Carbohydrate Polymers 112 (2014) 721–728

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Thermal degradation and stability of cationic starches and their complexes with iodine

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ARTICLE INFO

Article history:
Received 3 February 2014
Received in revised form 16 May 2014
Accepted 6 June 2014
Available online 20 June 2014

Keywords:
Cationic starch
Cationic starch–iodine complex
Thermal degradation
Kinetics

ABSTRACT

Thermal degradation processes of cationic starch (CS) and CS–iodine complex were investigated by thermogravimetry (TG) in air and under nitrogen atmosphere at 10 °C min^{-1} heating rate and compared. Moreover, the thermal stability of CS with different degree of substitution (DS) and their complexes with iodine was studied by TG under nitrogen atmosphere at different heating rates. The average E_a values for CS were found to be slightly lower as compared to native starch, suggesting lower thermal stability of modified starches due to cationisation. The main thermodegradation event of native starch–iodine and CS–iodine complexes can be separated in two steps: the release of iodine in the range of 137–196 °C, followed by the subsequent iodine induced thermochemical degradation of polysaccharide macromolecules, which appears at lower temperatures than in the absence of iodine. "Blue" inclusion complex showed higher thermal stability than ionic CS–iodine complex.

1. Introduction

Cationic starches are important industrial derivatives in which the starch is given a positive ionic charge by introducing ammonium, amino, imino, sulfonium, or phosphonium groups. CS are used on a large scale by the paper industry as wet-end additives, surface size, and coating binders. Cationic starches containing quaternary ammonium groups are one of the most important commercial derivatives (Xie, Liu, & Cui, 2005). They can also be potentially used in medical applications in antimicrobial products formulations. The use of such polymeric materials with antimicrobial properties gains an increasing interest from both academic and industrial point of view. Polymers can act as matrix holding the antimicrobial agents, or polymers can possess antimicrobial activity themselves (Munoz-Bonilla & Fernandez-Garcia, 2012). In the previous study, it has been shown that starch derivatives containing quaternary ammonium groups show the antimicrobial activity; however, they are more bacteriostatics, rather than bactericides (Bendoraitiene et al., 2013). Therefore, in order to enhance the antimicrobial activity, an effective antimicrobial agent such as iodine could be introduced, and complexes of polysaccharide with iodine could be obtained. Polysaccharide containing positively charged quaternary ammonium compounds can bind negatively charged triiodide anions (I_3^-) through electrostatic interaction; hence, iodophors can be formed in such a way (Klimaviciute, Bendoraitiene, Rutkaite, & Danilovas, 2011). It is well known that single helix V-amylose has a central hydrophobic cavity in which the polyiodide chains can also reside (Immel & Lichtenthaler, 2000; Putseys, Lamberts, & Delcour, 2010). However, anhydrous V-amylose can absorb only ~30% of its weight of iodine vapour to form an unstable complex (Murdoch, 1992). Moreover, our previous investigation showed that cationic starch–iodine complexes showed greater antimicrobial activity, than non-cationic starch–iodine complexes (Bendoraitiene et al., 2013). Therefore, the use of cationic starch in the formation of iodophores is promising. Such complexes, as antimicrobial additives, could be introduced into antimicrobial products during thermal processing of plastic films, coatings, etc.

Conventional preparation of thermoplastic materials are carried out at relatively high temperatures, which could cause the degradation of the antimicrobial additive. The extent of degradation depends on temperature and length of time used in the processing, which have a significant influence on the properties and technological applications that can be utilized (Pineda-Gomez, Coral, Ramos-Rivera, Rosales-Rivera, & Rodriguez-Garcia, 2011). Therefore, being aware of thermal degradation and stability of cationic starches and especially their complexes with iodine is important. To date, there are no reports of such investigation of these cationic starch-based bactericides. It is of great interest for scientists and engineers to understand the changes in thermal degradation and

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http://dx.doi.org/10.1016/j.carbpol.2014.06.038
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stability that take place during any modification of starch in order to have proper control of the thermal processing of starch-based materials.

This paper aims at investigating the influence of the degree of substitution on the thermal degradation and stability of cationic starches and their complexes with iodine. Both thermal decomposition processes of CS and CS–iodine complexes in air and under nitrogen atmosphere have been investigated and compared. The apparent activation energies in the decomposition process were calculated by applying different methods.

2. Materials and methods

2.1. Materials

The native potato starch (Antanavas Starch Plant, Lithuania) was dried at 105 °C before use. 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) (70%, Fluka), epichlorohydrin (99%, Aldrich) were used as received. I_2–KI fixanal were purchased from Fluka. All other chemicals were of analytical grade and prepared or purified by standard procedures.

2.2. Preparation of cationic starch and their complexes with iodine

The *N*-(2-hydroxyl)-propyl-3-trimethyl ammonium starch chloride (CS) was obtained by starch cationization with EPTMAC in the presence of sodium hydroxide as a catalyst (the molar ratio anhydroglucoside unit (AGU):EPTMAC:catalyst:H_2O was 1:0.2–0.52:0.044:3–6) at 45 °C for 24 h. The molecular mass of the AGU was assumed as a mole of starch. After the reaction, CS microgranules were washed five times with water–isopropanol mixture, purified by Soxhlet extraction with methanol for 24 h and dried. The number of cationic groups in CS was expressed as the degree of substitution (DS), which was calculated from the nitrogen content estimated by the Kjeldahl method (Houben-Weyl, 1953). The data on the preparation of CS and their properties were previously published in Bendoraitiene et al. (2013) and Kavaliauskaite, Klimaviciute, and Zemaitaitis (2008). Cationic starch complexes with iodine were prepared by reaction of CS with iodine present in aqueous iodine–potassium iodide solution. The iodine content in samples was determined using iodometric titration with sodium thiosulfate. The iodine content in samples was 6.7–6.9 wt%.

