

Thermal properties of starch succinates

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Abstract

Starch succinates are starch derivatives used as binders and thickening agents in foods, tablet disintegrants in pharmaceuticals, surface sizing agents and coating binders in paper. A series of starch esters with different degrees of substitution (DS = 0.008–0.639) prepared by reactive extrusion were studied. Potato, wheat and corn starch were investigated. Thermooxidative behaviour of starch succinates was studied by simultaneous thermal analysis–mass spectrometry (STA–MS) method. The thermal stability of starch esters depends on the degree of substitution (DS). With an increase in DS, thermal stability increases. The major differential thermogravimetric (DTG) peaks are observed below 300 °C. The most abundant ions found are H₂O⁺ and CO₂⁺.
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1. Introduction

Starch succinates are starch derivatives used as binders and thickening agents in foods, tablet disintegrants in pharmaceuticals, surface sizing agents and coating binders in paper [1–3].

Depending on the degree of substitution (DS), properties of starch esters e.g. solubility vary significantly. The degree of substitution is defined as the number of moles of substituents per D-glucopyranosyl structural unit of starch with a theoretical maximum of DS = 3. The esterification of starch with organic acids, results in thermoplastic and hydrophobic materials when the DS is high enough.

Thermal behaviour of starch derivatives, including starch esters is usually studied in an inert atmosphere [4–10]. Thermal properties of starch octanoates and dodecanoates were studied by the TG method [4,5]. Šimkovic and Jakab used the thermogravimetry/mass spectrometry technique to study the decomposition process of cross-linked starch [8]. They

found that the presence of inorganic acids enhanced the char and water formation. The most important primary reaction observed was dehydration. Similar results were obtained during studies of thermal decomposition of native and modified starch by ¹³C high-resolution solid-state NMR spectroscopy [9]. It was reported that thermal reactions for starch started around 300 °C with thermal condensation between hydroxyl groups of starch chains to form ether segments with a loss of water molecules and other small molecular species.

Thermal stability under an air atmosphere was determined for lauroylated potato starch (DS = 1.5) [11] and tosylated amylo maize starch (DS = 1.09) [12]. Thermooxidative degradation of the tosylated amylo maize starch was initiated at a lower temperature than in the case of the native amylo maize starch; conversely for the lauroylated starch the onset of decomposition appeared at a higher temperature in comparison with the unmodified potato starch.

The aim of the work was to study thermal behaviour of starch succinates in an oxidative environment using the STA–MS technique. Simultaneous thermal analysis/mass spectrometry (STA–MS) system allows the detection of the thermal effects recorded from thermogravimetry (TG) and differential thermal analysis (DTA) and monitoring of the

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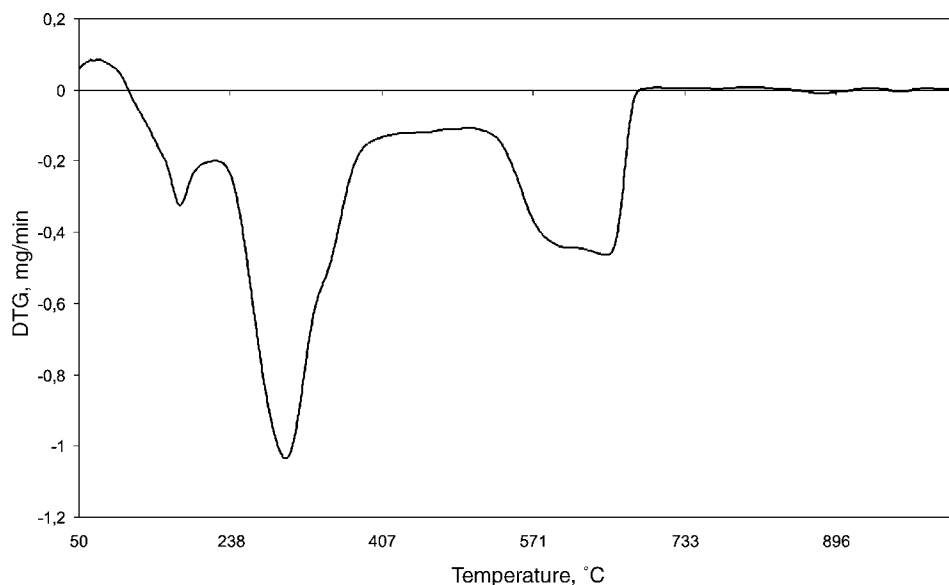


