Effect of processing on the microstructure of finger millet by X-ray diffraction and scanning electron microscopy

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Abstract Finger millet is one of the important minor cereals, and carbohydrates form its major chemical constituent. Recently, the millet is processed to prepare hydrothermally treated (HM), decorticated (DM), expanded (EM) and popped (PM) products. The present research aims to study the changes in the microstructure of carbohydrates using X-ray diffraction and scanning electron microscopy. Processing the millet brought in significant changes in the carbohydrates. The native millet exhibited A-type pattern of X-ray diffraction with major peaks at 2θ values of 15.3, 17.86 and 23.15°, whereas, all other products showed V-type pattern with single major peak at 2θ values ranging from 19.39 to 19.81°. The corresponding lattice spacing and the number of unit cells in a particular direction of reflection also reduced revealing that crystallinity of starch has been decreased depending upon the processing conditions. Scanning electron microscopic studies also revealed that the orderly pattern of starch granules changed into a coherent mass due to hydrothermal treatment, while high temperature short time treatment rendered a honey-comb like structure to the product. However, the total carbohydrates and non-starch polysaccharide contents almost remained the same in all the products except for DM and EM, but the individual carbohydrate components changed significantly depending on the type of processing.

Keywords Finger millet · Microstructural parameters · Hydrothermal treatment · High temperature and short time treatment

Introduction

Finger millet or ragi (*Eleusine coracana*), one of the important millets, was traditionally used to prepare flour based products. Recently, the millet is hydrothermally treated and polished to prepare decorticated millet and the decorticated millet was subjected to high temperature and short time treatment to prepare expanded finger millet (Malleshi 2006; Ushakumari et al. 2007). Decorticated and expanded finger millet being new generation products are slowly gaining prominence nowadays. A significant portion of the millet produce is also used to prepare popped product (Malleshi and Desikachar 1981). During the preparation of these products, the millet undergoes hydrothermal and also high temperature short time treatment leading to a series of changes in its bio-components namely carbohydrates, proteins and lipids. Among these nutrients, carbohydrates form a major component. The millet carbohydrates consist of free sugars, starch and non-starch polysaccharides. The millet starch consists of amylose and amylopectin fractions, normally present in the ratio of 25:75. Many of the starch granules of the millet are compound and rigid in nature and this contributes towards the nutritional advantages of the millet food in terms of slow digestion of its carbohydrates or lower glycemic index of the millet meal (Lakshmi Kumari and Sumathi 2002).

Normally, hydrothermal treatment causes gelatinization of starch within the ambit of cellular structure where as high temperature and short time (HTST) treatment causes burst opening of the cell walls and expansion of the starch granules. Basically, starch is a semicrystalline polymer with

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low and imperfect crystallinity (Frost et al. 2009). Due to this nature of starch, two phase transitions are likely to occur during thermal treatment of starch-water systems: glass transition that concerns the amorphous phase (mainly branching regions of amylopectin and most of the amylose chains) and the melting of crystallites (formed by adjacent short chains of amylopectin intertwined into double helices) (Maache-Rezzoug et al. 2008). Different analytical tools have been used to study these changes in starch. X-ray scattering method is one of such tools which can be efficiently used to study the changes in the crystalline structure including the crystallite size. X-ray scattering of cereal products at small and wide angle provides qualitative and quantitative information on both the macro and micro-structure of their starchy component. X-ray scattering methods provide structural information that can be directly related to observed material properties. While the small angle X-ray scattering provides information about the sizes of repeating lamellar structure (10 to 50 nm) within the starch granules (Lopez-Rubio et al 2009), the wide-angle X-ray scattering throws light on the structure of the nanoparticles of the condensed matter with a special resolution ranging from angstroms to hundreds of nanometer (1 to 10 nm) whether they are in liquid or solid form. This aspect has been studied in the case of rice and it has been reported that, rice starch exhibits a typical A-type pattern of diffraction with peaks at 15, 23 and an unresolved doublet at 17,18 A° (Cheetham and Tao 1998), which changes into V-type pattern after parboiling (Priestly 1976). In case of finger millet also it has been reported that the millet starch exhibits a typical A-type pattern with strong peaks at 15.15, 17.15, 18.2, 20.3 and 23.5 A° but it retains the same pattern even after hydrothermal treatment at moisture level of below 30% (Adebowale et al. 2005). However, there is no information about the nature of its starch when it is steamed at moisture content higher than 30%. The structure and crystallinity of cereal starches are largely influenced by the type of processing and also its environment. Apart from X-ray scattering, scanning electron microscopic studies will be helpful to actually visualize the changes that take place after processing. Hence, the objective of the present work is to study the changes in the microstructure of the millet starch on hydrothermal processing, decortication, expansion and popping through X-ray diffraction method and scanning electron microscopy in relation with their carbohydrate components.

