PII: S0144-8617(97)00115-X

Carbohydrate Polymers 34 (1997) 303–308
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0144-8617/97/$17.00 + .00

Starch radicals. Part II: Cereals—native starch complexes

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(Received 20 January 1997; revised version received 18 July 1997; accepted 25 July 1997)

Several varieties of flours were subjected to thermolysis up to 400°C. The thermal characteristics of 13 flours were similar for all flours except soy. The weight loss of these flours up to 400°C ranged from 65 to 97%. Although flours began to decompose at lower temperatures than did corresponding starches, there was less radical decomposition in flours than in starches as proved by Electron Paramagnetic Resonance absorption (EPR) spectra. The order of heat resistance to the radical decomposition for starches and flours paralleled one another, however, flours generated radicals at temperatures approximately 20°C higher than in corresponding starches. The data showed that cereals did not form free radicals before carbonization and thus they could be safely processed in the temperature intervals generally used in baking, roasting, and frying. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Thermal treatment is the most common way of processing polysaccharides. At elevated temperature, polysaccharide depolymerization can proceed according to either ionic or/and a free radical mechanism (Tomasik *et al.*, 1989 and references therein). A mechanical treatment of starch such as milling or extrusion can also potentially cause free radical formation by decomposition (Tomasik & Zaranyika, 1995). We have demonstrated, for example, that thermolysis of starch produces free radicals (Ciesielski & Tomasik, 1996). Their count was dependent on starch variety, temperature, and heating time. All starch varieties except oat appeared to be fairly heat resistant: oat starch required heating up to 285°C for over 1 h to generate unpaired spins. Cereals and flours which are natural polysaccharide complexes with proteins and/or lipids (Tomasik & Schilling, 1997) are thermally processed more often than starch itself. Data on the thermal stability of starch varieties should not evoke any concern about their radical decomposition on food preparation (Barabasz *et al.*, 1990). However, this statement may not necessarily be true for cereals which contain other components. Therefore, we have investigated cereal flours for their stability at elevated temperatures and for a possible effect due to starch complexes. This paper presents the thermal behaviour of 13 flours on heating up to 400°C.

MATERIALS AND METHODS

Materials

Maize flour (M) as well as two rye flours (R1 and R2), soy flour (S), and all wheat flours (W1–W5) were commercial products. The other flours, i.e., oat (O), barley (B), rice (R), and triticale (T) were prepared in the laboratory by milling cereals using the RG-109 Hungarian mill. Chemical composition of all flours was determined according to officially recommended AOAC methods (AOAC, 1990).

Thermolysis

Samples of flours (0.2 g) were heated in porcelain crucibles at 250, 285, 300, 320, 335 and 350°C with a precision of ±0.5°C for 30, 60, 90, and 120 min in all

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possible combinations of parameters. The ELF 11/6 Eurotherm Carbolite oven was used.

EPR spectra

The spectra of thermolyzed samples were run at room temperature in the range of X-band $(\nu) = 9.5\,\mathrm{GHz}$, $\lambda = 3.2\,\mathrm{cm}$) using the spectrometer made by Politechnika Wroclawska, Poland. Diphenylpicrylhydrazyl (DPPH) was applied as the standard for the spectral splitting (g-factor) and $CuSO_4$ (2.4×10^{21} spins/g) as the standard for the estimation of unpaired spin counts. The spectral curves were processed using the MicroCal Origin, version 2.8β program.

Thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA)

Thermal analyses of flours (0.200 g) in the range of 20–400°C were carried using a Hungarian Paulik-Paulik-Erdey D1500Q derivatograph. Samples were heated in an air medium at a rate of 5°C/min with corrundum ($\phi = 8\,\mu\mathrm{m}$) serving as a reference material.

RESULTS

Table 1 reports chemical characteristics of flours.