2.3. Thermogravimetry (TG)

The thermogravimetric analysis was performed with a Perkin Elmer (TGA 4000) instrument. The measurements were carried out at heating rates of 2.5 °C min^{-1}, 5 °C min^{-1}, 10 °C min^{-1} and 20 °C min^{-1} under nitrogen atmosphere (flow rate 20 cm^3 min^{-1}) and at heating rate of 10 °C min^{-1} in air. About 10.0 mg of sample was loaded in the ceramic pan. The apparent activation energy E_a was determined according to Flynn–Wall–Ozawa (*F–W–O*), modified Coats–Redfern and Kissinger methods.

3. Theoretical approach of kinetics

The fundamental rate equation used in all kinetic studies can be described as

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where k is the rate constant and $f(\alpha)$ is the reaction model, a function which depends on the actual reaction mechanism. Eq. (1) expresses the rate of conversion, $d\alpha/dt$, at a constant temperature as a function of the reactant concentration loss and rate constant. In this study, the conversion rate α is defined as

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \quad (2)$$

where W_t, W_0, and W_f are sample weight at certain time t, initial weight, and final weight, respectively. The rate constant k is generally given by the Arrhenius equation:

$$k = A \quad \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

where E_a is the apparent activation energy (kJ/mol), R is the gas universal constant (8.314 J K^{-1} mol^{-1}), A is the pre-exponential factor (min^{-1}), and T is the absolute temperature (K). By combining Eqs. (1) and (3) the following relationship is obtained:

$$\frac{d\alpha}{dt} = A \quad \exp\left(\frac{-E_a}{RT}\right) f(\alpha). \quad (4)$$

For dynamic TGA data obtained at a constant heating rate, $\beta = dT/dt$, this term is inserted into Eq. (4), to obtain

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \quad \exp\left(\frac{-E_a}{RT}\right) f(\alpha). \quad (5)$$

Eqs. (4) and (5) are the fundamental expressions to calculate the kinetic parameters based on TGA data.

The methods used to obtain kinetic parameters of cationic starches and their complexes with iodine are summarized in Table 1.

The isoconversional Flynn–Wall–Ozawa (*F–W–O*) integral method is a relatively simple method for determining the E_a directly from mass loss versus temperature curve at multiple heating rates (Erceg, Kovacic, & Klaric, 2005), without a *priori* assumption of the mechanistic model. The plot of log β versus $1/T$ produces a straight line for each selected conversion. E_a was calculated from the slope of the linear plots for every selected rate of conversion. The modified Coats–Redfern method is a multi-heating rate application of the Coats–Redfern equation producing a model-free isoconversional approach. Plotting the left hand side for each heating rate versus $1/T$ at that heating rate gives a series of straight lines of slope (E_a/R). The full solution is to be done iteratively by first assuming a value of E_a and then recalculating the left hand side until convergence occurs. A quick solution is also available by moving $((1 - 2RT)/E_a)$ into the intercept and assuming that it is a constant (Yao, Wu, Lei, Guo, & Xu, 2008).

4. Results and discussion

4.1. Thermal degradation of cationic starches

The TG curves of cationic starch (DS = 0.34) at 10 °C min^{-1} in air (dotted line) and under nitrogen atmosphere (solid line) are shown in Fig. 1. The inset figure on the right is the corresponding derivative (DTG) curve for the degradation process.

Thermal events of cationic starch in air and under nitrogen atmosphere proceed in three and two stages, respectively. The characteristic temperatures and mass losses (M_l) in every temperature domain and stage, obtained from TG and DTG curves in air and under nitrogen atmosphere, are given in Table 2. From this data, the conclusion can be drawn that the first stage of $CS_{(DS=0.34)}$ mass loss develops within the same temperature range in air and in nitrogen, namely at 35–127 °C and 35–126 °C, respectively. Moreover, in these two cases the temperature ranges and the corresponding mass losses are almost identical. This thermal event was related to the elimination of physically retained water. The dehydration is usually not considered to affect thermal degradation of starch in most of the studies (Liu et al., 2010, 2013; Liu, Yu, Liu, Chen,

Table 1
Kinetic methods used to evaluate activation energy.

Method	Expression	Plots	References
Flynn–Wall–Ozawa	$\log \beta = -0.4567 \left(E_a/RT\right) - 2.315 + \log \left((A \times E_a)/(R \times g(\alpha))\right)$	$\log \beta = \text{against} 1/T$	Flynn and Wall (1966), Ozawa (1965)
Coats–Redfern (modified)	$\ln \left[\beta/\left(T^2\left(1 - 2RT/E_a\right)\right)\right] = \ln \left[-AR/(E_a \ln(1-\alpha))\right] - E_a/RT$	$\ln \left(\beta/T^2\right) = \text{against} 1/T$	Brown et al. (2000), Coats and Redfern (1964)
Kissinger	$\ln \left(\beta/T_m^2\right) = \ln \left((A \times R)/E_a\right) + \left(1/T_m\right) \times \left(-E_a/R\right)$	$\ln \left(\beta/T_m^2\right) = \text{against} 1/T_m$	Kissinger (1956)

Table 2
Characteristic data for the thermal degradation of $CS_{(DS = 0.34)}$ from TG–DTG analysis at 10 °C min^{-1} heating rate.

