

Cassava starch snack formulation using functional shell fish by-products: mechanical, sorption and geometric properties

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Abstract: Utilisation of by-products of the shrimp industry, namely shrimp head protein and chitosan, could lead to a functional snack with substantial market in Asia. Produced on a cassava starch base this would lead to a product with shrimp flavour and chitosan's lipid adsorption capacity. The characteristics of such a mixture with 82% deacetylated chitosan and salt was investigated by Rapid Visco Analyser and instrumental Texture Profile Analyser using the Doehlert Uniform Shell experimental design. Polynomial models explained more than 88% of variability of responses. A significant effect of salt, shrimp head proteins and chitosan was observed on cassava starch gelling characteristics. A corresponding heat and shear stress resistance ability was observed while there was a reduction in its specific swelling power. Snacks prepared in the form of chips and extruded product confirmed their good potential for added value to snack foods in respect of their 90–94% linear expansion ratio, up to 1.1 kg maximum breaking force and up to 4.5 radial expansion ratio. Adsorption isotherm of extrudates had a maximum water content target of 115 g kg⁻¹ dry matter at 25 °C for a later formulation and extrusion optimisation, in order to guarantee consumer texture acceptability. Corresponding shelf-lives of extrudates were calculated at three storage conditions.

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Keywords: cassava; functional snacks; chitosan; formulation; texture

INTRODUCTION

Cassava is widely grown around the world, with a production around 168×10^6 tons in 1999.¹ The tuber has until recently been used mainly as a feed in the form of dried chips or pellets.² However, with export restrictions, there is a necessity to look for alternative applications for this resource in South East Asia. In recent years, because of health concerns and health consciousness among consumers, the food industry has been attempting to produce 'lighter' diet products. Uses of functional ingredients^{3,4} which not only add sensory characteristics but are also good from a nutritional benefit are increasing. However, waste management has become a tremendous concern for industry.⁵ Utilisation of the by-products of the shrimp industry, namely the protein from the head and the chitosan fraction which can be obtained from the shell by fermentation,^{6,7} will meet both these requirements. Shrimp head protein might provide a good flavour while the chitosan could act as a slimming agent because of its capacity to absorb lipids *in vivo* from food.^{8,9}

In this work, the physical and functional properties of cassava starch along with other components for snack production were compared with that of corn, wheat, rice and potato starch. This was done in terms of the viscosity and textural characteristics of the resultant gels. These followed evaluation of some geometric characteristics, such as linear and radial expansion, and also textural characteristics, such as maximum breaking force, for both fried chips and extrudate. The effect of added ingredients was estimated by appropriate experimental design. The extrudate adsorption isotherms and shelf-life estimates will contribute to an optimised formulation for a product that can be industrially developed.

MATERIALS AND METHODS

Starches and flour

Commercial cassava starch, corn starch, rice and wheat flour (Table 1) were obtained from a local market. Chitosan (Chs 82% minimum deacetylated) was kindly supplied by Bioprocess Technology Programme

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Table 1. Starch and flour analysis

	Moisture ^a (g kg ⁻¹ dm)	a_w ^b	Amylose ^b (g kg ⁻¹ starch)	Ash ^b (g kg ⁻¹ dm)	pH ^b
Cassava starch	120.9 ± 2.9	0.57 ± 0.01	177 ± 2	2.0 ± 0.7	5.9 ± 0.1
Corn starch	123.0 ± 2.3	0.55 ± 0.01	245 ± 3	3.4 ± 0.1	6.2 ± 0.1
Rice flour	124.3 ± 0.7	0.55 ± 0.01	194 ± 1	6.3 ± 0.5	6.7 ± 0.1
Wheat flour	127.3 ± 1.8	0.58 ± 0.01	220 ± 0	7.4 ± 1.0	5.9 ± 0.1

^a Data are means of four determinations.

^b Data are means of two determinations (at 27.0 ± 0.4 °C for a_w and at 26.6 ± 0.1 °C for pH).

(AIT, Bangkok, Thailand) and shrimp head proteins (Shp) by Fishery International Development Institute, Department of Fisheries (Kasetsart University, Bangkok, Thailand). All samples were sieved through a 180- μ m standard sieve (0.007 inch nominal opening screen).

Amylose content was determined by a modified iodine binding method which is a standard colorimetric method.¹⁰ Starches and flour moisture content were obtained by drying to constant weight at 104 °C in a convective oven and ash by burning in a furnace at 550 °C. Water activity (a_w) was measured using an AquaLab apparatus at ambient temperature (model CX-2, Decagon Devices, Pullman, Washington, USA) and pH using a portable pH meter (model pH320, WTW, Weihen, Germany) using 5 g of properly mixed starch to 25 ml of distilled water at room temperature.

