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Effects of thermal treatments and germination on physico-chemical properties of corn flour

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Certain physico- chemical properties including viscoelasticity, crystallinity and maltose content of corn depends on the gelatinization of starch under different treatments. Three different treatments were performed; boiling in water, steam heating, and germination. The effects of gelatinization on viscoelastic property of corn starch were measured and the morphological changes of corn after different treatments were determined by scanning electron microscope (SEM). Various grooves and fissures on the exterior surface of the granules were noticed in the treated sample compared to control. The crystallinity of corn after different treatments was determined by X-ray diffraction studies (XRD). The control showed higher crystallinity than that of thermal treated samples.

Key words: Crystallinity, viscoelastic property, Instron Texture Analyzer, scanning electron microscope, and X-ray diffraction.

INTRODUCTION

Starch in abundant quantity is available in India. Starchy foods are staple foods for the growing millions of Indians. Starch, is an extraordinarily versatile polymer used in a wide array of products from paper to prepared foods (Mua and Jackson, 1995). In addition, starch is one of the most economic carbohydrates in nature (Hve Young et al., 2001), biosynthesized in granular form by plants. Whether modified or in its native state starches are used for thickening, stabilizing and gelling abilities in a wide variety of food and nonfood products (Jennings et al., 2002). Again in response to concerns about health implications of excess dietary fat and calories, a variety of fat substitutes were developed in recent years (Duxbury, 1990; Duxbury, 1990; Chun et al., 1997). Modified food starches partially replace fat to reduce calories and provide desirable textural qualities, mouth feeling appeal, etc. Rapid advances continue in acquisition of new knowledge of starch and a vigorous expansion in the use of starch is proceeding in food applications. Some remarkably significant and interesting practical developments have occurred. Consequently it is important to explore

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again the accumulated knowledge of starch and its practical use (Grist, 1975).

Availability makes dent corn the grain of choice for food starch manufacture, thus allowing corn starch to be an inexpensive food starch available in India. Corn flour is extensively used to produce products such as corn tortillas, corn chips, and tortilla chips, etc (Sahai et al., 2001; Serna et al., 1990). It is generally recognized that physical characteristics of corn are important factors influencing product characteristics (Sahai et al., 2001). The major component of the corn kernel is starch, and according to Trejo-Gonzales et al. (1982), starch is responsible for the mechanical properties of the dough (Cory and Bruce, 1997) and consequently plays an important role as a determinant of the food product quality. Functional properties of starch have considerable effects on the quality of starch-based products. Starch gelatinization is most important in a number of food modifications inclusive cooking, baking and extruding starch-based foods. The overall starch gelatinization process is generally supposed to be obeying a first order kinetics and depends on temperature. Nonetheless the phenomenon is very complex and implies significant changes in physical, chemical and nutritional properties of starch as well as water and heat diffusivity, viscosity, rheological behavior, swelling and deformation of the

original shape of starchy products and susceptibility to enzymatic digestion. Actually the crystalline order of starch granules is lost during gelatinization (Bhattacharyya et al., 2004).

Cereal grains synthesize -amylase during germin-ation, which enhances the starch degradation process. This enzyme enhances the conversion of insoluble gra-nules to soluble starch and dextrin. Hence it is important to study the effect of germination on quality of the grains (Dona et al., 1991; Beck and Ziegler, 1989; Hill and MacGregor, 1988).

The present paper has studied the effects of thermal treatments and germination on gelatinization of corn starch, which affect viscoelastic property. The viscoelastic properties of starch-based doughs were measured by Instron Texture Analyser (London, U.K.). Starch crystallinity was determined by X-ray diffractometer (XRD). Scanning electron microscope (SEM) was applied to observe the morphological changes of corn after different treatments.

MATERIALS AND METHODS

Materials

Corn seeds (*Zea mays* L) were procured from local market. 3,5dinitrosalicylate (Loba Chemie, Mumbai), potassium iodide (E. Merck India Pvt. Ltd, Mumbai), and iodine (Qualigens Fine Chemicals, Mumbai, India) were purchased.

Different treatments on corn kernel

Corn seeds were used throughout the experiments. The proportion of corn flour and water was kept constant (1:5, w/v) in each case. Corn was treated in boiling water for 5, 10 and 15 min followed by drying at 60°C in Tray Drier (International Commercial Traders, Kolkata, India) for 5- 6 h. Another portion of corn was steam heated at 15 psi for 10, 20 and 30 min before drying at 60°C for 5-6 h. Beside steam heating another portion of corn was allowed to germinate in dark for 2,3 and 4days respectively at 37°C and then dried at 60° c for 5-6 h.

