EFFECT OF SELECTED SAGO STARCH MODIFICATIONS ON ITS PROPERTIES AND QUALITY OF INSTANT ‘KEROPOK LEKOR’

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ABSTRACT

‘Keropok lekor’ is a perishable food which has short shelf life at room temperature. Therefore, this research was conducted to produce instant powder of ‘keropok lekor’ that are shelf stable at room temperature by incorporating modified sago starch in the formulation. Thus, this study was carried out to evaluate the sago starch properties after being modified chemically and the effect of its incorporation on the final properties of ‘keropok lekor’. Sago starch was modified using cross-linking and succinylation methods before incorporated into the ingredients. Sago starches used were in its unmodified (native), cross-linked, succinylated and a mix of cross-linked and succinylated form. Results showed that sago starch retained its morphological features after modifications. Cross-linking increased the swelling power of sago starch. Both cross-linking and succinylation decreased oil absorption capacity and retarded starch retrogradation. Thermal scanning temperatures of cross-linked sago starch were elevated to higher degree of onset (T_0) and peak temperatures (T_p). Cross-linking and succinylation of sago starch brought some changes in the physicochemical properties of the fried samples. The most significant result was the improvement of expansion property where the sample with cross-linked starch showed the highest (15.0%) with low hardness values. In conclusion, the application of modified sago starch had shown its potential in the development of acceptable instant ‘keropok lekor’.

Key words: Sago, starch modification, instant starch

INTRODUCTION

‘Keropok lekor’ has been identified as popular local food and consumed as appetizer or snack. It has a great potential to be commercialize as the demand and intake of ‘keropok lekor’ is increasing parallel with the increasing popularity of this traditional snack (Khaizura, 2010). ‘Keropok lekor’ has a sausage like texture but it does not undergo the similar processing as sausage. Nowadays, they are fresh ‘keropok lekor’ and frozen ‘keropok lekor’ being commercialized in the market. Fresh ‘keropok lekor’ can be purchased on the road side stall (Khaizura, 2010) and usually have short shelf life (Embong et al., 1990). Frozen ‘keropok lekor’ is in frozen state and usually have longer shelf life. However, it is not a convenient form for transportation and storage.

There are several basic ingredients for the making of ‘keropok lekor’ such as fish, starch and salt. The types and amount of ingredient used play a major role in the quality of the final products. Starch is one of the important ingredients in the production of ‘keropok lekor’. It is a mixture of two polymers, amylose, a linear polysaccharide and amyllopectin, a highly branched polysaccharide (Copeland, 2009). Native starch or starch that has not been modified is a good texture stabilizer and regulator in food systems but the disadvantages are it has low shear resistance, thermal resistance, thermal decomposition and high tendency of retrogradation (Singh et al., 2007). Those disadvantages can be improved by modifications. Chemical modification such as succinylation and cross-linking can be carried out by using chemical reagents to enhance the functional properties of starch (Kaur et al., 2012). Starch succinate is produced from the reaction of succinic anhydride with starch producing a few of desirable properties.
such as high viscosity, better thickening power, low gelatinisation and retrogradation (Olayinka et al., 2011; Bhandari & Singhal, 2002; Lawal, 2004). Cross-linking treatment can stabilize and strengthen starch granule because it is intended to add intra- and inter-molecular bonds at random places in the granule. It minimizes granule rupture, loss of viscosity and formation of stringy paste during cooking (Singh et al., 2007).

‘Keropok lekor’ has short shelf life with only one day at room temperature as it favours the growth of microbial with pH 6-7 and water activity of 0.96-0.99 (Khaizura, 2010). By transforming ‘keropok lekor’ into dry powder form, instant ‘keropok lekor’ can be prepared easily by consumer at home and thus, it is more convenience than the traditional one. Other than that, instant ‘keropok lekor’ has low water activity of lower than 0.6 which can inhibit the growth of microorganisms and gives dry powder product a longer shelf life without refrigeration. However, it was thought that the main challenge faced is the ability of the dried ingredients to perform in the ‘keropok lekor’ making procedure when rehydrated and fried before consumed. Thus, this current study was carried out to determine the functional properties of cross-linked and succinylated sago starch and their effect on the properties of ‘keropok lekor’ after cooking.