Soy flour contained more protein and fat but significantly less carbohydrates than the other flours. Also the composition of oat flour differed markedly from an average composition of other cereals listed in Table 1. Simultaneously, both soy and oat flours had the highest content of minerals and fibre. Table 2 presents thermogravimetric characteristics of flours under study.

Table 3 collects unpaired spin counts.

The g-factor at $\nu = 9.5\,\mathrm{GHz}$ being 2.003 was calculated according to the formula:

$$g = (h\nu)/(\mu B)$$

It was close to the g-factor for DPPH signal (g = 2.0023 for free electron).

DISCUSSION

In this paper the susceptibility of cereals to thermal free radical decomposition is presented. Moreover, the links between the thermal properties of flours and their affinity to the free radical decomposition are attempted.

Zhukhman & Kovalenko (1983) have ascribed particular thermal effects in the thermograms of maize and waxy maize starch to structural changes taking place in starch. Thus, between 200 and 220°C constitutional water was assumed to leave. A small DTG peak at about 250°C was ascribed to the combustion of lipids complexed to starch. The evolution of volatile carbon-containing products [CO, CO_2 and organic compounds (Bryce & Greenwood, 1964; Picon, 1953)] started suddenly at 270°C and continued up to 310°C. At 310–330°C and then up to 500°C two-step combustion of starch took place. According to Zhukhman & Kovalenko (1983), among the two main polysaccharide components of maize starch amylopectin was more thermally stable than amylose.

The thermogravimetric investigations of cereals delivered the following facts. All cereals but soy resembled one another in their moisture content (see also Table 1). All began to lose water starting from 35–40°C. Their first weight loss, from water sorbed on the surface and in capillaries, varied from 7% (soy flour) to 13% (maize and wheat 650-type flours) as resulting from the analysis of the TG line. This loss was manifested by an endothermic effect on the DTG curve which was broad and of medium intensity; DTA peaks were centered between 100 and 110°C. In a few cases

Table 1. Chemical composition, %, of cereal flours[a]

Flour	Moisture	Protein	Carbohydrates	Fat	Fibre	Minerals
Barley (B)	14.8	9.5	71.2	2.2	1.3	1.1
Maize (M)	14.4	9.7	68.8	4.0	1.9	1.2
Oat (O)	14.3	10.5	64.9	4.9	2.2	3.2
Rice (R)	14.8	7.2	76.1	0.4	0.7	0.8
Rye:						
720 (R1)	13.9	5.0	78.6	1.4	0.5	0.6
2000 (R2)	14.9	7.9	71.8	2.3	1.4	1.7
Soy (S)	9.6	40.1	27.3	18.2	2.0	2.8
Triticale (T)	13.1	7.7	76.2	1.3	0.2	0.8
Wheat:						
500 (W1)	12.8	8.3	76.5	1.5	0.4	0.5
550 (W2)	13.2	8.5	75.7	1.7	0.4	0.5
650 (W3)	13.8	8.7	74.4	1.8	0.4	0.6
750 (W4)	14.3	8.8	73.8	1.9	0.5	0.7
850 (W5)	15.0	9.0	72.5	2.2	0.6	0.8

[a] The data in this table are averages of, at least, triplicate estimates.