Experimental

Raw material

Finger millet (variety GPU 28) procured from the University of Agricultural Sciences, Bangalore, was cleaned to remove

the immature grains, extraneous and foreign particles, deglumed in an Engelberg huller (Sri Ganesha Engineering Works, Chennai, India) and used for the studies.

Sample preparation

Finger millet was soaked in water to raise its moisture content to 35±1%, steamed for 30 min at atmospheric pressure, dried at about 40±1°C to 12% moisture level to prepare hydrothermally processed millet (HM). The HM was moist conditioned and decorticated in a carborundum disc mill as per Malleshi (2006) to prepare decorticated millet (DM). The DM was equilibrated to about 40% moisture, steamed for about 10 min and pressed between rolls of cereal flaker just to create minute fissures, dried to about 9% moisture content and subjected to HTST treatment according to Ushakumari et al (2007) to prepare expanded millet (EM). On the other hand, the native millet (NM) was equilibrated to 18% moisture content and popped following high temperature and short time (HTST) treatment (Malleshi and Desikachar 1981) to prepare popped millet (PM).

The NM, HM, DM, EM and PM were pulverized in a domestic flour mill to prepare a meal of less than 250μ particle size. The whole meals were defatted using petroleum ether (60–80°) and the defatted samples were used for the estimation of free sugars, total and soluble amylose, starch and total carbohydrates as well as the non-starch polysaccharides. Whole meals were used for X-ray diffraction studies with isolated starch from the millet as a reference material, whereas, the whole grains were used for scanning electron microscopic examination.

Isolation of starch Finger millet was soaked in 0.01 M aqueous HgCl₂ solution overnight (to prevent incipient sprouting of grains during steeping) for 16 h at ambient conditions. The steeped material was mashed with five volumes of water in a Waring blender and the slurry was screened through a sieve of 105 μm openings. The residue was again dispersed in water, wet ground and sieved through screens of 75, 45 and 73 μm openings respectively, and the process was repeated until it tested negative to iodine. The residue was dispersed in water, washed with mild alkali, followed by salt solution and toluene treatment to free the starches from protein and pigment contamination. After ensuring the purity by microscopic examination, the starch was dried over methanol (Singh and Ali 2008).

Carbohydrates

Free sugars Twenty five gram each of the defatted samples was refluxed with 70% ethanol (w/v) for about 2 h. The extraction was repeated with the residue till the extract

tested negative for sugars. The extracts were pooled and freed from the colored matter as well as the non-sugar constituents by passing through dowex (H^+) and dowex (OH^-) resins successively and concentrated under reduced pressure at 40°C. The total sugar contents of the extract were determined by phenol sulphuric acid method (Ford 1981).

Starch The total starch contents of the samples were estimated following the enzymatic digestion method (Holm et al. 1986). Defatted samples (100 mg) were dispersed in 15 ml of water containing 0.1 ml of heat stable α -amylase. To the mixture, 15 ml of 0.05 M acetate buffer (pH 4.8) containing 10 mg of glucoamylase was added and incubated at 60°C for 16 h. The contents were made up to 100 ml and the reducing sugars were estimated using dinitrosalicylic reagent. The total and soluble amylose contents of the samples were determined according to Sowbhagya and Bhattacharya (1971).

Non-starch polysaccharides The residue from the free sugar extraction was used for isolation of non-starch polysaccharide (NSP) fractions. The residue was sequentially extracted with water, 0.5% ethylene diamine tetraacetic acid and 10% NaOH solution to isolate water soluble NSP, pectic polysaccharides followed by that the starch was digested and subsequently the residue was treated with alkali and used for isolation of hemicelluloses and cellulose fractions (Malleshi et al. 1986).

