Morphological and physico-chemical properties of modified white sorghum (Sorghum bicolor) starch.

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Abstract
The chemically modified acid-thinned (aWSS), oxidized (oWSS) and acetylated-oxidized (aoWSS) white sorghum starch were investigated in the present study. These chemical modifications caused roughness on the surface of sorghum starch granules. The size of surface pores in nWSS granules ranged between (178-289) nm which increased to 300-438 nm in dual modified aoWSS granules. The increase in pore diameter could be due to higher degree of substitution in dual modified starch altering the structure of starch on microscale. An increase in solubility was found following modifications indicating ease of amyllose leaching. The reduction in pasting temperature and time to reach peak viscosity indicate that functional groups actually weaken the structure of starch granule. The decline in setback viscosity was also observed suggesting decline in retrogradation phenomenon in chemically modified sorghum starches. In case of oxidized and acetylated-oxidized starches, no gel network was formed whereas as acid-thinned starches formed a weaker gel compared to native sorghum starch gel.

Keywords: Sorghum, starch, morphological properties, physicochemical properties.

1. Introduction
The functional properties of sorghum (Sorghum bicolor) starch are similar to corn starch and thus could be a good alternative to corn starch [1]. Sorghum is a good competitor of maize as it can grow in those drought hit areas where it is difficult to grow maize. Also sorghum requires less water than maize. Similar to maize, sorghum is also gluten free thus could be beneficial for celiac who are allergic to gluten proteins. They could be used to prepare gluten free foods like tortillas, cakes, breads, snacks etc. Therefore, keeping in view the impact of global warming, the advantages of sorghum can never be neglected.

The objective of this study was to investigate the effect of different chemical modifications on morphological and physicochemical properties of white sorghum starch.

2. Materials and Methods
Type I sorghum cultivar (Johar) provided by Pakistan Agriculture and Research Council was used for isolation of starch using the method of Ali and Hasnain Ali [2].

2.1. Chemical modifications
2.1.1. Acid thinning
Acid thinned starches were prepared using 0.1M HCl solution out using the procedure of Gunaratne and Corke [3].

2.1.2. Oxidation
The method of Forssel et al.[4] was used for preparing oxidized white sorghum starch using sodium hypochlorite solution.

2.1.3. Dual modified acetylated oxidized starch
Oxidized white sorghum starch prepared by using the aforementioned method was further modified by acetylation using the procedure of Philips et al.[5]. The acetic anhydride added was 6% w/w on starch (dry basis).

2.2. Percent Carboxyl Content
The method of Chattopadhyay et al.[6] was used for determining carboxyl content of oxidized starches.

2.3. Percent Carbonyl Content
The procedure of Smith.[7] was employed for estimating carbonyl content.
2.4. Percent Acetyl Content
Percent acetyl content in AOWSS was determined using the procedure of Wurzburg [8].

2.5. Morphological Properties
The morphology (granular and pore diameter) of modified and unmodified starches was studied through Scanning Electron Microscopy (SEM) using the method of Ali and Hasnain [2].

2.6. Swelling power and solubility
Swelling power and solubility of starch was determined using the method of Bello-Perez et al. [9].

2.7. Micro-Viscoamylography
Pasting properties of chemically modified sorghum starches were studied using Ali and Hasnain [2].

2.8. Paste clarity
Paste Clarity of 1% (w/v) starch solutions in boiling water bath was determined employing the procedure described by Perera and Hoover [10].

2.9. Gel hardness

2.10. Statistical analysis
Analysis of variance was used to calculate significant differences between the mean values followed by Duncan’s Multiple range test at P ≤ 0.05 was used to separate the means using SPSS software (SPSS version 17, Inc., USA).

3. Results and Discussion

3.1. Percent acetyl, carboxyl and carbonyl groups
According to USDA (United States Food and Drug Administration), the percentage of acetyl groups in starches must not exceed 2.5% while in oxidized starches the carboxyl groups must not exceed 1.3%. Therefore the modified sorghum starches prepared in this study are within the limits prescribed by FDA (Table 1) as percentage of acetyl groups in aoWSS was found to be 0.06% and % carboxyl groups in oxidized starches is only 0.9%.

3.2. Morphological characteristics
The results of SEM are presented in Fig 1 and Fig 2, respectively. The results showed presence of pores on the surface of sorghum granules similar to those reported for corn starch by Huber and BeMiller [11] (2000). The size of starch granules ranged between (6-20)µm while the diameter of pore was found to range between (178-350) nm. Chemical modifications of sorghum starches had no effect on granular size. However, roughness was evident from scanning electron microscopy. The pore diameters of acid-thinned, oxidized and acetylated-oxidized starch granules were found to be (200-245) nm, (225-275) nm and (300-438) nm, respectively. This indicates that dual modification could alter the nanostructure of starch granules resulting in increment of pore size.

3.3. Swelling power and solubility
Swelling power and solubility of sorghum starch granules were estimated in the range of (60-90)°C. It could be observed from the graphs (Fig 3 & 4) that both swelling power and solubility of control and modified starch granules increased linearly with the rise in temperature owing to gelatinization of starch granules. However, acid thinned starches did not exhibit much rise in swelling power with temperature which could be due to increased crystallinity of starch granules. Also it could be observed that oxidized (oWSS) also showed restricted swelling compared to control at all temperatures owing to depolymerization of long starch chains. The highest rise in solubility was observed for aoWSS as acetyl, carbonyl and carboxyl groups were introduced on starch chains which cause immense weakening of granule and subsequent rise in their solubility. Acid-thinned starches also showed high solubility due to hydrolysis of starch chains under acidic conditions.

