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Thermal degradation of carbohydrate polymers in amorphous states: A physical study including colorimetry

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Abstract

The early stages of the thermal decomposition of dense matrices of maltodextrin are studied as a function of the molecular weight and the water content using colorimetry and near-infrared reflectance (NIR) spectroscopy. Dense matrices of maltodextrin prepared by solvent casting equilibrated at 25 °C at various water activities are subjected to elevated temperatures for various time intervals using specifically constructed, hermetically sealed cells. The degradation of the maltodextrins is followed colorimetrically and state of water in the thermally treated samples is investigated using NIR spectroscopy. The results are discussed in terms of kinetic models including matrix viscoelasticity and reaction order. The data show that to a good approximation the color formation can be modelled using an Arrhenius' type activation energy, independent of the physical state of the matrix (rubbery or glassy). The relevance of the results for carbohydrate processing and storage is highlighted.

Keywords: Maltodextrin; Water activity; Glass transition; Kinetics; Caramelization; Maillard reaction; Near infrared reflectance spectroscopy

1. Introduction

Carbohydrate polymers and mixtures of carbohydrates polymers and simple sugars are increasingly used as biodegradable polymers (Wikes, 2001) and as matrices for the encapsulation, stabilization and release of active ingredients, like flavors (Ubbink & Schoonman, 2003), drugs (Levine, 2002) and nutrients (Risch & Reineccius, 1995). For these applications, carbohydrates generally are used in the amorphous state. Principal advantages of using amorphous carbohydrates are that they combine interesting mechanical properties with the ability of forming films, particles and matrices of adjustable morphology. In addition, under controlled conditions in the glassy state, they combine high physical and chemical stability (Roos, 1995) with very high barrier properties for gases like oxygen and nitrogen (Schoonman, Ubbink, Bisperink, Le Meste, & Karel, 2002), and organic molecules (Gunning, Parker, & Ring, 2000).

A variety of processing techniques like extrusion, spray-drying, fluidized-bed drying is used to produce carbohydrate matrices for the various applications (Ubbink & Schoonman, 2003). During processing, amorphous carbohydrates are often subjected to significant stresses including shearing and elevated temperatures. Whereas the effect of for instance shear is well-understood, much less is known about the impact of thermal decomposition on the properties of carbohydrate polymers in dense states.

The effects of thermal stresses on systems containing carbohydrates are strongly dependent on the composition. Of principal importance to the food technologist is Maillard reaction, which comprises a whole plethora of reactions between reducing sugars and amino acids leading to the formation of brown color and the generation of taste and aroma compounds (Buera, Chirife, Resnik, & Wetzler, 1987a; Buera, Chirife, Resnik, &

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Lozano, 1987b; Kroh & Schulz, 2001; Lievonen, Laaksonen, & Roos, 2002; Schebor, Buera, Karel, & Chirife, 1999). A second general class of thermally induced reactions of relevance mainly for systems consisting of pure carbohydrates is the caramelization of carbohydrates, which leads, by mechanisms different from the Maillard reaction, also to the formation of brown color and flavor compounds (Kroh, 1994). Whereas the Maillard reaction has been extensively investigated both in aqueous solutions (Buera et al., 1987a) and in amorphous matrices above and below the glass transition temperature (Chung, Ruan, Chen, & Wang, 1999; Ibarz, Pagan, & Garza, 2000) virtually all current knowledge on the caramelization of sugars is from solution studies or from studies on crystalline solids (Chung et al., 1999; Ibarz et al., 2000; Kroh, Schröder, Mügge, Westphal, & Baltes, 1992; Kroh, 1994; Tschiersky & Baltes, 1989).

Caramelization comprises the reactions involved in the thermal decomposition of carbohydrates, in particular reducing mono- and disaccharides. Various stages of the caramelization reaction may be discerned (Kroh, 1994). The first step in most caramelization reactions involves internal reorganizations with the carbohydrates which are known as enolizations. The second step comprises the formation of the anhydro form of the carbohydrate via the elimination of a water molecule. This is followed by variety of chemical reactions which depend strongly on the precise sugar composition, sample conditions like pH and the temperature. In these intermediate stages, most of the volatile compounds associated with caramel flavor are formed. In a fairly late stage of the caramelization reaction, brown-colored polymeric substances are formed via radical polymerizations.

The caramelization of carbohydrate polymers and their mixtures with low-molecular-weight sugars is of interest for food processing not only because of the caramel flavor and color, but also because the changes in sugar structure and the liberation of water during the caramelization reaction could have a potentially significant effect on the mechanical and barrier properties of the carbohydrate system. In particular, the water liberated during caramelization could decrease the glass transition temperature of the amorphous carbohydrate matrix.

In the present paper, we focus on the early stages of the thermal decomposition of dense matrices of maltodextrin as a function of the molecular weight and the water content. Maltodextrins are interesting model systems for our studies because of their wide industrial use, their availability in large quantities in relatively pure form and their well-defined molecular weight distributions. Dense matrices of maltodextrin of four different molecular weight distributions which are equilibrated at 25 °C at various water activities are subjected to elevated temperatures for various time intervals using specifically constructed, hermetically sealed cells. The degradation of the maltodextrins is followed colorimetrically and state of water in the thermally treated samples is investigated using NIR spectroscopy. The results are discussed in terms of kinetic models including matrix viscoelasticity and reaction order.

