Universidade Estadual de Londrina

DAFNE GARCIA PEREIRA

HIDRÓLISE ÁCIDA DO AMIDO DE MANDIOCA, CARACTERIZAÇÃO DAS PROPRIEDADES E APLICAÇÃO

Londrina
2020

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Tese apresentada ao Programa de Pós-Graduação em Ciência de Alimentos, da Universidade Estadual de Londrina, como requisito parcial à obtenção do título de Doutor em Ciência de Alimentos.

Orientadora: Profª. Drª Adelaide Del Pino Beleia.

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Aos meus pais Adoica e José Carlos, ao meu irmão Mateus e ao meu namorado Matheus por todo amor e incentivo DEDICO.

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PEREIRA, Dafne Garcia. **Hidrólise ácida do amido de mandioca, caracterização das propriedades e aplicação.** 2020. 64 f. Tese (Doutorado em Ciência e Tecnologia de Alimentos) – Universidade Estadual de Londrina, Londrina, 2020.

RESUMO

O amido é o componente em maior quantidade da raiz da mandioca, porém há limitações no uso industrial de amidos nativos. A hidrólise ácida é um importante método químico de modificação de amidos que permite a alteração significativa das propriedades funcionais alterando pouco a morfologia dos grânulos, o amido resultante pode ser chamado de ácido-modificado. A principal aplicação do amido ácido-modificado é na produção de balas de goma, atuando como um agente gelificante contribuindo para a estrutura e textura final da bala, onde maciez e mastigabilidade são desejáveis. O objetivo deste trabalho foi obter amido de mandioca ácido-modificado, caracterizá-lo quanto às propriedades físicas antes e após o processo de hidrólise, avaliar seu comportamento em uma solução de açúcares e aplicar o amido ácido-modificado na formulação de balas de goma. Após a modificação, alguns dos efeitos observados no amido de mandioca ácido-modificado foram: aglomeração dos grânulos após a hidrólise ácida, detectado pelos resultados das determinações de distribuição, tamanho de partícula, área superficial e span, entretanto, em microscopia eletrônica de varredura não foi visualizado alterações no formato dos grânulos. Em soluções de açúcares o amido ácido-modificado apresentou aumento no índice de absorção, poder de inchamento a 90 ºC, aumento da temperatura de pico de gelatinização e não houve desenvolvimento de viscosidade detectável em RVA. O amido de mandioca ácido-modificado foi aplicado em balas de goma nas proporções de 12 e 16% e comparado com balas de goma produzidas com amido de milho ácido-modificado na proporção de 8% (controle). Com as análises das propriedades físico-químicas foi encontrado diferenças na cor e no perfil de textura das balas, pode-se destacar que as balas produzidas com amido de mandioca a 12% apresentaram dureza e mastigabilidade semelhantes à bala de amido de milho 8% e maior porcentagem de amido de mandioca (16%) resultou em bala de goma com quase o dobro da dureza e mastigabilidade. No teste sensorial, ordenação da preferência, as balas de amido de milho 8% e mandioca 12% foram igualmente preferidas pelos avaliadores. Após a hidrólise ácida, o amido de mandioca ácido modificado apresentou propriedades adequadas para a aplicação em balas de goma e a produção de balas com 12% de amido é promissora.

Palavras-chave: Amido de milho. Análise Sensorial. Bala de goma. *Manihot esculenta* Crantz. Solução de açúcares.

PEREIRA, Dafne Garcia. **Characterization of properties and application of acidthinned cassava starch.** 2020. 64 p. Thesis (Doctoral Degree in Food Science) – Universidade Estadual de Londrina, Londrina, 2020**.**

