Carbohydrate Polymers **21** (1993) 157-167

Basis of cereal starch expansion*

Rangan Chinnaswamy‡

Departments of Biological Systems Engineering, and Food Science and Technology, University of Nebraska-Lincoln, Lincoln, NE 68583-0726, USA

Expansion of cereals and starches has been known to us for several centuries. Various high-temperature short-time methods have been applied to bring about the desired expansion of cereals. A few decades ago, extrusion technology replaced most of the conventional technologies to produce expanded cereals and other similar products. Since extrusion processing is a versatile process, it has found a permanent place in Food Industries. However, all cereals and starches do not expand equally, due to raw material quality differences. The branched structures of starches and their contents seem to control extrusion-expansion of cereals. Various methods, processing variables, chemical additives, γ-irradiation and their combinations, have been used to alter the branched structures of starch and their relationships to starch expansion properties have been studied. Overall, it appears that changes in their branched fraction of starches affect expansion volume greatly.

INTRODUCTION

It is believed that extrusion technology was invented by Joseph Baramat in England in 1797. He then used a piston-driven device to produce lead pipes. Since then the technology and the device have undergone numerous modifications and have found many applications in the plastics, food and pharmaceuticals industries. With the introduction of twin screw extruders in the 1960s, extrusion technology has revolutionized the snack food industry in the western hemisphere. Today, over $20 000 million worth of snack foods are produced using this technology and consumed in the continental United States alone. This consumption rate increases by 3% every year in the USA.

Extrusion cooking technology is applied extensively in manufacturing cereal or starch-based crispy foods. The texture and mouthfeel of most expanded or puffed, extruded snacks depends on their expanded volume (Owusu-Ansah *et al.*, 11984). Several studies have investigated the role of extrusion processing variables and the expansion volume of cereal starches (Meuser *et al.*, 1982; Owusu-Ansah *et al.*, 1983; Chinnaswamy & Hanna, 1988*a,b*; Wen *et al.*, 1990). Among the variables studied, those that most prominently control expansion volume are the barrel temperature and moisture content of the raw material (Mercier & Feillet, 1975; Owusu-Ansah *et al.*, 1983, 1984; Chinnaswamy & Hanna, 1988*a,b*). Guy and Horne (1988) extensively reviewed extrusion processing variables and their relationships with cereal product qualities. Other studies further indicated that the qualities of raw materials such as contents of protein, lipid and starch and their composition and type are also important in controlling expansion volume (Faubion *et al.*, 1982; Launay & Lisch, 1983; Chinnaswamy & Hanna, 1988*a*). Models have been developed considering mainly the extrusion processing variables (Owusu-Ansah *et al.*, 1983; Bhattacharya & Hanna, 1987*a,b*), but they are inadequate to explain the raw material quality differences and changes that take place during extrusion cooking. It is generally accepted that extrusion cooking of starches or starchy cereals involves extensive degradation of macromolecules (Gomez & Aguilera, 1983; Colonna *et al.*, 1984; Davidson *et al.*, 1984). Another set of studies indicated that the viscosity changes in starch during extrusion cooking also control expansion (Launay & Lisch, 1983). Chinnaswamy and Hanna (1988*c*) used sodium chloride to promote the expansion

*Published as Paper No. 10061, Journal Series, Nebraska Agricultural Research Division.
‡Present address: Midwest Grain Products, Inc., 1300 Main Street, Atchinson, KS 66002, USA.

Carbohydrate Polymers 0144-8617/93/$06.00

volume of the starches. The compositions of starch, amylose and amylopectin seem to influence expansion volume (Chinnaswamy & Hanna, 1988*a*,*c*).

Mercier and Feillet (1975) observed that starches with low (waxy) and high amylose contents expanded the best at 135 and 225°C, respectively. Bhuiyan and Blanshard (1982), however, reported that corn flours and grits with 35% amylose content expanded the best. In contrast, Bhattacharya and Hanna (1987*b*) reported that waxy corn starch expanded better than normal corn starch. Thus, the effects of quality factors on the expansion of starches were not clear. The objectives of many systematic studies have been to understand the effect of amylose and amylopectin on the expansion properties of corn starches, and to determine whether the expansion volume of such varieties that expand poorly could be increased by altering extrusion processing conditions or by modification of starch with chemical additives or gamma-irradiation.

This review includes the work done at the University of Nebraska and elsewhere in the United States and Europe. The discussion covers the changes in expansion ratio with respect to amylose content and starch modifications by physical, chemical and atomic treatments. Changes in molecular structures during extrusion cooking are monitored closely in relationship to product quality. Interrelationships among various functional, chemical and molecular properties are also evaluated.

OPTIMUM EXTRUSION COOKING CONDITIONS

A C.W. Brabender model 2802 laboratory extruder with a 1·90 cm barrel diameter and a 20:1 ratio of barrel length to diameter was used for the study at the University of Nebraska-Lincoln. The extruder screw had a compression ratio of 3:1. The die diameter and length were 3 mm and 15 mm, respectively. The barrel temperatures of the compression and die sections were either held at 150°C or varied from 110 to 200°C while the feed section was held constant at 70°C. Starch samples were fed into the extruder at the rate of 60 g/min, using a vibrating feeder, keeping the screw speed constant at 140 rpm. These optimum extrusion cooking conditions were arrived at after a preliminary study using normal corn starch (25% amylose). The temperatures, moisture contents, screw speeds, and feed rates were run at different combinations and the above stated conditions were arrived at as an overall optimum extrusion cooking condition for the maximum expansion of normal corn starch (Chinnaswamy & Hanna, 1988*b*). These conditions were kept constant throughout the study unless otherwise stated in the text.

Four different corn starches were used for the study. Most of the studies were conducted using Waxy, Normal, Amylomaize V and Amylomaize VII starches. These starches henceforth will be referred to in the text by their respective amylose contents, that is 0% amylose starch for waxy, 25% starch for normal corn starch, and so on. The starches were agglomerated before extrusion cooking to facilitate the flow of the samples into the extruder. The desired sample moisture contents, 10–30% (dry basis), were obtained by adding distilled water and equilibrating overnight in sealed containers. All extrusion cooking experiments were conducted with samples having 14% (dry basis) moisture content unless otherwise stated in the text. The radial expansion ratios of the extrudates were generally calculated by dividing the cross-sectional area of the extrudates by the cross-sectional area of the die orifice. Each value was an average of 10 or more readings. The radial expansion ratio henceforth will be referred to simply as the expansion ratio. Chinnaswamy *et al.* (1993*a*) have clearly shown that the radial expansion pattern followed more or less the overall and/or bulk density pattern under normal extrusion processing conditions. Thus the radial expansion volumes reported in this paper may well represent the overall expansion ratio of starches.

