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# THERMAL STABILITY AND DEGRADATION OF STARCH DERIVATIVES

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Thermal behaviour of different starch derivatives, i.e. starch esters and ethers having degree of substitution (DS) in the range of 0.02–0.18 were studied. Potato, maize and wheat starches were used. Measurements were carried out by coupled thermal analysis/mass spectrometry method (STA-MS) in air atmosphere.

The major DTG peak during the investigation for starch derivatives is observed below 300°C. The mass loss up to a temperature of 300°C is about 50%. The most abundant ions found are $H_2O^+$ and $CO_2^+$. For the studied starch derivatives with a low degree of substitution (DS<0.18) no correlation was found between thermal stability and the level of substitution regardless of the nature of substitution.

**Keywords:** *starch derivatives, starch esters, starch ethers, thermal degradation*

## Introduction

Starch is used by man mostly in food applications, but there is a growing interest in the utilization of starch as a renewable raw material for industrial applications. For non-food uses starch is modified in order to obtain products with properties suitable for various applications, for example, in the pulp and paper industry. The modification can be carried out by chemical methods by introducing small amounts of ionic or hydrophobic groups into the molecules. These modifications, normally present at very low concentrations in starch preparations, produce dramatic differences in the physical and chemical properties of starch and lead to a multitude of uses in both food and nonfood applications [1–3]. Depending on the nature of the substituents and on the degree of substitution (DS), properties of modified starch can be varied extensively, e.g. solution viscosity, association behaviour, film forming properties or thermal stability. The DS indicates the average number of hydroxyl (OH) group substituted per *D*-glucopyranosyl structural unit in starch polymer. Since each D-glucose unit possesses three reactive hydroxyl groups, so the maximum possible DS-value is 3. Most of the starch derivatives which are available commercially have low DS (DS=0.01–0.02).

Thermal analysis method was applied to study thermal behaviour of native starch [4–6]. Earlier studies have investigated the rheological, thermal and mechanical properties of a series of fatty-acid esters of high-amylose starch by DSC [7]. Cationically modified corn starch was characterised by thermal analysis [8]. Oleoyl, palmitoyl, lauroyl, capryloyl and butyryl modified starches have been synthesised and their thermal stabilities were studied [9]. The thermal properties of etherified amylose and etherified high-amylose starch was studied also by DSC and TG [10, 11]. A series of starch esters prepared by acylation of the polysaccharide with octanoic, dodecanoic and octadecanoic acid chlorides were prepared and their thermal properties were characterized [12]. However, the reported studies were mostly performed in an inert atmosphere.

The aim of this work was to study the thermal behaviour of starch derivatives under an oxidative environment. The other purpose was to study the influence of nature of substituent and DS on the thermal stability of starch derivatives. Different starch derivatives were studied i.e. starch esters and ethers having DS in the range of 0–0.18. Potato, maize and wheat starches were used.

## Experimental

### *Materials*

Starch derivatives were laboratory made samples prepared by reactive extrusion method. The following starch derivatives were used:

- starch esters, i.e. starch acetates (STAA) with DS ranging from 0.03 to 0.08.
- starch ethers, i.e. carboxymethyl starch (KMS) with DS ranging from 0.02 to 0.18.

### *Methods*

A simultaneous differential thermal analysis/thermogravimetry system Netzsch STA 429 coupled with

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Balzers QMG 420 quadrupole mass spectrometer (DTA/TG/MS) was used for thermoanalytical characterization of starch derivatives. Measurements were performed in an air atmosphere (flow rate: 130 mL $\text{min}^{-1}$). The sample mass was ca. 25 mg. Samples were heated from 30 to 1000°C with a heating rate of 10°C $\text{min}^{-1}$.

## Results and discussion

Figures 1 and 2 present DTG and DTA curves of starch acetate. The decomposition of starch acetate takes place in two steps. The main mass loss has its maximum (DTG) at about 250°C and is related to a mass loss of 30–40%. Up to temperature of 300°C approximately 50% mass loss occurs. The temperature for the second DTG peak was above 500°C.

