal reaction pathways of starch are important; the results play a fundamental role in understanding the thermal behaviour and physical properties of the materials. To our knowledge, the chemical structure changes during the heating process and associated decomposition pathways in the thermal decomposition chemistry of starch have not been examined comprehensively.

In this paper, we concentrate on the study of chemical structure changes of starch during thermal decomposition up to 600 °C. Further temperature increases result in formation of carbonaceous structures. Four varieties of starch samples are examined including both native
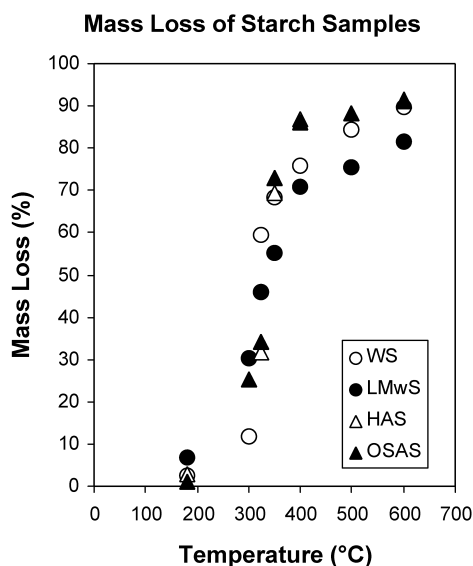
Mass Loss of Starch Samples

Fig. 1. Mass loss of starch samples after being heated up to 600 °C.

(unmodified) and modified starches. Possible thermal reaction pathways are postulated for these starch samples based on how the observed chemical structure changed with temperature. High-resolution solid-state NMR spectroscopy was applied for detecting the chemical structures of the starch samples after exposure to high temperatures. The results provided in this study are critical for extending the
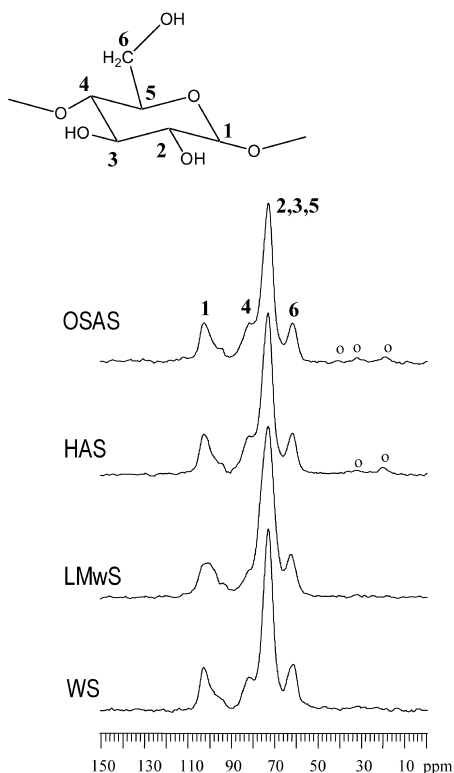

Fig. 2. ^{13}C NMR CP/MAS spectra of WS, LMwS, HAS and OSAS sample before heating. The peaks marked with circles represent minor resonances attributed to chemical modification.

applications of starch materials as packaging or binding materials for use at high temperatures.

2. Experimental

2.1. Starch

Starch samples used in this study included native wheat starch (amylose content of 25% from Manildra Group, Australia), and the following modified starches — low molecular wheat starch (MW of 2000, hydrolysed under acidic conditions, from Manildra Group, Australia), high amylose-content corn starch (amylose content of 80%, from Starch Australasia Ltd) and octanyl succinic anhydride (OSA) substituted corn starch (low amylose content of ~20%, from Starch Australasia Ltd). These four starch samples are referred to as WS, LMwS, HAS and OSAS, respectively, in the text. For HAS the C-6 (or −CH$_2$OH group) of the glucose units is hydroxypropylated to a level of ~5%. OSAS is also a modified corn starch with ~5% of octanyl succinic anhydride substituted at the C-6 position of the glucose rings. The substitution of starch at C-6 positions normally stabilizes the gelatinized state, enhancing the water-binding capabilities and improving the flexibility of the starch when forming films. The water content in the untreated starch samples was around 13%. Each sample was pre-gelled (one part of starch with two parts of water) in water bath, stirred mechanically at approximately 70–80 °C for 1 h, since starch is utilized in its gelatinized state in many applications. The pH of the LMwS gel was 2.9 while the values of the other starch gels were 6.1 (OSAS), 6.3 (WS) and 6.6 (HAS). After drying at 110 °C overnight, the starch was further heated at 180 °C for 2 h. In the decomposition study about 2 g of each sample was heated in a quartz glass tube furnace at a pre-set temperature (300, 325, 350, 400, 500, 600 °C) and held at this temperature for 5 min under a flowing Argon atmosphere. The samples were then removed from the furnace into a dry, nitrogen atmosphere (dry box) and allowed to cool to room temperature. The tube furnace temperature was maintained using a type K thermocouple and a digital temperature controller. The furnace itself was attached directly to the dry box.