DIE NOZZLE *L*/*D* RATIO

Expansion properties of cereals and starches have always been related to process variables including the die size and shape. Many studies have reported the effect of barrel temperature, moisture content, feed rate and screw speed on expansion properties. However, there were only a few studies related to die nozzle configuration effect on extrusion pressure, and its impact on the expansion volume. To study the effect of die nozzle configuration and *L*/*D* ratio, 25% amylose starch was used. In Fig. 1(a), the extruder nozzle die configuration is cited. At the end of the die there was a screw-in cylindrical die nozzle with a narrow opening. The length (*L*) of the cylindrical opening and the diameter (*D*) of the cylindrical tube were varied. Nine different combinations of *L*/*D* ratio, varying from 2 to 10, were used for the study (Chinnaswamy & Hanna, 1987).

The relationships between expansion ratio and extrusion pressure of starch, and nozzle *L*/*D* ratio are given in Fig. 1(b). The expansion ratio increased sharply from 4·5 to 13 as the nozzle *L*/*D* ratio increased from 2·5 to 3·4 and then declined gradually to 8·5. The extrusion pressure (measured in the extruder compression section), however, increased proportionally from 4·6 to 14·6 MPa, with increasing *L*/*D* ratios. It is known that the expansion ratio of starch is mainly dependent on its degree of gelatinization (Harper, 1981; Chinnaswamy & Bhattacharya, 1983*a*,*b*, 1984; Gomez & Aguilera, 1984). In Fig. 1(b), the initial

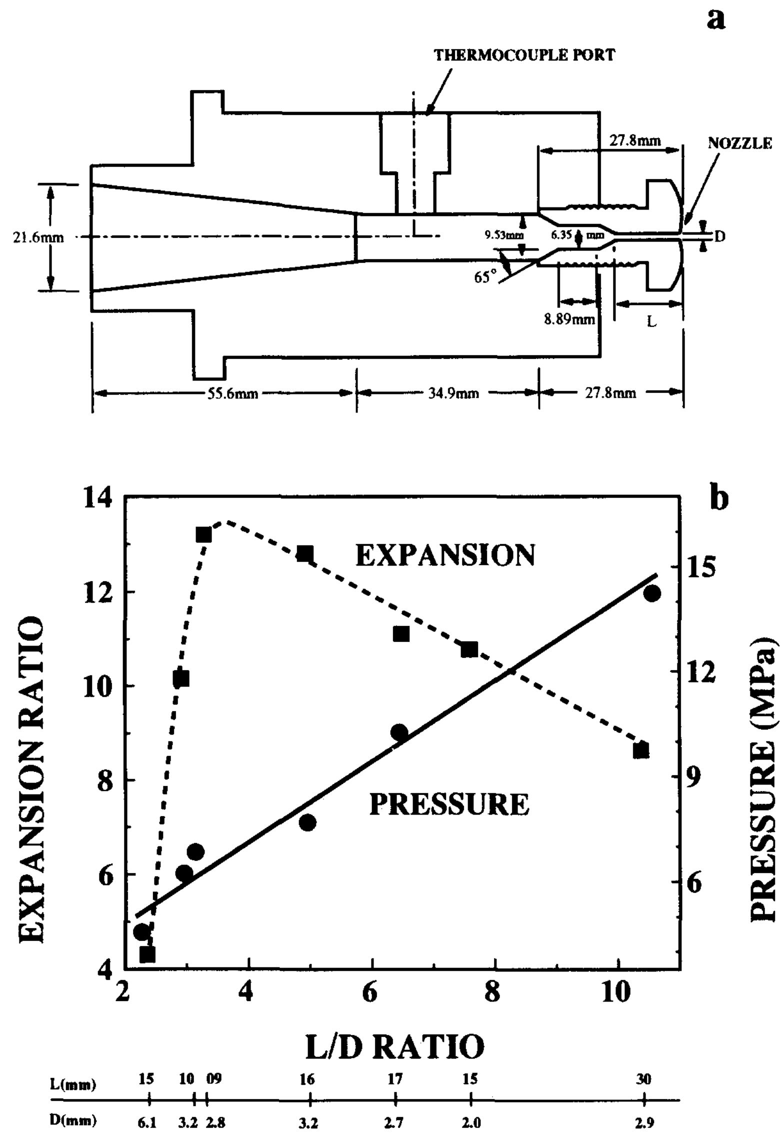

Fig. 1. (a) Die-nozzle '*L*' and '*D*' configuration; (b) relationships among *L*/*D* ratio, extrusion pressure and expansion ratio.

increase in expansion ratio with *L*/*D* ratio and extrusion pressure may be due to such an increase in degree of starch gelatinization, since high extrusion pressures increase the residence time and eventually subject the starch to high shear rates within the extruder which ultimately increase the degree of starch gelatinization (Chaing & Johnson, 1977). However, at extrusion pressures over 7 MPa and *L*/*D* ratios over 3·4, the expansion ratio gradually decreased. At such high extrusion pressures, the residence times and shear rates were high enough to cleave the starch molecules and thus reduce the expansion ratio. High shear rates and residence times are known to induce starch degradation (Colonna *et al*., 1983; Gomez & Aguilera, 1983) and reduce expansion ratio (Davidson *et al*., 1984). Kokini *et al.* (1992) also stated that the starch viscosity is related to the *L*/*D* ratio which in turn influences the expansion.