Fig. 1. DTG curves of starch succinate. Sample: PSTSA2 (potato starch, DS = 0.689).

mass spectra of the volatile products simultaneously [13]. The coupling of thermal analysis with MS is a powerful tool for polymer analysis, especially helpful in understanding the thermal degradation pathway of the polymers. The influence of the degree of substitution and the source of the starch (i.e. potato, corn and wheat starch) on the thermal stability of starch succinates was also studied.

2. Experimental

2.1. Materials and methods

Starch succinates were obtained by the reactive extrusion method [14].

Degree of substitution (DS) for succinylation was measured by alkaline titration for the carboxyl group according to method described by Kweon et al. [15].

A simultaneous differential thermal analysis/thermogravimetry/mass spectrometry (DTA/TG/MS) system NETZSCH STA 429 coupled with Balzers QMG 420 quadrupole mass spectrometer was used for thermoanalytical characterization of starch esters. The principles of the technique are described elsewhere [13]. Measurements were performed in an air atmosphere (flow rate: 130 ml/min). The sample mass was ca. 25 mg. Samples were heated from 30 to 1000 °C with a heating rate of 10 K/min.

3. Results and discussion

Typical DTG and DTA curves for the starch succinates are shown in Figs. 1 and 2, respectively. The thermooxidative degradation proceeds in two stages for all investigated starches, regardless of their botanical source. The DTG curve

has two peaks with a first maximum at 262 °C and a second one at 611 °C. The additional stage observed at 144 °C is due to the loss of water contained in the starch sample. A broad exothermic peak appears in the DTA curve with a maximum at 590 °C overlapping with the second DTG peak. This region termed “glowing combustion” produces simple gases, CO, CO₂ and H₂O due to reactions of carbonaceous residues with oxygen. It was observed by Aggarwal and Dollimore [16] that during thermooxidative degradation of corn starch and cellulose gaseous combustion is followed by glowing combustion, both being sufficiently exothermic to cause appreciable distortion in the imposed temperature program.

The mass spectra for starch succinate are shown in Fig. 3. The most abundant ions found are H₂O⁺ and CO₂⁺. They have maxima at about the same temperature as the DTG curve. The water is the main product of decomposition at temperatures below 300 °C, formed by intermolecular or intramolecular condensation of starch hydroxyls. Temperature dependence of the ion current intensities for the measured fragment of the $m/z = 56$ is given in Fig. 4 for starch succinates with different DS. The $m/z = 56$ peak at 250 °C is related to C₃H₄O succinyl group. The maximum intensity for the fragment $m/z = 56$ at 250 °C overlaps with the main DTG peak. It was observed that its intensity correlates to the degree of substitution, i.e. to the succinyl group contents.

In order to determine the thermal stability of the starch succinates, the following values were determined: $T_{x\%}$ —temperature corresponding to $x\%$ mass loss and W_T —mass loss at a given temperature T . The results for the different types of starch and for different DS are summarized in Table 1.

Starch succinates are stable up to 200 °C, followed by 50% mass loss at 350 °C. The thermal stability is similar regardless of the source of starch with approximately the same DS (cf. PSTSA1, CSTSA4 and WSTSA8).