Total carbohydrates The total carbohydrates were estimated by dissolving 50 mg of the defatted sample in 4 ml of 90% dimethyl sulphoxide followed by boiling in a water bath for 15 min. The contents were centrifuged and an aliquot of the supernatant was used for the estimation of carbohydrate contents by phenol-sulphuric acid method (Ford 1981).

X-ray diffractometry

The isolated starch and the meals from NM, HM, DM, EM and PM, were packed in rectangular glass crucibles and exposed to X-ray beam (8 keV) generated by a X-ray diffractometer (MiniFlex –II, Desktop X-ray diffractometer, Japan) equipped with a θ - θ goniometer at 25 mA and 30 kV, with Cu α filtered radiation. The scanning range for 2θ was set to 6–45° to cover all the significant diffraction peaks of sample crystallites with a scan speed of 3°/min. A single order method based on Warren-Averbach (Warren and Averbach 1952) Fourier theory was used to compute the crystallites size from the broadening of X-ray reflection. For this purpose, a known analytical function for crystal size distribution was used (Somashekarappa et al 1999; Singh et al 2006). The necessary equations for the computations of the microstructural parameters namely,

crystal size, width of the size distribution and the strain were the same used by Smitha et al (2008) for the millet flour milled in different pulverizers. The strain was calculated by the line profile analysis employing exponential distribution function. The present method of computing the microstructural parameters was also well documented in the report on Round-Robin test by IUCr, UK (Balzar 2002).

Microscopic studies

The grains from NM, HM, DM, EM and PM were cut transversely and also longitudinally into two halves using a sharp blade. The cut portions were mounted on the metallic stubs with the aid of double-sided scotch tape to expose the seed coat and also the endosperm portion. The samples were gold coated (about 100 Å) in a KSE 2AM Evaporation Seevac gold sputter (Polaron SEM Sputter Coating System, Hertfordshire, UK) and scanned in a LEO 435VP scanning electron microscope (Leo Electron Microscopy Limited, Cambridge, UK) and the selected portions depicting morphological features of the seed coat and also the endosperm were selectively photographed (Meek 1976).

Statistical methods

Values were calculated per 100 g of dry matter. The experiments were performed with three independent trials, and data are presented as means $\pm$ standard deviation (SD). Data were assessed for significant difference employing *t*-tests and were considered to be statistically significant at $p \leq 0.05$. The statistical analysis was done using Microsoft Excel 2007 (Microsoft Corp., Redmond, WA, USA).

Results and discussion

Carbohydrates

The carbohydrate characteristics of NM, HM, DM, EM and PM are presented in Table 1. The NM contains 1.09% free sugars which decreased to 0.71 on hydrothermal treatment and decortication. During soaking the millet, a part of the free sugars may leach out and also may undergo Maillard reaction during steaming, which may be the reason for the decreased free sugar content. Decortication did not influence the free sugar content of the millet but expansion slightly reduced it, which may be due to the browning reactions of Maillard type during expansion. A slight decrease in the free sugar content of the millet after popping was observed but it was not significant. No significant difference was observed in the starch content of NM (60.31%), HM (62.19%) and PM (60.68%) but in the case of DM the removal of seed coat resulted in an

Table 1 Carbohydrate characteristics of finger millet products (g/100 g)

Parameter	NM	HM	DM	EM	PM
Free sugars	1.1±0.04 ^c	0.71±0.061 ^b	0.70±0.012 ^b	0.63±0.012 ^a	0.95±0.021 ^c
Starch	60.3±1.20 ^a	62.2±1.00 ^a	72.3±1.10 ^b	71.5±0.90 ^b	60.7±1.20 ^a
Total carbohydrates	61.4±0.90 ^a	61.9±0.81 ^a	73.0±1.10 ^b	72.2±1.00 ^b	61.6±1.00 ^a
Total amylose	16.7±0.20 ^a	18.2±0.30 ^b	20.4±0.12 ^c	21.0±0.10 ^c	18.3±0.20 ^b
Soluble amylose	11.0±0.10 ^d	8.5±0.10 ^b	9.8±0.11 ^c	7.5±0.10 ^a	7.1±0.09 ^a
Insoluble amylose	5.7±0.10 ^a	9.4±0.13 ^b	10.3±0.10 ^c	13.5±0.08 ^d	11.2±0.06 ^c
Non starch polysaccharides	20.3±0.80 ^b	20.1±0.91 ^b	17.1±1.00 ^a	17.5±0.80 ^a	20.5±1.30 ^b