Pasting properties

Pasting properties of starch suspensions of 80 g kg⁻¹ dry matter (2 g dry basis adjusted to 25 g of distilled water) were determined in a Rapid Visco Analyser (RVA) model 4 (Newport Scientific Pty Ltd, Warriewood, Australia). The standard profile 1 selected included a pre-mix period, a constant stirring with increasing temperature, a holding and then a cooling stage. After mixing at 960 rev min⁻¹ for 10 s at 50 °C and holding for 50 s at 160 rev min⁻¹, the temperature was increased at the rate of 0.2 °C s⁻¹ to 95 °C. This temperature was held for 150 s. The temperature was then cooled at a rate of 0.2 °C s⁻¹ to 50 °C. Peak time (P_{time}), peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV), breakdown (BD) and pasting temperature (T_{paste}) were recorded for all samples in triplicate.

Gel texture analysis

Texture analysis was performed using a TA-HD texture analyser (Stable Micro Systems Ltd, Godalming, Surrey, UK) that recorded a force–time curve equivalent to instrumental texture profile analysis (TPA).^{11,12} The analysis was done in the RVA canister itself on gels obtained by RVA and cooled at 6 °C for 2 h. Strong gels obtained with rice flour and corn starch were not cooled in order to avoid gel disruption. The soft gelled structure obtained with cassava starch allowed the full standard profile 1 to be applied. Samples in the canister were placed onto the texture analyser platform and punctured twice with a 25-mm diameter plastic

cylindrical plunger to 10 mm depth. Hardness (Hrd, maximum peak force at first puncture in g), adhesiveness (Adh, negative force area of first bite in g) and springiness (Spg, ratio of second bite time to the time elapsed between end of the first bite and start of the second one) were recorded. A pre-speed of 3 mm s⁻¹, a speed of 5 mm s⁻¹ and a post-speed of 8 mm s⁻¹ were selected within a minimum 10 g strength for texture profile to be recorded.

Experimental design

An experimental design based on that of the Doehlert Uniform Shell¹³ with response surface methodology was used to assess formulation.¹⁴ Salt and chitosan were chosen in the range 5 to 100 g kg⁻¹ total dry matter and shrimp head protein ration in the range 5 to 160 g kg⁻¹ total dry matter.

Chip preparation

Two doughs were prepared for chip production according to a process suggested by Ruksakulthai *et al.*¹⁵ One dough used only ingredients whose effects were assessed at the centre point of the experimental design (corresponding to 500 g of cassava starch, 155 g water, 28.5 g of chitosan, 28.5 g of salt and 46 g of shrimp head protein) and named SD for ‘simple dough’. The second formulation, name CD for ‘complex dough’, had in addition to the previous compounds 20 g of water, 65 g of wheat flour, 12.5 g of pepper, 12.5 g of freeze-dried garlic and 25 g of commercial fish sauce (containing 60% fish, 37% salt and 3% sugar). The two recipes were then compared with a commercial chip, named ‘Commerce’ and with a local one named KD ‘Kasetsart dough recipe’. Both were deep-fried under identical conditions. The latter two chips did not contain the functional additives, shrimp protein and chitosan, under study in this work.

Cassava starch was mixed and hand-stirred with boiling water until sticky. In a separate vessel, a mixture containing additives (salt, shrimp head protein and partially soluble chitosan in acetic acid 5% (v/v)) were prepared and then combined with the sticky starch–water mixture. The remaining cassava starch and water were then added to get the required consistency. The dough was formed into rolls and steamed for 30 min at 100 °C. This was then taken out of the steam chamber and cooled to room temperature before being placed on damp cloth for refrigeration at approximately 2 °C for 12 h. It was then cut into 1-mm slices for chips making. Slices were oven dried at 50 °C

until a brittle consistency was achieved. Stabilised slices were then put into a commercial palm oil bath at $150 \pm 5^\circ\text{C}$ until puffing was achieved after 30 s.

Chip texture evaluation

Texture analysis of chips was obtained at 25°C using the Stable Micro Systems TA-HD immediately after deep fat frying. Punch test was made on the chips, which are mounted over a three-point-support using a 5-mm aluminium probe. The test cross-head speed was 0.001 m s^{-1} (pre-test 0.0015 m s^{-1} and post-test 0.01 m s^{-1}) and, in all cases, maximum breaking force (Mfb) and deformation were recorded from the force–deformation curve similarly to Instron Universal Testing Machine conditions.¹⁶ Texture analysis was performed randomly on 20 chips in duplicate.

Measurement of linear expansion

Puffing potential of simple and complex dough were investigated with calculation of a linear expansion percentage (%LE) deep-fried chips. Unpuffed samples were ruled with three lines across them using a permanent fine pen prior to length measurement before and after deep fat frying.¹⁷ This process was repeated on 20 crackers to obtain a significant standard deviation, due to low measurement precision and unequal puffing.