Temperature range (°C)	Stage	Characteristic parameters[a]	Values of characteristic parameters	
			In air	In N_2
35–127	I	T_i (°C)	35	35
		T_m (°C)	74	73
		T_f (°C)	127	126
		M_l (%)	3.9	4.0
245–359	II	T_i (°C)	245	245
		T_m (°C)	285	287
		T_f (°C)	359	358
		M_l (%)	62.7	69.5
359–607	III	T_i (°C)	359	–
		T_m (°C)	519	–
		T_f (°C)	607	–
		M_l (%)	30.6	–
Sample residue at 700 °C (%)			2.4	11.3

[a] T_i is the initial thermal degradation temperature; T_m is the temperature at the maximum degradation rate; $T_f$is the final thermal degradation temperature; $M_l$is the mass loss.

& Li, 2008; Liu, Yu, Liu, Chen, & Li, 2009; Soares, Lima, Oliveira, Pires, & Soldi, 2005). As we can see the investigated sample after loss of adsorbed and bound water was stable up to 245 °C and the real chemical degradation of $CS_{(DS=0.34)}$ began above this temperature at the second stage, which corresponds to 60–70% of mass loss. During the degradation in air, the intermediary resulted in the second stage is further burned by glowing combustion in the third stage, while under nitrogen atmosphere a thermally stable carbonaceous residue remains (11.3 wt% at 700 °C). However, the degradation mechanism in air up to the temperature of the maximum degradation rate of the second stage should be identical to that under nitrogen atmosphere since the thermograms are identical within the 35–287 °C temperature range (Fig. 1). Thus, the conclusion could be made, that initiation of the polysaccharide breakdown is a non-oxidative process.

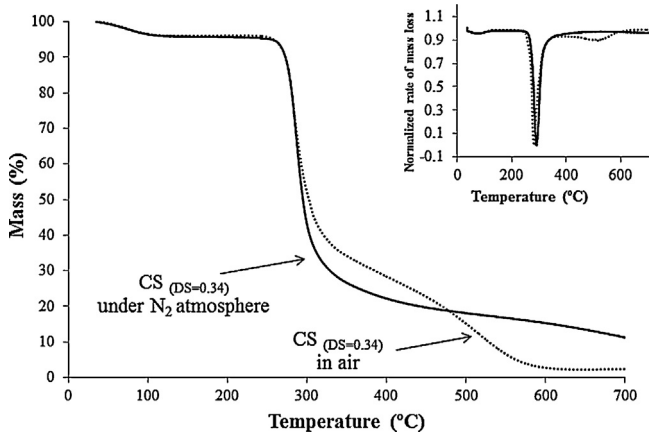

Fig. 1. Thermal decomposition detected by TGA for $CS_{(DS=0.34)}$ in air (dotted line) and under nitrogen atmosphere (solid line), heating rate 10 °C min^{-1}.

It has been shown earlier that at higher temperatures, depolymerization of the macromolecules of native starch takes place with the formation of β-(1,6) anhydro D-glucopyranose (levoglucosan), 2-furaldehyde (furfural) and a range of lower molecular-weight volatile and gaseous fragmentation products (Aggarwal & Dollimore, 1998). In nitrogen atmosphere a carbonaceous residue remains after all the volatile products have been driven off. Pyrolysis of native starch at 300 °C in a stream of nitrogen was shown to give volatiles, such as CO_2, CO, water, acetaldehyde, furan and 2-methyl furan. The distribution of products formed showed little difference when the pyrolysis was conducted in air or oxygen. Aggarwal, Dollimore, and Heon (1997) in thermal degradation studies of native starch or cellulose in air and under nitrogen atmosphere also investigated, that initiation of the breakdown of native polysaccharides is non-oxidative process. In this study we observed that similarly to native starch, oxygen present in air does not induce thermal degradation of cationic starch.

In Fig. 2, the TG and DTG curves for the main stage of degradation of native starch and cationic starches with different DS obtained under nitrogen atmosphere at 5 °C min^{-1} heating rate are presented. The TG and DTG curves of CS showed the main stage of degradation occurred in the range of 230–341 °C, corresponding to ca. 62–66% mass loss. Despite some differences in terms of residual mass, similar profiles of the curves of mass loss were observed. Meanwhile, it could be clearly seen that native starch decomposes at higher temperatures, as the main stage of degradation is in the range of 250–345 °C, with residual mass being 66%, which is almost the same as in the case of CS. Consequently, the thermal decomposition temperature of native starch is ca. 15–20 °C higher than that of CS, showing that thermal decomposition temperature of polysaccharide decreases after cationisation.

Liu et al. (2010) suggest that in the native starch-conversion process, the primary attack is the hydrolysis of α-1,4 glycosidic linkages in the amylose and amylopectin molecules. In addition, the scission of α-1,6 linkages may occur, and α-1,4 linkages are more susceptible to hydrolysis than α-1,6 linkages. Yang et al. (2013)