NM Native finger millet, HM Hydrothermally treated finger millet, DM Decorticated finger millet, EM Expanded finger millet, PM Popped finger millet
Mean values with different superscripts for a particular row vary significantly ($p < 0.05$)

apparent increase in the starch content from 62.9 to 73% which remained almost same (72.15%) on expansion of the millet. The total carbohydrate content also followed the similar trend. The total amylose content of the millet increased from 16.7 to 18.18 on hydrothermal processing and further increased to 20.4 on decortication. It is interesting to note that HTST treatment also increased the total amylose content compared to the control sample. This increase in the total amylose content may be due to the thermal degradation of amylopectin equivalent portion of starch (Usha Dharmaraj and Malleshi 2011). Considerable decrease in the soluble amylose content from 11 to 8.48% in case of HM and 9.8% in case of DM was observed. However, EM and PM exhibited comparatively lower values for soluble amylose. Similar results had been reported for rice during parboiling (Ali and Bhattacharya 1972). But, the total non-starch polysaccharides remained almost the same in NM, HM and PM samples, except for that of DM and EM for which a decrease of about 16% was observed which may be mainly due to the removal of the seed coat during decortication of the millet.

X-ray diffraction

According to diffraction theory, the intensity of peak depends on the amount of ordered semicrystalline structures and/or on the differences in electron density between amorphous and crystalline lamellae (Feign and Svergun 1987). Therefore the sharp peaks can be directly correlated to crystalline region and the diffused peaks to amorphous region of the samples. The X-ray diffractograms of the whole meals from NM, HM, DM, EM and PM as well as the isolated starch from the native millet are presented in Figure 1 and the corresponding microstructural parameters are indicated in Table 2. The diffraction patterns of the native millet is comparable with a triplet pattern observed for the isolated starch at 2θ of 15, 17 and 23° exhibiting A type pattern. Contrary to this, in case of HM the absence of peaks at 15 and 17° are conspicuous and it exhibited only a

diffused peak at 19.8° of 2θ . The peak at 2θ of 20° is typical to V-type pattern and this is commonly observed in the case of parboiled cereals. Similar to HM, DM also exhibited a V type pattern for diffraction with a diffused peak at 2θ of 19.81° . Decortication of HM involves only removal of the outer seed coat and hence, no significant difference between the endosperm structure of HM and DM was observed. The X-ray diffractogram of EM was also similar to DM with a peak at slightly lower 2θ value of 19.46° . The PM also exhibited a single peak at 2θ of 19.39° , still lower to that of EM. The diffraction peaks of HM, DM, EM and PM were invariably small and of lower area compared to that of the NM. This shows that the starch in these products is largely of amorphous nature with very little crystallinity. The lower peak intensities indicate the presence of lower degree of crystallinity. The degree of crystallinity of the native millet was less than that of the starch and it decreased on hydrothermal treatment. Decortication of the millet did not influence the degree of the crystallinity. But, HTST treatment further decreased the crystallinity, which may be due to complete gelatinization of starch.

The values for lattice spacing for the isolated starch, indicated by 'd', were 5.9, 5.0 and $3.9 \text{ \AA}$ at 2θ values of 15.1, 17.6 and 23.0° respectively. The corresponding values for NM were 5.8, 5.0 and $3.9 \text{ \AA}$ respectively, more or less comparable to the native starch. The 'd' values for both HM and DM were only $4.5 \text{ \AA}$ but was $4.6 \text{ \AA}$ for EM indicating a marginal increase on expansion of DM. However, in the case of popped millet, 'd' value ($4.6 \text{ \AA}$) was significantly lower than the native millet ($5.9 \text{ \AA}$) at 15.3° . The number of unit cells in a particular direction of reflection indicated by N were highest (9.4) for the initial peak, decreased significantly (5.8) for the second peak and again increased to the initial value (9.3) at the third peak in case of starch. The NM also exhibited similar trend but for the slightly lower values for 'N'. However, the 'N' values were significantly lower (1.8) in the case of HM and DM compared to that of the NM. The EM and PM also