To see the individual effects of nozzle *L* and *D* on the expansion ratio and extrusion pressure, starch was extruded with nozzles having different lengths but nearly the same diameter dimensions and vice versa. A review of Fig. 1(b) shows *D* values of 2·8, 2·7 and 2·9 mm with corresponding *L* values of 9, 17 and 30 mm. The operating pressures attained with these nozzles were 6·3, 10·2 and 14·6 MPa and the expansion ratios were 10·3, 11·1 and 8·6, respectively. Similarly there were *L* values of 15, 16 and 15 mm with corresponding *D* values of 2·0, 3·2 and 6·1 mm. For these, the operating pressures were 11·6, 7·7 and 4·6 MPa, and the expansion ratios were 10·7, 12·9 and 4·5, respectively. As would be expected, the operating pressure increased with increasing nozzle length or decreasing nozzle diameter. Looking at *L* and *D* independently, with respect to expansion ratio, would suggest that there was an optimum operating pressure for maximum expansion. The results in Fig. 1(b) indicate that a pressure of 7 MPa, generated as a result of any combination of nozzle length and diameter, resulted in the greatest expansion of the starch. Further, it should be noted that an increased *L/D* ratio would reflect either a decrease in nozzle diameter or an increase in length or a combination thereof. In other words, the *L/D* ratio and its relationship with starch expansion and extrusion pressure are limited to the actual values reported in Fig. 1(b) (bottom horizontal axes), for the reason that similar *L/D* ratios can be obtained with different sets of *L* and *D* nozzle values. However, the extrusion pressure would vary. Therefore, it is suggested that extrusion pressure instead of nozzle *L/D* ratio would serve as a better indicator for predicting starch expansion ratio.

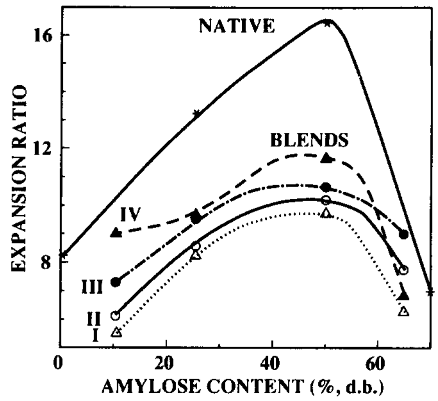

Fig. 2. Relationship between amylose contents of native, blended starches and expansion ratio. For blends I-IV explanations, see Table 2.

EFFECT OF AMYLOSE

The proximate compositions of the corn starches including their amylose contents are given in Table 1. The starch amylose contents ranged from 0 to 70% (dry basis). Residual protein content, as well as the phosphorus content of some corn starches, increased with increasing amylose content of starch.

All corn starches were extruded under the optimal conditions specified above. The relationship between expansion ratio and the amylose content of the native starches is shown in Fig. 2. The expansion ratio of the different native starches vaired from 7 to 16·4. Expansion ratio initially increased from 8·3 to 16·4, as amylose content of native starch increased from 0 to 50% and then decreased sharply. This clearly shows that the amylose content of starch could be a controlling factor for expansion ratio.

To simulate the amylose content of native starches, different native corn starches (0, 25, 50 and 70% amylose starches) were mixed in the appropriate ratios to result in an overall mixture of amylose levels of 10–65% (dry basis). Four blends were prepared: Blend I from the 0 and 70% amylose native starches: Blend II from the 0, 25 and 70% amylose native starches; Blend III from the 0, 50 and 70% amylose native starches; and Blend IV from the 0, 25, 50 and 70% amylose native starches. Within each blend, starch samples with amylose levels of 10, 25, 50 and 65% (dry basis) were prepared. These samples will be referred to in the text as a 10% amylose blend, 25% amylose blend, and so on. The exact percentages of the various native starches mixed to attain these amylose levels are given in Table 2. As one can see in Fig. 2, the blended starch samples show trends similar to those of the native starches when they were extruded under optimal conditions, but with much lower expansion ratios. Mercier and Feillet (1975) observed in a similar experiment that the expansion ratio of the 50% amylose blended starch was lower than the expansion ratio of 50% amylose native starch. The maximum expansion ratio obtained with the 50% amylose blended starch samples, for example, was 11·8, which was far lower than the corresponding expansion ratio of 16·4 for 50% amylose native starch. The differences in expansion ratios for blended starch samples and native starches at the same amylose levels show that amylose content alone was not controlling the expansion of the starch. Amylose did, however, have some influence on starch extrusion expansion, as the

Table 1. Composition of various corn starches[a]

Component	Starch sample			
	Waxy	Normal	Amylomaize V	Amylomaize VII
Amylose, % (d.b.)[b]	0	25	50	70
Protein, % (d.b.)	0·2	0·3	0·5	0·8
Phosphorus, mg/100 g	4·2	14·0	22·8	19·1
Fat, g/100 g	0·1	0·1	0·4	0·3
Ash, g/100 g	0·1	0·2	0·1	0·1
Moisture, % (d.b.)	10·6	9·5	11·0	10·6

[a]Manufacturer's specifications.
[b]d.b. = Dry basis.

Table 2. Blending of starches

Amylose content of blended starch (%, d.b.)	Blend type	Proportion of native starches in the mixture (%)[a,b]				
		0	25	50	70	Expansion ratio[c]
10	I	85·7	—	—	14·3	5·6
	II	79·3	10·0	—	10·7	6·2
	III	82·9	—	10·0	7·1	7·3
	IV	76·4	10·0	10·0	3·6	9·0
25	I	64·0	—	—	36·0	8·6
	II	58·0	10·0	—	32·0	8·8
	III	61·0	—	10·0	29·0	9·5
	IV	55·0	10·0	10·0	25·0	9·7
50	I	29·0	—	—	71·0	9·9
	II	22·0	10·0	—	68·0	10·4
	III	26·0	—	10·0	64·0	10·0
	IV	19·0	10·0	10·0	61·0	11·8
65	I	7·1	—	—	92·9	6·5
	II	0·7	10·0	—	89·3	7·9
	III	4·9	—	10·0	85·1	9·1
	IV	2·5	5·0	5·0	87·5	6·9

[a]Percentage (d.b.) of various starches in the blended starch samples.
[b]Amylose contents (d.b.) of native starches are indicated by column headings.
[c]Expansion ratios of blended starches were obtained at optimal extrusion conditions, i.e. 140°C barrel temperature and 14% moisture content.

optimum amylose content for greatest expansion remained at 50% (dry basis) for all the samples studied.

PHYSICAL MODIFICATIONS

For the best product quality, extrusion cooking of cereals and starches requires control of numerous processing variables, such as barrel temperature, moisture content of ingredients, screw speed and die configuration. Of these variables, screw design and its elements, the moisture content of the ingredients prior to extrusion cooking, and extrusion temperature are known to drastically affect the functional qualities of the products. The optimum conditions used were arrived from experimenting only with 25% amylose starch. These optimum conditions may perhaps vary for starches with different amylose contents as did their gelatinization temperature. Therefore, it was of interest to understand the effects of barrel temperature and moisture content on the expansion properties of starches differing in amylose contents. The temperature and moisture content might play a greater role in changing the viscoelastic properties of the starches which in turn affect the expansion volume (Kokini *et al.*, 1992). In other words, if there is a physical modification in the starches due to changes in barrel temperature and moisture content, it might help poorly expanding starch varieties such as 0% amylose and 70% amylose starches to expand more.