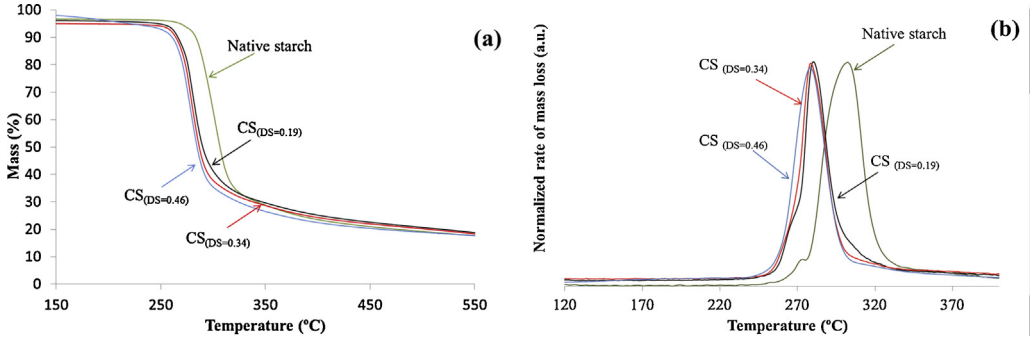

Fig. 2. The TG (a) and DTG (b) curves of the non-isothermal degradation process of native starch and CS with different DS, recorded at the heating rate of 5 °C min^{-1}.

proposed the mechanism of native starch thermo-degradation, which starts first with a scission of glycosidic bonds, namely the primary formation of the glycosidic radicals. Yang et al. (2013) suggest that starch macromolecules are not directly converted to low molecular weight volatile products, char and levoglucosan, but undergo intermediate physical and chemical changes. However, during thermal degradation of cationic starch, additional reactions could be envolved due to the scission of cationic groups, which lower the thermal degradation temperature of the polysaccharide. Quaternary ammonium-containing cationic groups can start to decompose according to the Hofmann elimination reaction or a nucleophilic attack of the ammonium counter-ion on the ammonium in a reverse Menschutkin-type reaction (Sowmiah, Srinivasadesikan, Tseng, & Chu, 2009). Furthermore, the amines resulting from either Hofmann elimination or from nucleophilic attack of chloride could then enhance the mechanism of random chain scission due to their nucleophilic character (Hablot, Bordes, Pollet, & Averous, 2008). A reduction in decomposition temperature with increasing substitution was also reported for cellulose (Yan, Tao, & Bangal, 2009), hemicelluloses (Ren, Sun, Liu, Chao, & Luo, 2006) and agarose (Pradoa, Matulewicz, Bonelli, & Cukierman, 2011), modified with the same cationic group. The lower molecular weight of polysaccharides after chemical modification could have influenced their thermal stability. Ren et al. (2008) suggest that the lower thermal stability of the modified hemicelluloses was due to the fact that the hydrogen bonds were destroyed by chemical modification. Such conclusions could also explain the decreasing thermal decomposition temperature with increasing DS of cationic starches used in this study.

4.2. Thermal degradation of cationic starch–iodine complexes

Fig. 3 shows TG mass loss curves for $CS_{(DS=0.34)}$–iodine complex at the heating rate of 10 °C min^{-1}. Multistep pattern was characteristic for degradation of this complex.

TG curves of CS–iodine sample in air and under nitrogen atmosphere could be fragmented into at least five and three stages, respectively. The first one is related to the loss of absorbed water in the range of 35–128 °C, and second one is due to the thermal degradation of $CS_{(DS=0.34)}$–iodine complex in the range of 168–203 °C. During this event, the released iodine from the complex was shown to induce the thermochemical degradation of cationic starch, and its main degradation event occurred at the third stage in the range of 203–319 °C (see Table 3). In this case, the observed main degradation stage of CS occurred at much lower temperatures than compared to the CS, where no iodine was present in the sample (see Fig. 1 and Table 2). The initial degradation temperature (T_i) of CS influenced by the iodine released from decomposed $CS_{(DS=0.34)}$–iodine complex was observed to be lower by more than 42 °C, compared to the T_i of $CS_{(DS=0.34)}$ sample. On the other hand, it could be clearly seen from Fig. 3 that TG curves in air and under nitrogen atmosphere are essentially identical for all three degradation stages. Therefore, the conclusion can be made that oxygen does not induce the start of thermal decomposition of $CS_{(DS=0.34)}$–iodine complex. The differences in TG data can be seen only at the temperatures above 318 °C, where the mass of the sample in the air decreases more rapidly, than under nitrogen atmosphere.

Fig. 4 shows the TG and DTG thermograms for the main stage of degradation of native starch–iodine and CS–iodine complexes, under nitrogen atmosphere at 5 °C min^{-1} heating rate. It may be seen that the mass loss which is attributed to the complex degradation appears at lower temperatures in the case of CS–iodine complexes, as compared to that of native starch–iodine complex. When complexes brake down, the iodine released from the complex further induces thermochemical degradation of the polysaccharide, which occurs at much lower temperatures than compared to the sample, where no iodine was present (Figs. 2 and 4). Our recent studies have shown that in CS with low DS, iodine could be introduced both into an inclusion complex and into an ionic complex due to interaction with cationic groups (Bendoraitiene et al., 2013; Klimaviciute et al., 2011). However, by increasing the DS, more iodine is bound into an ionic complex and less iodine could be introduced into inclusion complex. In this study, the sequence of thermal decomposition temperature of complexes with iodine was observed to be native starch–iodine > $CS_{(DS=0.19)}$–iodine > $CS_{(DS=0.34)}$–iodine > $CS_{(DS=0.46)}$–iodine, which is in accordance with the cationic groups content. Such results indicate that inclusion complex breaks at higher temperature, than ionic complex.