Fig. 1 X-ray diffractograms of different finger millet products

cps: counts per second

exhibited lower values (1.9) for 'N' but slightly higher than that of the HM and DM. The probability of the occurrence of the unit cells, represented by 'P', also followed the similar trend. The intrinsic strain (g%) varied from 0.1 to 0.3 for starch and NM, exhibiting their anisotropic nature. The 'g' value for HM, DM, EM and PM was 0.1 indicating that, these samples are largely isotropic in nature. The lattice size, indicated by the 'D' values was highest (54.8) for starch at 2θ of 15.1, which decreased to 29.2 Å at 2θ of 17.6 and again increased to

35.9 Å at 2θ of 23.0. The lattice size of the NM also followed a similar pattern. The corresponding 'D' values for HM and DM were 7.8 and 8.0 Å respectively. However, the EM and PM exhibited a slightly higher values for 'D' (8.5 and 8.5 Å) compared to HM and DM. The 'Δ' indicates the goodness of the fit of experimental profiles and the reliability of the microstructural parameters given in Table 2.

Native cereal starch granules display quite complex structure with several levels of organization, normally

Table 2 Microstructural parameters of finger millet products using exponential distribution function

Samples	2 θ in Deg.	'd' (Å)	<N>	P	'g' (%)	Δ (%)	D = N.d (Å)	Degree of crystallinity (%)
Starch	15.1	5.9	9.4±0.38	8.4±0.34	0.2	4.1	54.8±2.23	33±1.4
	17.6	5.0	5.8±0.26	4.9±0.22	0.3	4.5	29.2±1.32	
	23.0	3.9	9.3±0.38	8.3±0.34	0.2	4.1	35.9±1.53	
Native millet	15.3	5.8	8.1±0.32	7.3±0.29	0.1	4.0	46.8±2.30	27±2.1
	17.9	5.0	5.0±0.24	4.2±0.20	0.2	4.8	24.6±1.21	
	23.2	3.8	7.5±0.31	6.7±0.28	0.1	4.2	28.7±1.20	
Hydrothermally treated millet	19.8	4.5	1.8±0.04	1.4±0.04	0.1	2.57	7.8±0.21	16±1.4
Decorticated millet	19.8	4.5	1.8±0.04	1.4±0.03	0.1	2.51	8.0±0.20	16±0.7
Expanded millet	19.5	4.6	1.9±0.04	1.5±0.03	0.1	2.36	8.5±0.20	13±0.7
Popped millet	19.4	4.6	1.9±0.05	1.5±0.04	0.1	2.57	8.5±0.20	14±0.7

d: lattice spacing

<N>: number of unit cells in a particular direction of reflection

P: probability of occurrence of the unit cells

g: intrinsic strain

D: lattice size

 Δ : the goodness of fit of experimental profiles

linear amylose being amorphous and amylopectin being semicrystalline (Lopez-Rubio et al. 2007), but processing the cereals generally disrupts the crystallinity of its starch and parboiling normally transforms the crystalline structure to amorphous one. Parboiling also causes a perceptible shift in the crystalline phases of the granule of the native starch including all microstructural parameters. This observation was in concurrence with the increase in the amorphous portion of the starch (amylose) on hydrothermal and high temperature short time treatment. Hence, the processed starch majorly exhibits amorphous structure. It was reported that V-type X ray pattern occurs during parboiling of rice as a consequence of amylose-lipid complex (Priestly 1976). Parboiled rice exhibits either V type or mixed A and V type X-ray pattern (Ong and Blanshard 1995), probably due to the presence of both ungelatinized and gelatinized starch or also may be due to the recrystallization of the starch. However, in the case of the millet, only a single peak at 2 θ of 19.8° was observed after hydrothermal treatment and no mixed type patterns were recorded. Thus, it may be concluded that almost all the starch present in the millet has undergone gelatinization during the treatment under the experimental conditions and the extent of recrystallization of the starch on hydrothermal treatment is less. It may be opt to state here that, Singh et al. (2006), who studied the nature of crystallinity in native and acid modified starches, reported relatively higher degree of crystallinity in finger millet starch (30%) compared to other cereal starches. Similarly, Mohan et al. (2005) reported that, the crystallinity of finger millet starch (30%) was considerably higher than the rice starch (22%). Mahanta et al. (1989) studied the