ABSTRACT

Starch is the major component of the cassava root, but there are limitations in the industrial use of native starches. Acid hydrolysis is an important chemical method of starch modification that allows a significant change in the functional properties of the starch with little change in the morphology of the granules, the resulting starch is called acid-thinned. The main application of acid-thinned starch is in the production of gummy candies, acting as the gelling agent that contributes to the structure and final texture of the candy where softness and chewiness are desirable. The objective of this work was obtain acid-thinned cassava starch, characterize it in terms of physical properties before and after the hydrolysis process, evaluate its behavior in a sugar solution and apply acid-thinned starch in the formulation of gummy candies. After the modification, some of the effects observed in the acid-thinned cassava starch were: granules agglomeration after the hydrolysis, detected by the results of the determinations of distribution, particle size, surface area and span, however, in scanning eléctron microscopy there were no changes in the shape of the granules. In sugar solutions, acid-thinned starch showed an increase in absorption index, swelling power at 90 ºC, an increase in peak gelatinization temperature and there was no development of detectable viscosity in RVA. Acid-thinned cassava starch was applied in gummy candies in the proportions of 12 and 16% and was compared with gummy candies produced with acid-thinned corn starch in the proportion of 8% (control). With the analysis of the physical-chemical properties, differences were found in the color and texture profile of the gummy candies, it can be highlighted that the gummy candies produced with 12% cassava starch showed hardness and chewiness similar to 8% corn starch candies, higher percentage of cassava starch (16%) led to gummy candy with almost twice the hardness and chewiness. In the sensory Preference-Ranking test, candies of corn starch 8% and cassava 12% were equally preferred by the assessors. After acid hydrolysis, acid-thinned cassava starch showed properties suitable for application in gummy candies and the production of candies with 12% of starch is promising.

Keywords: Corn starch. Gummy candy. *Manihot esculenta* Crantz. Sensory analysis. Sugar solution.

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1.1. INTRODUÇÃO

O amido é o componente em maior quantidade da raiz da mandioca e quando extraído pode chegar até 80% do peso seco da raiz, devido a isso, provavelmente as características de muitos produtos à base de mandioca sejam em grande parte afetada pela qualidade e propriedades do amido (ZHU, 2015). A modificação do amido é realizada para melhorar as propriedades e as funcionalidades do amido, pois há limitações no uso industrial de amidos nativos, que suportam pouco aos processos tecnológicos industriais. A modificação do amido está em constante evolução com possibilidades de gerar amidos com diferentes propriedades e com maior valor agregado (KAUR, et al. 2012; ZHU, 2015).

A hidrólise ácida é um método químico de modificação de amidos, sendo os ácidos mais utilizados o clorídrico ou sulfúrico. Tal modificação é importante, pois pode alterar as propriedades estruturais e funcionais do amido nativo sem alterar significativamente sua morfologia granular, o amido resultante pode ser chamado de amido ácido-modificado (WANG; COPELAND, 2015). O ácido clorídrico age quebrando as ligações glicosídicas da região amorfa primeiro, pois essa é facilmente permeável, as ligações glicosídicas da região cristalina são hidrolisadas por último (JIANG et al., 2018). Após a hidrólise ácida, de modo geral os amidos ácido-modificados apresentam menor viscosidade, maior lixiviação de amilose, temperaturas maiores de gelatinização e menor poder de inchamento, porém, quando observado em microscopia eletrônica de varredura apresenta pouco ou nenhum sinal de destruição visível na superfície dos grânulos (ZHANG et al., 2017; ULBRICH, LAMPL, e FLÖTER, 2016; MEHBOOB et al., 2015).

As novas pesquisas sobre as modificações químicas em amidos buscam criar variações mais amplas nas propriedades e na estrutura dos amidos, além de incorporar novas tecnologias para melhorar o processo de hidrolise ácida (ZHU, 2015; LeCORRE et al., 2012). As principais aplicações de amido ácido-modificado na indústria de alimentos são como agentes gelificantes na fabricação de balas de goma, substitutos parciais de gordura em produtos com teor reduzido de gordura e ainda como aditivos alimentares, agindo como: espessante, estabilizador coloidal, agente encapsulante e agente de retenção de água (ALMEIDA et al., 2013; OLAYINKA; ADEBOWALE; OLU-OWOLABI, 2013; WANG; COPELAND, 2015).