Extrusion process, radial expansion ratio and colour appreciation

Extrusion processing was carried out using a single-screw laboratory extruder (Brabender 20 DN, Duisburg, Germany) under constant conditions, where feed moisture was 150 g kg^{-1} dry matter, barrel temperature $150\text{--}170^\circ\text{C}$ and feed rate 27 rev min^{-1} . The screw was of decreasing pitch with a compression ratio of 1:4 and length to diameter of 20:1 (L/D). The extruder consisted of four jacketed head sections, controlled by thermocouples mounted inside the barrel. A feed hopper with paddle agitator ensured uniform feed flow into the extruder barrel at variable screw speed between 115 and 220 rev min^{-1} . A Do Corder E system controller (Brabender, Duisburg, Germany) ensured uniform screw speed rotation. Samples were hand cut without cutting device at standard 4-mm extruder die.

Dough composition prior to extrusion was similar to the simple dough used for chip production. In order to get target feed moisture, the salt used was dried overnight at 104°C before mixing and chitosan was partially solubilised overnight with 2% acetic acid by mixing.

During extrusion, screw speed was increased from 115 to 220 rev min^{-1} , keeping feed rate, temperature and other parameters constant. The ratio of the cross-section area of the extruded rods to that of the die was measured to assess expansion quality as $(ER)_{\text{radial}}$ the radial expansion ratio.^{18,19} Five samples were randomly chosen for each screw speed and 13 determinations of diameter' were done for each

using a digital Vernier calibre (Monostat Corp, New York, NY, USA), before being sealed in plastic bags and stored at ambient temperature prior to moisture content determination in triplicate.

Using a HunterLab Colorimeter (ColorQUEST Software 3.1, Hunter Associates Laboratory Inc, Reston, VA), unsieved crushed extrudate colour was estimated using the CIE 1976 $L^*a^*b^*$ measuring mode and colour space with a white colour standard ceramic in D65 illuminant mode.²⁰

Extrudate sorption isotherms

According to the standard static gravimetric method, equilibrium moisture content of crushed extrudates were evaluated in the a_w range $0.11\text{--}0.90$ at the stabilised temperatures of $25.0 \pm 0.1^\circ\text{C}$, $30.0 \pm 0.1^\circ\text{C}$ and $35.0 \pm 0.1^\circ\text{C}$ using standard saturated salt solutions.²¹ Extrudates were initially dried by static desiccator method using pure phosphorus pentoxides (Merck Eurolab SA, Darmstadt, Germany) and stabilised to equilibrium with nine saturated solutions in hermetic low vacuum conditions during 15 days. Experimental data were then fitted to the three-parameter Guggenheim–Anderson–Boer (GAB) model for hygroscopic properties prediction and a later extrusion optimisation, using non-linear regression with Excel solver software (Microsoft Corp, USA) and water analysis Series v97.4 software (Shanaglen, Webb Tech Pty Ltd, Oxenford, Australia). The goodness-of-fit was estimated using the relative root-mean-square error (%RMS) according to Bizot.²²

Extrudate crispness and shelf life estimation

Extrudates stabilised during 15 days at $25 \pm 0.1^\circ\text{C}$ in closed desiccators containing various saturated solutions in the range $11.1\text{--}70.8\%$ relative humidity were submitted to crispness evaluation using a Stable Micro Systems TA-xT2 texturometer. Compression test were made on the extrudates, which were mounted over a platform using a 50-mm diameter plastic cylinder, with a probe distance of 10 mm through the samples. The test cross-head speed was 0.001 m s^{-1} (pre-test 0.002 m s^{-1} and post-test 0.02 m s^{-1}) and in all cases, average drop-off force was computed from the force–deformation curve. This function calculated the average drop in force between consecutive peaks and troughs over the selected region (Stable Micro Systems Ltd) as an indicator of products crispness.²³

Texture analysis was performed randomly on ten extrudates for each relative humidity. The critical water activity (a_c) was then graphically estimated according to the safe storage borderline with the tangent on the linear stage of the adsorption isotherm²⁴ and confirmed by crispness limit of acceptability.

Using the Heiss and Eichner model,^{25–27} the potential storage time based on a_c was estimated at isothermal temperatures and relative humidity of 0.7 for storing conditions using 0.04-m^2 polyethylene bags with a permeance of $2.28 \times 10^{-3}\text{ kg H}_2\text{O m}^{-2}\text{ Pa}^{-1}\text{ day}^{-1}$.

Statistical analysis

A Fisher test at 95% confidence level was computed using Statgraphics Plus v 2.1 (Statistical Graphics Corporation, Manugistics Inc, Rockville, USA) in order to estimate whether there are significant differences among means and a Duncan's multiple-range test to estimate which means are different from each other.