To see whether poorly expanding native starches, that is 0, 25 and 70% amylose native starches, could be made to expand more by altering the processing temperature, all native starches were extrusion cooked at barrel temperatures ranging from 110 to 200°C. The results are presented in Fig. 3(a). For all native starches, the expansion ratio increased from 3·4 up to 16·4 with increasing barrel temperature; however, the maximum expansion ratio for each native starch type varied from 11·2 to 16·4 and occurred at different temperatures. The maximum expansion ratios obtained with the different native starches were 11·9 for 0% native amylose (waxy), 14·2 for 25% native amylose, 16·4 for 50% native amylose, and 11·8 for 70% native amylose starch, occurring at temperatures of 130, 140, 150, and 160°C, respectively. The overall greatest expansion (16·4) was obtained with 50% amylose native starch extrusion cooked at 150°C barrel temperature. Extrusion temperature affects various properties of starch. Mercier and Feillet (1975) reported the appearance of a new structure similar to butanol–amylose complex at different temperatures for different starches. Launay and Lisch (1983) observed a relationship between the viscoelastic properties of melted starch in the extruder and the expansion ratio. The viscoelastic and flow properties of melted starch increased with increasing amylose content (Kokini *et al.*, 1992). Such differences in flow properties of starches could alter the residence time in the extruder and eventually their degree of gelatinization, which is known to affect expansion. This could be

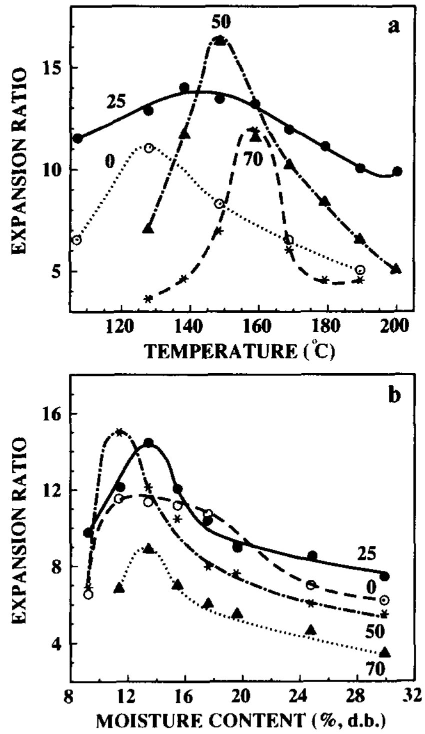

Fig. 3. Effect of (a) extrusion temperatures, and (b) starch moisture contents, on the expansion ratio of starches with different amylose contents (indicated).

a reason why our starches, with different amylose contents, expanded better at different extrusion cooking temperatures.

Moisture content of the starch before extrusion was an important factor controlling the expansion volume of starch. It was of interest to see whether optimum moisture content for starch expansion (like barrel temperatures as seen earlier) varied for different starches. Figure 3(b) clearly shows that all starches expanded more at a uniform moisture content of 13–14% (dry basis). The overall greatest expansion was still obtained with 50% amylose content starch; therefore it appears that the expansion ratio of poorly expanding starches cannot be improved satisfactorily by changing starch moisture content.

CHEMICAL MODIFICATIONS

From the previous sections it is clear that extrusion temperature and moisture content could improve the expansion ratios of poorly expanding starch types. The overall greatest expansion was still obtained with the starch having 50% amylose content. Thus, it is apparent that the varietal differences could not be overcome completely by altering the processing conditions alone. Degree of gelatinization of starch was also related to expansion qualities of starches and cereals (Chaing & Johnson, 1977). Degree of gelatinization of starch can also be altered by the addition of chemical substances. To alter the raw material quality, chemical substances such as urea, which is a hydrogen bond breaking agent; sodium bicarbonate, which decomposes to carbon dioxide (increased pressure) at extrusion temperatures; and sodium chloride, a metallic salt known for its efficient heat conduction, were mixed with starches before extrusion cooking. One gram of each of these substances was mixed with 100 g of the various corn starches which were then extrusion cooked under the optimum conditions reported elsewhere (25% amylose starch). The relationships between expansion ratio and amylose contents of starches with different chemical substances are given in Fig. 4. Sodium chloride increased the expansion ratio by 0·5 to 5·5 units among the starches studied. In general, all the starch–sodium chloride mixtures showed higher expansion ratios than their native starch counterparts. Overall, the highest expansion ratio of 17·5 was obtained with 50% amylose starch. A closer look at the data in Fig. 4 shows that the addition of 1% sodium chloride to normal corn starch caused it to expand as much as native 50% amylose starch, which has been found to expand the most. Corn starches with 0 and 25% amylose showed expansion ratio increases of 5·5 and 3·4 units, respectively, over those of their native starch counterparts. However, 70% amylose starch (Amylomaize VII) showed an increase of only 2·8 units over its native state expansion. Urea, in contrast, decreased the expansion ratio of all starches by 1 to 6 units. The maximum decrease of 6 units in expansion ratio occurred with 50% amylose starches. The 0% (waxy) and 70% amylose starches were affected the least. Sodium bicarbonate affected the expansion of various starches irregularly. The expansion ratios of the 0 and 70% amylose starches were increased by 3 and 3·2 units, respectively, but the 25 and 50% amylose starch expansion ratios were decreased by 1 and 1·5 units, respectively. Although sodium chloride increased the expansion ratios of 25% and 70% amylose, overall

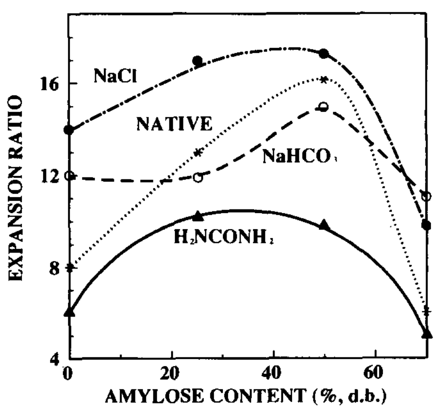

Fig. 4. Effect of chemical additives (indicated) on the expansion ratio of native starches with different amylose contents.

maximum expansion ratio was still the greatest for 50% amylose starch. Therefore, from the study it is clear that the 50% amylose still gives the highest overall expansion ratio. The reason for this, however, is not clear.