Quando um amido é modificado, há diversas possibilidades de aplicações, por isso é importante investigar como o amido irá se comportar na presença de outros ingredientes simulando uma condição próxima do uso real deste amido. Para os amidos de trigo e mandioca, avaliou-se o efeito da adição de açúcares e/ou polióis no comportamento do amido nativo, e foi observado o aumento na temperatura de gelatinização e na viscosidade medidas por RVA (ALLAN; RAJWA; MAUER, 2018; POURMOHAMMADI et al., 2018). Porém, não foram encontrados estudos que investigaram amidos ácido-modificados na presença de açúcares.

O mercado de confeitaria abrange um grupo grande e heterogêneo de consumidores no mercado, de crianças a idosos (PERICHE et al., 2014). Balas de goma são importantes e há estudos com diferentes formulações, como por exemplo balas produzidas com alginato e pectina (AVELAR; EFRAIM, 2020), balas com mel e gelatina (MUTLU; TONTUL; ERBAS, 2018) e balas produzidas com a combinação de amido e gelatina ou amido e pectina (PICCONE; RASTELLI; PITTIA, 2011). Nesses trabalhos diferentes aspectos das balas são avaliados de acordo com o objetivo de cada estudo, tais como requisitos de energia para a secagem, liberação e/ou percepção sensorial do aroma e acidez. Entretanto, os parâmetros comumente investigados em balas são a aceitação sensorial e as características físicas, tais como análise do perfil de textura, cor instrumental, teor de umidade, pH e atividade da água.

Para a produção de balas de goma a característica fundamental que um amido precisa ter no processamento é a baixa viscosidade a quente em altas concentrações de sólidos (EISLEY, 2014). Na formulação de balas de goma, o alto teor de sólidos é devido principalmente aos açúcares, usado de forma única ou em combinação com xarope de glicose. Juntamente com outros ingredientes, os açúcares desempenham um papel importante na formulação, pois afetam a textura e também na percepção de palatabilidade dos alimentos (YANG et al, 2015).

1.2. OBJETIVOS

1.2.1. Objetivo Geral

Obter amido de mandioca ácido-modificado, caracterizá-lo quanto às propriedades físicas antes e após o processo de hidrólise, avaliar seu comportamento em uma solução de açúcares e aplicar o amido ácido-modificado na formulação de balas de goma.

1.2.2. Objetivos Específicos

- Efetuar a hidrólise ácida do amido de mandioca nativo;
- Avaliar os efeitos da hidrólise ácida nas propriedades físicas e morfológicas do amido nativo e ácido-modificado;
- Simular uma condição semelhante ao uso real do amido ácido-modificado com o auxílio de uma solução de açúcares (sacarose e xarope de glicose);
- Analisar as propriedades de pasta e tecnológicas do amido ácido-modificado em água e em solução de açúcares;
- Aplicar o amido ácido-modificado na formulação de balas de goma e comparar com balas de goma produzidas com o amido de milho ácido-modificado (controle);
- Analisar as balas de goma física e sensorialmente.

1.3. REVISÃO BIBLIOGRÁFICA

1.3.1. Amido de mandioca nativo

A mandioca (*Manihot esculenta* Crantz*)* pertence à família das *Euphorbiaceae,* que é considerada como uma das mais importantes dentro do grupo das Angiospermas, é uma raiz tuberosa, que consiste basicamente em uma polpa de amido envolvida por uma casca fina que pode ser facilmente retirada (CONCEIÇÃO, 1983). Segundo o relatório da FAO realizado em novembro de 2018, a produção mundial da raiz da mandioca foi de 277,1 milhões de toneladas e o consumo per capita mundial foi de 19,8 kg por ano (FAO, 2018). Zhu (2015), estudou a composição, a estrutura e as propriedades físico-químicas do amido de mandioca, e relatou que em peso seco a mandioca pode ter rendimento de até 80% de amido, o conteúdo de amilose pode variar entre 16-26%, cinzas entre 0,07-0,77%, proteínas 0,05-0,77%, lipídeos entre 0,04-0,51% e fibras 0,11-1,9%.