2. Materials and methods

2.1. Preparation of matrices

All maltodextrin materials were obtained from Roquette Frères (Lestrem, France). The following dextrose equivalents (DE) were used: DE 6 (Glucidex IT-6, lot. no. E4489); DE 12 (Glucidex IT-12, lot. no. E8950); DE 21 (Glucidex IT-21, lot. no. 729083) and DE 33 (Glucidex IT-33, lot. no. 729084. The degree of hydrolysis of maltodextrins is indicated by the dextrose equivalent (DE) (Chronakis, 1998) which denotes the percentage fraction of reducing sugars in the sample (DE 1 is equivalent to non-hydrolyzed starch, DE 100 is equivalent to glucose), and is thus proportional to the number average molecular weight. The molecular weights of the samples and information on the content of glucose, maltose and maltotriose are given in Table 1. All materials were used without further purification as the carbohydrate content of all lots was higher than 98% on dry weight. The protein and amino acid content

Table 1
Molecular weight of maltodextrin samples and content of glucose (degree of polymerization (DP) = 1); maltose (DP = 2) and maltotriose (DP = 3)

DE	M_n (Da)[a,b]	M_w (Da)[a,c]	$Q_{DP=1}$[d]	$Q_{DP=2}$[d]	$Q_{DP=3}$[d]
6	n.d.	9.3×10^4	0.002	0.013	0.022
12	1.9×10^3	1.9×10^4	0.009	0.028	0.048
21	1.0×10^3	8.1×10^3	0.014	0.065	0.091
33	6.3×10^2	2.0×10^3	0.103	0.094	0.096

[a] The molecular weight distribution is determined by gel permeation chromatography with pullulan molecular weight standards.
[b] Number average molecular weight.
[c] Weight average molecular weight.
[d] Weight fractions; determined by high-pressure liquid chromatography.

of the maltodextrin samples is generally in the ppm-range or below and Maillard reactions may thus be safely be disregarded as principal mechanism of color formation.

Matrices were prepared by solvent casting and controlled evaporation as previously described (Kilburn et al., 2004). The maltodextrins were dissolved in demineralized water at 60 °C at a total solids content of 70 wt% using a Stephan VM60 mixer (Stephan, Germany). After dissolution by slow stirring (≈1 rpm) for 1–2 h, the samples were slowly concentrated by evaporation under reduced pressure (≈200 mbar) until the viscosity of the solution became too high for the mixer (after about 6 h). The concentrated solutions were then transferred into stainless-steel trays (layer thickness ≈1 cm) and dried at 60 °C under reduced pressure (400 mbar) using a Vacutherm vacuum oven (Hereaus Instruments, Germany). The cast samples were ground and further dried until a final water activity of about 0.1 was reached. The ground samples were sieved into size fractions; the size fractions between 200 and 300 μm were used for water-activity equilibration and all further experiments.

2.2. Sample equilibration and determination of the glass transition temperature by differential scanning calorimetry

Samples were equilibrated at 25 °C at various water activities in desiccators containing saturated salt solutions of known water activity ($a_w = 0.11$ (LiCl); $a_w = 0.22$ (CH_3COOK); $a_w = 0.33$ ($MgCl_2$); $a_w = 0.43$ (K_2CO_3); $a_w = 0.54$ ($Mg(NO_3)_2$); $a_w = 0.75$ (NaCl)) (Greenspan, 1977). The sorption of water was followed gravimetrically until equilibrium was achieved (generally within 35 days).

The water content was determined using a home-built extraction unit. This apparatus comprises a thermostated oil bath in which glass vacuum tubes are halfway inserted. The part of the tube within the oil bath contains the sample of which the water content needs to be determined; the part of the tube which protrudes out of the apparatus and consequently remains at room temperature contains the desiccant P_2O_5. Prior to the drying experiment, the tubes were evacuated to about 70 mbar. Full extraction of the water was achieved after 6 h at 102 °C.

The extraction of water was followed as a function of time by monitoring the decrease of the water peak at $\lambda = 1940$ nm in near infrared reflectance spectroscopy (see below). The variation between duplicates was <0.1% w/w on initial weight.

Calorimetric measurements were carried out using a Seiko 220C DSC (Seiko, Japan) as described previously (Kilburn et al., 2004). The T_g was determined from the onset of the change in heat flow observed at the second heating ramp.

2.3. Near infrared reflectance spectroscopy

A near infrared reflectance (NIR) spectrum was recorded between 1400 and 2400 nm using an InfraAlyzer 500 (Bran & Lübbe, Germany). In order to observe the effect of the thermal treatment on the state of water and carbohydrate in the spectra, a two-point normalization on the spectrum of non-treated powder was carried out at $\lambda = 1680$ and 2232 nm. The peaks at $\lambda = 1940$ and 2100 nm were analyzed as provide information on the state of water and carbohydrate, respectively. Both peaks are related to a combination of secondary and tertiary harmonics of the fundamental vibrations of water and the C–O bond, respectively.

