Oxidation by Hydrogen Peroxide Changes Crystallinity and Physicochemical Properties of Banana Flour

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Abstract. Banana flour var nangka has been oxidised using hydrogen peroxide at concentration of 1 to 3 % using native banana flour as a control. Functional and pasting properties and the change in crystalline type have been compared following the modification. Investigation using XRD showed that oxidation by hydrogen peroxide decreased the crystallinity from 56.9% in the native to around 52% in the oxidised flour. The crystalline type however remained unchanged (B type). There was no remarkable difference of properties following oxidation at various concentration of hydrogen peroxide, suggesting that the smallest concentration in the present study (1%) was sufficient to modify the banana flour. In terms of functional properties, oxidation increased swelling volume, freeze thaw stability and gel strength but decreased solubility, water absorption capacity and whiteness degree. Other parameters of pasting properties were not significantly affected by oxidation in the present range of concentration except the setback and breakdown viscosity which decreased compared to the native flour.

Keyword: banana flour, oxidation, crystallinity, physicochemical properties

1. Introduction

Starch constitutes the main source of energy and carbohydrate in the human diet. Extensive studies on starch have been well documented with the reports revealing its different sources [1-3] as well as type of starch modification [4-5]. Amongst the modification techniques, oxidation is a common approach to ameliorate native starch properties. Oxidising agents commonly applied to modify starch was hydrogen peroxide.

Starch modification by hydrogen peroxide has been so extensively carried out that there are numerous literatures available. The literature on oxidation to flour by hydrogen peroxide is however rarely available. It is thus important to examine the oxidation to the flour form by hydrogen peroxide, particularly when we consider that the flour form has been applied into food production in the higher quantity than in the form of starch which is purer form with less non-starch components. Our present study focused on the effect of oxidation in the concentration range of 1-3% H₂O₂ on the change of
flour properties including pasting and functional properties. The change of supramolecular structure was also investigated.

2. Materials and methods

2.1. Materials
Banana flour used in this study were extracted from unripe green banana var nangka, local name known as pisang nangka. For the present study, green banana samples with a diameter of around 3 cm, length of 15–20 cm were chosen. Reagents used in the present study were of analytical grade and used directly without further purification.

2.2. Preparation and oxidation of banana flour
The method to prepare banana flour was referred to that of previous study [4]. The peel of banana fruit was first of all stripped off. The pulp was then cut into transverse slices approx. 2mm thick, followed by dipping the slices of pulp in water for 10 min, draining and drying at 50 °C overnight in an oven (Shel Lab). After that, the pulp slices were milled to produce flour (Fomac miller machine FCTZ-300) and passed through 80 mesh screens.

The oxidation process followed the method as explained in a previous study [6]. Briefly the flour suspension was exposed to oxidation for around 30 minutes with the concentration of H₂O₂ 1, 2 and 3 %. Following the netralisation and washing with destilated water, the flour was oven-dried at 50°C for 24 h. The dry flour was then sieved to 80 mesh and stored for later experiment.

2.3. X-ray diffraction pattern
Diffraction patterns were observed using XRD (PANalytical X’Pert PRO seri PW3040/x0) with Cu Ka value of 1.54 radiation with a range of 3 –50° (2θ), using a voltage of 40 kV and filament current 30 mA.

2.4. Functional and pasting properties
Functional and pasting properties were examined using the method of previous study [4] except the gel strength which referred to another study [7] using Texture Analyzer (TA-XT2). Pasting properties were characterised using a Rapid Visco Analyzer (RVA-SM2), Warriewood Australia.

2.5. Statistical Analysis
Data were analysed by the statistical package software (SPSS), using Anova followed with post hoc test of Duncan.

3. Results and Discussion

3.1. X-ray diffraction pattern
The diffactograms of native and oxidised-banana flour are presented in Fig 1. Native banana flour was characterised by a small peak at 5.51°, strong peaks at 15° and 16.95° and a broad peak at 22.98°(2θ), corresponding to a B-type pattern [8]. Previous study also found a B crystalline type of banana starch from different cultivar [5].
Figure 1. X-ray diffractograms of banana flour following oxidation by H$_2$O$_2$ at concentration 1-3%.

When the flour was exposed to oxidation by hydrogen peroxide at concentration of 1-3%, it was noticeable that the diffraction pattern did not change compared to that of the native. It suggested that the crystalline type of starch remained in the B-type. The present finding was in agreement with another study on ozonated banana starch and flour which also found that crystalline type was not affected by oxidation [5].

In terms of crystallinity, it was obvious that the crystallinity of banana flour decreased from 56.92% to around 52-53% following the oxidation by hydrogen peroxide. The decrease in crystallinity due to oxidation was also observed in another study when banana starch and flour were oxidised by gaseous ozone [5]. The crystallinity decreased by 4-5% when banana starch was oxidised by hydrogen peroxide while it decreased by 1.6 % when oxidised by ozone at 200 ppm [5]. It suggested that oxidation by hydrogen peroxide at the present range of concentration was more effective than by gaseous ozone at 200 ppm.