Os grânulos de amidos nativos possuem tamanhos e formas variados conforme a fonte e até entre os grânulos de uma mesma fonte. Os grânulos de amidos de tubérculos e raízes tendem a ser maiores, como por exemplo, o grânulo de mandioca pode variar entre 2-32 µm, sendo que tamanhos entre 7-20 µm são os mais frequentes (BEMILLER; HUBER, 2010; ZHU, 2015). As características morfológicas dos grânulos de amido de mandioca de diferentes variedades foram resumidas por Zhu (2015), há grânulos com polimorfismo tipo A ou C, cristalinidade entre 15,3 e 49%, tamanho entre 2,4 e 32 µm com média próxima de 15 µm, e as formas dos grânulos foram descritas como esféricas, ovais, truncada, cilíndrica, superfícies lisas, parcialmente deprimidas e arredondadas.

As características físicas e químicas dos amidos nativos dependem da sua composição, pois os grânulos são formados por dois polímeros: a amilose que é um polímero relativamente linear e a amilopectina que é um polímero ramificado. A estruturação dessas cadeias forma nos grânulos regiões cristalinas devido ao empacotamento das duplas hélices da amilopectina e regiões amorfas principalmente constituídas por amilose, e as proporções de cada um desses polímeros variam conforme a fonte vegetal do amido (BEMILLER; HUBER, 2010). A amilose do amido de mandioca pode ter o peso molecular médio de $2,1 \times 10^6$ g/mol e a amilopectina, que é uma molécula maior pode ter o peso molecular médio de 19×10^6 g/mol. Pesos moleculares medidos pelo método de fracionamento por campo de fluxo assimétrico, mas esses valores podem variar em função da genética das culturas e do método utilizado para a medição (JUNA; HUBER, 2012).

1.3.2. Modificação e caracterização de amidos ácido-modificados

A hidrólise ácida é uma das modificações químicas mais importante, os ácidos mais utilizados são o ácido clorídrico e o sulfúrico. O procedimento normalmente inicia pelo tratamento dos grânulos de amido com o ácido na concentração desejada, em temperatura menor que a de gelatinização, durante um ou vários períodos de tempo pré-determinados, o amido resultante é recuperado por lavagem e secagem. A hidrólise ácida altera as propriedades funcionais dos amidos, durante a hidrólise ácida, as regiões amorfas são as primeiras a serem afetadas pelo ácido, por isso são hidrolisadas preferencialmente, e por consequência aumenta a cristalinidade relativa e o teor de duplas hélices do amido hidrolisado (WANG;

COPELAND, 2015). Na comparação entre diferentes artigos científicos (Tabela 1), todos utilizaram o ácido clorídrico para realizar a hidrólise ácida, nas concentrações de 0,1 M até 1,5 M, nas proporções de 30-45% (p/v) e os principais efeitos encontrados foram resumidos.

Quadro 1.1 – Comparação entre artigos científicos que realizaram a hidrólise ácida de amidos de diferentes fontes.

