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RESEARCH ARTICLE

IMPACT OF CROSS-LINKING ON PHYSICO-CHEMICAL AND FUNCTIONAL PROPERTIES OF CASSAVA STARCH

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Abstract

Starch had been isolated from cassava that was modified using two different cross-linking agents such as ginger and garlic at two different concentrations (5 and 10 %). Physico-chemical and functional properties of cross-linked cassava starches were analyzed by standard methods and crystalline structure was determined by X- ray diffraction method. Cross-linking decreased moisture, protein, fat, swelling power, solubility, water and oil absorption capacity and paste clarity. Ash content was significantly increased in cross-linked starches as concentration of cross-linking agents increased. However crystalinity was decreased with higher concentration of cross-linking agents. Protein and fat predicts the Swelling power in native and cross-linked starches. Though starch is a common ingredient used in many food and non-food applications, and native cassava starch lacks the versatility necessary to function adequately under industrial processing conditions, the cross-linked cassava starch could more effectively meet the functional property demands in food and non-food products.

Introduction

Cross-linking is a common approach to improve the performance of starch for various applications. Starch and starch products have been cross-linked with cross-linking agents, such as phosphorus oxychloride, sodium trimetaphosphate, sodium tripolyphosphate, epichlorohydrin, and 1,2,3,4-diepoxybutane, to improve the mechanical and functional properties of starch and starch products (Seker and Hanna, 2006).

The current consumer and worker safety requirements, the use of some new synthetic chemicals have been prohibited including use of high concentrations of the existing agents. This has led to the need for research into naturally occurring starch-modifying agents. Some natural products, e.g. alum used in water processing for home or industrial needs and ginger used as a seasoning agent and as preservative have been reported to improve the functional properties of cassava and rice starches (Lee et al., 1995; Daramola and Osanyinlusi, 2006).

Cross-linking considerably reduced swelling power, solubility, water-binding capacity and paste clarity. The decrease became greater as the reagent concentration increased. (Kaur et al., 2006). Cross-linking treatment is intended to add chemical bonds at random locations in a granule. The cross-linking stabilises the granules and strengthens the relatively tender starch (Acquarone and Rao, 2003). The objective of this study was to evaluate the effect of cross-linking with ginger/garlic on physicochemical and functional characteristics of cassava starch.

Materials and methods

Sample preparation

Native cassava starch (NCS) was isolated from cassava roots according to the method of Vasanthan (2001). Ginger and garlic were purchased from local market in Salem, Tamil Nadu. Starches were modified with two cross linking agents such as ginger/garlic at two different concentrations (5% and 10%), according to the method described by Daramola and Osanyinlusi (2006) with slight modification. Ginger and garlic were cleaned, peeled and crushed then mixed with starch-water suspension and stirred periodically for 30 minutes at room temperature. Residues had been filtered, starch milk was washed, and the excess water was removed using suction pump. The starch obtained was dried using air oven and grounded with mortar and pestle to obtain modified starch, namely A (cassava native starch with 5% ginger), B (cassava native starch with 10% ginger), C (cassava native starch with 5% garlic) and D (cassava native starch with 10% garlic) respectively.

Pysico-chemical and functional properties

Moisture (%)**,** Dry matter (%), Ash (%), protein (%) and fat (%) contents were estimated by AOAC Method (1990). Swelling power (g g^{-1}) and solubility (%) were measured as per the method described by Leach et al., (1959). Paste clarity (%) was determined by Bhandari and Singhal (2002).

Powder X-ray Diffraction (XRD)

X-ray diffraction patterns were obtained by a Powder X-ray diffractometer (Rigaku Mini Hex-II, Japan). Crystallinity Index (CI) was calculated using Equation proposed for cellulose by Segal et al., (1959) and applied to starch, by using the equation with slight modification:

$$CI = 100 \times \frac{I_{max} - I_{am}}{I_{max}}$$

Statistical analysis

Data were analyzed using one way ANOVA. All the analyses were done in triplicates. A multiple regression model was employed to investigate the prediction of swelling power by protein and fat.