Table 2. Thermogravimetric (TG, DTG, and DTA) characteristics of cereal flours

Flour	Characteristics[a,b]
Barley	TG: 35–135 (−9%), 135–200 (−11.5%), 200–270 (−62%), 270–400 (−82%)
(B)	DTG: 90, 250, 370
	DTA: 100, 170s, 190s, 225s, 250w, 315s, 365w, 400s
Maize	TG: 35–135 (−13%), 135–185 (−14%), 185–285 (−68.5%), 285–400 (−85.5%)
(M)	*230–285 (−35%), 285–336 (−51%), 336–400 (−72%)*
	DTG: 90, 250, 400
	243, 254s, 271, 324s
	DTA: 100, 195s, 250w, 360w, 400w
	247w, 254s, 330w, 350s, 361w, 380w, 396w
Oat	TG: 45–135 (−8.5%), 135–190 (−10%), 190–265 (−49%), 265–400 (−68.5%)
(O)	DTG: 95, 235, 340w
	DTA: 105, 175vw, 210 vw, 235vw, 285vw, 305w, 315w, 360w
Rice	TG: 35–135 (−10%), 135–210 (−12%), 210–265 (−73%), 265–365 (−82%), 365–400 (−97%)
(R)	DTG: 85, 235, 405
	DTA: 100, 235vw, 275s, 355w
Rye 750	TG: 40–135 (−9%), 135–180 (−10%), 180–280 (−60%), (R1)
(R1)	280–400 (−75%)
	244–276 (−31.5%), 276–326 (−49.5%), 326–400 (−63.5%)
	DTG: 90, 245, 340s,
	246, 253, 263, 267, 322s, 328s
	DTA: 105, 150s, 180s, 205s, 250vw, 315s, 380w
	247w, 253s, 274s, 322w
Rye 2000	TG: 45–135 (−8%), 135–180 (−9.5%), 180–290 (−59%), 290–400 (−71%)
(R2)	DTG: 95, 255, 325s
	DTA: 100, 115, 165s, 215s, 235s, 270s, 325s, 365vw, 390vw, 400vw
Soy	TG: 40–100 (−7%), 100–155 (−8%), 155–290 (−48.5%), 290–375 (−58.5%), 375–400 (−62%)
(S)	DTG: 90, 225, 420
	DTA: 85, 100, 140s, 260s, 280vw, 315vw, 375w
Triticale	TG: 50–140 (−9%), 140–195 (−10%), 195–290 (−60%), 290–400 (−73%)
(T)	DTG: 95, 255
	DTA: 100, 150s, 185vw, 210vw, 220s, 245s, 300s, 400w
Wheat 500	TG: 35–140 (−9%), 140–190 (−10%), 190–265 (−63%), 260–400 (−83%)
(W1)	*219–278 (−32%), 278–305 (−43%), 305–400 (−64%)*
	DTG: 95, 240, 300vw, 400
	250s, 257, 268, 305s
	DTA: 95, 110, 175vw, 190vw, 240w, 310s, 365w
	255s, 267s, 271s, 276s, 305w, 315w, 320w, 340w
Wheat 550	TG: 35–130 (−9%), 130–185 (−10%), 185–270 (−61%), (W2)
	270–375 (−79%), 375–400 (−82%)
	DTG: 100, 250, 400
	DTA: 105, 165s, 205vw, 250w, 275s, 320s, 350vw, 355vw
Wheat 650	TG: 50–135 (−13%), 135–200 (−14%), 200–270 (−63%), 270–400 (−80%)
(W3)	DTG: 95, 255, 420w
	DTA: 110, 190vw, 250w, 320s, 375w
Wheat 750	TG: 50–140 (−9%), 140–195 (−10%), 195–275 (−57%), 275–400 (−72%)
(W4)	DTG: 95, 250, 310s
	DTA: 105, 195s, 250w, 310s, 385w
Wheat 850	TG: 45–140 (−10%), 140–195 (−11%), 195–275 (−55%), 275–400 (−71%)
(W5)	DTG: 95, 250, 315s
	DTA: 105, 175s, 195vw, 225vw, 250w, 280s, 300s, 365vw, 395w

TG, thermogravimetry; DTG, differential thermogravimetry; DTA, differential thermal analysis.

[a] In the TG characteristics, temperatures (in °C) relate to characteristic shoulders on the TG-curve. In the parentheses the total weight loss in % is given from the origin up to the given temperature. Temperatures characterizing the DTG and DTA curves relate to the minima of the peaks. All of them are endothermic. The shoulders on the DTG and DTA curves are denoted by "s". The weak and very weak bands are denoted by "w" and "vw", respectively.