Artigos científicos	Fonte
• Amido de milho ceroso • Suspensão de 40% (p/v) de amido e ácido clorídrico 0,2 M, mantidos em banho Maria a 50 ºC por 8 h. • Os amidos apresentaram baixa viscosidade, perfil de cadeias de ramificação curtas, a estrutura granular não apresentou sinais de destruição visível, cristais tipo A e cristalinidade relativa de 45,5%, pequena diminuição nos valores de temperatura de gelatinização inicial, de pico e de conclusão no DSC, não houve variação de entalpia em comparação ao amido nativo e apresentou baixíssimo teor de amido resistente (0,7%).	Zhang et al. (2017)
• Amido de milho • Suspensão de 40% de amido com ácido clorídrico nas concentrações de 0,25, 0,5, 1,0 e 1,5 mol/L, o pH da suspensão foi ajustado para 6,0–6,5 com NaOH 1 mol/L, por 3 h a 50 °C, o amido foi lavado e seco a 45 °C em estufa a vácuo. • O diâmetro médio dos grânulos diminuiu com o aumento da concentração do ácido de 28,5 para 3,5 µm. Não houve diferença nos padrões de cristalinidade. Foi realizada uma mistura dos amidos ácido-modificados com goma xantana (40:1), todos os parâmetros de pasta diminuíram com o aumento da concentração do ácido, todas as misturas tiveram um comportamento de um fluido pseudoplástico e uma típica estrutura de gel fraca, a mistura de goma com amido hidrolisado com ácido 1M apresentou melhor estabilidade, a digestibilidade foi semelhante para todas as misturas.	Jiang et al. (2018)
• Amido de batata • Suspensão 40% de amido usando ácido clorídrico 0,54 M, mantido em 3 diferentes temperaturas 2, 25 e 50 °C por 4 h. • Maiores danos foram observados na superfície dos grânulos de amido com o aumento da temperatura de hidrólise, também houve maior solubilização de carboidratos lixiviados, aumento nas temperaturas de gelatinização, a transição sol-gel da pasta de amido e a capacidade de formar um gel firme foram determinadas exclusivamente para a amostra tratada a 50 ºC, ocorreu significativa diminuição do peso molecular dos polímeros das amostras tratadas a 50 ºC e em menor intensidade para as amostras a 25 e 2 ºC.	Ulbrich, Lampl, e Flöter (2016)

• Amido de sorgo branco • Suspensões de amido foram elaboradas com 35% (p/v) de amido em ácido clorídrico 0,1 M, 0,5 M e 1,0 M, mantidos a 45 ºC por 3 h sob agitação constante. • A hidrólise do amido reduziu o poder de inchamento, reduziu a claridade das pastas de amido, o pico de viscosidade e a dureza do gel, mas não houve alterações significativas na solubilidade. Inicialmente não foi observada a coesão nos géis de amido, mas a coesão foi desenvolvida após o armazenamento a frio, a elasticidade também aumentou durante o armazenamento, a modificação ácida reduziu a entalpia de gelatinização e resultou em maiores porcentagens de retrogradação.	Mehboob et al. (2015)

Observa-se nos artigos do quadro 1 sobre hidrólise ácida, que nenhum trabalho utilizou o amido de mandioca, aplicou ou indicou qual seria o melhor uso para o amido ácido-modificado, apenas estudaram os efeitos provocados pela modificação nas propriedades. Os principais efeitos estudados podem ser resumidos da seguinte forma: no geral os amidos ácido-modificados apresentaram reduzida ou nenhuma viscosidade, pouca ou nenhuma modificação visível nos grânulos pela análise de microscopia eletrônica de varredura, alterações nas características físico-químicas dos amidos foram detectáveis e os tempos de hidrólise foram entre 3 e 8 horas.

As propriedades dos amidos ácido-modificados estudadas dependem do objetivo da pesquisa, como por exemplo, Ulbrich, Natan e Flöter. (2014), estudaram quais seriam os impactos da modificação ácida com o uso de ácido clorídrico e sulfúrico por 4 ou 24 h em amidos de trigo, batata e ervilha. Os autores descreveram que a hidrólise ácida aumentou o teor de carboidratos dissolvidos, principalmente com o uso do ácido clorídrico e com o aumento do tempo de hidrólise, reduziu a viscosidade das pastas de amidos a quente e observaram que a principal degradação molecular ocorreu na fase inicial resultando na desramificação da amilopectina. Em outro estudo de Ulbrich, Wiesner e Flöter (2015), foi estudado o efeito causado pela modificação ácida com ácido clorídrico e ácido sulfúrico em diferentes concentrações (0,36 e 0,72 N) e tempos (4 e 24 h) nas propriedades dos géis de amido de trigo, batata e ervilha, e como resultado foi obtido géis com maior resistência e claridade após a hidrólise ácida, com exceção do amido de batata.