For the experimental design, calculations were also performed using Statgraphics. A second-degree polynomial model was chosen to correlate the response variables (P_{time} , PV, HPV, CPV, BD, SB, T_{paste} and Hrd, Adh, Spg) with the process variables (salt concentration, C_{st} ; shrimp head proteins concentration, C_{shp} ; chitosan concentration, C_{cts}).

$$Y = a_0 + \sum_i a_{ii}X_i^2 + \sum_i a_iX_i + \sum_{i,j} a_{ij}X_iX_j \quad (1)$$

where

Y : a response (P_{time} , PV, HPV, CPV, BD, SB, T_{paste} , Hrd, Adh or Spg)

X_i : factor i (C_{st} , C_{shp} or C_{cts})

a_0 : constant

a_i : linear effect of X_i

a_{ii} : quadratic effect of X_i

a_{ij} : interaction effect of X_i and X_j

RESULTS AND DISCUSSION

Preliminary characterisation

As expected, cassava starch pasting properties were significantly different from those obtained from corn starch and rice flour. The starch/flour paste variation coefficient below 5.3% (except from rice BD) confirmed good reproducibility of RVA results (Table 2).²⁸ Higher PV and BD were observed for cassava starch due to weak internal organisation inducing higher swelling power and then lower heat and shear stress resistance.²⁹ In order to fulfil conditions for extrusion such as that obtained from corn starch, selected ingredients in formulation that lower PV and BD would be required.

Similarly, preliminary TPA curves indicated significant differences due to starch/flour type used (Fig 1). Higher gel hardness testified that corn *ca* 1104 g, and rice, *ca* 564 g, have better get resistance than cassava, *ca* 142 g.³⁰ In addition, the adhesive properties of cassava starch, as the small negative area under the TPA

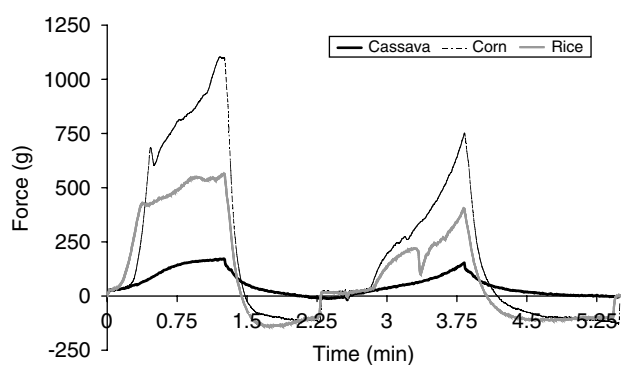


Figure 1. TPA curves of starches and flour.

curve verified, shows a wide range of possible application in industry as a smooth, stable and fluid adhesive³¹ compared with corn and rice. The significant adhesion force was in the range 120–140 g. The use of selected ingredients for extrusion could amplify both cassava hardness and adhesion properties to obtain functional properties similar to corn and fit common extrusion conditions as well.

Experimental design

The experimental design gives ten response regression coefficients (P_{time} , PV, HPV, CPV, BD SB, T_{paste} , Hard, Adh and Spg) with reduced co-ordinates (Table 3). Except for adhesiveness at 84%, adjusted regression coefficients indicate that the fitted polynomial models explained more than 88% of response variability.

P_{time} and T_{paste} : All linear effects were positive and significant. C_{shp} had a clear linear effect. The effects of salt and C_{cts} concentrations were similar. No linear ingredients effects were enhanced by quadratic terms and interactions due to poor significance levels.

PV and SB: A strong linear negative effect was observed for both C_{shp} and C_{st} without any significant quadratic and interaction between ingredients. Respectively, 96 and 97% of the variability of PV and SB were explained by polynomial model coefficients.

HPV and CPV: Both linear effects concerning C_{shp} and C_{st} were negative, but positive for C_{cts} . The negative interaction between C_{shp} and C_{cts} confirmed their significant antagonistic influence. No significant interactions between factors and quadratic effects were marked. The influence of salt on both HPV and CPV was opposite to that observed on starch paste with water-soluble non-starch polysaccharides.³²

Table 2. Pasting properties of starches and flours^a

	P_{time}^b	PV ^b	HPV ^b	CPV ^b	BD ^b
Cassava	4.2 ± 0.1a	227.8 ± 3.8a	96.3 ± 1.4a	155.9 ± 3.8a	131.5 ± 2.8a
Corn	5.9 ± 0.1b	116.5 ± 1.2b	99.2 ± 1.8a	112.3 ± 1.5b	17.3 ± 0.6b
Rice	6.9 ± 0.1c	163.3 ± 0.8c	127.2 ± 6.7b	234.8 ± 3.9c	36.11 ± 5.9c

^a P_{time} in min, PV, HPV, CPV and BD in RVU.