Results and Discussion

Moisture and dry matter

Native cassava starch (8.88 %) had significantly higher moisture content than cross-linked (4.73-6.73%) starches (Table 1). This result is confirmed with Carmona-Garcia et al., (2009) who stated that native banana starch had high moisture than cross-linked starch. This pattern is related to the reaction between the OH groups of glucose units of starch and the bi- or poly-functional chemical reagent used in this chemical modification, decreasing the possibility of reaction between OH of starch chains and the water molecules and consequently the join of water to this polymer (Carmona-Garcia et al., 2009). However cross-linking significantly increased the dry matter of starch.

Ash content

Ash content of cross-linked starches was significantly increased with increasing the concentration of cross-linking agents. Native cassava starch (0.33%) had significantly lower ash content than the cross-linked starches (1.33-1.47). Ash level is increased in the cross-linked starch, this pattern is due to the introduction of some phosphate groups in the amylopectin molecule during the modification process. That might be due to the sub-products of the reaction contain Na and P, that might be retained in the modified starch, thus increasing the ash amount (Carmona-Garcia et al., 2009).

Protein content

Protein content of cross-linked starches (0.21-0.57%) was significantly lower than that of native cassava starch (0.60%). These results are confrmed with Yousif et al., (2011) who stated that native corn starch had high protein than acid modified starch. Increasing concentration of cross-linking agents, the protein content decreased. The protein content in the cross-linked starches was less when compared to native sample. This effect is due to partial solubilization of the proteins with the reagents used in the chemical modification.

Fat content

Similarly cross-linked starches recorded statistically the least lipid content (0.16 - 0.22 %). This result is on par with Yousif et al., (2012) who stated that the cross-linked starches reduced the fat content, and the type of cross-linking agent used in the modification plays an important role in the proximal composition.

Table 1. Physico-chemical properties of native and cross-linked cassava starches.

Samples	Moisture (%)	Dry matter (%)	Ash (%)	Protein (%)	Fat (%)
N C S	8.88±1.92[a]	88.99±2.02[a]	0.33±0.02a	0.60±0.09[a]	0.23±0.04[a]
A	5.36±1.12[b]	94.63±1.12[b]	1.33±0.20b	0.44±0.07 [b]	0.19±0.01[b]
B	4.73±0.68[b]	95.26±0.68[b]	2.30±0.55c	0.11±0.02 [c]	0.15±0.03[c]
C	6.73±0.75[cb]	93.26±0.75[cb]	1.47±0.36db	0.57±0.01 [d]	0.22±0.01[d]
D	5.56±0.25[cb]	94.43±0.25[cb]	2.23±0.18ec	0.21±0.08 [e]	0.16±0.02[e]
F- value	6.61*	14.76*	18.44*	34.14*	5.20*
CD- value	1.55	1.60.	0.45	0.08	0.03

Mean values superscripted by the same letter are not significantly different within the columns.
Mean values of three measurements± standard deviation, NCS= native cassava starch, A = cassava native starch with 5% ginger, B = cassava native starch with 10% ginger, C = cassava native starch with 5% garlic and D = cassava native starch with 10% garlic, *= significant difference at 5%

Swelling power

Swelling power was decreased significantly with increasing level of cross-linking reagents (Table 2). Native cassava starch (15.41 g g^{-1}) had significantly higher swelling power than the cross-linked (10.95-11.08 g g^{-1}) starches. This result is in agreement with the finding of Mirmoghtadaie et al., (2009) who reported that the reduced swelling factor of cross-linked oat starch with increasing degree of cross-linking. Regression analysis exhibited that the swelling factor was linearly related to the concentration of cross-linking reagent used (R^2 = 0.878). It is well known that cross-linking strengthens the bonding between starch chains, thus allowing them to resist against swelling. Therefore, the reduced swelling factor would be related to the formation of inter-molecular bridges by phosphorous residual after cross-linking reaction (Chung et al., 2004). Amylose lipid complexes reduce swelling power. (Zuluaga et al., 2007).