Moreover, it could be seen that degradation process runs differently in the case of native starch–iodine inclusion complex. For

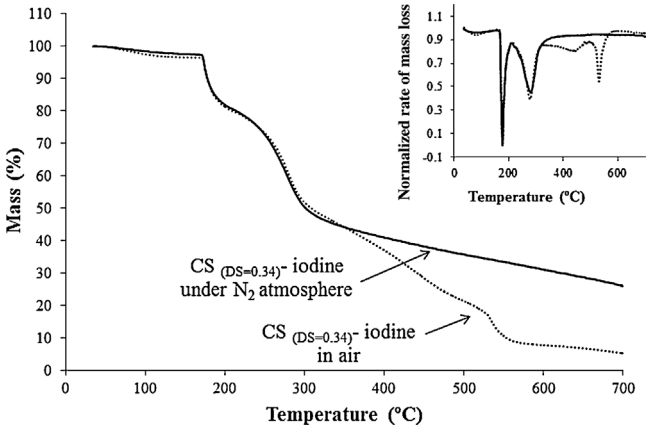

Fig. 3. Thermal decomposition detected by TGA for $CS_{(DS=0.34)}$–iodine complex in air (dotted line) and under nitrogen atmosphere (solid line), heating rate 10 °C min^{-1}.

Table 3
Characteristic data for the thermal degradation of $CS_{(DS=0.34)}$–iodine from TG–DTG analysis at 10 °C/min heating rate.

Temperature range (°C)	Stage	Characteristic parameters[a]	Values of characteristic parameters	
			In air	In N_2
35–128	I	T_i (°C)	35	35
		T_m (°C)	78	79
		T_f (°C)	128	127
		M_l (%)	3.2	2.1
168–203	II	T_i (°C)	169	168
		T_m (°C)	175	174
		T_f (°C)	203	203
		M_l (%)	15.7	15.9
203–319	III	T_i (°C)	203	203
		T_m (°C)	279	279
		T_f (°C)	318	319
		M_l (%)	32	34
318–499	IV	T_i (°C)	318	–
		T_m (°C)	441	–
		T_f (°C)	499	–
		M_l (%)	26.8	–
499–584	V	T_i (°C)	499	–
		T_m (°C)	535	–
		T_f (°C)	584	–
		M_l (%)	13.5	–
Sample residue at 700 °C (%)			5.4	26.1

[a] T_i is the initial thermal degradation temperature; T_m is the temperature at the maximum degradation rate; T_f is the final thermal degradation temperature; M_l is the mass loss.

CS–iodine decomposition process distinct peaks in DTG curves can be clearly observed at degradation stage 2 and stage 3, whereas native starch–iodine complex shows multistep degradation process corresponding to a peak with shoulders, due to the overlapping peaks (Fig. 4b). It could be hypothesized that iodine from native starch–iodine complex is released at higher temperatures having higher kinetic energy, therefore, inducing rapid thermooxidative destruction of polysaccharide.

4.3. Kinetic analysis of thermal degradation of CS and their complexes with iodine

The kinetic parameters were calculated for the second thermal event of native and cationic starches. However, in the case of CS–iodine complex degradation, the DTG peaks at stage 2 and stage 3 partially overlap, so further separation of these thermal degradation processes by the deconvolution of DTG curves was necessary (Katsikas & Popovic, 2003). The deconvoluted DTG curve peaks were then integrated, and the E_a was calculated for the thus-formed TG curves of the second thermal event. As could be seen from Fig. 4b, many thermal events for native starch–iodine complex degradation overlap, resulting in a broad peak with shoulders. Therefore, the DTG curves for native starch–iodine complex could not be deconvoluted. Instead, the activation energy for the second thermal event of "blue" inclusion complex was calculated for 6.9% mass loss, which corresponds to iodine content in the sample. The reaction limits employed are presented in Tables 4 and 5.

Fig. 5 represents the typical isoconversional plots based on *F–W–O* and modified Coats–Redfern methods for $CS_{(DS=0.34)}$ and $CS_{(DS=0.34)}$–iodine complex, which show a general trend of activation energy.

In the case of $CS_{(DS=0.34)}$, (Fig. 5a and c) it can be seen that the fitted lines are nearly parallel when the conversion rate is $\alpha < 0.5$, which indicates approximate activation energies at different conversions and consequently implies the possibility of single reaction mechanism or the unification of multiple-reaction mechanisms (Liu et al., 2010). In the case of the second thermal event of $CS_{(DS=0.34)}$–iodine complex (Fig. 5b and d), the fitted lines are nearly parallel at all conversion rates, in the range of 0.1–0.9. This also shows a high possibility of single reaction mechanism, which could be attributed to the release of iodine from the complex.

Fig. 6 shows the dependence of E_a on conversion rates based on *F–W–O* and modified Coats–Redfern methods. Fig. 6a and d clearly shows that the thermal decomposition of native and cationic

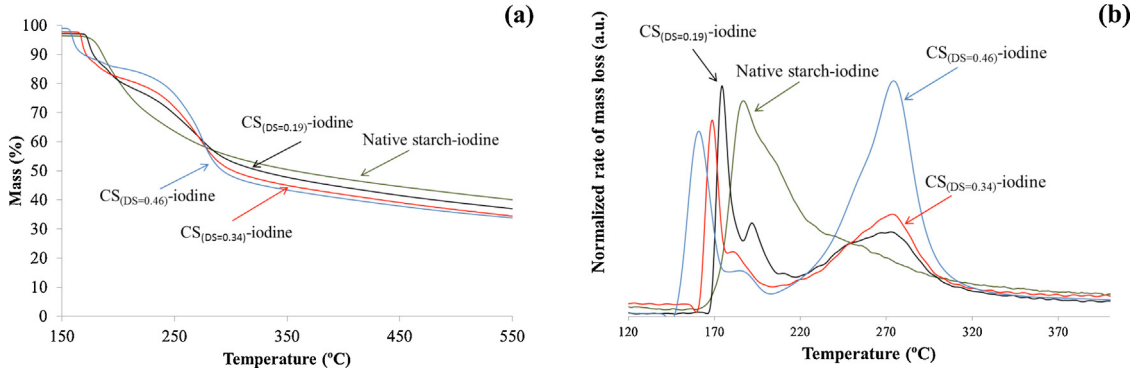

Fig. 4. The TG (a) and DTG (b) curves of the non-isothermal degradation process of native starch–iodine and CS–iodine complexes, recorded on the heating rate of 5 °C min^{-1}.