The DTA curve shows a large exothermic event with a maximum corresponding to the second DTG peak. For cationically modified starch also a two-step degradation process was observed in an air atmosphere [8]. It was reported that for both inert and air atmosphere, the major mass loss, corresponding to the complete breakdown of starch, starts at the temperature (about 250°C), indicating that initiation of the breakdown of starch is a non-oxidative process. The second stage does not occur in inert atmosphere, thus, it was supposed that the oxidation of the partially decomposed starch takes place. The second region of mass loss observed at above 500°C is related to the oxidation reaction of the solid carbonaceous residue and is termed as a region of ‘glowing combustion’.

The mass spectrum of the volatiles released from starch acetate at the main DTG peak at 250°C is shown in Fig. 3. The maximum intensities are observed for $CO_2$ and water (peaks at $m/z=18$ and $m/z=44$). The evolution profiles of water and $CO_2$ follow the features of the DTG curves in agreement with the fact that water and $CO_2$ are the main volatile products (cf. Fig. 4).

The DTG and DTA curves for carboxymethyl starch are presented in Figs 5 and 6, respectively. The thermooxidative decomposition process of carboxymethyl starch proceeds in three consecutive steps, the first one being the main one. The first step is at temperature 200°C with a mass loss of 15% and the second at temperature 320°C with a mass loss of 50%. The third step observed at 400°C coincides with a large exothermic peak in the DTA curve (cf. Figs 5 and 6). The mass spectrum of the volatiles released from carboxymethyl starch is shown in Fig. 7. The main products are water and carbon dioxide released in stages overlapping with those observed for the DTG curves. However, it can be observed that $CO_2$ is