ATOMIC MODIFICATIONS

Adams (1983) reported that gamma-irradiation caused a number of chemical and molecular changes in carbohydrates. Adams (1983) further reported that irradiation produced radiolytic products, such as dihydroxy acetone, formaldehyde and hydrogen peroxide. However, low levels of irradiation probably can relocate the branch points in carbohydrate polymers, such as starch, or even create more branching as was reported by Grant and D'Appolonia (1991). They suggested that the increased intrinsic viscosities of pentosans treated with low irradiation levels were due to increased branching in pentosans. Sabularse *et al.* (1991) attributed increased water solubility of rice starch to the degradation of the starch granular structure due to gamma-irradiation. Thus, irradiation appears to have promise as a way to modify the molecular size of starches to nullify varietal differences in expansion qualities.

Starch samples differing in amylose contents from 0 to 70% were used in this study (Sokhey & Chinnaswamy, 1992). Samples were subjected to 10, 20 or 30 kGy gamma-irradiation dosages at room temperature using a Cobalt^{60} irradiator (Nuclear Materials and Equipment Corp., Apollo, PA). The relationships between expansion ratio and starch amylose content at the different irradiation dosages are given in Fig. 5. All irradiation-modified starches showed lower expansion volumes than their counterparts (compare Figs 2 and 5). However, it is interesting to note that the irradiation

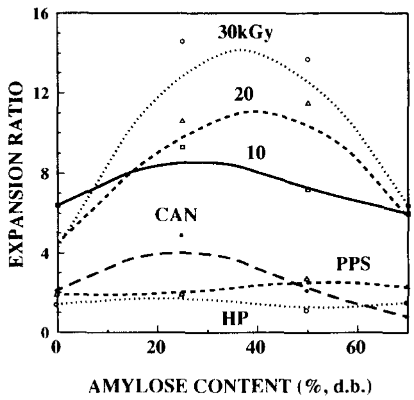

Fig. 5. Relationship between amylose content and expansion ratio of irradiation modified corn starches with and without chemical additives (indicated). Ceric ammonium nitrate (CAN), potassium persulfate (PPS) and hydrogen peroxide (HP) are mixed at a rate of 2·5 g per 100 g of irradiated starches (20 kGy).

dosage had an impact on all the starches. The expansion ratios of the 0% amylose starches decreased from 6 to 2·1 as irradiation dosage increased from 10 to 30 kGy. The expansion ratios of 25% amylose and 50% amylose starches increased significantly, from 2·9 to 7·9 and from 6·5 to 14·5, respectively, with irradiation dosage. The 70% amylose starch, however, did not exhibit any significant difference in expansion ratios with increasing irradiation dosages from 0 to 30 kGy. The maximum expansion volume was observed for 50% amylose starch while the minimum expansion volume was observed for 0% amylose starch, both irradiated at a level of 30 kGy. Therefore, the overall maximum expansion ratio was still given by 50% amylose starch.

Grant and D'Appolonia (1991) reported crosslinking in pentosans after irradiation with gamma rays. It was, however, suspected that debranching of the starch molecules occurred at higher irradiation dosages. Free-radical formation on starch by the gamma irradiation (O'Meara & Shaw, 1957; Sabularse *et al.*, 1991) could result in degradation and formation of crosslinks between the adjoining chains of the starch molecules during extrusion cooking. This perhaps reduced the molecular sizes considerably and allowed the product to expand differently (Fig. 5). The formation of bonds with free radicals was explained by Sonntag (1979). Free radicals are formed when bonds possess high levels of energy imparted by irradiation. These free radicals then lose energy with time, and as soon as the energy falls below a certain level, covalent bonds are formed. Overall it appears that the irradiation modifications differed with amylose content of starches, which could partially explain the differences in their expansion properties.

It was of interest to see whether free-radical inducing or enhancing chemicals such as potassium persulfate (PPS), hydrogen peroxide (HP) and ceric ammonium nitrate (CAN), when added to irradiation modified starches (20 kGy), could increase free-radical activity further during extrusion cooking which might, in turn, alter the expansion properties of starches. Such increased free-radical activity may increase the crosslinking of starch molecules or degrade the starch molecules or both. These chemicals were thus expected to alter the molecular weights and sizes of the starches, any of which are known to have implications on the starch expansion properties. To test this, irradiation (20 kGy) modified starches differing in amylose contents were first mixed with the chemicals noted previously at a level of 2·5% on a dry weight basis in a Hobart blender for 5–10 min before extrusion cooking. All samples were then extrusion cooked under optimal conditions (Sokhey & Chinnaswamy, 1992).

The expansion ratios of the blends of irradiated starches and chemicals are shown in Fig. 5. The expansion ratios of all starches extruded with chemicals were reduced to a value of 4 or less, irrespective of amylose contents. Although the aim was to increase the expansion ratio of the poorly expanding starch types (0 and 70% amylose starches), the results showed decreased expansion ratios for all starches, including the 25 and 50% amylose starches which are known to expand better. In other words, the differences in the expansion ratios due to amylose contents were minimized or eliminated. There may have been too much alteration of starch molecular structures due to the combined effects of irradiation modifications and chemical treatments. Among the three free-radical inducing or enhancing chemical additives studied, CAN appeared to have the most adverse effect, followed by PP and then HP. There are no reports available on the effects of CAN, PP and HP on the expansion ratios of starch to compare. It appears that the high amylose starches were more affected by the addition of chemicals, as indicated by the magnitude of reduction in the expansion ratios. Chinnaswamy and Hanna (1988*c*) reported that the sodium chloride caused a slight increase in the expansion ratio of 0 and 25% amylose starches and no change or decreases for 50 and 70% amylose starches. Further study is necessary on the finite molecular changes that have occurred among starches during extrusion cooking with and without various modifications to understand the basis of starch expansion.