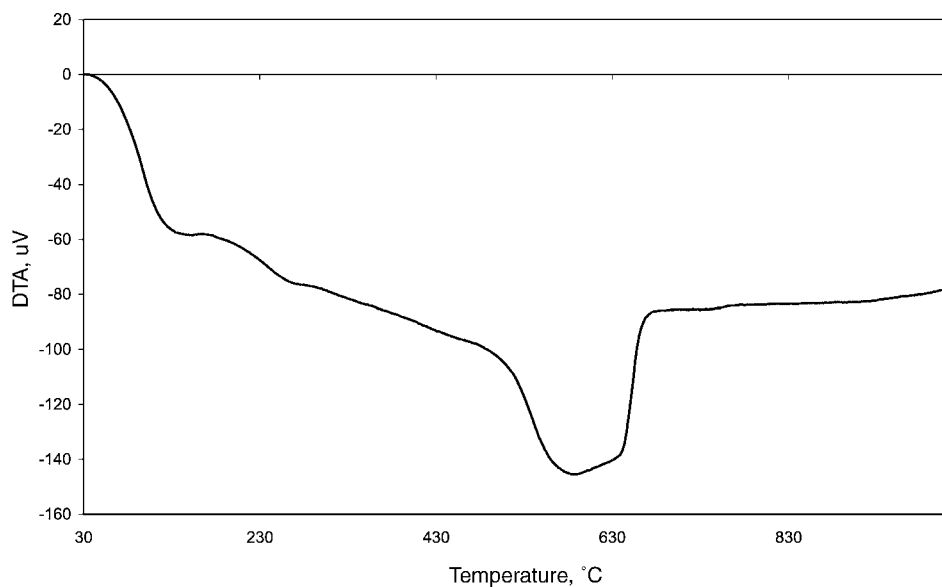


Fig. 2. DTA curves of starch succinate. Sample: PSTSA2 (potato starch, DS = 0.689).

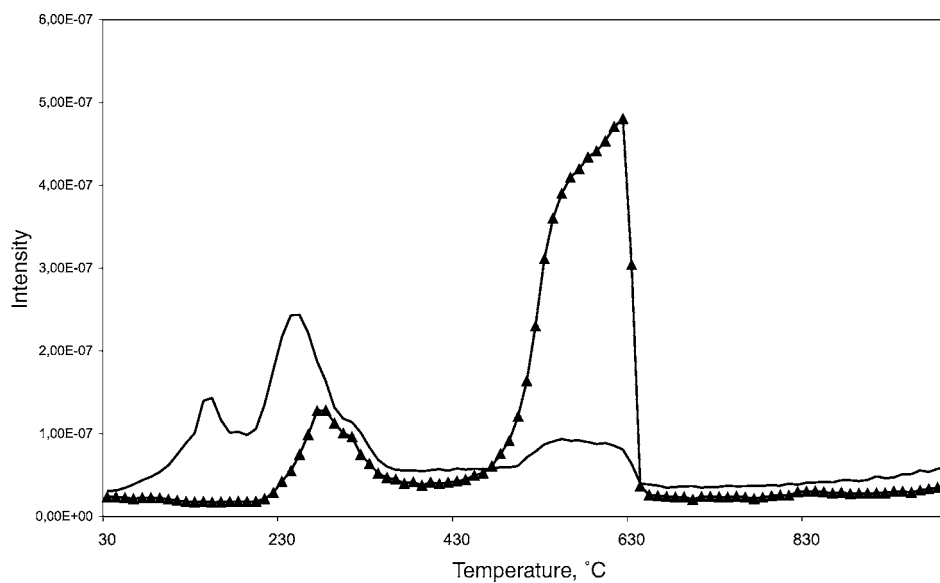


Fig. 3. Temperature dependence of the ion current intensities for the measured fragments of the m/z . Sample: PSTSA2 (potato starch succinate, DS = 0.689). (—) $m/z = 18$; (\blacktriangle) $m/z = 44$.

Table 1
Thermal characteristics of starch succinates

Sample	Starch	Humidity (%)	DS	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$W_{150^\circ\text{C}}$ (%)	$W_{200^\circ\text{C}}$ (%)	$W_{250^\circ\text{C}}$ (%)	$W_{300^\circ\text{C}}$ (%)	$W_{350^\circ\text{C}}$ (%)
PSTSA1	Potato	11.3	0.285	155.6	214.2	241.2	-4.4	-8.4	-24.3	-42.9	-50.4
PSTSA2	Potato	5.1	0.639	168.3	212.0	242.9	-2.9	-8.3	-23.1	-44.7	-53.2
CSTSA3	Corn	20.9	- ^a	89.4	152.1	206.6	-9.9	-18.4	-33.6	-45.4	-48.3
CSTSA5	Corn	16.2	0.222	155.0	221.2	249.1	-4.4	-8.1	-20.5	-38.9	-44.8
CSTSA6	Corn	16.1	0.401	186.1	220.6	246.2	-1.9	-6.3	-21.6	-42.4	-49.6
WSTSA7	Wheat	21.1	- ^a	112.1	158.9	203.7	-7.9	-22.8	-36.2	-48.6	-53.3
WSTSA8	Wheat	15.8	0.247	147.2	211.1	238.5	-5.3	-8.7	-25.9	-43.4	-49.9
WSTSA9	Wheat	16.2	0.381	200.4	228.4	250.4	-2.6	-4.9	-19.8	-38.4	-46.3