2.4. Thermal treatment

The samples were subjected to controlled thermal treatments using a hermetically sealed home-built cell consisting of two aluminium discs containing a space for the samples which are sealed with an O-ring. One of the cells was equipped with a thermocouple located in the center of the sample space in order to monitor the temperature evolution in the powder. Approximately 4 g of powder was wrapped in aluminium foil and inserted in the sample chamber. The aluminium foil was used to avoid sticking of the sample to the walls of the cell. The cell was heated to the operating temperature before the experiment in order to minimise the time to thermal equilibrium. After the thermal treatment in a laboratory oven (Hereaus), the cells were cooled down to room temperature and left to stabilize for a minimum of two days. Immediately after opening of the cell, a NIR spectrum was recorded and the water activity was determined. The conditions for the thermal treatment of the samples were chosen in such a way as to have temperatures below T_g as well as above T_g. A first series of samples of maltodextrin DE 12 at $a_w = 0.15$ and $a_w = 0.57$ was treated at temperatures of 58, 88, 118 and 188 °C for various times between 0.5 and 72 h. The second and third series of samples comprising maltodextrin matrices of various DE equilibrated at various water activities were heated for 4 h at $T = 95$ °C and $T = T_g + 30$ °C.

2.5. Color measurements

Color measurements were performed at 25 °C using a handheld surface colorimeter (ColorEye CE 7000, Macbeth, Germany). The ColorEye is a small, portable colorimeter allowing the rapid measurement of the color parameters of surfaces including powders. Measurements were performed with the following setting: optical geometry = $d/8$, aperture diameter = 14 mm, illumination standard D65. The observer standard was CIE 2° and the color metric were set according to CIELAB.

The measurements were carried out using a measuring cuvette made of optical glass (LZM012, Lange, Germany).

Color measurements imply the measurement of three independent parameters L^*, a^* and b^*, where L^* signifies the luminosity of the surface, and varies between 0 (black) to 100 (white) (Joshi, 2001). The parameter a^* quantifies the redness ($a^* > 0$) and greenness ($a^* < 0$) of the sample and b^* records how yellow ($b^* > 0$) or blue ($b^* < 0$) a sample is. As we expect that brown color will develop in our samples, we thus anticipate shifts towards higher values of L^* and b^*.

A useful approach to quantitatively study the color evolution of a sample as a function of time is to combine all three-color parameters in one parameter. For this purpose, the so-called Hunter–Scotfield equation is often used (Ibarz, Pagan, & Garza, 1999)

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}, \quad (1)$$

where $\Delta L^* = L^*(\text{final}) - L^*(\text{initial})$; $\Delta a^* = a^*(\text{final}) - a^*(\text{initial})$; $\Delta b^* = b^*(\text{final}) - b^*(\text{initial})$.

In particular with samples heated to above the glass transition temperature, we have to be careful in order to avoid changes in the color parameters due to changes in the structure of the sample surface (and which do not originate in the 'intrinsic' color of the sample). For this purpose, we have ground all samples to approximately the same particle size before the color measurements.

3. Results and discussion

As it is our aim to investigate the relation between the degree of thermal degradation and the physical state of the carbohydrate matrix, we have determined the water sorption isotherm and the glass transition of the maltodextrin matrices as a function of the molecular weight and the water activity.

In Fig. 1, the water sorption isotherms of water on dense granules of maltodextrin are shown for the four degrees of hydrolysis (DE 6, DE 12, DE 21 and DE 33). Characteristic is the sigmoidal shape of the isotherms, which gets more pronounced with increasing degree of hydrolysis (i.e., with increasing DE). The moisture sorption data are fitted using the Guggenheim–Anderson–De Boer equation (GAB) (Anderson, 1946; Roos, 1995)

$$Q' = \frac{KCW_m a_w}{(1 - Ka_w)(1 - Ka_w + KCa_w)}, \quad (2)$$

where K, C and W_m are constants characterizing the system. Experience has shown that the GAB equation is particularly suited to fit the sigmoidal moisture sorption isotherms of water on biopolymeric matrices.