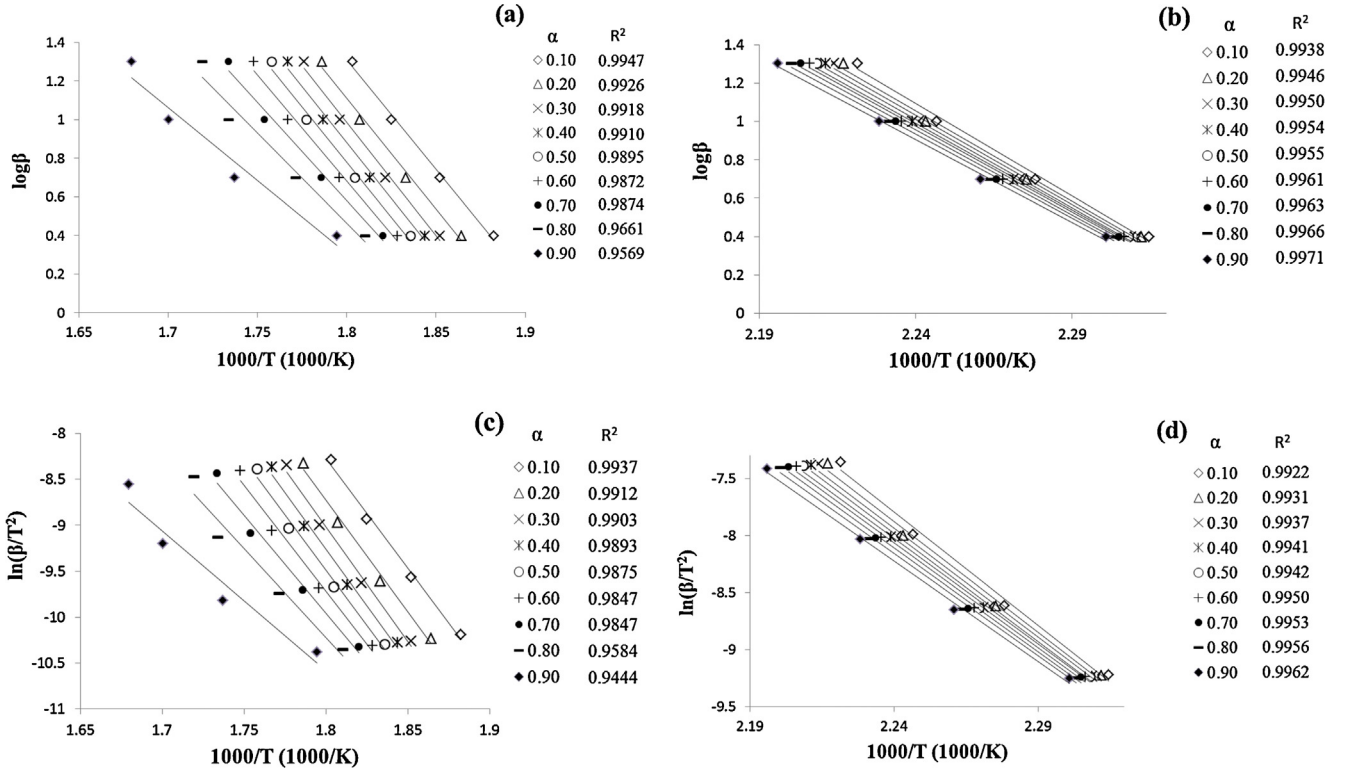

Fig. 5. Typical isoconversional plots of *F–W–O* method for $CS_{(DS=0.34)}$ (a) and $CS_{(DS=0.34)}$–iodine (b), modified Coats–Redfern method for $CS_{(DS=0.34)}$ (c) and $CS_{(DS=0.34)}$–iodine (d).