^b a–c, Means with different lower case letters in the same column are significantly different at 95% confidence level; Means are obtained from data in triplicate.

Table 3. Regression coefficients of the second-order experimental design describing pasting properties and textural profile of cassava starch

	a ₀	a ₁ (C _{shp})	a ₂ (C _{st})	a ₃ (C _{cts})	a ₁₁	a ₂₂	a ₃₃	a ₁₂	a ₁₃	a ₂₃	\bar{R}^2
P _{time} (min)	5.29	0.43***	0.33***	0.25***	-0.07	-0.09	-0.07	-0.11	0.13	0.08	
±	0.04	0.03	0.03	0.03	0.06	0.06	0.06	0.08	0.09	0.09	0.96
PV (rvu)	127.30	-36.12***	-33.87***	-1.25	7.35	10.49	3.46	9.09	-2.54	-7.40	
±	3.19	2.76	2.76	2.76	5.05	5.05	4.79	6.38	7.14	7.14	0.96
HPV (rvu)	79.11	-9.54***	-9.36***	10.25***	-5.14	2.64	-4.51	0.96	-8.2*	0.43	
±	1.33	1.15	1.15	1.15	2.10	2.10	1.99	2.66	2.97	2.97	0.94
CPV (rvu)	110.84	-19.63***	-15.40***	8.84**	-3.09	3.16	-1.94	1.11	-8.99	0.02	
±	2.00	1.73	1.73	1.73	3.17	3.17	3.00	4.00	4.48	4.48	0.94
BD (rvu)	47.86	-26.57***	-24.50***	-11.51**	12.82*	8.18	8.31*	8.13	5.66	-7.82	
±	2.14	1.85	1.85	1.85	3.39	3.39	3.21	4.28	4.79	4.79	0.97
SB (rvu)	31.72	-10.03***	-5.96***	-1.27	2.06	0.53	2.75	0.14	-0.54	0.02	
±	0.89	0.78	0.78	0.78	1.42	1.42	1.34	1.79	2.00	2.00	0.94
T _{paste} (°C)	79.45	1.15**	1.79***	1.74***	-0.14	0.23	-0.11	-0.46	0.12	0.53	
±	0.24	0.20	0.20	0.20	0.37	0.37	0.35	0.47	0.53	0.53	0.93
Hard (g)	134.97	22.84***	-15.79***	23.80***	11.84*	-0.07	-17.65**	-9.76	21.59*	0.51	
±	2.84	2.46	2.46	2.46	4.50	4.50	4.26	5.69	6.36	6.36	0.96
Adh (g)	-4.86	-2.81**	0.34	-3.83**	-1.55	2.37	1.12	-0.96	-7.00**	-2.20	
±	1.07	0.93	0.93	0.93	1.69	1.69	1.61	2.14	2.40	2.40	0.84
Spg	2.69	-0.40	0.17	-1.81***	0.01	0.78	1.93**	-0.81	-1.45*	-0.56	
±	0.03	0.03	0.03	0.03	0.05	0.05	0.05	0.07	0.08	0.08	0.88