1.3.3. Aplicação de amidos ácido-modificados

Os amidos são produzidos comercialmente para a indústria a cerca de 100 anos, mas somente entre 50-75 anos atrás, que a introdução de amidos modificados foi aprimorada, principalmente para a indústria de alimentos. O motivo principal da maior aplicação de amidos modificados é a sua maior resistência e/ou estabilidade a diferentes parâmetros de processamento, tais como acidez, condições térmicas e cisalhamento mecânico. Um exemplo de modificação e aplicação de amido modificado é o uso de amidos ácido-modificados em balas mastigáveis (LUALLEN, 2018).

Segundo Eisley (2014) o efeito benéfico da hidrólise ácida de amidos nativos, reside no fato de que é possível reduzir a viscosidade da pasta quente em maior medida do que é reduzida a resistência do gel quando frio, o peso molecular diminui, mas o conteúdo de amilose permanece praticamente inalterado. Isto permite a utilização de amidos hidrolisados com ácido em altas concentrações de sólidos e na presença de açúcares, em comparação do que seria possível com o mesmo amido não hidrolisado. No processamento de balas de gomas essa característica é fundamental, porque permite que a solução seja cozida rápida e eficazmente sem dificuldades no bombeamento, devido a isso tem como principal aplicação confeitos de gelatina e de goma.

No estudo de Marfil, Anhê e Telis (2012) foi avaliada a textura e a microestrutura de balas de goma a base de amido e/ou gelatina, neste trabalho foi utilizado o amido de milho ácido-modificado comercial (Candymil®). As balas foram formuladas em dois grupos, sendo o grupo 1 gelatina: amido variando entre 10:0; 9:1; 8:2; 7:3; 0:10 e no grupo 2 foi fixada a porcentagem de gelatina em 8% (baseado no peso final da formulação) e o amido variou entre 0-5%. Como resultados esses autores relataram que as balas elaboradas somente com amido são mais rígidas e adesivas, nas balas elaboradas com gelatina e amido, a adição de 1% de amido não modificou as propriedades mecânicas das balas, porém com o aumento da proporção de amido houve o aparecimento de zonas ocas com grânulos de amido isolados dentro dessas zonas, mostrando incompatibilidade dos dois polímeros. Pelos resultados dos testes de perfil de textura os autores concluíram que a adição de amido modificado aos géis de gelatina em proporções adequadas pode ser uma alternativa viável na formulação de balas de goma.

1.3.4. Produção de balas de goma

As balas e doces são populares e estão presentes no dia-dia dos consumidores de 3 a 5 vezes por semana, porém, não há registros exatos sobre a história das balas no Brasil, podendo ser dividida em três fases: inicialmente produzidas de forma artesanal, seguido das primeiras fábricas e ampliação do setor, e atualmente com a industrialização, mecanização e consolidação do setor no mercado (ABICAB, 2020a). As balas e doces em geral são uma categoria de produtos que possui uma grande variedade de modelos, formas e sabores. Podem existir balas dos tipos macias, dura, sabor de frutas, de hortelã, recheadas, entre outras. De acordo com o balanço anual da Associação Brasileira da Indústria de Chocolates, Cacau, Amendoim, Balas e Derivados (ABICAB), o mercado de balas e gomas fechou em 2019 com o volume de 257 mil toneladas de doces produzidos, consumo aparente de 181 mil toneladas, volumes de exportação e importação de 86 e 10 mil toneladas, respectivamente (ABICAB, 2020b).

Os doces de gomas geralmente são produzidos pela fervura sob altas temperaturas, aproximadamente 100 °C dos agentes gelificantes e dos açúcares, xaropes de glicose e/ou frutose. Somente depois de ferver, que o aromatizante e/ou agentes corantes podem ser adicionados à mistura (RIEDEL; BÖHME; ROHM, 2015; MUTLU; TONTUL; ERBAS; 2018). Os principais agentes gelificantes utilizados descritos na literatura são: a gelatina, Ƙ-carragena, pectina, goma de guar, goma xantana, amido e seus derivados, estes servem para fornecer estrutura de gel na produção dos doces (CHAROEN et al, 2015; HABILLA; CHENG, 2015; UTOMO et al; 2014). Por fim, a mistura obtida é moldada, na maioria das vezes são usados moldes formados de amido de milho. Os doces são secos a 50-65 ºC por um certo período de tempo, que pode demorar até 3 dias e então são cortadas (HABILLA; CHENG, 2015; MUTLU; TONTUL; ERBAS; 2018).