starch crystallinity in rice subjected to different degree of parboiling and observed the shift from A to V or A to mixed type X-ray pattern depending upon the severity of parboiling. They also observed comparatively low degree of crystallinity in all the samples. The X-ray diffractograms and microstructural parameters are totally dependent on the nature of starch present in the cereals and in the case of hydrothermally treated and decorticated millet, the only difference is removal of seed coat. Since, the seed coat is mainly non-starch material, it may not affect the X-ray diffractogram. High temperature and short time treatment to the millet, converts it to a ready-to-eat product containing completely gelatinized starch, which further decreases the crystallinity. Hoover and Vasanthan (1994), subjected starches of different origins to heat-moisture treatment and studied the X-ray diffraction patterns and observed that, the treatment induced changes not only in the crystalline regions but also in amorphous regions of all the starches irrespective of their origin. They also noticed decrease in the intensities of the peaks as the severity of heat treatment increased. The decreased intensity of the peaks on treatment may either be due to crystallite disruption or reorientation of the double helics forming the crystalline array due to the hydrothermal treatment that gelatinizes its starch.

Scanning electron microscopy

The observations of X-ray diffraction were confirmed by the scanning electron microscopic studies. The microstructure of the native as well as the processed millet products are illustrated in Figure 2. The transverse section of the NM

Fig. 2 Scanning electron photomicrographs of finger millet products; **a** native, **b** hydrothermally processed, magnified images of **c** native, **d** hydrothermally processed, **e** expanded, **f** popped, and magnified images of **g** expanded and **h** popped millet

endosperm indicates two distinctly different cellular arrangements, one towards the central core and the other towards the periphery (Fig. 2a) which disappears completely on hydrothermal treatment leaving a void at the center portion (Fig. 2b). The magnified image of the NM shows the granular arrangement of the starchy endosperm (Fig. 2c) and

clearly brings out the enclosure of the starch granules by the papery thin cell walls. The HM endosperm looks like a coherent mass with completely lost morphological features of the endosperm constituents, or in other words, the orderly crystalline arrangement of the starch granules and other constituent tissues of the seed change into a homogeneous

amorphous mass (Fig. 2d). The photograph of EM indicates the presence of a large void resembling like a thin soap bubble surrounded by a net work of irregular sized voids (Fig. 2e). The high temperature short time treatment of the native kernel changes its endosperm into a honey comb structure with a net work like structure (Fig. 2f) in case of PM. Even though both PM and EM were prepared by HTST treatment, the structure of the kernel differ because of the basic difference in their preparation method. The expanded millet was devoid of seed coat (Fig. 2g) since it is prepared from DM but the popped millet contains seed coat (Fig. 2h) since it is prepared from native millet.

Thus, the decrease in the degree of crystallinity of NM on hydrothermal treatment and decortication could be visualized by the transformation of the endosperm from granular structure to an amorphous homogenous mass. Even though, high temperature and short time treatment to the millet, converts the endosperm into a net work like structure the degree of crystallinity decreases further. These observations are in line with the decreased microstructural parameters recorded by the X-ray diffractograms.

Conclusions

The X-ray and microscopic studies of the finger millet carbohydrates indicate that, the structure of the millet endosperm undergoes significant changes during hydrothermal and high temperature short time treatment. The degree of crystallinity decreased on processing and the three major reflection peaks observed in the native millet, were disappeared. A noticeable decrease in the lattice spacing and lattice size was also observed as a result of processing conditions. These observations were confirmed by the scanning electron microscopy through which the shift of the endosperm from orderly granular arrangement to a coherent homogeneous mass was visualized. Popping and expansion of the millet resulted in an orderly network like structure resulting further decrease in the microstructural parameters. These results were quantified by the increase in the amorphous portion of the starch, namely, the amylose, on processing. However, the total carbohydrates and non-starch carbohydrate contents almost remained the same on processing except for the decorticated millet. The study gives an insight to the changes occurred in the structural components of the finger millet due to processing conditions, which may be helpful to understand the functional properties of these products.

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