Elemental analysis was conducted on these starch samples after thermal treatment. The C/H and C/O atomic ratios were calculated from these elemental analysis data.

2.2. NMR experiments

High-resolution solid-state NMR experiments were conducted using a Varian Unity plus spectrometer at resonance frequencies of 75 MHz for carbon-13 and 300 MHz for H-1. ^{13}C NMR spectra were observed under cross-polarization (CP), magic angle sample spinning (MAS) and high power decoupling (DD) conditions. The
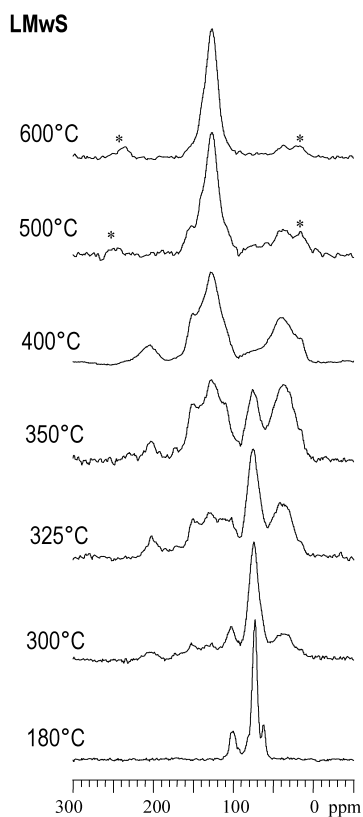
LMwS

Fig. 3. ^{13}C NMR CP/MAS spectra of LMwS sample after being heated at different temperatures. The peaks marked with stars represent MAS spinning side bands.

90° pulse is of 3.4 μs whereas the spinning rate of MAS was set at a value in the range of 9–12 kHz. The chemical shift of ^{13}C NMR spectra was determined by taking the carbonyl carbon of solid glycine (176.03 ppm) as an external

C/H & C/O Atomic Ratios of LMwS

Fig. 4. The C/H and C/O atomic ratios of LMwS sample after being heated up to 600 °C.

reference standard. All the experiments were conducted at room temperatures.

3. Results and discussion

The mass loss data of four starch samples after being heated up to 600 °C are shown in Fig. 1. Note that a significant mass loss (70–90 wt%) occurred around 300–400 °C in all samples. This result is consistent with the thermal analysis studies reported previously [12–17]. Note that the mass lost by the unmodified WS at 300 °C was slightly lower as compared to the other samples, suggesting that the thermal decomposition of WS begins at a slightly higher temperature. Above 400 °C, further mass loss increased slowly with rising temperature. This is consistent with the modified starches (HAS and OSA starch); however, LMwS appears to lose slightly less mass in the higher temperature ranges, possibly due to its low pH (2.9) — a result of residual acid remaining after the hydrolysis (cutting) of the polymer chains under acidic conditions in its preparation.

The ^{13}C NMR CP/MAS spectra of four starch samples before pyrolysis were assigned as shown in Fig. 2. The basic spectrum features of the four samples are similar besides some weak intensities around 10–40 ppm for the HAS and OSAS samples which are attributed to the substitution at C-6 position of the glucosyl units (the –COO– group was detected at 174 ppm). The relatively wide resonance of C-1 at 94–103 ppm is attributed to the glycosidic conformation and polymorphism thus resulting in a wide distribution of the chemical shift [8,10,18–20]. Note that the resonance of C-1 LMwS at low field (100–103 ppm) is broader than those of the other three starch samples, and is due to the large numbers of end groups in LMwS since the hydrolysis has lowered the molecular weight to around 2000. Usually the molecular weight of starch is of the order of several million.