MATERIALS AND METHODS

Sample preparation
Surimi, sago starch and tapioca flour were purchased from Mapero Sdn. Bhd. Kuala Terengganu. Surimi was dried at 60°C using cabinet dryer, ground and sieve using sieve shaker. Surimi powder, tapioca flour, sago starch, water and salt were mixed together and shaped into 1.5 cm in diameter and 5 cm in length cylinder. The shaped dough was boiled in water for 5 min followed by frying at 180°C for 1.5 min. Samples were allowed to cool down at room temperature before further analysis.

Similar composition of tapioca flour and sago starch was used in all formulations. Different forms of sago starch were applied i.e. in its native form, cross-linked, succinylated and mix of cross-linked and succinylated sago starch form. The ingredients of instant ‘keropok lekor’ and the proportion of starches used are shown in Table 1 and 2.

Preparation of modified starches
The cross-linked sago starch was prepared using sodium trimetaphosphate (STMP) and sodium sulphate (Carmona-Garcia et al., 2009). About 50 g of sago starch, 70 ml of water, 6.0 g of sodium trimetaphosphate (STMP) and 5.0 g of sodium sulphate were mixed in a round-bottom flask. The mixture was adjusted to pH 11.5 by adding 1.0 M sodium hydroxide. The slurry was stirred continuously, warmed up to 45°C and held at this temperature for 3 hours. The slurry was neutralized to pH 6.5 with 1.0 M hydrochloric acid. After drying overnight at 40°C in vacuum oven, the cross-linked starch was ground (< 250μm) and sieved.

Whereas, for succinylated starch, method of Šubaric´ et al (2014) with modifications was followed. About 100 g of sago starch was dispersed in 300 ml of distilled water and stirred magnetically for 1 hour. The pH of the slurry was adjusted to pH 9.0 using 1 M NaOH. About 10 g of succinic anhydride was used to treat the starch suspension for 2 hours while maintaining a pH range of 8.0 – 9.0. The pH of the slurry was adjusted to pH 6.0 using 0.5 M HCl at the end of the reaction. The mixture was filtered and the modified starch was washed six times with distilled water, oven dried for 24 hour at 50°C and ground to a fine powder (<250 μm).

Analyses
Analyses that were carried out for the individual modified starch powder including microscopic evaluation, determination of oil absorption capacity, swelling power as well as gelatinisation and retrogradation properties of the starch granules. Whereas, ‘keropok lekor’ that were formulated with native, cross-linked, succinylated and the mix of cross-linked and succinylated starches were evaluated for their expansion and hardness values.

Table 1. Ingredient of instant ‘keropok lekor’

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surimi</td>
<td>100.00</td>
</tr>
<tr>
<td>Tapioca Starch</td>
<td>50.00</td>
</tr>
<tr>
<td>Sago Starch</td>
<td>50.00</td>
</tr>
<tr>
<td>Ice water*</td>
<td>75.00</td>
</tr>
<tr>
<td>Salt*</td>
<td>2.63</td>
</tr>
</tbody>
</table>

*Based on the amount of surimi.

Table 2. Composition of starches in the formulation of instant ‘keropok lekor’

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tapioca starch, %</th>
<th>Sago starch, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50.0</td>
<td>50.0 (Unmodified)</td>
</tr>
<tr>
<td>B</td>
<td>50.0</td>
<td>50.0 (Cross-linked)</td>
</tr>
<tr>
<td>C</td>
<td>50.0</td>
<td>50.0 (Succinylated)</td>
</tr>
<tr>
<td>D</td>
<td>25.0 (Succinylated) + 25.0 (Cross-linked)</td>
<td></td>
</tr>
</tbody>
</table>
Microscopic evaluation of starch granules

The morphological features of the native, cross-linked and succinylated sago starch were observed using a scanning electron microscopy (JEOL JFC-1600, Japan). The samples were placed on a double sided adhesive tape mounted on a specimen holder and coated with a 100-200 Å thickness of gold. Micrographs were recorded at suitable magnification.