1.3.5. Caracterização física de balas de goma

A análise do perfil de textura (APT) se baseia na aplicação de uma força controlada a um produto em estudo e registra sua resposta com o tempo. A APT é uma técnica comumente utilizada na indústria para a avaliação do comportamento da textura de alimentos, pois pode dar uma indicação das propriedades sensoriais do alimento (LAU; TANG; PAULSON, 2000). A APT é útil para análise de diferentes tipos de géis, pois os parâmetros obtidos nas curvas do APT têm sido positivamente correlacionados com a avaliação sensorial. Com a APT é possível gerar uma condição similar a de uma mastigação oral, alguns dos parâmetros obtidos são dureza, coesão, elasticidade e mastigabilidade (CHANDRA; SHAMASUNDAR, 2015).

A análise da cor de um produto alimentício é importante, pois pode influenciar a aceitação pelo consumidor. Os corantes são muito utilizados em produtos de confeitaria, e devem estar associados às propriedades aromáticas do produto. Apesar da atual tendência em utilizar aditivos e corantes de origem natural, os corantes sintéticos ainda são utilizados. Em produtos em que o processo de produção passa por tratamento térmico sob altas temperaturas, esse tipo de corante é particularmente eficaz (SILVA et al., 2016).

Em seu estudo Mutlu, Tontul e Erbas (2018) estudaram produtos tipo bala de mel, feitas por duas diferentes técnicas de mistura (fria e quente), três porcentagens de gelatina (15, 20 e 25% do peso do mel) e três sucos de frutas (laranja, morango e amora). Os autores realizaram as análises de conteúdo de umidade, atividade de água, determinação de cor, análise do perfil de textura, acidez, pH, teor de açúcar e prolina, determinação do número de diástase e aceitação sensorial. Em outro estudo com balas sabor pera elaboradas a frio com alginato e pectina, Avelar e Efraim (2020) utilizaram as análises de microscopia eletrônica de varredura, requisitos de energia do processo, aceitação sensorial e características físicas (textura e cor instrumental, teor de umidade, pH e atividade da água). Apesar de não utilizarem o mesmo agente gelificante que foi utilizado neste trabalho, podem-se observar nesses trabalhos quais as análises mais utilizadas para a avaliação de produtos tipo balas em geral.

1.3.6. Análise sensorial

De acordo com a Associação Brasileira de Normas Técnicas (ABNT) a análise sensorial é uma ciência que evoca, mede, analisa e interpreta as reações humanas frente às características dos alimentos e materiais, percebidas pelos cinco sentidos: paladar, olfato, tato, visão e audição (ABNT, 2014). Os métodos na análise sensorial classificam-se em: métodos de discriminação, que analisam as diferenças entre amostras; métodos descritivos que caracterizam como as amostras diferem em termos sensoriais específicos e métodos afetivos que analisam quanto e quais amostras são preferidas (LAWLESS; HEYMANN, 2010). Diferentes métodos sensoriais rápidos foram desenvolvidos nos últimos anos para descrever diferentes tipos de amostras. Entre eles, o Perfil Flash é um método sensorial rápido e descritivo, que se baseia na combinação do método de Perfil Livre e o teste de ordenação (DELARUE, 2014).

O Perfil Flash foi primeiramente proposto por Williams e Langron (1984), os avaliadores têm a liberdade de utilizar os termos descritivos na quantidade e como desejarem. Este método tem como princípio que os avaliadores conseguem perceber as mesmas características numa amostra mesmo que expressem de forma diferente, nesse método não é necessário consenso e treinamentos na seleção dos avaliadores (OLIVEIRA; BENASSI, 2010). Com o objetivo de aumentar o desenvolvimento de termos descritores individuais e a interpretação dos resultados, algumas modificações foram aplicadas ao Perfil Flash, conforme relatado por Liu et al. (2016) e Di Monaco et al. (2015). Essas modificações consistiram em uma sessão preliminar, usada para permitir que os avaliadores analisassem antes as diferenças ou semelhanças entre as amostras.