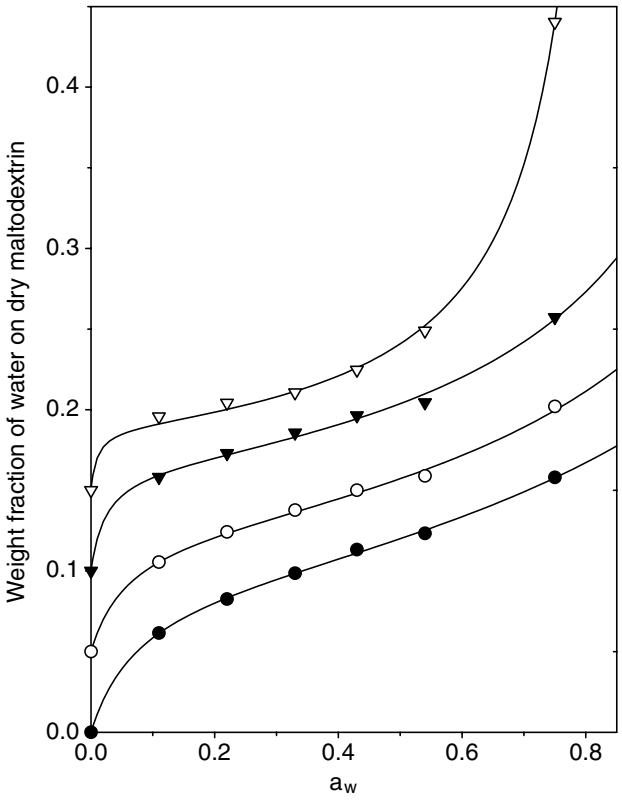

Fig. 1. Water sorption isotherms of maltodextrin matrices at 25 °C. Filled circles: DE 6; open circles: DE 12; filled triangles: DE 21; open triangles: DE 33. The isotherms for the DE 12, DE 21 and DE 33 matrices are vertically shifted by 0.05, 0.1 and 0.15 units, respectively. The solid lines represent the optimal fit using the GAB model.

The glass transition of amorphous biopolymers is a strongly decreasing function of the water content and decreases with decreasing molecular weight. An often-used relation to correlate the moisture sorption and glass transition data is the so-called Gordon–Taylor equation (Gordon & Taylor, 1952; Roos, 1995)

$$T_g = \frac{w_1 \cdot T_{g_1} + k_{GT} \cdot w_2 \cdot T_{g_2}}{w_1 + k_{GT} \cdot w_2}. \quad (3)$$

In Eq. (3), w_1 and w_2 are the weight fractions of maltodextrin and water, respectively, and k_{GT} is a system specific parameter. T_{g_1} is the glass transition temperature of the dry maltodextrin and T_{g_2} is the glass transition temperature of water (−134 °C). We observe an improved fit in the in the domain $0.11 < a_w < 0.75$ by leaving T_{g_1} as a free parameter. Values for T_{g_1} and k_{GT} are reported in Table 2. The glass transition data obtained on the maltodextrin matrices are shown in Fig. 2, together with the optimized fit to the Gordon–Taylor equation.

The most extensive heating experiments where carried out on maltodextrin DE 12, for which two samples with different water activities were available ($a_w = 0.15$ and $a_w = 0.57$). In order to study the effect of the glass–rubber transition on the kinetics of thermal degradation, experiments were carried out both below and

Table 2
Coefficients of the fit of the moisture sorption data in the range $0.11 \leqslant a_w \leqslant 0.75$ to the Gordon–Taylor equation. The T_g of the dry materials is somewhat higher than the T_g as obtained from the fit of the data to the Gordon–Taylor equation and is provided for reference purposes (Roos & Karel, 1991)

Parameter	DE 6	DE 12	DE 21	DE 33
k_{GT}	5.75	5.85	6.13	6.19
T_{g_1} (°C)	197.7	164.3	137.4	102.8
T_g(dry) (°C)	n.d.	200	158	119

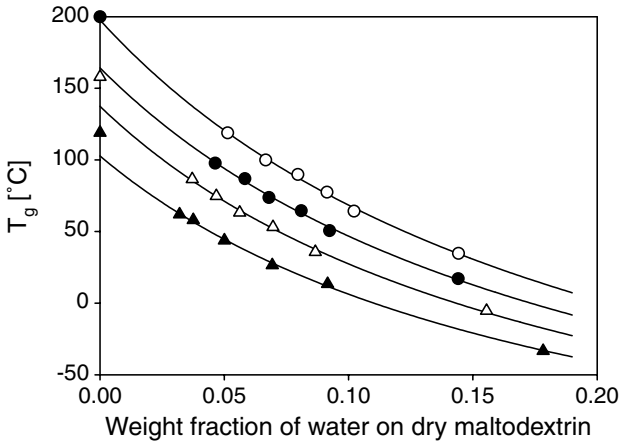

Fig. 2. Dependence of the glass transition temperature of the maltodextrin matrices on the water content. The solid line is the best fit to the experimental data using the Gordon–Taylor equation. Open circles: DE 6; filled circles: DE 12; open triangles: DE 21; filled triangles: DE 33. The T_g data for the fully dry state have been excluded in the Gordon–Taylor fit.

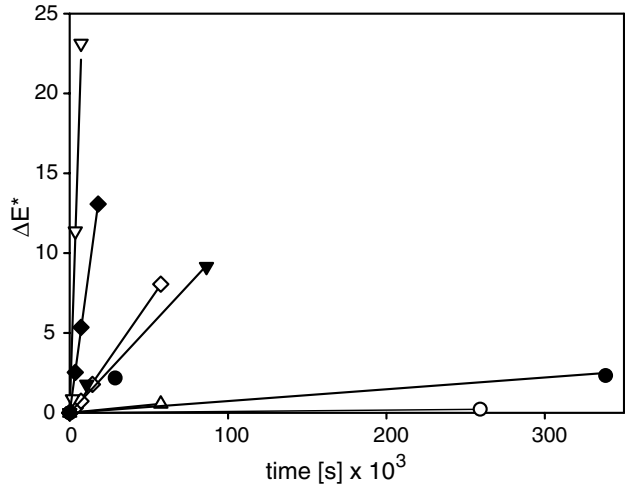

Fig. 3. Color evolution parameter ΔE^* as a function of heating time for maltodextrin DE 12 at two different water activities. Open symbols: $a_w = 0.15$; filled symbols: $a_w = 0.57$. Open circle: $T = 58$ °C; open triangle up: $T = 88$ °C; open diamonds: $T = 118$ °C; open triangles down: $T = 188$ °C; filled circles: $T = 50$ °C; filled triangles: $T = 100$ °C; filled diamonds: $T = 130$ °C. With one exception, the correlation coefficients R^2 of the linear fit to the data are all higher than 0.98.