Developments of doughs

All the dried samples were milled finely with a blender (Bajaj Mixer Grinder, GM- 550) for 1 min and used for dough development. The proportion of corn flour and water was kept constant (1:1, weight basis) in each case. Doughs were formed by mixing flour and water in a twin Z arm mixer for 0.5 min. This produced a (just) cohesive very undeveloped dough that was finally shaped by hand into a 1cm cube.

Moisture content

Moisture content of control and treated corn seed powders were measured using standard air oven (Model No-06104, S.C.Dutta andCo, Kolkata, India) according to AOAC NO14.002 (AOAC, 1965).

Texture analysis

Texture analysis (viscoelasticity) of all the doughs were made using Instron Texture Analyser 4301 (London, U.K.) of maximum load 100 N and operating at 25%. The dough was placed onto the flat platform under a stainless steel probe with rounded end. The probe traveled at 15 mm/min until the force detected 10 N and then traveled upward until the gap between dough and probe was 2 mm. Finally the probe traveled downward until the force was 10N. The difference between the forces of these two bites was the viscoelasticity of that dough.

Determination of starch digestion

Effects of different treatments on corn starch damage were estimated by determining reducing sugar (maltose) content of each sample. Reducing sugar content was determined by standard AOAC NO 14.023 method.

Enzyme assay

Alpha-amylase activity was assayed at 40° C by measuring the reducing sugar released during the reaction, using starch as the substrate, according to Somogyi-Nelson method (Nelson, 1994). The reaction mixture contained 0.5 ml of 1.1% soluble starch in 0.05 M imidazole-HCl buffers, pH 7.0 and 2.5 ml of enzyme solution. After incubating for 1 h at 60° C the reaction was stopped by heating the reaction mixture in boiling water bath for 10 min. This reaction mixture was diluted with distilled water. 1 ml of dinitrosalicylic acid solution (Miller, 1959) was added in each 3 ml of dilutions (samples) and heated in boiling water bath for 5 min. Absorbance at 540 nm wavelength was measured (Spectrophotometer, U- 2000, Hitachi, Japan) after cooling the DNS-sample mixture at room temperature (Shaw et al., 1995).

One unit of alpha-amylase activity is defined as the amount of enzyme that releases 1 m (micromole) of reducing sugar per minute from soluble starch at pH 6.9 and 40° C.

X-ray diffraction patterns

The X-ray patterns of the flours were obtained with copper, nickel foil filtered, K radiation using a diffractometer (Rigaku, Miniflex, Japan). The diffractometer was operated at 10 mA and 30 kV. The scanning region of diffraction angle (2θ) was $4 - 40^{\circ}$ at a 0.05° step size with a scanning speed 1° per min (McPherson et al., 2000; Jane et al., 1997).

Scanning electron microscope (SEM)

Scanning electron microscope (JEOL, JSM5200, TOKYO, JAPAN) were taken at an accelerating voltage of 20 km to view the corn flour in three dimensions and to determine the shape and surface features of the granules. Corn flour from all the treatments and the control sample were mounted stubs with adhesive tape and sputters coated gold approximately 190 A⁰ thick for 2.5 min at 10 mA before observation with SEM. One micrograph was taken for each starch sample at 1000 X magnification. All the images for each sample showed representative results.

Statistical analysis

Data were analyzed using single factor ANOVA in EXCEL (Micro-

soft Office 2000). Significance level at P 0.05 was applied to the results to test the significant difference.

RESULTS AND DISCUSSION

Texture analysis

Figure 1 shows the viscoelasticity of doughs prepared from corn powder. It is evident from the figure that viscoelasticity of doughs prepared from corn under different treatments were influenced by starch damage. It was also found that in the case of boiling and germin-ation, the viscoelasticity of doughs decreased rapidly. In Figure 1 two bars showed effect of each treatment and difference between the values of two bars is the elasticity of that sample. The stress values were: 2.5±0.11, 3.75±0.041. 3.27±0.15 N for 5, 10 and 15 min boiling and 4.86±0.33 N for 3-days germination, respectively, than that of steam treatment where the stress values were: 1.02±0.024, 1.25±0.071, 2.5±0.041 N for 10, 20 and 30 min at 15psi. Again it was found that the viscoelasticity of doughs made by control corn was the highest, with corresponding stress value of 0. 99±0.061 N.