***, **, * Significance level for $p < 0.001$, $p < 0.01$ and $p < 0.05$, respectively.

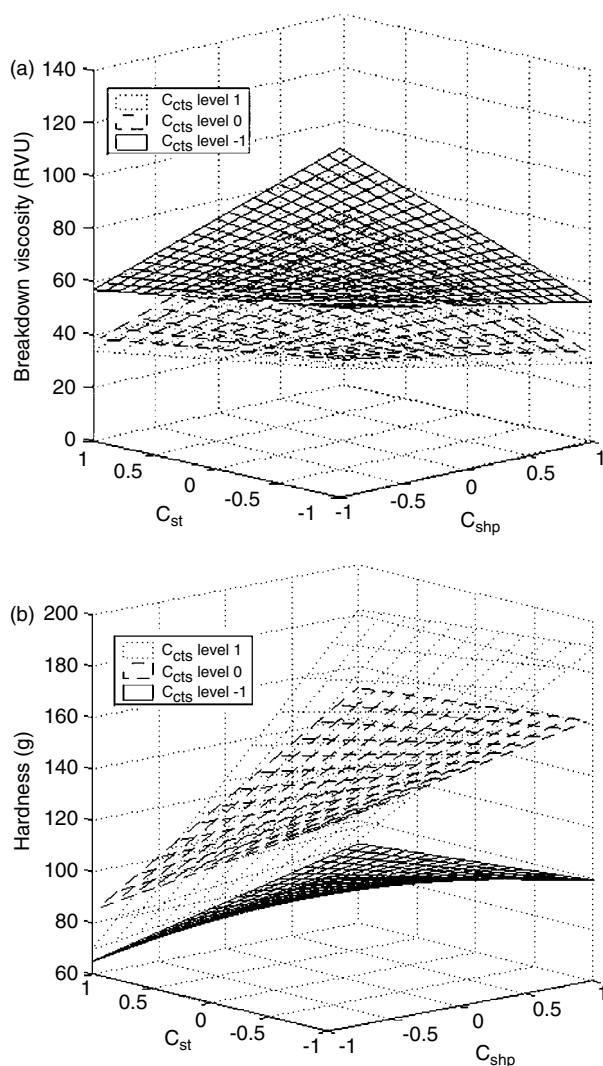


Figure 2. Salt and shrimp head protein influence on (a) BD and (b) Hrd.

BD: All linear effects were negative and significant. C_{cts} and C_{shp} linear effects were slightly reduced because of their respective significant quadratic effects (Fig 2a).

Hrd: Salt had a marked linear negative effect, whereas C_{cts} and C_{shp} had a positive linear effect (Fig 2b). The interaction between C_{cts} and C_{shp} showed that they were synergistic. Antagonistic quadratic effects of C_{cts} and C_{shp} were observed.

Adh: The polynomial model was not well correlated with the experimental results (adj $R^2 = 0.84$). Since adhesiveness corresponds to the small negative area after the first bite (Fig 1), its computation introduced a significant error by approximation. Slight linear effects were observed negatively for C_{shp} and C_{cts}, as well as for their interaction. No significant effect was found for C_{st} or for quadratic terms.

Spg: Chitosan concentration had a linear negative effect on elasticity, synergistic to its interaction with proteins. A slight positive effect was found for chitosan quadratic term.

The implementation of shrimp head proteins and chitosan were then shown to be beneficial and suitable for their respective effect on raising textural characteristics (Hrd and Adh) as well as their interaction. The results of extrudate quality indicate lowering of mixture swelling power, while reinforcing cassava starch mixture heat and shear stress resistance. Such functionality were also commonly observed with sorghum and corn starches using monoglycerides or stearic acid complexation, interfering with granule tightening up before swelling.²⁹

Chip quality evaluation

The comparative study carried out for the two recipes with a local production and a commercial product deep fried under the same conditions showed intermediate

Table 4. Chips characteristics before/after deep-fat frying

	a_w^a before frying	a_w^a after frying	Mfb (kg) ^b	Final moisture content (g kg ⁻¹ fresh matter) ^c	% LE ^b
SD	0.55 ± 0.01	0.39 ± 0.01	1.22 ± 0.33a	44.3 ± 2.1	89 ± 9a
CD	0.54 ± 0.01	0.42 ± 0.01	1.16 ± 0.27a	49.6 ± 0.5	94 ± 11a
KD	0.67 ± 0.01	0.41 ± 0.01	1.53 ± 0.39b	44.3 ± 1.1	70 ± 12b
Commerce	0.60 ± 0.01	0.42 ± 0.01	1.16 ± 0.26a	40.2 ± 4.8	120 ± 12c

^a Data are means of two determination at 26.5 ± 0.4 °C.

^b Data are means of 20 determinations in duplicate.

^c Data are means of three determinations; a–c means with different lower case letters in the same column are significantly different at 95% confidence level.

maximum force of break Mfb and linear expansion percentages (% LE) compared with the local and commercial recipes (Table 4).

While the addition of wheat flour facilitated the hand-mixing during rolls forming with a lower friability of dough and higher elasticity, the %LE values obtained were high and significantly different from one recipe to the other, except from the simple to the complex recipes. With the exception of the hand-mixing improvement, wheat flour did not significantly influence %LE. Higher moisture content found after frying should be due to additional compounds and especially to higher salt concentration and wheat flour acting as water networking retainer.

The lower %LE obtained for KD could be due to the heat resistance of the fish protein's network and, to a lesser extend, to the absence of chitosan. The observed Mfb seemed to confirm such hypotheses. Concerning the commercial product and the two recipes, equivalent Mfb values were observed, indicating a slight influence of ingredients added to the second mix.

Even though no triangular test was carried out for consumer acceptability, the use of shrimp head protein combined with chitosan seems to act as a flavour exhauster into the final product. That the %LE values of the two recipes were greater than 77% indicates their potential good mouth feel with an acceptable level of crispness according to Siaw *et al* as cited by Sriburi and Hill.³³ Some visual heterogeneity of chip colour was observed and will need to be improved by further mixing or use of complementary additives.