High-resolution solid-state NMR is a powerful technique to study the structure change in a highly cross-linked polymer system where many other techniques fail to provide detailed structural information. This NMR technique has also been applied in the investigation of polymer thermal decomposition and carbonization process for many systems [21–25]. The ^{13}C NMR CP/MAS spectra of LMwS sample after being heated at different temperatures are shown in Fig. 3. No significant structure change was observed in the NMR spectra of LMwS samples after heating at 180 °C (seen in Figs. 2 and 3), indicating that no observable chemical reactions at this stage. Thermal analysis reported previously [15,16] indicated that degradation of starch could commence around 250 °C and a significant mass loss occurred above 300 °C that is consistent with the result obtained in this study. Heating the LMwS sample at 300 °C did generate a significant chemical structural change as seen in Fig. 3. The broadness of the resonances at 103, 75 and
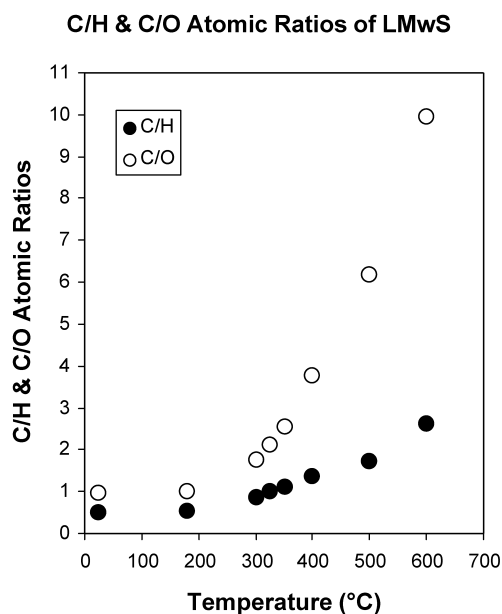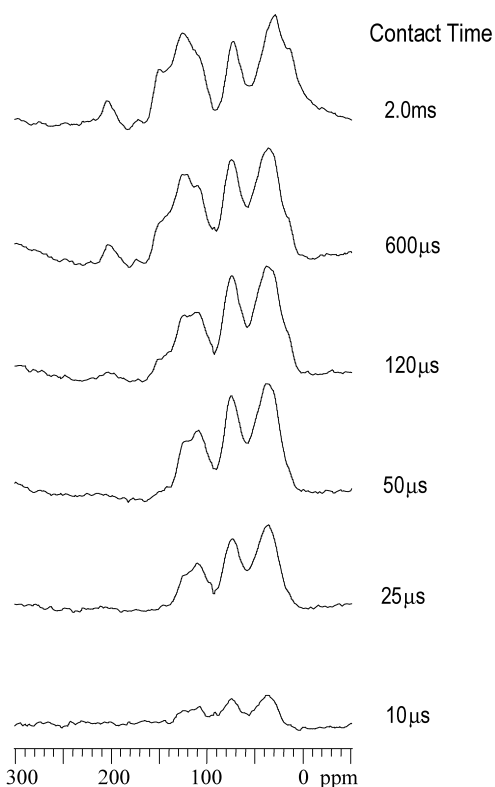
Fig. 5. ^{13}C NMR CP/MAS spectra observed at varied cross-polarization contact time for LMwS sample after heating at 350 °C.

60 ppm indicates the thermal condensation or cross-linking between starch chains/repeat units that generated a complex chemical shift distribution. The main thermal reactions could be due to the formation of ether bonds via the elimination of H_2O molecules from starch chains, following the elimination of residual water from the starch structure. Fig. 4 shows the atomic ratios of C/H and C/O of LMwS after being treated at each temperature. Note that the atomic ratio of C/H and C/O increased from 0.5 and 1.0 at 180 °C to 0.86 and 1.8 at 300 °C, respectively. Various new resonances across a wide range were also observed in the NMR spectra for LMwS after being heated at 300 °C. The broad peak at 205 ppm is due to aldehyde group(s) (−CHO) while the resonance at 178 ppm is assigned to −COOH groups. Since the pyrolysis was conducted under an argon atmosphere, the oxygen involved in the formation of −COOH group should come from within the starch, following a possible radical reaction mechanism. A group of new resonances at 110−155 ppm could be attributed to the formation of $>$C$=$C$<$ and possibly aromatic structures. The appearance of new resonances at 20−40 ppm suggest the formation of −CH$<$ and −CH$_2$− linkages or −CH$_3$ end groups in the starch polymer chains due to the thermal degradation process. Heating the sample at 325 °C resulted in a decrease of the relative intensity at 75 ppm while the intensity increased for all other resonances. The strong intensities of the resonances at 110−155 ppm indicate the