Solubility

Semi-crystalline structure of the starch granules is responsible for their low solubility even at high temperatures (Ferrini et al., 2008). The solubility of native and modified cassava starches are presented in Table 2. The highest solubility was noticed in native cassava starch 8.46**%**, followed by cross-linked cassava starches 7.08, 6.41, 7.07 and 6.85**%** (A, B,C and D) respectively. Due to the strengthening of the starch granules through cross-links, less disintegration took place during gelatinization and lowering of solubility. Cross-linking reduces the solubility which leach out of the swollen granules on cooking and the extent of solubilization is affected by the degree of cross-linking (Wurzburg, 1986).

Paste clarity

Paste clarity at T650 of the native cassava starch exhibited 47.36% (Table 2). However, the use of ginger and garlic cross-linking agent led to a substantial decrease in the paste clarity. This result is consistent with the reports by Lim and Seib, (1993) and Kaur et al., (2006) who found that cross-linked starches showed lower paste clarity than their native starches. The significant decrease in the paste clarity was possibly attributed to a change in the starch granular structure by cross-linking (Morikawa and Nishinari, 2000). Furthermore, it has been suggested that the reduced swelling of cross-linked starches might be partly responsible for their reduced paste clarity (Kaur et al., 2006; Reddy and Seib, 2000).

Table 2. Functional properties of native and cross-linked cassava starches

Samples	Swelling power (g g^{-1})	Solubility (%)	Past clarity (%)
N C S	15.41±2.88[a]	8.46±0.44[a]	47.36±1.16[a]
A	11.03±0.20[b]	7.08±0.62[b]	45.02±1.04[b]
B	10.95±0.20[b]	6.41±0.72[b]	43.06±1.78[c]
C	11.08±0.50[b]	7.07±0.27[b]	39.56±1.32s[d]
D	10.99±0.19[b]	6.85±0.83[b]	36.26±1.01[e]
F- value	6.65*	4.67*	34.38*
CD- value	1.86	0.86	1.83

Mean values superscripted by the same letter are not significantly different within the columns. Mean values of three measurements± standard deviation, NCS= native cassava starch, A = cassava native starch with 5% ginger, B = cassava native starch with 10% ginger, C = cassava native starch with 5% garlic and D = cassava native starch with 10% garlic, *= significant difference at 5% and $^{NS=}$ significant difference

X-ray diffraction

The X-ray diffraction of the native and cross-linked starches are presented in Fig 1. The X-ray patterns of A type starches present the stronger diffraction peaks at around 15, 17, 18 and 23°.2θ. Native cassava starches showed peaks at the 2θ diffraction angles around 11.47, 14.96, 16.93, 17.91 and 23.17° 2θ and cross-linked starches showed peaks at the 2θ diffraction angles 11.13, 14.78, 16.98, 17.78 and 22.71° 2θ (Sample A), 10.11, 11.52, 15.02, 17.10 and 23.09° 2θ (Sample B), 15.20, 17.09, 17.94 and 23.06° 2θ (Sample C) and 14.87, 17.03, 17.98 and 22.96° 2θ (Sample D) respectively. These 2θ values were compared with corn starch 2θ values of JCPDS database (Joint Committee on Powder Diffraction Standards). These patterns was considered as an A type crystalline structures. Rickard et al., (1991); Defloor et al., (1998) were reported that cassava starch is A-type diffraction patterns with characteristic peaks at 15.3,17.1 and 23.5° 2 θ angles. Starches having an A-type diffraction pattern are described as having an arrangement of helices in the unit cells with monoclinic symmetry (Bello-Perez et al., 2005). Crystallinity of native cassava starch (32.25%) had higher than the cross-linked starches (12.95, 12.16, 15.27 and 12.68) respectively. Cross-linking agents increase the amorphous content (Delval et al., 2004).