Table 3
k value for maltodextrin DE 12 $a_w = 0.15$ and $a_w = 0.57$

$a_w = 0.15$		$a_w = 0.57$	
T (°C)	k (s^{-1})	T(°C)	k (s^{-1})
58	8.70×10^{-7}	50	4.25×10^{-6}
88	9.77×10^{-6}	100	1.03×10^{-4}
118	1.45×10^{-4}	130	7.28×10^{-4}
188	4.00×10^{-3}		

above the glass transition temperature. For instance, heating experiments on the $a_w = 0.15$ sample were carried out at 58 °C ($T - T_g = -40$ °C), 88 °C ($T - T_g = -10$ °C), 118 °C ($T - T_g = 20$ °C) and 188 °C ($T - T_g = 90$ °C).

In Fig. 3, the kinetics of browning is plotted for the two water activities at which the maltodextrin DE 12 matrix was equilibrated. Interestingly, the degree of color formation, represented by the parameter ΔE^* (see Section 2) increases linearly with time for all samples. The degree of color formation is fitted according to $\Delta E^* = k \cdot t$, where t is the time and k is a constant characteristic for the temperature and water activity. Values for k are summarized in Table 3. Possibly, the kinetics of degradation may be described as the initial stages of a monomolecular reaction in which the amount of reactant (the undegraded carbohydrate) is available in virtually unlimited quantity. Carbohydrate degradation by a monomolecular mechanism seems to be logical way of color formation and not the reaction of two distinct molecular species like in the Maillard reaction where a sugar and a protein react together. The thermal degradation or caramelization of carbohydrates may thus be considered to be effectively a monomolecular process although it proceeds through various stages (Kroh, 1994). Caramelization only differs from Maillard reaction in the first steps. After formation of reductones and hydroxymethylfurfural, the condensation reaction leading to the formation of melanoidins are of similar mechanism in both reactions (Ponder & Richards, 1993).

Because of its size and weight, the sample cell requires a certain time before the final temperature of the experiment is reached. We have attempted to minimize the time lag in the thermal treatment due to the thermal equilibration of the sample cell by heating the cell before the sample is loaded but nevertheless we need to assure that the time of thermal equilibration is not significant compared to the experimental time scale. In Fig. 4(a), the kinetics of heating of a sample cell filled with maltodextrin powder to the final temperature of the experiment (58, 108 and 118 °C) is plotted. In Fig. 4(a), we have expressed this thermal equilibration in terms of a reduced temperature difference $(T_{final} - T)/(T_{final} - T_{initial})$. Interestingly, we observe that for the temperature differences studied, the kinetics