3.4. Differential scanning calorimetry
The results of differential scanning calorimeter are presented in Table 2. Except acid-thinning all other treatments reduced the peak gelatinization temperature (T_p) of starch granules indicating that insertion of functional groups resulted in early gelatinization of starch granules owing to increased or less restricted percolation of water into starch granules. However, acid-thinning increased the gelatinization temperature which could be due to the restricted swelling power and higher relative crystallinity of these granules. But, enthalpy which is the energy required to gelatinize the starch granules was reduced significantly. Acetylation was however found to sort of stabilize oxidized starch granules as there were almost insignificant changes in gelatinization enthalpy, indicating that acetyl groups might have improved hydrogen bonding with other starch chains leading to stabilization of starch granules [2].

3.5. Pasting properties
The results of pasting properties are presented in figure 5. The pasting profile elaborates the behavior of starch granules under cooking and cooling conditions. Pasting temperature and time to reach peak viscosity were both reduced owing to chemical modifications while dual modification having a more pronounced effect. Peak viscosity, hot paste viscosity and cold paste viscosities were also reduced due to chemical modifications. Similar to calorimetric investigations, the pasting profile also suggest slight stabilization of oxidized starch granules after acetylation. This is evident by increase in peak and hot paste viscosity of aoWSS compared to oWSS. Also cold paste viscosity and setback viscosity value of aoWSS was higher than aWSS. This shows that swollen and rigid granules on cooling were responsible for a firm gel network. Acid-thinning of starch granules increased the breakdown viscosity of starches due to hydrolysis of starch chains. All modifications decreased the setback viscosity as presence of functional groups interfere with the reassociation of starch chains and thus reduces retrogradation of modified starch granules.

3.6. Paste clarity
Paste clarity improved significantly due to chemical modifications (Fig.6). The clarity of starches followed the order aoWSS>oWSS>aWSS>nWSS implying that functional groups resulted in higher clarity compared to depolymerization alone as among chemically modified starches acid-thinned sorghum starch showed the least percent transmittance. The results also showed that transmittance reduced on storage for 72 hours. Acetylated-oxidized starch showed the least decline in percent transmittance (10%) from 24 to 72 hours of storage followed by OWSS (23%) and aWSS (27%). The highest decline in clarity was observed for native sorghum starch of 30%. These results suggest that retrogradation tendency or ability of solubilized starch chains to reassociate with each other reduced on chemical modifications.

3.7. Gel hardness
The results of gel hardness show that due to introduction of functional groups on starch chains during oxidation (carboxyl and carbonyl groups) and acetyl-oxidation (carbonyl, carboxyl and acetyl), the reassociation tendency was hindered. Thus gel network was not formed and thus no firmness was observed for oWSS and aoWSS gels (Fig 7). These modified starches (oWSS and aoWSS) could be used to increase the solid content without giving excessive thickening like in food confections. For aWSS gels, it was observed that firmness of gels was reduced compared to native sorghum starch which is an indication that hydrolysis of long chains reduced the gel forming capability. On storage of gels, it was observed that hardness increased. The increase in hardness is due to the retrogradation phenomenon.

4. Conclusion
It could be observed from the results that owing to modifications, undesirable characteristics of starches are reduced and thus could improve the applications of starches in a variety of food products. Paste clarity of modified starches also increased significantly while setback viscosity which is the measure of retrogradation was significantly reduced which can lead to utilization of modified sorghum starches in refrigerated and frozen food products.

<table>
<thead>
<tr>
<th>Percent carboxyl, carbonyl and acetyl groups in oWSS and aoWSS</th>
<th>% Carboxyl groups</th>
<th>% Carbonyl groups</th>
<th>% Acetyl groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>oWSS</td>
<td>0.19</td>
<td>0.07</td>
<td>ND*</td>
</tr>
<tr>
<td>aoWSS</td>
<td>0.19</td>
<td>0.07</td>
<td>0.06</td>
</tr>
</tbody>
</table>

*Not determined
Figure 1: Scanning electron micrographs of sorghum starches observed under 1600X magnification: a) nWSS b) aWSS c) oWSS d) aoWSS

Figure 2: Scanning electron micrographs of sorghum starches observed under 8000X magnification: a) nWSS b) aWSS c) oWSS d) aoWSS
Figure 3: Swelling power of native and modified white sorghum Starches

Figure 4: Solubility of native and modified white sorghum starches

Figure 5: Pasting Properties of native and modified white sorghum starches. PT (pasting temperature), PV (Peak viscosity), TTP (time to reach peak viscosity), HPV (hotpaste viscosity), CPV (cold paste viscosity), BD (breakdown), SB (Setback viscosity).

Figure 6: Paste clarity of native and modified white sorghum starches
Figure 7: Gel hardness of native and chemically modified white sorghum starch.

Table 2
Thermal characteristics of native and chemically modified white sorghum starches.

<table>
<thead>
<tr>
<th>Starch</th>
<th>T₀ (°C)</th>
<th>Tₚ (°C)</th>
<th>Tₛ (°C)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nWSS</td>
<td>68.1a</td>
<td>71.2</td>
<td>82.8a</td>
<td>13.3a</td>
</tr>
<tr>
<td>aWSS</td>
<td>71.6b</td>
<td>76.2b</td>
<td>88.6b</td>
<td>6.7b</td>
</tr>
<tr>
<td>oWSS</td>
<td>60.3c</td>
<td>64.9c</td>
<td>77.9c</td>
<td>10.0c</td>
</tr>
<tr>
<td>aoWSS</td>
<td>64.2d</td>
<td>68.7d</td>
<td>82.4a</td>
<td>13.6a</td>
</tr>
</tbody>
</table>

Different superscript letters within a column are significantly different at p≤0.05.

References