[b] Data in italics are these from our recent paper (Tomasik *et al.*, 1986) in which the results were reported on thermogravimetric studies of a given starch variety. Only high temperature portions of the TG, DTG and DTA curves are quoted.

Table 3. The unpaired spin count in cereal flours depending on time and heating temperature[a,b]

Heating time (min)	Unpaired spin count × 10^{15}/g												
	B	M	O	R	R1	R2	S	T	W1	W2	W3	W4	W5
285°C													
120			5	1									
		1	*20*		*8*			*5*	*6*	*4*			
300°C													
60			6										
90			10										
			10		*2*			*2*	*2*	*6*			
120			20	20	10		6	10	5	8			4
		3	*30*		*4*			*3*	*3*	*5*			
320°C													
60			10	4	1								
90			20	15	3				6				
		2	*80*		*4*			*4*	*3*	*70*			
120			60	40	8	4	10	20	10	10	4	2	8
		7	*1000*		*60*			*200*	*40*	*600*			
335°C													
30			10					2					
60	3	4	30	15	6	2	7	10	6	8	10		
90	10		80	30	10	10	20	20	10	20	5	8	30
120	40	20	200	40	40	30	60	70	60	50	10	20	80
350°C													
30	10	5	20		10			10	10	8	3		20
60	20	10	60	8	15	3	5	20	30	10	10	8	30
90	30	20	200	20	40	20	10	50	60	30	20	10	80
120	90	50	500	50	80	40	70	90	100	80	70	40	200

[a] See Table 1 for abbreviations of flours.

[b] The figures in italics are these from our recent paper (Ciesielski & Tomasik, 1996) on starch radicals.

(Table 2) these peaks split into a doublet with minima at 100 and 110°C showing that there were at least two different types of water sorption. Three types of sorbed water in several starch varieties have been identified and four types in potato starch (Schierbaum *et al.*, 1962). On the DTG curves, humidity loss was reflected by the first endothermic medium-intensity peak centered between 90 and 100°C, regardless of cereal variety. Further heating of flours resulted in a rapid weight loss, the beginning of which was more dependent on the variety. Soy flour was clearly exceptional in this respect as the weight loss caused by the decomposition of organic matter started at 155°C, and the endothermic effect was manifested by a relevant peak with its minimum at 225°C. The other flours began to decompose between 180 and 200°C with a peak minima between 235 and 255°C depending on flour variety. Rice flour was the most heat resistant as its decomposition began at 210°C. Figure 1 presents thermograms of soy and rice flour.

Our studies showed that the Zhukhman & Kovalenko (1983) assignments of the thermal DTG effect at 250°C to the decomposition of starch lipids should be declined. This peak appeared in thermograms of all flours under investigation and its magnitude was comparable in all cases, regardless of whether the flours contained either 18.2% of lipids (soy flour) or 0.4% of lipids (rice flour) (see also Table 1). In our opinion just this peak corresponded to the loss of constitutional water. An inspection of the flour compositions (see Table 1) suggested that the low thermal stability of soy flour i.e., low temperature of the decomposition beginning might be accounted for by the protein present in a high quantity. In this case, protein and the products of their thermal decomposition reacted with amylose, amylopectin and various products of their decomposition gave humus-like products of considerable thermal stability. Thus, soy flour lost 62% of its weight up to 400°C, whereas rice flour with a low protein content was almost totally decomposed (97% weight loss) at 400°C as shown by the course of the TG lines.