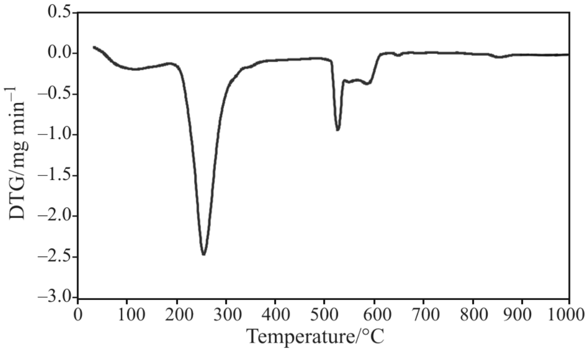

**Fig. 1** DTG curve of starch acetate (potato starch; DS=0.030)

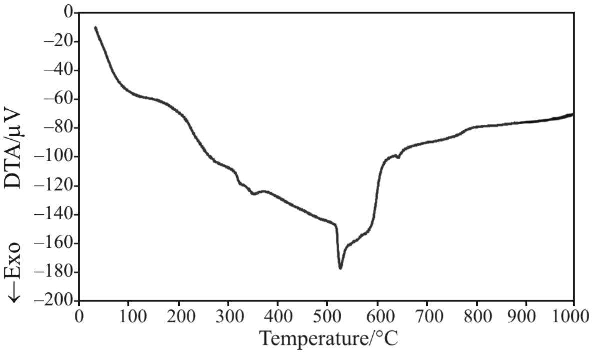

**Fig. 2** DTA curve of starch acetate (potato starch; DS=0.030)

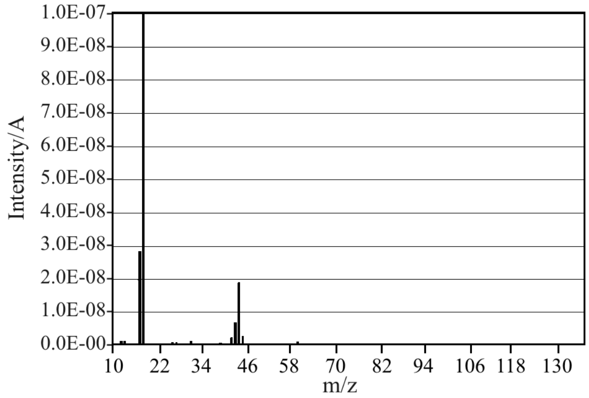

**Fig. 3** Mass spectra of starch acetate at 250°C (potato starch; DS=0.030)

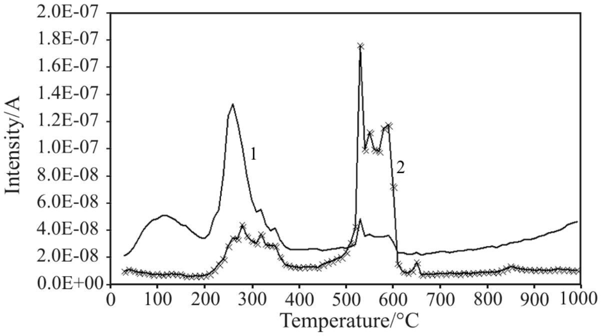

**Fig. 4** Temperature dependence of the ion current intensities for the measured fragments of the $m/z$. Sample: starch acetate; DS=0.030. 1 – $m/z=18$, 2 – $m/z=44$

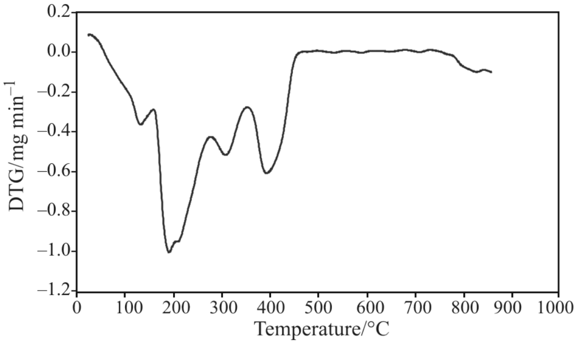

**Fig. 5** DTG curve of carboxymethyl starch (corn starch; DS=0.184)

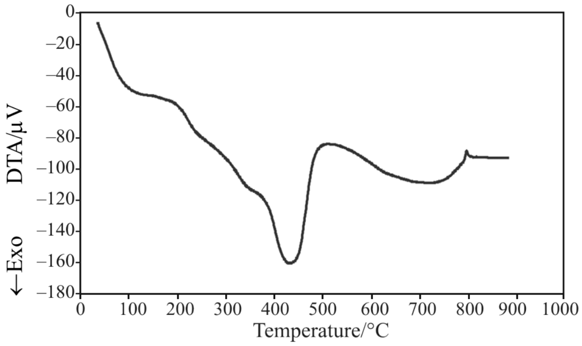

**Fig. 6** DTA curve of carboxymethyl starch (corn starch; DS=0.184)

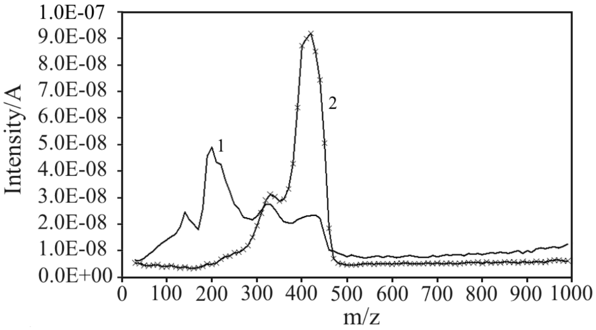

**Fig. 7** Temperature dependence of the ion current intensities for the measured fragments of the *m*/*z*. Sample: carboxymethyl starch; DS=0.184. 1 – *m*/*z*=18, 2 – *m*/*z*=44

evolved mainly at the second and the third step corresponding to temperatures 320 and 400°C, respectively. The modification of OH groups in starch by etherification changes the decomposition patterns. Furthermore, the presence of sodium cation in carboxymethyl starch may altered the thermal decomposition of etherified derivative of starch. It was reported that the cations play a key role in the decomposition of lignins [13].