formation of aromatic structures such as substituted phenol and benzene rings. The resonances of aliphatic carbons at 15−40 ppm also increased their relative intensities and the aldehyde group at 205 ppm was still present. It was reported that furfuryl and furaldehyde structures could be formed around 350 °C as dominant pyrolysis products [26]. Early GC/MASS study on thermal decomposition of cellulose also showed that furfuryl compounds in conjunction with various small molecular species were detected in volatiles products [27,28]. Strong intensities of the resonances at 115 and 155 ppm are consistent with the formation of furfuryl structures (C-3/C-4 and C-2/C-5 of furfuryl rings, respectively) since these peaks should not be that pronounced if only phenol/benzene structures were formed. The broad peak at 70−75 ppm observed at 325 °C are mainly due to the −CH$_2$−O−CH$_2$− segments, and its intensity further decreased when the sample was heated at 350 °C while other resonances keep increasing their intensities.

Fig. 5 shows the ^{13}C CP/MAS NMR spectra with different cross-polarization contact time (10 μs−2.0 ms) of the LMwS sample after being heated at 350 °C, which provided additional information for the resonance assignment. The ^{13}C resonances observed at very low contact times (10 and 25 μs) such as the intensities at 130, 110, 75 and 35 ppm are due to the protonated carbons with strong cross-polarization capability. The peaks at 155 ppm observed at longer contact time (above 120 μs) is attributed to non-protonated carbons such as the hydroxyl carbon of phenol (or C-1 of phenol), or the C-2 and C-5 of substituted furan structures. Some protonated carbons such as −CHO (205 ppm) and −CH$_3$ (15−20 ppm) appeared only when using a longer contact time (above 120 μs) due to their mobility as end groups. The non-protonated carbon at 178 ppm should be assigned to the −COOH group.

When the LMwS sample was heated at 400 °C, the peak at 75 ppm disappeared in the ^{13}C CP/MAS NMR spectra (Fig. 3) while three major resonances were detected at 205 ppm (−CHO), 152/128 ppm (aromatic groups such as phenols) and 30/15 ppm (aliphatic carbons, −CH$<$, −CH$_2$− and −CH$_3$). Note that 70% of the original sample mass was lost after the sample was heated to 400 °C (Fig. 1), and the atomic ratio of C/H and C/O had further increased to 1.35 and 3.77, respectively (Fig. 4). Furfuryl structures could breakdown at this temperature and be converted to substituted phenol/benzene structures [25]. Further heating the sample above 400 °C mainly resulted in carbonization. As seen in Fig. 3, above 500 °C the LMwS sample generated a strong and broad aromatic resonance at 150 and 130 ppm in conjunction with a weak aliphatic carbon resonance at 30 ppm in ^{13}C CP/MAS NMR spectra, but the −CHO group at 205 ppm disappeared. At 600 °C the aliphatic carbon intensities became very weak, a strong peak at 130 ppm was observed with an even narrower linewidth, indicating some ordered structure of carbon had formed at this stage. The atomic ratios of C/H and C/O for the sample were 2.63 and 9.97, respectively. When the samples were heated at 800 °C
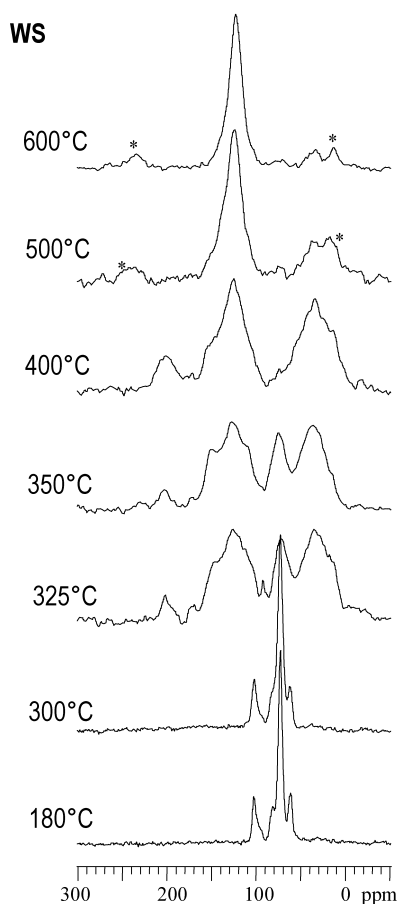
Fig. 6. ^{13}C NMR CP/MAS spectra of WS sample after being heated at different temperatures. The peaks marked with stars represent MAS spinning side bands.

the C/H and C/O ratios increased, but there were no further changes in ^{13}C CP/MAS NMR spectra (data not shown).