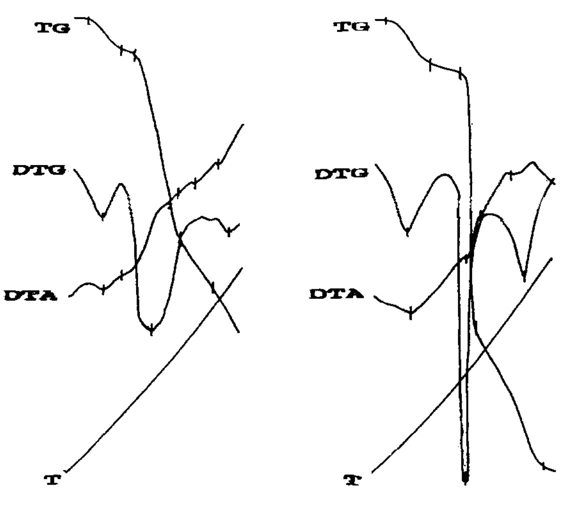

Fig. 1. The thermograms of soy (left) and rice (right) flours recorded from 20 to 420°C in the air. Crucial temperatures should be identified based on Table 3.

The majority of flours under study lost weight up to 400°C from 69% (oat flour) to 75% (rye flour) in spite of the similarity of their composition to that of rice flour. The data suggest that apart from composition, the distribution of the components i.e. amylose, amylopectin, lipids and proteins in granules and their mutual relations might be involved. The complexation and/or entanglement of the components (Lii *et al.*, 1996) and/or their non-uniform distribution inside granules influences the availability of the components for their mutual reactions (Lii *et al.*, 1996). Such effects on rheological properties of rice starch varieties have been observed by Lii *et al.* (1996).

The thermal behaviour of oat and soy flours also could be related to their mineral content. Studies by Bryce & Greenwood (1966) evidenced that minerals (2%) added to starch facilitated its decomposition by lowering the threshold temperature of decomposition.

Inspection of earlier studies on the thermal analysis of some starch varieties (Tomasik *et al.*, 1986) showed that for starch of a given origin decomposition always began at a temperature higher than that found for flour of the same origin. Higher thermal characteristics, however, were generally comparable. The weight loss of starch also was lower than that of its corresponding flour.

Insight developed in Table 3 indicated that oat and rice flours most readily generated free radicals. The sensitivity of oat flour to such a mode of decomposition was the highest within the whole range of heating. On the other hand rice flour which had begun to decompose under mild conditions, at higher temperatures appeared to be more resistant. Wheat 650-type and rye 2000-type flours were the most resistant. Soy flour, the least thermally stable material, did not readily generate free radicals. Thus, there is no direct link between protein content and the generation of free radicals.

Thermogravimetric stability of flours did not parallel their affinity for free radical decomposition. The reason being perhaps that the radicals were generated locally and on a micro scale, whereas, thermograms reported an overall macro scale effect. The thermal effect of the process responsible for the formation of a low population of unpaired spins could not be distinguished from thermal effects of many other simultaneous and concerted processes.

Heating of flours changed their original colour. They turned from white through creamy white (around 250°C), yellow, and to many shades of brown to black. Similarly, as formerly observed for starch varieties (Ciesielski & Tomasik, 1996), free radicals could be found only in fairly carbonized samples. The susceptibility order of flours to the free radical decomposition resembled that for starch varieties. However, flours with their probable native complexes required a higher temperature and extended time to generate radicals. Possibly the components present in flours and absent in starch stabilized rather than disrupted the polysaccharide molecules. Complexation then could dissipate and consume the energy transmitted to polysaccharides for conformational changes, vibrations, and translocations; additionally, complexes may act as radical scavengers. The g-factor (2.003) of the developed radicals was very close to that for free electron ($g = 2.0023$). Also, the EPR spectral patterns were very similar to the spectra of free radicals generated from starch described in our former paper (Ciesielski & Tomasik, 1996). Several weeks air exposure did not result in a loss of free radicals, suggesting their stabilization due to delocalization of unpaired spins.

CONCLUSIONS

Cereals were more thermally stable to free radical decomposition than starch isolated from them. They did not form free radicals before carbonization and thus they could be safely processed in the temperature intervals generally used in baking, roasting and frying.

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