Determination of oil absorption capacity and swelling properties of starch

About 1 g of starch sample was mixed with 10 ml cooking oil for 30 sec. The sample was allowed to stand at 21°C for 30 min before being centrifuged at 5000 × g (30 min) and the volume of the supernatant in a 10 ml graduated cylinder was recorded. Result was expressed on a dry weight basis (Acuna et al., 2012). The percentage of oil absorption capacity was calculated according to equation below:

\[
\% \text{ oil absorption capacity} = \frac{\text{Weight of the wet article} - \text{weight of the dry article}}{\text{Weight of the dry article}} \times 100
\]

For swelling property, about 100 mg starch powder was mixed and suspended in 10.0 ml of distilled water followed by incubation at 30°C in a dry cabinet for 1 hour. The mixture was allowed to cool to room temperature (27°C) before centrifuged at 3000 × g for 10 min (Autio et al., 1992). Swelling power was calculated according to equation below:

\[
\text{Swelling power} = \frac{\text{Weight of sediment}}{\text{Weight of dry sample solids}}
\]

Physical analysis of ‘keropok lekor’

Expansion of ‘keropok lekor’ was determined by measuring the diameter of ‘keropok lekor’ before and after frying (Huda et al., 2003) and was calculated as:

\[
\frac{\text{Diameter after frying (cm)} - \text{Diameter before frying (cm)}}{\text{Diameter before frying (cm)}} \times 100\%
\]

For textural analysis, a cylinder probe P36/R (Textural Analyser TA-TX 2i, Stable Micro System, UK) was used to measure hardness of the samples. Fried ‘keropok lekor’ with the size of 1.5 cm x 2 cm long were cooled down at room temperature prior to testing. The probe was located at the central point of the fried sample. A 5 kg force load with pre-test speed of 1.0 mm/s was applied. The penetration depth of measurement was 2 mm at 1.00 mm/s of speed.

Statistical analysis

All analysis, except microscopic observation and thermal properties were carried out in triplicate. The data were subjected to one-way analysis of variance (ANOVA) at 95% confidence limit using Minitab Statistical Software version 13 (Minitab Inc., USA). Results with significant difference were further analyzed using Fisher’s LSD multiple comparison test.

RESULTS AND DISCUSSION

Figure 1 shows the scanning electron micrographs of unmodified, cross-linked and succinylated sago
starches. SEM showed that the sago starch consisted of oval granules with diameters in the range of 28-30μm. No significant differences were observed in the shape or average diameter for the starch granules after modifications. The micrograph revealed that sago starch granules manage to retain their original structure after modification process.

Both of the modified sago starches were similar in oil absorption capacity and the values were lower than the unmodified sago starch (Figure 2). Primo-Martin (2012) also found lower oil absorption (20-23%) of cross-linked wheat starch as compared to its native starch (28%). The chemical cross-linking reaction within the starch granules makes them more resistant to deformation during heating and thus, promoting its oil barrier property (Gamonpilas et al., 2013). Whereas, for succinylated starch, Awokoya et al (2011) reported the same finding where the succinylated cocoyam starch was also had lower oil absorption (12-14%) as compared to its native starch (17%). According to Awokoya et al (2011), modification using succinylation resulted in the introduction of bulky functional group and inhibits oil absorption. These might be the reason which support the lower oil absorption capacity of cross-linked and succinylated sago starch in this study.

Swelling analysis showed significant higher swelling index of cross-linked sago starch as compared to others (Figure 2). It is suggested that cross-linked starch had undergone an inclusion of phosphate groups inside the starch granules creating repulsive forces that might enhance penetration of water molecules inside the core of starch (Singh & Nath, 2012).

Table 3 shows the gelatinisation and retrogradation temperatures of unmodified and modified sago starches. The melting temperatures of unmodified sago starches were between 69.4 to 89.6°C. Thus, the temperatures were referred to gelatinisation temperature (67-89°C) of sago starch (Abdorreza et al., 2012). All samples had single transition corresponds to the dissociation of the amylose and amylopectin molecules within the starch granules and leaching out of amylose to the

![Fig. 2. Percentage of oil absorption capacity and swelling power index for unmodified, cross-linked and succinylated sago starch.](image)

(Histogram with the same superscript are not significantly different (p > 0.05).