Extrudate quality evaluation

(ER)_{radial} was influenced by extruder screw speed as previously observed.^{34,35} Screw speed induced a higher expansion (Table 5), at low moisture content,^{11,35} as found earlier. Nevertheless, the screw speed can significantly and negatively influence expansion at

higher moisture content. Hashimoto and Grossmann observed such phenomenon and reported other researcher's similar conclusions.³⁶ No significant differences were observed concerning final moisture content which should guarantee extrudates stability subject to critical water activity.

Even though SD chips and extrudates have an equivalent initial composition, at equivalent a_w , they reached different final moisture contents, around 44.3 and between 96.7–99.5 g kg⁻¹ fresh matter, respectively. Two explanations can be suggested. At first, a significant fat absorption is expected during deep-fat frying³⁷ as well as a partial gelatinisation of cassava starch. This should induce a major decrease in a_w . This phenomenon should be enhanced by the presence of chitosan, known with chitin for its fat adsorption capacity,⁸ up to 12 times their weight in fat, in contrast to the extrusion process where no fat income is expected as well as a full starch gelatinisation during the residence time. Moreover, the extrusion process with high pressure should induce a massive molecular disruption with macromolecular degradation³⁸ inducing a higher water bonding capacity onto the matrix, so raising its hygroscopicity.

Regarding extrudates appearance, lightness variable L ca about 64.7 ± 0.2 and chromacity co-ordinates a and b ca 6.8 ± 0.1 and 19.9 ± 0.3 respectively, confirmed the light brown-red aspect, similar to that of chips. Lightness and chromacity variables were similar to that obtained by twin-screw extrusion of air-classified pea protein.³⁹ At equivalent barrel temperature (between 150 and 160 °C) and screw speed (135 to 245 rev min⁻¹), L , a and b variables indicated a potential acceptability of final protein extrudates.

Snacks sorption isotherm

Equilibrium moisture content (g kg⁻¹) at variable a_w were obtained at 25, 30 and 35 °C, respectively. As expected, adsorption isotherms fluctuate with

Table 5. Extrudates characteristics

Screw speed (rev min ⁻¹)	115 ± 6	150 ± 8	200 ± 10	220 ± 11
Water activity ^a	0.39 ± 0.01	0.39 ± 0.01	0.40 ± 0.01	0.40 ± 0.01
Moisture content (g kg ⁻¹ fresh matter) ^a	96.7 ± 2.4a	96.8 ± 1.2a	99.0 ± 1.8a	99.54 ± 2.1a
(ER) _{radial} ^b	4.49 ± 0.20a	5.38 ± 0.28b	5.95 ± 0.24c	6.16 ± 0.13c

^a Data are means of three determination (at 27 ± 0.2 °C for a_w).

^b Data are means of ten determinations with four replicates; a–c means with different lower case letters in the same row are significantly different at 95% confidence level.

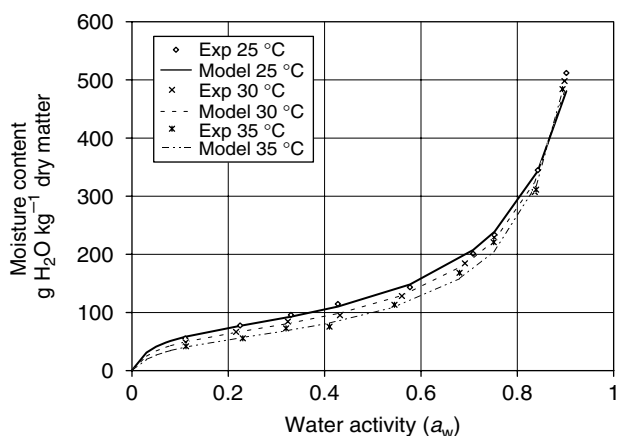


Figure 3. Adsorption isotherm at 25, 30 and 35 °C fitted to GAB model.

Table 6. Estimated GAB model coefficients at 25, 30 and 35 °C

$\alpha * 10$	-1.326	-1.525	-1.805
$\beta * 10$	1.340	1.492	1.702
$\gamma * 10^3$	5.755	7.682	10.738
RMS (%)	0.132	0.097	0.242
Monolayer water content $g\ kg^{-1}(X_m)$	68.98	60.92	52.19
Guggenheim constant C	26.498	21.954	17.881
Correcting factor K	0.951	0.973	0.998
Regression variance	0.319	0.184	0.141

temperature (Fig 3). For the same equilibrium moisture content, a_w will shift while the storing temperature rises. At moisture content of $100\ g\ kg^{-1}$ dry matter, the computed magnitude of a_w shift²⁴ is ca 0.13 from 25 to 35 °C.