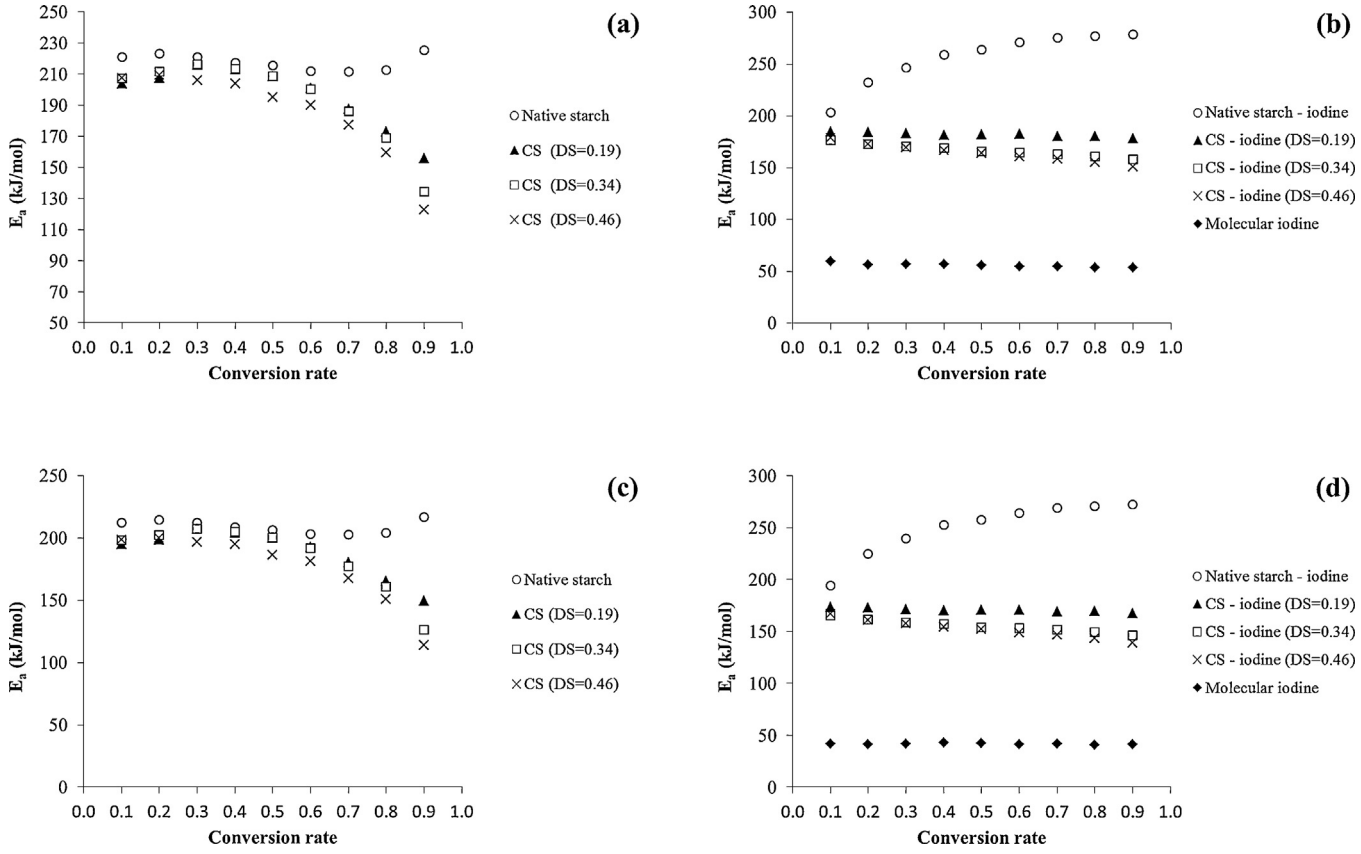

Fig. 6. Plots of apparent activation energy as a function of decomposition conversion rate (α), calculated by different methods: *F–W–O* method for (a) and (b), modified Coats–Redfern method (c) and (d).

Table 4
E_a calculated according to different methods at reaction limits taken from TG/DTG curves of native starch and CS.

Sample	Heating rate (°C min^{-1})	Temperature range (°C)	Mass loss (%)	F–W–O		Modified Coats–Redfern		Kissinger	
				E (kJ mol^{-1}) (α = 0.1–0.4)	R^2	E (kJ mol^{-1}) (α = 0.1–0.4)	R^2	E(kJ mol^{-1})	R^2
Native starch	2.5	241–335	61.3	220.4 ± 2.4	0.9887 ± 0.0018	211.8 ± 2.5	0.9867 ± 0.0021	223.1	0.9885
	5	250–345	66.1						
	10	257–350	67.9						
	20	261–363	69.4						
$CS_{(DS=0.19)}$	2.5	224–336	62.6	209.9 ± 5.3	0.9933 ± 0.0023	201.2 ± 5.4	0.9920 ± 0.0027	213.9	0.9930
	5	231–341	65.1						
	10	235–363	68.8						
	20	244–370	72.2						
$CS_{(DS=0.34)}$	2.5	233–302	58.3	211.9 ± 3.9	0.9925 ± 0.0016	203.2 ± 3.9	0.9911 ± 0.0019	215.9	0.9628
	5	241–334	63.9						
	10	245–358	69.5						
	20	251–401	73.9						
$CS_{(DS=0.46)}$	2.5	233–299	59.7	206.5 ± 2.4	0.9885 ± 0.0016	197.5 ± 2.3	0.9863 ± 0.0019	212.2	0.9885
	5	237–317	62.8						
	10	241–341	67.5						
	20	244–359	72.7						

starches may be a multiple-step events since the relationship between E_a and α does not give a straight horizontal line . For cationic starches at conversion rates $\alpha > 0.4$, the decrease in E_a values could be noticed, whereas for native starch such behaviour has not been observed. This indicates different thermal degradation mechanisms of native and cationic starches. During thermal degradation of CS, the nitrogenous substances can be formed according to Hofmann elimination reaction or nucleophilic attack of chloride. Such substances can further take part in polysaccharide degradation reactions with lower activation energies.

However, linear relationship between E_a and α could be seen for all samples at conversion rates $\alpha \leq 0.4$. Therefore, the E_a values for the decomposition of CS and CS–iodine complexes (Tables 4 and 5) were determined in the conversion range of $0.1 \leq \alpha \leq 0.4$. Results show that E_a of cationic starches based on *F–W–O* and modified Coats–Redfern methods in the conversion range of $0.1 \leq \alpha \leq 0.4$ are about 11 kJ mol^{-1} lower than the E_a of native starch.