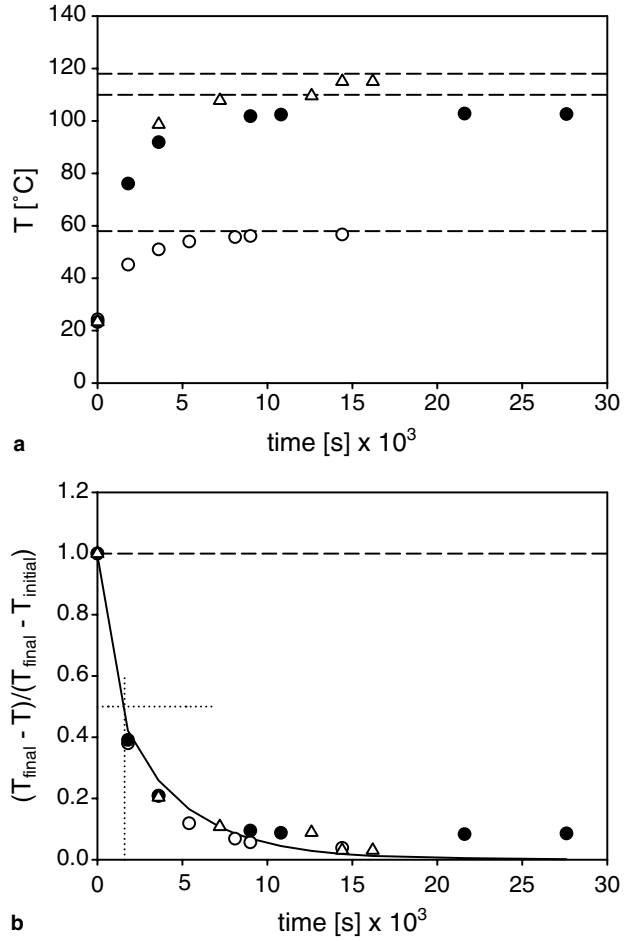

Fig. 4. Time lag in heating the sample cell to its final temperature. (a) Approach to the final temperature (T_{final}) from room temperature ($T_{initial}$). The dashed lines indicate the final temperatures ($T_{final} = 58$, 110 and 118 °C). (b) Approach to the equilibrium temperature in terms of the reduced variable $(T_{final} - T)/(T_{final} - T_{initial})$. The solid line is the fit to the experimental data using the equation for thermal conductivity. Note that no differences between the rate of thermal equilibration are observed for the three different values of T_{final}. The 'half life' of the thermal equilibration is approximately 1.6×10^3 s, as indicated by the dotted lines.

of thermal equilibration is virtually identical. The kinetics of thermal equilibration may well be modelled by the equation of thermal conductivity (Carslaw & Jaeger, 2001), as shown by the continuous line in Fig. 4(b). The dotted lines in Fig. 4(b) indicate the half life or lag time of the thermal equilibration, which is 1.6×10^3 s, i.e., about 27 min. This time lag therefore does not appreciably influence the kinetics of caramelization in the time frame relevant for the present study.

Fig. 5 represents the Arrhenius plot of the kinetic parameter ln k versus $1/T$, where T is the temperature on the Kelvin scale. We observe that at both $a_w = 0.15$ and $a_w = 0.57$ the kinetics of degradation are linear functions of $1/T$. As the experiments were carried out both above and below T_g, we conclude that there is no direct effect of the glass transition on the kinetics

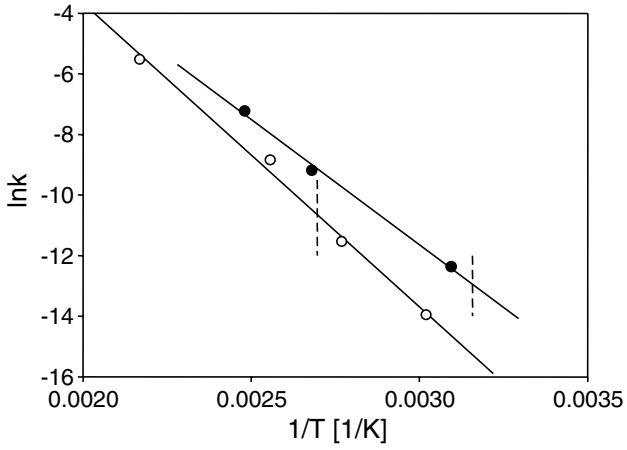

Fig. 5. Arrhenius plot of the rate constant of color formation in maltodextrin DE 12 matrices. Open symbols: $a_w = 0.15$; filled symbols: $a_w = 0.57$. The glass transition temperatures of the matrices are indicated by the short dashed lines. Note that the rate constant is apparently not influenced by the glass transition.

of color formation. The activation energy of the color formation reaction E_a is determined from the following Arrhenius equation:

$$\frac{k}{k_0} = \exp\left(\frac{E_a}{RT}\right), \tag{4}$$

where R is the gas constant and k_0 the reaction rate extrapolated to zero temperature. We calculate E_a to be 83 kJ/mol for the sample equilibrated at $a_w = 0.15$ and 68 kJ/mol for the sample equilibrated at $a_w = 0.57$. These values are comparable but somewhat lower than the values for E_a determined for sugar in aqueous solution at $a_w = 0.90$, namely 104–125 kJ/mol for fructose and xylose and 146–240 kJ/mol for lactose, maltose and sucrose (Buera et al., 1987b).

We have corroborated our conclusions for the maltodextrin DE 12 matrix by carrying out experiments for other molecular weights and water activities. Instead of determining the full time and temperature dependence of the color formation, we have determined the color formation after heating for 4 h at $T - T_g = 30$ °C and at a fixed temperature of 95 °C. The data on ΔE^*, Δa^*, Δb^* and ΔL^* are collected in Table 4 ($T - T_g = 30$ °C) and Table 5 ($T = 95$ °C).

As the parameter ΔE^* from the Hunter–Scotfield equation combines the effects of the three independent parameters ΔL^*, Δa^* and Δb^*, it makes sense to look into the values of these latter three parameters. It is clear from Tables 3 and 4 that the principal effect of the thermal treatment is to increase the degree of yellowness and, somewhat less pronounced, the degree of redness. During the color formation, the brightness of the sample, as represented by the parameter ΔL^*, decreases quite strongly. There is some fluctuation in the values for Δa^*, which is possibly caused by the resolution of the colorimeter which is limited for the slight changes