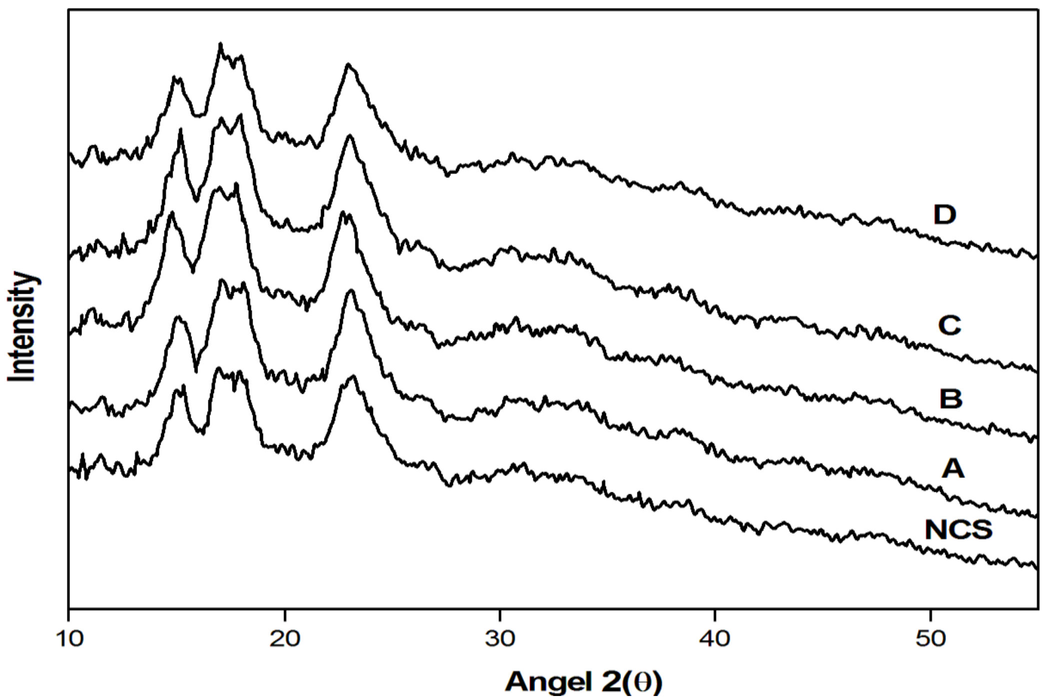

Figure 1. X-ray diffraction pattern of native and cross-linked cassava starch

Table3. Comparison of 2θ values of native cassava starch and cross-linked cassava starches with corn starch of JCPDS database

S.No	N C S	A	B	C	D	JCPDS Corn starch
1	11.47	10.11	11.13	15.20	14.87	10.10
2	14.96	11.52	14.78	17.09	17.03	11.50
3	16.93	15.02	16.98	17.94	17.98	15.30
4	17.91	17.10	17.78	23.06	22.96	18.20
5	23.17	23.09	22.71	-	-	20.30
6	-	-	-	-	-	23.50
7	-	-	-	-	-	27.00
8	-	-	-	-	-	31.00

NCS= native cassava starch, A = cassava native starch with 5% ginger, B = cassava native starch with 10% ginger, C = cassava native starch with 5% garlic and D = cassava native starch with 10% garlic,

JCPDS = Joint Committee on Powder Diffraction Standards

Multiple linear regression

Cross-linked cassava starch

The value of r= 0.75 indicated that the swelling power had positive relation with protein and fat. The linear relationship was strong but not very strong. The value of r^2 = 0.57 states that 57% of total variation in swelling power explained by protein and fat. The lower value of r^2 indicated that other variables such as amylose, phosphorus and solubility might be contributed to the swelling power determination.

Native cassava starch

The value of r= 0.79 indicated that the swelling power had positive relation with protein and fat. The linear relationship was strong but not very strong. The value of r^2 = 0.63 indicated that 63% of total variation in swelling power explained by protein and fat. The lower value of r^2 indicated that other variables such as amylose, phosphorus and solubility might be contributed to the swelling power determination.

Conclusion

The present study concluded that the cross-linking agents such as Ginger and Garlic decreased moisture, protein and fat content of native cassava starch. And cross-linked cassava starches had higher ash content than the native cassava starch. Swelling power, solubility, water and oil absorption capacity, paste clarity and crystalinity were decreased with increased concentration of cross-linking agents. Hence Cross-linked starches might be used for various food products such as snack foods, breads and cakes to improve their quality.

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