3.2. Functional properties of banana flour

The change in functional properties of banana flour following oxidation by hydrogen peroxide is presented in Table 1. The effect of hydrogen peroxide concentration in the range 1-3% was relatively small on functional properties. When compared to the functional properties of the native flour, it was however clear that oxidation changed the properties. The hydrogen peroxide concentration of 1% is thus apparently sufficient to change the functional properties.

| Properties                      | 1% (g/g) | 2% (g/g) | 3% (g/g) |
|---------------------------------|---------|---------|---------|
| WHC                             | 1.60±0.05$^a$ | 1.65±0.06$^a$ | 1.64±0.06$^a$ |
| Swelling volume (ml/g)          | 11.41±0.10$^b$ | 11.87±0.27$^a$ | 11.67±0.38$^{ab}$ |
| Solubility (%)                  | 7.75±0.59$^b$ | 8.84±0.34$^a$ | 8.19±0.59$^{ab}$ |
| Freeze thaw stability (% sineresis) | 5.99±1.96$^a$ | 3.92±2.30$^{b}$ | 4.37±2.76$^{b}$ |
| Gel Strength (gF)              | 3.65±0.71$^a$ | 3.08±0.56$^{ab}$ | 2.43±0.58$^{b}$ |
| Whiteness (%)                  | 44.05±1.04$^c$ | 46.26±1.07$^b$ | 49.37±1.08$^a$ |

Different letters in the compared values denote significant difference at p < 0.05
Water Holding Capacity (WHC) decreased from 2.51 g/g in the native flour to approximately 1.6% in the oxidised banana flour. Furthermore, solubility decreased from 9.4% in the native flour to approximately 8% in the oxidised flour. Whiteness degree was also found to be lower than that of the native flour which was approximately 54.1%. The decrease in the solubility of banana flour following oxidation by hydrogen peroxide was also found in the flour oxidised by gaseous ozone [5]. The author suggested a presence of cross-linking following oxidation on the granule surface particularly involving protein which served as a barrier and then hampered amylose and other dissolved solid from leaching hence the lower solubility.

Parameters that increased following oxidation were swelling volume, freeze thaw stability and gel strength. Swelling volume was augmented from 8.4 mL/g in the native flour to approximately 11 mL/g in the oxidised flour. This finding was in line with previous study using ozone as an oxidator [5]. The freeze thaw stability was expressed in the percentage of syneresis. Higher syneresis represents a less stable flour to the cold storage. Syneresis of the native flour in the present study was approximately 44.4%. This value decreased remarkably to approximately 4-6% when the flour oxidised, suggesting that oxidation by hydrogen peroxide to banana flour increased its stability to the retrogradation. This remarkable increase in stability following oxidation by hydrogen peroxide was in line with the finding on flour oxidation by gaseous ozone [5]. Compared to the extent of the gel strength increase from 1.38 gF to 2.4 to 3.6 gF, also to the magnitude of the decrease of other functional properties, freeze thaw stability was apparently the most sensitive property to the oxidation either by hydrogen peroxide in the present study or by ozone in the previous study [5].

3.3. Pasting properties of banana flour

Pasting properties of the native and oxidised flour are presented in Table 2. When compared to the values of the native flour, the change in pasting properties particularly breakdown and setback was interesting. However, similar to the role of hydrogen peroxide concentration to the functional properties, it was observable that the oxidator concentration role in changing pasting properties was also relatively small. Therefore it can be concluded that the concentration of 1% hydrogen peroxide is seemingly sufficient to change the pasting properties.

| Properties          | Treatments (H₂O₂) |
|---------------------|-------------------|
|                     | 1%                | 2%                | 3%                |
| Pasting point       | 72.92± 1.30 a     | 73.31± 0.45 a     | 74.37± 3.03 a     |
| Peak Viscosity      | 5929.5± 207.10 a  | 5613.75± 190.56 b | 5864.37± 235.97 a |
| Hold viscosity      | 3698.25± 153.07 a | 3742.37± 168.48 a | 3703.25± 510.18 a |
| Final viscosity     | 5131.87± 247.06 a | 4888.25± 553.25 a | 5290.00± 642.65 a |
| Breakdown           | 2231.25± 250.09 a | 1871.37± 289.61 b | 2161.12± 468.39 ab|
| Setback             | 1433.62± 160.70 b | 1145.87± 413.55 b | 1586.50± 273.82 a |

Different letters in the compared values denote significant difference at p < 0.05

Small decrease in pasting point from 75°C in the native flour following oxidation by hydrogen peroxide was also observed in another study when banana flour was oxidised by gaseous ozone [5]. No remarkable change of peak viscosity following oxidation was observed. The oxidation however pronouncedly decreased breakdown (3155 cP in the native flour) and setback viscosity (2295 cP in the native flour). Given that the peak viscosity did not strongly change following oxidation (5303 cP in the native flour), the decrease in the breakdown had to be related to the increase in hold viscosity. Indeed, the hold viscosity of the native flour (2148 cP) augmented by approximately 1500-1600 cP
following oxidation by hydrogen peroxide. This finding demonstrated that oxidation by hydrogen peroxide ameliorated the flour stability to heating and shearing process.

4. Conclusion

Banana flour oxidation by hydrogen peroxide resulted in a lowered crystallinity from 56.9% in the native to around 52% in the oxidised flour. The crystalline type of B however remained unchanged following oxidation. There was no remarkable difference of properties following oxidation at various concentration of hydrogen peroxide, suggesting that the smallest concentration in the present study (1%) was sufficient to modify the banana flour. Compared to the native flour, oxidation increased swelling volume, freeze thaw stability and gel strength but decreased solubility, water absorption capacity and whiteness degree. Freeze thaw stability of flour was pronouncedly ameliorated to be much more stable to the retrogradation following oxidation. Amongst parameters of pasting properties, breakdown and setback viscosity were significantly decreased compared to that of the native. The decrease in the breakdown was linked to the increase of hold viscosity following oxidation. The oxidation by hydrogen peroxide thus increased the stability of flour to the pasting process.

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