Corresponding isothermal coefficients using GAB model are given in Table 6. The root mean-square percentage, <5%, confirmed that the GAB model fitted the experimental data satisfactorily (Table 6).⁴⁰ The characteristic sigmoidal-shaped curve (type II) indicated a large hygroscopicity of extrudates above 60% relative humidity in common with most foods.²⁴ The estimated monolayer moisture content decreased from 69 to $52\ g\ kg^{-1}$ dry matter in the range 25–35 °C. The value at 25 °C corresponds to the estimated coefficient for tapioca recipe available in the literature.⁴¹ Extrudates should be dried below a target moisture content to achieve the desired consistency and storability, as will be apparent later by shelf life simulation and crispness evaluation. Nevertheless, similar moisture content with dough prior to extrusion will require its optimisation in order not to remove too much water detrimental to the process cost and mass balance. Further studies could then be focused on technological parameters, such as temperature, feed moisture content and additives, to limit water removal during extrusion, beneficial to energy savings and extrudate quality.

Crispness evaluation and shelf-life estimation

Computed average drop-off plotted versus corresponding water activity were superimposed on the

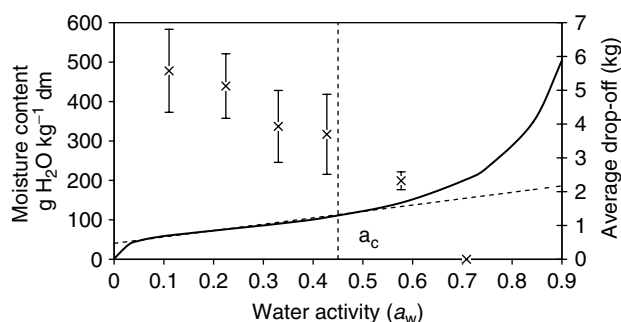


Figure 4. Fitted adsorption isotherm at 25 °C and average drop-off.

adsorption isotherm at 25 °C as shown in Fig 4. Antagonistic evolutions of the average drop-off with water activity, as expected, clearly indicated a loss in extrudate crispness during a_w rise. If 0.7 represents the a_w where no more crispness could be measured through the instrumental method, a critical water activity, a_c around 0.45, could be graphically estimated as the safe storage borderline with the tangent on the linear stage of the adsorption isotherm (Fig 4). This limit is confirmed by the average drop-off in the same a_w range. It corresponds to literature values on snack foods where transformations from amorphous to crystalline sugar food systems usually occur.⁴² At 25 °C, a moisture content below $115\ g\ kg^{-1}$ dry matter could maintain cassava extrudates crispness as required for consumers acceptability and might be confirmed by some later hedonic investigation.

Using the Heiss and Eichner model, the corresponding potential storage time based on the a_c could be estimated under given storage conditions, usually available for such commercial products.

The corresponding calculated shelf-life of extrudates at three storage conditions and a_w 0.7 are shown in the Table 7. If such storage conditions were applied to extrudates with corresponding initial moisture content, the estimated shelf-life might be estimated in the range of 38–10 days at ambient temperature, 26–1 and 15 days to initial instability, at respectively 30 and 35 °C. The absence of crossing-over (intersection) among adsorption isotherms suggests it is

Table 7. Estimated shelf-life of extrudates with increasing temperature and constant a_w 0.7

	25 °C	30 °C	35 °C	
Estimated critical Eq moisture content ^a	114.8	102.4	88.6	
Estimated Eq moisture content ^a	202.3	187.2	169.1	
Initial moisture content ^a	Corresponding estimated shelf-life (days)			
	40	38	26	15
	80	21	11	3
	100	10	1	0

^a $g\ kg^{-1}\ dm$.

preferable to avoid high temperatures during storage, as well as high feed moisture content, to ensure a better extrudate stability. The moisture content is also a determinant to ensure a correct expansion, since a drop in barrel temperature induces a lower vapour pressure in the dough, resulting in less moisture flashing at the extruder die and then expansion, as earlier demonstrated by Launay and Lisch.⁴³ Nevertheless, the appearance of extrudates might be later lightened by reducing the extrusion operating temperature and increasing initial moisture content as reported by Linko *et al.*⁴⁴ Taking into account all incidences of feed moisture content prior to the extrusion process as well as final one that might be detrimental to product stability, quality and acceptability, Later optimisation will then require, especially if extrudate are to be stored at high temperature.

If higher costs can be afforded, a packaging with lower water permeance such as polypropylene or multilayer packaging (polyethylene, polypropylene and aluminium foil) could be assumed, potentially improving product shelf life.

CONCLUSION

Chitosan, shrimp head protein and salt lowered the natural high peak viscosity and breakdown of cassava starch and led to functional properties close to that of corn starch during extrusion process. Hardness and adhesiveness enhancement were also valuable. Selected quality criteria of chips and extrudates demonstrated their good potential for by-products valorisation as well as new potential for local cassava starch use in Thailand. High extrudates hygroscopicity should be taken into account to optimise extrudate formulation and processing when consumer acceptability and technological costs determined.

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