### Table 3. Gelatinisation (G) and retrogradation (R) properties of unmodified, cross-linked and succinylated sago starch

<table>
<thead>
<tr>
<th>Starch</th>
<th>T_o (°C)</th>
<th>T_p (°C)</th>
<th>T_f (°C)</th>
<th>T_f–T_o (°C)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified (G)</td>
<td>69.39±0.02b</td>
<td>73.98±0.092c</td>
<td>89.57±0.77a</td>
<td>20.18</td>
<td>4.20±0.77a</td>
</tr>
<tr>
<td>(R)</td>
<td>48.31±0.25</td>
<td>57.6±0.53</td>
<td>70.26±1.54</td>
<td>21.95</td>
<td>1.34±0.29</td>
</tr>
<tr>
<td>Cross-linked (G)</td>
<td>74.62±0.13a</td>
<td>82.12±0.07a</td>
<td>90.19±1.34a</td>
<td>15.52</td>
<td>2.70±0.01a</td>
</tr>
<tr>
<td>(R)</td>
<td>Nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Succinylated (G)</td>
<td>68.71±0.13c</td>
<td>74.15±0.035b</td>
<td>89.97±0.30a</td>
<td>21.26</td>
<td>3.60±0.24a</td>
</tr>
<tr>
<td>(R)</td>
<td>Nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

Note: T_o = Onset temperature; T_p = Peak temperature; T_f = Final temperature; T_f–T_o = Temperature taken to complete gelatinisation process; ΔH = Heat enthalpy; nd = not detected. Mean values with small letters (a-c) in the same column showed significant difference at p<0.05.
continuous phase (Carmona-Garcia et al., 2009). The magnitudes of onset and peak temperatures (T_o and T_p) of cross-linked sago starch were elevated to higher degree, showing their resistance to heat applied. This could be possibly due to the introduction of phosphate groups (STMP) into starch granules contributing to the formation of additional cross-linked covalent bonds that tightened the molecular organization of starch molecules and thus reinforced the integrity of starch granules. Though, this sample only required about 15.6°C to complete granule dissociation as compared to the other sago starch samples (20-21°C) with lower energy for the melting process (ΔH of 2.7 J/g). This could be explained by the increase of the free volume in the starch chain in the presence of bulky groups of cross-linking agents (Detduangchan et al., 2014). Thus, less energy is required for dissociation of the starch granules.

For retrogradation study, storage sago starches showed that enthalpy for molecule dissociation of unmodified sago starch was lower compared with first gelatinisation enthalpy (Table 3). Besides that, the melting peak appeared at lower temperature of between 48.3°C to 70.3°C. According to Olayinka et al. (2011), starch molecule recrystallization occurred in a less ordered manner in stored starch gels than in native starch. Thus, less heat is required resulting in lower melting temperatures and heat enthalpy. Therefore, in this finding the lower single melting point observed was considered as the temperature for the dissociation of retrograded starch granules. The enthalpy of retrogradation is generally corresponds to order-disorder transition of crystallites formed at low temperature during storage. Such transitions are generally attributed to the melting of recrystallised amylopectin.

In contrast, there was no distinctive peak was observed in the thermogram of re-scanned cross-linked and succinylated sago starches. Thus, it could be assumed that both of these treatments reduced the potential of retrogradation from occurred even after 21 days of storage at low temperature. This might be related to the reduced mobility of amorphous chains in the starch granule to re-align themselves as a result of intermolecular bridges in the cross-linked starches (Singh et al., 2007). Besides, according to Olayinka et al. (2011), succinylation result in the inhibition of ordered structure of starch paste, thus retarding retrogradation. Therefore, the starch became more stable.

For the characteristics of ‘keropok lekor’, it has been observed that sample made with cross-linked starch incorporation showed significant higher expansion percentage as compared to the samples with unmodified and succinylated sago starches (Figure 3), contributing to lower hardness values of final product (Figure 4). This finding was in accordance with Nurul et al. (2009) who reported that the hardness of fried crackers decrease with increase in linear expansion. However, the incorporation of mixed modified starch has no impact on the expansion property and texture of fried ‘keropok lekor’. Significant effect was only showed by sample incorporated with cross-linked sago starch. The introduction of phosphate group by cross linking process reinforces the hydrogen bonds in the granules, thus make them rarely breaks down during cooking and become resistant to deformation during heating (Neelam et al., 2012;
Singh et al., 2007; Gamonpilas et al., 2013). This might probably the main reason contributing to the higher expansion property of ‘keropok lekor’ with cross-linked starch incorporation, showing its suitability in the production of instant ‘keropok lekor’.

CONCLUSION

Cross-linking of sago starch strengthen the structure of starch against heat treatment. Though, both modification techniques studied were successfully inhibit retrogradation of starch during storage. In the attempt of developing instant ‘keropok lekor’, overall findings agreed to choose cross-linking as a suitable starch modification that potentially produced acceptable properties of fried ‘keropok lekor’.

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REFERENCES