In order to determine the thermal stability of the starch derivatives, 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 investigated starch esters and ethers, i.e. starch acetates and carboxymethyl starch derived from starch of different botanical source and with different DS are summarized in Table 1.

It was reported that the thermal degradation in air of the tosyl amylomaize starch (DS=1.09) was initiated at a lower temperature (196°C) than in the case of the unmodified amylomaize starch (303°C) [2]. However, with increasing content of tosyl groups (DS=0.61–2.02), an increase in stability from 166 to 213°C was observed. The similar observation was reported by others [9, 12, 14]. These findings were explained by the lower amount of remaining hydroxyl groups after esterification. A previous study showed that water is the main product of decomposition of starch below 300°C, formed by intermolecular or intramolecular condensation of starch hydroxyl [13]. Thus, the increase in thermal stability of starch esters with increasing the degree of substitution was observed. This relationship was also observed in the etherified high amylose corn starch [10, 11].

Otherwise, comparing the thermal stability of the studied starch derivatives with different DS, no correlation appear between them. The increase in the level of substitution does not cause the increase in the thermal stability of esterified and etherified starches. It can be explained by the low DS (<0.18) of the investigated starch derivatives in comparison with those re-

**Table 1** Thermal characteristics of derivatives

| Sample | Starch | DS | $T_{5\%}$/°C | $T_{10\%}$/°C | $T_{20\%}$/°C | $W_{150}$/% | $W_{200}$/% | $W_{250}$/% | $W_{300}$/% | $W_{350}$/% |
|---|---|---|---|---|---|---|---|---|---|---|
| Starch acetate | corn | 0.089 | 166.5 | 188.9 | 212.6 | –2.1 | –11.8 | –39.1 | –52.2 | –55.7 |
| | potato | 0.030 | 171.4 | 224.8 | 244.7 | –3.7 | –6.6 | –24.2 | –54.6 | –59.8 |
| | potato | 0.036 | 174.4 | 222.4 | 242.9 | –1.7 | –6.9 | –24.9 | –55.9 | –61.4 |
| | wheat | 0.052 | 140.3 | 195.5 | 231.5 | –6.5 | –10.6 | –31.3 | –54.1 | –57.2 |
| | wheat | 0.081 | 133.4 | 173.1 | 226.7 | –7.8 | –13.4 | –30.4 | –56.0 | –59.9 |
| Carboxymethyl starch | corn | 0.181 | 155.6 | 185.3 | 207.2 | –4.2 | –16.4 | –35.9 | –46.0 | –54.9 |
| | corn | 0.184 | 158.8 | 187.2 | 199.1 | –3.8 | –15.5 | –34.5 | –45.3 | –54.9 |
| | potato | 0.029 | 154.3 | 212.2 | 247.7 | –4.7 | –8.2 | –20.9 | –35.4 | –44.1 |
| | potato | 0.059 | 168.2 | 188.6 | 209.1 | –3.6 | –15.4 | –34.2 | –43.6 | –53.5 |
| | potato | 0.076 | 168.7 | 190.9 | 210.4 | –3.2 | –14.3 | –33.7 | –44.3 | –54.8 |
| | wheat | 0.059 | 152.4 | 183.8 | 204.8 | –4.7 | –17.5 | –38.7 | –49.5 | –61.1 |
| | wheat | 0.088 | 134.2 | 159.5 | 198.6 | –8.4 | –20.5 | –38.6 | –48.7 | –58.3 |

ported in the literature. The reported starch derivatives have much higher DS (>1).

## Conclusions

The major DTG peak observed for starch derivatives is observed below 300°C. The mass loss up to this temperature is about 50%. The most abundant ions found are $H_2O^+$ and $CO_2^+$. For the starch derivatives of low degree of substitution (DS<0.18) of this study no correlation was found between thermal stability and the level of substitution regardless of the nature of substitution.

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