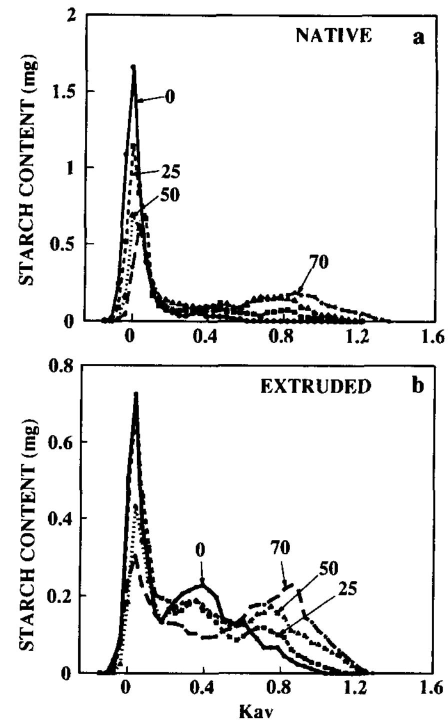

Fig. 6. GPC profiles of starches differing in amylose contents (indicated) (a) before and (b) after extrusion-cooking. All values in this and subsequent figures are expressed on 5 mg basis.

MOLECULAR PROPERTIES

To study the molecular properties of native and extruded normal corn starch, samples were fractionated by gel permeation chromatography on a Sepharose CL2B column. Generally, all starch samples gave two peaks, one eluting at the void volume and the other eluting at the later part of the gel. The void volume peak and the second peak will be referred to as Fraction I and Fraction II, respectively. Any fraction eluting between these two peaks will be referred to as intermediary fraction or Fraction III. Biliaderis *et al.* (1979, 1981) and Chinnaswamy & Bhattacharya (1986) concluded that Fraction I on a Sepharose CL2B gel was the branched component of starch (mostly amylopectin), whereas Fraction II was mainly the linear component of starch (mostly amylose). Any fraction between these two was most likely a degraded product of Fraction I. The GPC fractionation patterns of native, extrusion cooked and starches variously modified by gamma-irradiation and chemical treatments (Sokhey & Chinnaswamy, 1992) are shown in Figs 6 and 7, respectively. The fractionation patterns of native starches (Fig. 6(a)) show that Fraction I, the branched component of starch, was the highest for 0% amylose starch, followed by 25%, 50% and 70% amylose starches. Consequently, Fraction II increased with increasing amylose content of starches. It is interesting to note that Fraction I, or the branched fraction of starch, appears to be a major structural factor to be considered in addition to amylose content of starches for any meaningful interpretation of the expansion properties of starches. With extrusion cooking, Fraction I was degraded further. The degraded products of Fraction I eluted at the later part of the gel. Sometimes it was mixed with Fraction II. Overall it appears that the Fraction I of starch seems to be more important than the Fraction II in terms of its composition and structural entity. In Fig. 6(b) one can easily see the degradation patterns of 0, 25, 50 and 70% amylose starches after extrusion cooking treatments. All starches underwent degradation but the amount of degradation and the molecular size of the degraded products appear to vary. Further it was thought of interest to see how irradiation modifications and chemical treatments such as CAN change the molecualr properties of starch. In Fig. 7 one can see the progressive degradation of the Fraction I with different starch modifications and treatments. The example given in Fig. 7 is for waxy starch. Native waxy starch has the highest Fraction I content. After extrusion cooking Fraction I was reduced almost to one-half of its original content. The degradation product eluted at the latter part of the gel as shown in Fig. 7. When 0% amylose starch was subjected to irradiation modifications at a level of 20 kGy and then extrusion cooked, Fraction I was completely degraded and a new fraction appeared in

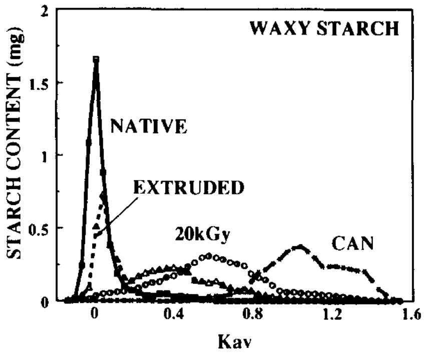

Fig. 7. Comparative GPC profiles of variously processed waxy starch. Native (no modification), native starch after extrusion-cooking (extruded), irradiation modified at 20 kGy dosage and extruded (20 kGy), irradiation modified at 20 kGy and extrusion cooked with ammonium nitrate (CAN) are indicated.

the later part of the gel as shown in Fig. 7. The molecular weight of Fraction I of waxy starch was reduced almost to one-half of its original molecular weight. When the irradiation-modified starch was further treated with CAN and then extrusion cooked, the molecular weight was reduced so much that the entire fraction eluted at the total volume of the gel. In other words, combinations of modifications, physical, chemical, atomic and/or extrusion cooking, progressively reduced the Fraction I content of starch and its molecular size.

Similar changes in Fraction I contents of 25, 50 and 70% amylose starches were also seen (graphs not shown). It should be noted that the degraded products of Fraction I sometimes became mixed with the Fraction II, which mostly represented amylose counterpart of starch (Blue value). Thus it was not clear about the degree of degradation of amylose, especially in mere extrusion cooked starches. Chinnaswamy *et al.* (1989), however, have shown that the branched component, amylopectin, underwent more degradation than its linear counterpart, amylose, during extrusion cooking. When these starches were subjected to gamma-irradiation or chemical treatment and/or extrusion cooking, both Fraction I and Fraction II underwent considerable degradation. Further study is necessary to precisely characterize the amylose degradation pattern in these samples. In any case, molecular degradation of starch during different treatments is clear. This could have a profound influence on the starch expansion properties.