Table 4
Color formation in maltodextrin DE 6, 12, 21, 33 after heating for 4 h at $T - T_g = 30$ °C

a_w	DE 6				DE 12				DE 21				DE 33			
	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*
0.11	50.16	−44.29	7.78	22.22	31.88	−21.81	4.05	22.90	21.26	−13.48	1.31	16.39	8.47	−5.11	−0.35	6.75
0.22	26.92	−19.23	3.25	18.56	22.99	−15.10	2.58	17.14	n.d.	n.d.	n.d.	n.d.	6.96	−3.72	−0.46	5.86
0.33	22.80	−17.15	2.96	14.73	16.37	−11.63	1.68	11.40	8.80	−6.35	−0.60	6.06	6.24	−5.88	−0.43	2.04
0.43	16.75	−10.46	1.96	12.93	10.40	−6.64	0.37	7.99	6.43	−5.48	−0.54	3.31	2.29	−2.29	0.02	−0.01
0.54	11.53	−7.78	0.66	8.49	5.67	−3.72	−0.21	4.27	4.78	−4.76	0.04	−0.37				
0.75	6.22	−6.19	0.09	−0.50	7.00	−6.98	−0.03	0.46								

Table 5
Color formation in maltodextrin DE 6, 12, 21, 33 after heating for 4 h at $T = 95$ °C

a_w	DE 6				DE 12				DE 21				DE 33			
	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*
0.11	1.11	−1.01	−0.03	−0.47	3.97	−3.97	−0.08	−0.23	n.d.	n.d.	n.d.	n.d.	0.14	−0.11	−0.02	0.08
0.22	0.30	−0.28	−0.02	−0.12	6.43	−6.43	−0.01	−0.21	2.39	−2.39	−0.07	0.03	1.59	−1.59	−0.02	−0.15
0.33	2.29	−2.29	0.00	−0.03	5.60	−5.60	−0.05	0.20	3.41	−3.38	0.07	−0.40	n.d.	n.d.	n.d.	n.d.
0.43	2.93	−2.81	−0.04	0.81	6.52	−6.51	−0.05	0.23	5.17	−5.14	0.03	−0.55	0.58	−0.56	0.02	−0.13
0.54	3.74	−3.46	0.01	1.43	5.34	−5.32	−0.05	0.43	3.83	−3.83	−0.03	−0.18				
0.75	4.20	−4.20	0.02	0.00	6.96	−6.92	−0.13	0.67								

in sample color of relevance in the study of the early stages of the thermal decomposition.

In Fig. 6(a), the degree of color formation ΔE^* is plotted as a function of the water activity for the samples heated at $T - T_g = 30$ °C. It is immediately obvious that the glass transition temperature does not play a significant role in the thermal degradation of the carbohydrates as the degree of color formation decreases strongly as a function of the water activity.

If we now plot the degree of color formation as a function of the water activity for $T = 95$ °C, we observe that the degree of color formation is an increasing function of the water activity, albeit slowly. This again demonstrates that the physical state of the matrix is not directly related to the kinetics of caramelization. In fact, in Fig. 6(b), samples in both the rubbery and glassy states are represented and no obvious correlation between the value for ΔE^* and the physical state of the matrix can be made. In addition, there is not much affect of the content of reducing sugars, which increases strongly with increasing molecular weight. For instance the content of glucose, maltose and maltotriose increases from 3.7% by weight for the DE 6 sample to close to 30% for the DE 33 sample.

The weak dependence of the degree of color formation on the water activity in addition indicates that the principal mechanism of color formation in caramelization is different from non-enzymatic browning. For non-enzymatic browning, the rate of reaction generally increases rapidly with water activity until $a_w = 0.7$–0.9, after which it levels off and starts to decrease at very high water activities because of the dilution of the reactants (Roos, 1995). In particular, a good correlation between

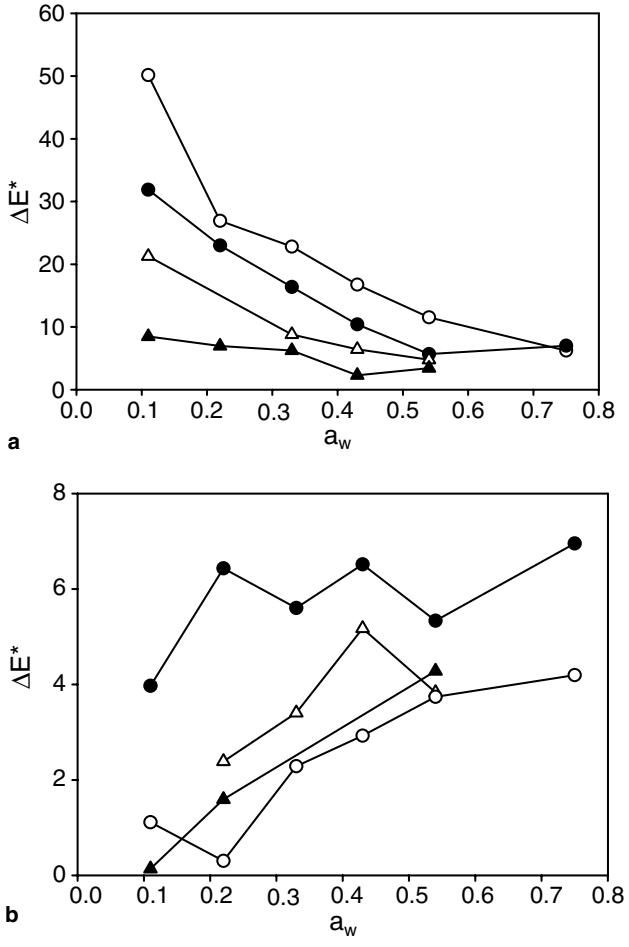

Fig. 6. Color evolution parameter ΔE^* as a function of the water activity for: (a) $T - T_g = 30$ °C and (b) $T = 95$ °C. Open circles: DE 6; filled circles: DE 12; open triangles: DE 21; filled triangles: DE 33.