Figure 1. Texture analysis of doughs. Pretreatments: Control (P1), Boiling in water for 5min (P2), Boiling in water for 10 min (P3), Boiling in water for 15 min (P4), 10 min team heating at 15psig (P5), 20 min steam heating at 15 psig (P6), 30 min steam heating at 15psig (P7), 3rd day germination (P8).

Starch crystallinity

The X-ray diffraction patterns of the treated starches showed that crystallinity decreased on thermal treatments (boiling and steam heating) . Native corn starch displayed an A-type X- ray diffraction pattern (Figure 5). The corn starch boiled in water for 10 min and steam heated for 10 min at 15 psi was gelatinized as indicated by the absence of crystalline peaks (Figure 5). The native corn starch exhibited intensified peaks at 18.15° and 23.1°. Jane and coworkers (1986) reported that the native double helical structure in starch was transformed into single helices during heating and this transformation occurred in both amylose and amylopectin molecules. The crystalline structure of native corn starch might be partially disrupted



Figure 2. Scanning electron microscopy of corn flour. A: P1, B: P2, C: P3, D: P4. See Figure 1 for the meaning of P1 to P4.



Figure 2. Scanning electron microscopy of corn flour. E: P5, F: P6, G: P7, H: 2nd germination (P9). See Figure 1 for the meaning of P5 to P7.



Figure 2. Scanning electron microscopy of corn flour. I: P8, J: 4th day germination (P10). See Figure 1 for the meaning of P8.

during heat treatments (boiling in water and steam heating) and as a result representing V- type diffractions (Figure 5). On the other hand the starch crystallinity was not significantly affected during germination.

Scanning electron micrographs

SEM pictures illustrate the effects of different treatments on the external structure of the individual starch granule compared to control (Figure 2). SEM showed that the corn starch granules under various treatments differed in shape from control one. Native corn starch was polyhedric (McPherson and Jane, 2000) in shape and had axial diameters of 5-20 µm (Figure 2A) as has been reported by Jane et al. (1994). Various grooves and fissures on the exterior surface of the granules are noticed in the treated samples compared to control. The control (Figure 2A) showed compact crystalline starch granules while in case of boiling and steam treatments the starch crystal granules were ruptured in the order Figures 2B to 2D and Figures 2E to 2G. These results agreed with those of Xray diffraction patterns as well as percent (%) maltose content. During germination corn starch granules were converted to small crystal fragments. Germination (Figure 2I) on 3rd day exhibits highest fragmentation.



Figure 3. Determination of maltose content (%). Series1: P1, Series2: P2, Series3: P3, Series4: P4. Series5: P5, Series6: P6, Series7: P7, Series8: P8, Series9: P9, Series10: P10.



Figure 4. Effect of germination on the activity of corn -amylase.

Effect of germination time on the activity of enzyme

During germination the seeds undergo pronounced metabolic changes and the structural profile of the various organic components are altered. Protein and carbohydrates are broken down during germination to simpler units mediated by hydrolytic enzymes (Jaya and Venkataraman, 1980). Studies were made on the effects of germination time on the activity of -amylase produced. It was found (Figure 4) that the enzyme produced showed maximum activity (58.967 unit) at 3- days germination. This result supported the fact that germinated sample for third day showed highest maltose content (%).

Starch digestion

During different treatments on starch, maltose (reducing sugar) free from corn starch to a great extent. Thus the starch damage during different treatments was determined by measuring percentage maltose content of each sample, which is shown in Figure 3. It is evident from the figure that in case of boiling in water and germination, percentage (%) maltose content of corn starch increased rapidly than that of steam-heated samples. The values of percentage (%) maltose content were: 11.88 ± 0.071 , 15 ± 0.085 , 21.75 ± 0.057 percentages (%) for 5, 10, 15 min boiling and 16 ± 0.092 , 30.25 ± 0.29 , $18.95\pm0.092\%$ for 2, 3 and 4-days germination respectively while in case of steam heated samples the values of maltose content were: 9.38 ± 0.38 , 10 ± 0.37 and $15.11\pm0.32\%$ for 10, 20 and 30 min at 15 psi.

CONCLUSION

Viscoelasticity (Figure 1), percent maltose content (Figure 3), surface structure of corn starch (Figure 2) and crystallinity (Figure 4) were influenced by the action of different pretreatments. Treatments in boiling water and germination show great changes in maltose content and viscoelastic property of cornstarch compared to steam heated samples. The crystallinity of cornstarch was



Figure 5: X-ray diffraction patterns (XRD) of treated samples. 10b:P3, 10s:P5, 3G:P8.

decreased during the thermal treatments; boiling in water and steam heating.

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