INTERRELATIONSHIPS

The molecular fractionation data showed that Fraction I of starch was a major starch quality factor, being altered during various processing and/or modification conditions for maximum expansion. Treatments such as barrel temperatures and moisture contents, chemical modifications with sodium chloride, sodium bicarbonate and urea, and atomic modifications (gamma-irradiation) altered the starch Fraction I content (amylopectin) more than the Fraction II content (amylose). The relationship between Fraction I content and the expansion ratio is shown in Fig. 8(a)–(d). In Fig. 8(a) the gamma-irradiation modified starches show decreased Fraction I content irrespective of amylose content and irradiation dosages with increasing expansion ratio. Similarly, when the gamma-irradiation modified starches show decreased Fraction I content irrespective of amylose content and irradiation dosages with increasing expansion ratio. When the irradiation modified starches were subjected to chemical modifications with HP, CAN, or PP, the Fraction I content of starch further decreased (Fig. 8(b)). Correspondingly the expansion ratios also decreased to 2 units or less. Similar results can be found in the literature for different barrel temperatures, moisture contents, native starches, sodium bicarbonate, and urea modifications (Chinnaswamy & Hanna, 1988*a,b*; 1990; Chinnaswamy *et al.*, 1993*b*). All those values were replotted against expansion ratio and the results are shown in Fig. 8(c). Expansion ratios generally decreased with decreasing Fraction I content irrespective of starch amylose content and/or treatments. Various other studies conducted at the University of Nebraska have used starch–fiber mixtures, starch–sodium chloride mixtures, starch–protein mixtures and starch–sugar mixtures which also showed changes in Fraction I contents of 0, 25, 50 and 70% amylose starches. The relationship between their Fraction I content and expansion ratio is given in Fig. 8(d). The expansion ratio varied as the Fraction I contents of variously treated starches were varied, and generally decreased with decreasing Fraction I content of starches irrespective of amylose contents and modifications.

However, from the results it was still not clear whether the Fraction I content of starch irrespective of the amylose content or starch modifications was responsible for maximum expansion ratio or not, although one can see in Fig. 8 that the values of Fraction I content generally decreased with increasing expansion ratio. Therefore, out of curiosity, all of the data were put together to see the overall trend. Such a figure was constructed (Fig. 9), where one can see that the Fraction I contents of starches and the expansion ratios are scattered, but in an orderly fashion. However, the overall trend is that with increasing Fraction I content, the expansion ratio generally increased. It should be noted that this picture contains more than 50 Fraction I content and expansion ratio values taken from different studies at different times. The work was conducted over a six-year period by seven different people. Thus the results represent the diverse nature of experimentation which, of course, may reinforce the validity

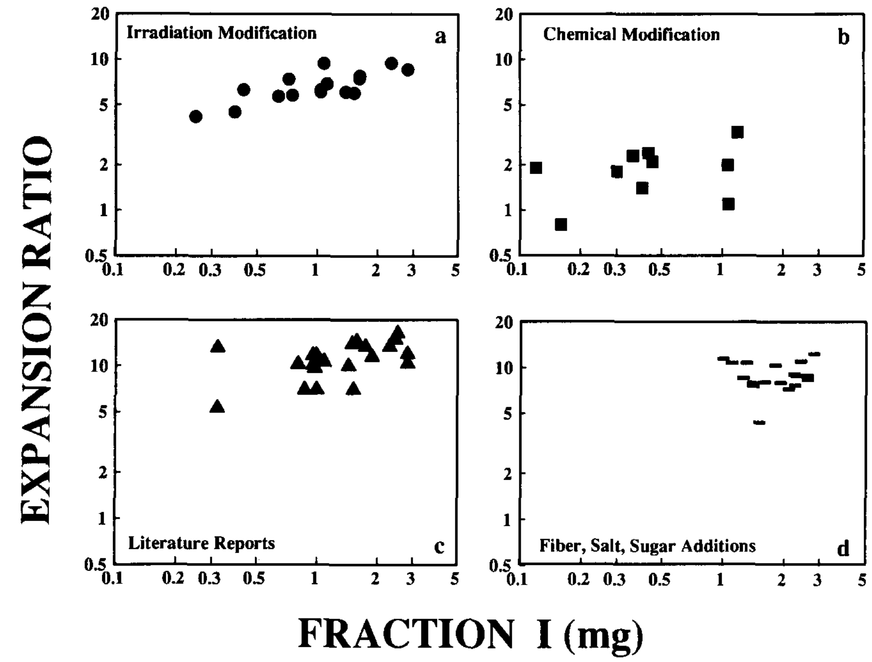

Fig. 8. Relationship between Fraction I content of variously modified starches (indicated) and expansion ratio. (a) Irradiation modifications, (b) chemical modifications, (c) data obtained for physical modifications from literature reports, and (d) modifications due to fiber, salt, and sugar additions are shown.

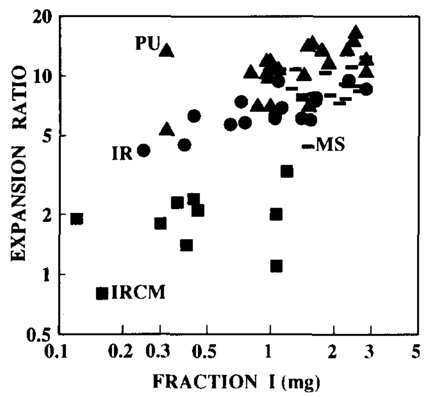

Fig. 9. Relationship between Fraction I content and expansion ratio of various starches with or without modifications and extrusion cooking. Literature reports (PU, ▲), irradiation modification (IR, ●), chemical additives (IRCM, ■), and fiber, salt, sugar, and protein additions (MS, ▬) are indicated.

of the trend. Overall, it appears that the best expansion of starch comes only from keeping the Fraction I structures and contents intact during extrusion processing. Therefore, any minimization of molecular degradations during extrusion cooking would help retain the good expansion qualities. However, it is not clear yet whether one can overcome the varietal differences among starches in their expansion ratios. Every modification procedure used in the study has mostly decreased the expansion ratio due to molecular degradations of starch. Sodium chloride modifications, however, have increased the expansion ratios of 25 and 70% amylose starch. There appears to be still some way to increase the expansion properties of poorly expanding types. Crosslinked starches might be one way to improve the stability of Fraction I content and thus expansion ratio.

In addition, the molecular weight ranges of Fractions I and II of native, extruded, gamma-irradiated starch before and after extrusion cooking have shown wide variations (Table 3). Native starch Fraction I molecular weight varied from $3{\cdot}5 \times 10^7$ to 1×10^7 while Fraction II molecular weight varied from $0{\cdot}14 \times 10^6$ to $3{\cdot}7 \times 10^6$. This gives some idea of the molecular sizes of Fractions I and II in various corn starches differing in amylose contents, with or without modifications.