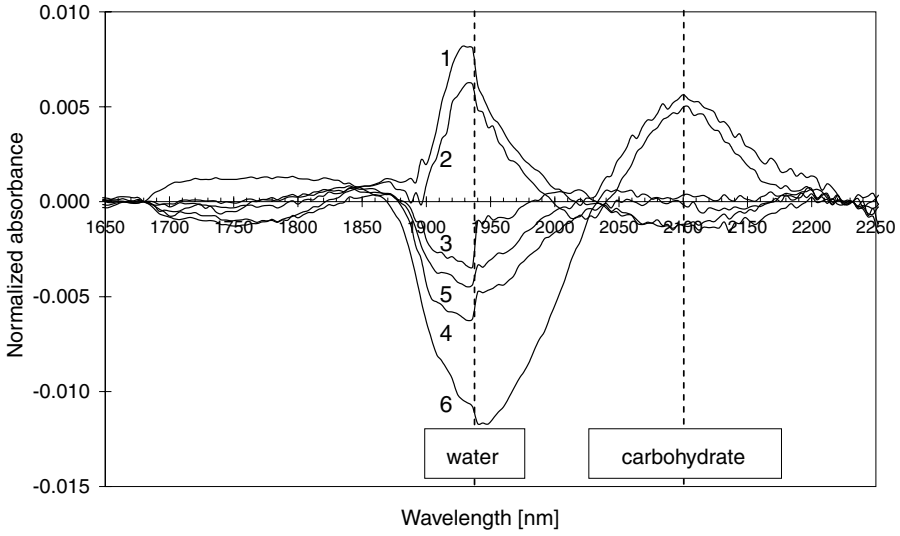

Fig. 7. Near infrared reflectance spectra of heat-treated maltodextrin DE 12 matrices as a function of the temperature and heating time. The spectra are normalized on the spectrum of non-treated maltodextrin DE 12. The absorbance peaks of water ($\lambda = 1940$ nm) and carbohydrate ($\lambda = 2100$ nm) are indicated. (1) Heating for 16 h at 88 °C; (2) heating for 72 h at 58 °C; (3) heating for 1 h at 118 °C; (4) heating for 4h at 118 °C; (5) heating for 2 h at 118 °C; (6) heating for 16 h at 118 °C. Observe the distinct behavior above and below T_g for the water peak. Whereas below T_g, the water peak increases with respect to the non-treated sample, above T_g it decreases. This is most likely related to the change in surface texture above T_g.

the onset of the Maillard reaction and the glass temperature is often found.

As the objective of this paper is to investigate the effect of the physical state of the matrix on the kinetics of caramelization, we have not analyzed the chemical pathways leading to the color formation. However, as one of the first steps in the thermal degradation of carbohydrates is the elimination of a water molecule from the sugars (Kroh, 1994; Ponder & Richards, 1993), we have investigated the possible effect of this reaction water by NIR spectroscopy (Fig. 7). From the peak at $\lambda = 1940$ nm, it is clear that the state and content of water are changing during the thermal treatment. It turns out that the state of water depends on the physical state of the matrix, as we observe that the samples which were heated below the glass transition temperature (95 °C) show an increasing water peak (as compared to the non-treated sample), whereas the samples which were heated to above the glass transition temperature show a decreasing absorbance at $\lambda = 1940$ nm. This latter observation most likely has to do with the change in the molecular structure of the sample, as we have recently observed that crystallization may be induced in a number of maltodextrin matrices. This phenomenon will be investigated in a future communication.

4. Concluding remarks

Thermal degradation of maltodextrin is phenomenon of potential importance during the processing of carbohydrate-based products under extreme conditions as they occur during, for instance, extrusion. The impact of the thermal degradation is observed in two principal ways: in the first place the formation of color and flavor of the polymers and in the second place the effect of water released during the caramelization on the physical properties of the carbohydrate matrix. This latter effect principally influences the glass transition of the matrix.

We have observed that the kinetics of caramelization obeys Arrhenius-type kinetics with an activation energy which is to a very good approximation independent of the physical state of the matrix. In other words, the overall mechanism of caramelization is most likely similar in both the glassy and the rubbery states, although small shifts in actual reaction pathways could of course occur. We have observed that the kinetics of degradation is increasing slowly with the water activity or the water content of the matrix and that they are almost independent of the molecular weight of the maltodextrin. The physical state of the matrix is apparently irrelevant for the caramelization reaction as we have not observed a significant correlation of the color formation with the molecular-weight and water activity dependent glass transition.

For future studies, we envisage a more detailed unraveling of the mechanism of the caramelization reaction. In particular, it would be of interest to identify the structure of the various intermediates in relation to the amount of water released into the matrix.

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