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

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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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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,