^aDegree of substitution (DS) not found (DS = 0).

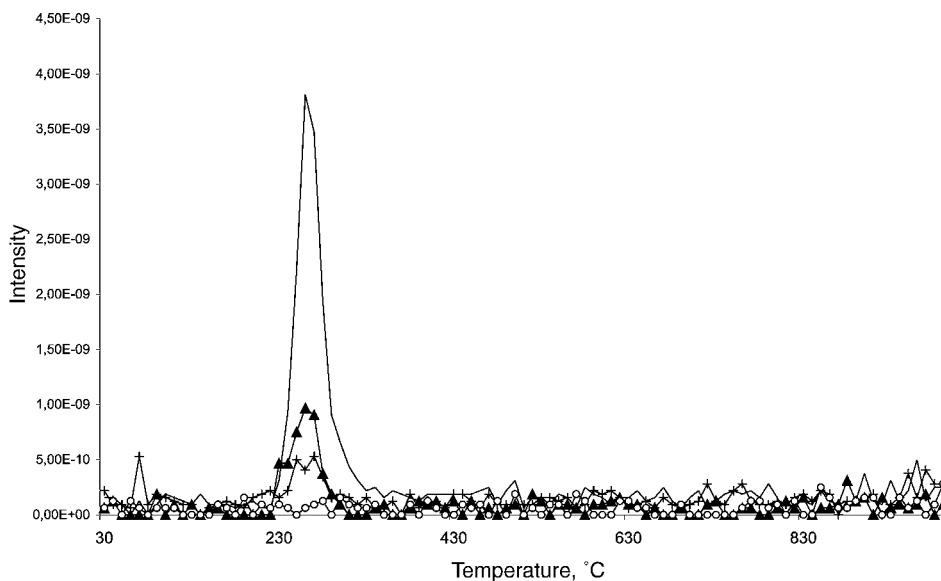


Fig. 4. Temperature dependence of the ion current intensities for the measured fragment of the $m/z=56$. (—) Sample: PSTSA2 (potato starch succinate, DS = 0.689); (\blacktriangle) sample: CSTSA5 (corn starch succinate, DS = 0.401); (+) sample: PSTSA1 (potato starch succinate, DS = 0.285); (\circ) sample: CSTSA3 (corn starch succinate, DS = 0).

Thermal stability of starch succinates increases with increasing the degree of substitution. For example for wheat starch succinate $T_{10\%}$ increases from 158 to 228 °C for ester with DS = 0.247 and 0.381, respectively. These results are in agreement with earlier studies concerning starch esters [4,11,12]. It was reported that with an increasing content of tosyl group [DS = 0.61–2.02] an increase in stability from 166 to 213 °C occurred [12]. The greater stability of the esters was explained by the lower amount of remaining hydroxyl groups after esterification. Since the main decomposition mechanism of starch is the dehydration reaction between starch hydroxyls, the lower the amount of hydroxyl groups remained, the better is the thermal stability of the starch esters.

4. Conclusions

It was found that the decomposition process of starch succinates under an air atmosphere takes place in two stages. The major DTG peak is observed below 300 °C. The most abundant ions found are H_2O^+ and CO_2^+ with maxima overlapping with those observed in the DTG curve.

The thermal stability of starch esters depends on the degree of substitution. With an increasing content of succinyl groups (i.e. higher DS) stability of starch succinates increases.

Moreover, it was observed that the thermal stability of starch succinates with approximately the same DS is similar regardless of the source of starch.

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