CONCLUSIONS

From this study one can draw a number of conclusions. Overall maximum expansion of starches was observed for 50% amylose content irrespective of physical, chemical or atomic modifications. Sodium chloride altered either the viscoelastic properties of starch or the molecular properties of starch, or both, to give an improved expansion of 25 and 70% amylose starch. The molecular degradation patterns of variously modified starches clearly showed that the Fraction I content, in addition to starch amylose content, plays a critical role in controlling the expansion properties of starch. The Fraction I content probably represents the average mean molecular weight of starch. The higher the Fraction I content, the higher the mean molecular weight of starch. Degradation of Fraction I contents

Table 3. Molecular weight changes with various modifications

Fraction	MW (daltons)
Fraction I:	
Native	$3\cdot5 \times 10^7$
Extruded	$3\cdot5 \times 10^7$
20 kGy Native	$2\cdot7–3\cdot5 \times 10^7$
Extruded	$1\cdot0–3\cdot5 \times 10^7$
Fraction II:	
Native	$0\cdot14–3\cdot7 \times 10^6$
Extruded	$0\cdot14–2\cdot8 \times 10^6$
20 kGy Native	$0\cdot23–1\cdot7 \times 10^6$
Extruded	$0\cdot14–0\cdot86 \times 10^6$

generally decreased the expansion ratio. Overall it appears that the amylose content, as well as the Fraction I content, and their structural properties form the basis of starch expansion properties, though further study is needed to explain how the Fraction I content and the amylose content of starches are interrelated with expansion.

REFERENCES

Adams, S. (1983). In *Recent Advances in Food Irradiation*, ed. P.S. Elias & A.J. Cohen. Elsevier Biomedical Press, Amsterdam, pp. 149–70.

Bhattacharya, M. & Hanna, M.A. (1987*a*). *J. Food Sci.*, **52**, 764–6.

Bhattacharya, M. & Hanna, M.A. (1987*b*). *Lebensm. Wiss. u. Technol.*, **20**, 195–201.

Bhuiyan, M.Z. & Blanshard, J.M.V. (1982). *Starch/Staerke*, **34**, 262–6.

Biliaderis, C.G., Grant, D.R. & Vose, J.R. (1979). *Cereal Chem.*, **56**, 475–80.

Biliaderis, C.G., Grant, D.R. & Vose, J.R. (1981). *Cereal Chem.*, **58**, 496–502.

Chaing, B.Y. & Johnson, J.A. (1977). *Cereal Chem.*, **54**, 436–43.

Chinnaswamy, R. & Bhattacharya, K.R. (1983*a*). *J. Food Sci.*, **48**, 1604–8.

Chinnaswamy, R. & Bhattacharya, K.R. (1983*b*). *J. Food Sci.*, **48**, 1600–3.

Chinnaswamy, R. & Bhattacharya, K.R. (1984). *J. Cereal Sci.*, **2**, 273–9.

Chinnaswamy, R. & Bhattacharya, K.R. (1986). *Starch/Staerke*, **38**, 51–7.

Chinnaswamy, R. & Hanna, M.A. (1987). *J. Food Sci.*, **52**, 1746–7.

Chinnaswamy, R. & Hanna, M.A. (1988*a*). *Cereal Chem.*, **65**, 138–43.

Chinnaswamy, R. & Hanna, M.A. (1988*b*). *J. Food Sci.*, **53**, 834–6, 840.

Chinnaswamy, R. & Hanna, M.A. (1988*c*).*Starch/Staerke*, **40**, 186–90.

Chinnaswamy, R. & Hanna, M.A. (1990). *Cereal Chem.*, **67**, 490–9.

Chinnaswamy, R., Hanna, M.A. & Zobel, H.F. (1989). *Cereal Foods World*, **34**, 415–22.

Chinnaswamy, R., Ali, Y. & Hanna, M.A. (1993*a*). *J. Food Engng.* (submitted).

Chinnaswamy, R., Tan, Y.L. & Jones, D. (1993*b*). *Stärke* (submitted).

Colonna, P., Melcion, J.P., Vergnes, B. & Mercier, C. (1983). *J. Cereal Sci.*, **1**, 115–25.

Colonna, P., Doublier, J.L., Melcion, J.P., De Monredon, F. & Mercier, C. (1984). *Cereal Chem.*, **61**, 538–43.

Davidson, V.J., Paton, D., Diosady, L.L. & Larocque, G. (1984). *J. Food Sci.*, **49**, 453–8.

Faubion, J.M., Hoseney, R.C. & Seib, P.A. (1982). *Cereal Foods World*, **27**, 212–16.

Gomez, M.H. & Aguilera, J.M. (1983). *J. Food Sci.*, **48**, 378–81.

Gomez, M.H. & Aguilera, J.M. (1984). *J. Food Sci.*, **49**, 40–3, 63.

Grant, L.A. & D'Appolonia, B.L. (1991). *Cereal Chem.*, **68**, 651–2.

Guy, R.C.E. & Horne, A.W. (1988).In *Food Structure: Its Creation and Evaluation*, ed. J.M.W. Blanshard & J.R. Mitchell. Butterworths, London, p. 335.

Harper, J.M. (1981). *Extrusion of Foods*, Vol. II. CRC Press, Boca Raton, FL.

Kokini, J.L., Chang, C.N. & Lai, L.S. (1992). In *Food Extrusion Science and Technology*, eds. J.L. Kokini, C.T. Ho & M.V. Karwe. Marcel Dekker, New York, pp. 621–42.

Launay, B. & Lisch, J.M. (1983). *J. Food Engng*, **2**, 259–80.

Mercier, C. & Feillet, P. (1975). *Cereal Chem.*, **52**, 283–97.

Meuser, F. Von Lengerich, B. & Koehler, F. (1982). *Staerke*, **34**, 366–72.

O'Meara, J.P. & Shaw, T.M. (1957). *Food Technol.*, **11**, 132–6.

Owusu-Ansah, J. Van de Voort, F.R. & Stanley, D.W. (1983). *Cereal Chem.*, **60**, 319–24.

Owusu-Ansah, J., Van de Voort, F.R. & Stanley, D.W. (1984). *Food Sci. Technol. J.*, **17**, 65–70.

Sabularse, V.C., Liuzzo, J.A., Rao, R.M. & Grodner, R.M. (1991). *J. Food Sci.*, **56**, 96–8, 108.

Sokhey, A.S. & Chinnaswamy, R. (1992). *Food Structure*, **11**, 361–71.

Sonntag, C.V. (1979). In *Radiation Biology and Chemistry: Research and Developments*, ed. H.E. Edwards, S. Navaratnam, B.J. Parsons & G.O. Phillips. Elsevier Scientific Publishing, New York, pp. 85–113.

Wen, L.F., Rodis, P. & Wasserman, B.P. (1990). *Cereal Chem.*, **67**, 268–75.