The ^{13}C CP/MAS NMR spectra of WS after being heated are shown in Fig. 6. As compared to LMwS, significant thermal decomposition of WS occurred at a relatively higher temperature, which is consistent with mass loss data show in Fig. 1. The reaction appears to start just above 300 °C, as a significant structural change was observed in the 325 °C sample. The spectral features of WS after being heated above 350 °C are quite similar to those observed for LMwS samples, indicating both WS and LMwS samples followed a similar decomposition pathway above 350 °C, although WS started to degrade above 300 °C but LMwS started below 300 °C. The thermal reactions of HAS and OSAS samples followed similar trends as observed from their ^{13}C CP/MAS NMR spectra after heating (see Fig. 7). The difference between these two starch samples appears in the reactivity at low temperatures; HAS started thermal reactions above 300 °C while OSAS started below 300 °C. Note that the amylose-content is quite different in these two starch samples besides the different chemical modification applied. There is no significant difference among the four starch samples at, and above, 350 °C. After samples of the
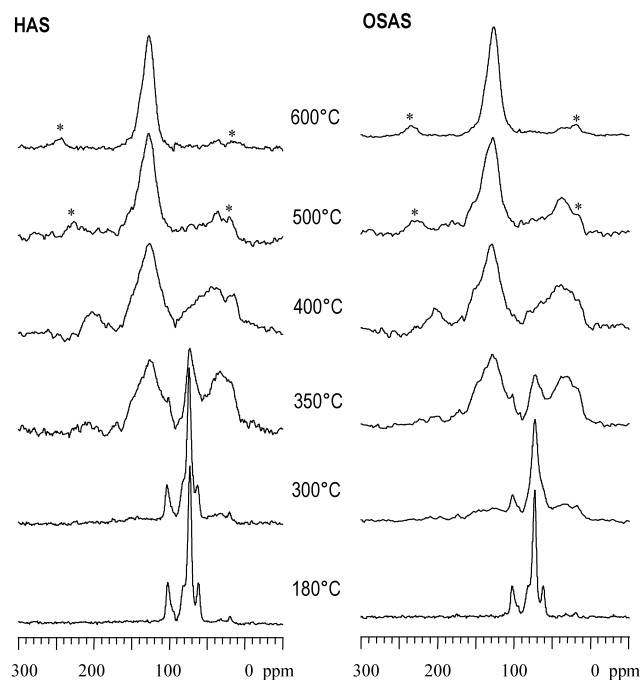

Fig. 7. ^{13}C NMR CP/MAS spectra of HAS and OSAS sample after heating at different temperatures. The peaks marked with stars represent MAS spinning side bands.

four starches were heated at 600 °C, the C/H and C/O atomic ratios were around 2.6–3.1 and 7.6–9.9, respectively. This data is similar to that of Novolac and furfuryl alcohol resins after heating at the same temperature (600 °C) [25].

In summary, thermal reactions for starch started around 300 °C with thermal condensation between hydroxyl groups of starch chains to form ether segments and lose water molecules and other small molecular species. Dehydration of neighbouring hydroxyl groups in the glucose ring also occurred resulting in the formation of >C=C< or breakdown of the glucose ring. Aldehyde groups were formed at the same time possibly as end groups if, and when, the glucose ring was fractured. Increasing temperature generated aromatic rings, such as substituted phenol/benzene and furan structures with either $-CH_2-$ or $-CH_2-O-CH_2-$ as main linkages between these aromatic groups. The starch structure disintegrated after heating at 400 °C, and above that temperature a highly cross-linked system was formed similar to thermally cross-linked phenol/benzene/furfuryl resins. Thereafter, the thermal reactions of the system would follow similar reaction pathways as phenol–formaldehyde resins and furfuryl alcohol resins undergoing thermal cross-linking and decomposition at increased temperatures. These polymer systems have been investigated comprehensively in previous reports [29–33]. Carbonization reactions of the system at temperatures above 500 °C increased the relative intensity of aromatic carbon resonances with the intensities of aliphatic carbons decreasing. Relatively large conjugated aromatic structures could be formed above 600 °C, and further heating generated amorphous carbon structures. The

initial thermal reactivity (at around 300 °C) relies on factors such as molecular weight, pH or structural modification of the glucose units of starch and probably amylose-content as well, however, the overall reaction pathway amongst these starch samples is similar. At temperatures above 350 °C, the four starch samples studied in the paper showed similar characteristics in chemical structure and reactivity, and generated identical carbon structures at 600 °C.

Acknowledgements

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