As could be seen from Fig. 6b and d, the linear relationship between E_a and α (calculated for 6.9% mass loss) for native starch–iodine complex has not been observed. Such results show that thermal decomposition of "blue" inclusion complex is a multiple-step mechanism from the beginning of complex degradation even at low conversion rates, probably due to the rapid thermooxidative destruction of polysaccharide, induced by released iodine. However, the relationship between E_a and α (calculated for the second thermal event of complexes from reconstructed TG curves) was observed to be linear for CS–iodine complexes with different DS. The obtained E_a for CS–iodine complexes based on *F–W–O* and modified Coats–Redfern method are about 112–118 kJ mol^{-1} higher than the obtained sublimation

Table 5
E_a calculated according to different methods at reaction limits taken from TG/DTG curves (for native starch–iodine sample) or deconvoluted DTG/reconstructed TG curves (for CS–iodine samples).

Sample	Heating rate (°C min^{-1})	Temperature range (°C)	Iodine content in sample (%)	*F–W–O*		Modified Coats–Redfern		Kissinger	
				E (kJ mol^{-1}) (α = 0.1–0.4)	R^2	E (kJ mol^{-1}) (α = 0.1–0.4)	R^2	E (kJ mol^{-1})	R^2
Native starch–iodine	2.5	152–183	6.9	235.4 ± 24.1	0.9842 ± 0.0014	227.7 ± 25.1	0.9815 ± 0.0018	–	–
	5	162–187							
	10	166–191							
	20	173–196							
$CS_{(DS=0.19)}$–iodine	2.5	143–172	6.7	183.4 ± 1.5	0.9945 ± 0.0018	171.8 ± 1.5	0.9932 ± 0.0022	170.7	0.9960
	5	161–178							
	10	171–184							
	20	176–191							
$CS_{(DS=0.34)}$–iodine	2.5	156–163	6.7	172.3 ± 3.3	0.9947 ± 0.0007	160.5 ± 3.4	0.9933 ± 0.0008	154.4	0.9958
	5	162–171							
	10	168–177							
	20	172–185							
$CS_{(DS=0.46)}$–iodine	2.5	137–156	6.9	172 ± 5.2	0.9949 ± 0.0016	159.8 ± 5.3	0.9935 ± 0.0020	149.5	0.9965
	5	146–164							
	10	158–170							
	20	160–177							
Molecular iodine	5	30–133	100	57.6 ± 1.4	0.9784 ± 0.0045	52.4 ± 2.1	0.9970 ± 0.0025	53.4	0.9738
	10	30–145							
	15	30–155							
	20	30–167							

energy of molecular iodine, which shows that iodine is strongly bound in the complexes. Moreover, the E_a for "blue" inclusion complex is much higher than for ionic CS–iodine complexes.

Kissinger's method is a special case in determining activation energy as it may not show the overall trend of E_a due to only some special conversion rate was used (Liu et al., 2010). However, the Kissinger is meaningful for determining E_a when the E_a is stable in certain conversion range. The results show fairly good linearity ($R^2 > 0.96$) for all samples (see Tables 4 and 5). The activation energy of cationic starches are similar, but lower by ~9.1 kJ mol^{-1} than that of native starch. The E_a values for CS complexes decrease with the increasing content of cationic groups (see Table 5). Results obtained by the Kissinger method support the data determined by other methods.

5. Conclusions

The apparent activation energies of thermal decomposition process determined using various kinetic methods including *F–W–O*, modified Coats–Redfern and Kissinger for cationic starches were found to be lower than that for native starch. E_a at low conversion rates ($\alpha \leq 0.4$) for cationic starches is lower by 9–11 kJ mol^{-1} than E_a for native starch. However, at higher conversion rates the significant decrease in E_a values for cationic starches could be noticed, which shows different mechanisms of thermal degradation of native and cationic starches. The sequence of thermal decomposition temperature of tested polysaccharides is native starch > $CS_{(DS=0.19)}$ > $CS_{(DS=0.34)}$ > $CS_{(DS=0.46)}$, which is in accordance with the cationic groups content. The results showed that the thermal stability of polysaccharide decreases with increasing content of cationic groups.

The thermal degradation processes of native starch and CS complexes with iodine were obtained to be multiple-step degradation events, with the decomposition of complexes and the release of iodine, followed by termochemical destruction of polysaccharide. An oxidizing action of the iodine molecules generated during the decomposition of complex was shown to reduce the degradation temperature of the polysaccharide. In addition, it was observed that the oxygen present in air does not induce the start of thermochemical decomposition of tested starches or their complexes with iodine. The sequence of E_a as well as thermal decomposition temperature of complexes is: native starch–iodine > $CS_{(DS=0.19)}$–iodine > $CS_{(DS=0.34)}$–iodine > $CS_{(DS=0.46)}$–iodine, which is also in accordance with the cationic groups content. The results showed that kinetic parameters of thermochemical destruction depend on the origin of the polysaccharide–iodine complex. E_a for thermal decompostion of CS–iodine complexes based on *F–W–O* and modified Coats–Redfern methods are similar and about 112–118 kJ mol^{-1} higher than the sublimation energy of molecular iodine. Such results show that iodine is strongly bound in the cationic starch complexes. Moreover, the "blue" inclusion complex was found to be more thermally stable than ionic CS–iodine complexes.

Acknowledgements

The authors are grateful to the Research Council of Lithuania and National Paying Agency under the Ministry of Agriculture for financial support of the project MT 1131.

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