Basicamente o procedimento do Perfil Flash pode ser dividido em 3 etapas. A 1º é para o avaliador identificar as diferenças e as similaridades entre as amostras, a 2º é uma entrevista individual para gerar os atributos e as suas respectivas definições e na 3º o avaliador ordena as amostras em ordem crescente de intensidade para cada um dos atributos de acordo com a sua própria ficha de avaliação que foi gerada anteriormente. Todo esse procedimento é feito em apenas uma única seção com o avaliador e pode durar de 30 a 60 minutos dependendo de cada avaliador (TERHAAG; BENASSI, 2010).

Os testes afetivos têm como objetivo medir o quanto uma população gostou de um determinado produto, avaliando a preferência ou a aceitabilidade dos mesmos (DUTCOSKY, 2019). Com o teste de ordenação da preferência é possível avaliar três ou mais amostras, que são ordenadas (crescente ou decrescente) em relação à intensidade de algum atributo ou de sua preferência de modo geral. Quando o teste de preferência é realizado em laboratório, recomenda-se no mínimo 30 avaliadores, pela soma das ordens obtidas é feita a avaliação estatística pelo teste de Friedman e pela tabela de Newell e MacFarlane para o cálculo do resultado final (IAL, 2008).

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CAPÍTULO 2 - CHARACTERIZATION OF ACID-THINNED CASSAVA STARCH AND ITS PASTE AND TECHNOLOGICAL PROPERTIES IN SUGAR SOLUTION

Characterization of acid-thinned cassava starch and its paste and technological properties in sugar solution

HIGHLIGHTS

• Particle size determination and the span detected granules agglomeration after acid hydrolysis.

• Higher gelatinization temperature and no detected viscosity increase in the RVA with sugars solution.

• The acid-thinned cassava starch had properties adequate to gummy candies production.

ABSTRACT

Cassava is a commodity high in carbohydrate and a source of commercial starch but for certain applications the starch needs to be modified. Acid hydrolysis is a type of chemical modification that allows the starch to become suitable for confectionary applications being gum candy a common product. The objective of this study was to obtain acid-thinned cassava starch, describe its characteristics and investigate the paste and technological properties in the presence of a mixture of sugars as used in candy industry (sucrose and glucose syrup). Electron scanning microscopy and polarized light microscopy did not visualize any alteration in granule form or size. Particle size determination and span detected starch granules agglomeration after the hydrolysis and the X-ray spectrum showed increase in crystallinity. In sugar solution absorption, swelling power at 90ºC and gelatinization temperature increased, in the RVA there was no detected viscosity increase even in high solids solution, a desirable property for this type of modification. The acid hydrolysis did not alter granule morphology, the paste and technological properties were changed after acid hydrolysis and provided desirable functional properties for application in confectionary products especially in gum candy.

Keywords: Glucose syrup. *Manihot esculenta* Crantz. Starch Agglomeration. Sucrose. X-Ray Diffraction.

2.1. INTRODUCTION

Cassava (*Manihot esculenta* Crantz) is an important food source in Africa, Asia, South America and the Caribbean, and the plant cultivation is extensive. The root grows under adverse climatic conditions and in poor soils and it is an important source of industrial starches (Abass et al. 2018; Aristizábal, García, & Ospina; 2017). Main properties of starch suspensions, when cooked are the gelatinization temperature and final texture, because they may determine the best applications, but for some industrial applications the starch must be modified by chemical, enzymatic, or physical methods to have adequate properties.

There are innumerous types of modified starches in the market for use in food, pharmaceutical and paper industries (Monroy, Rivero, & García, 2018). The most studied and utilized is corn starch but cassava starch although commercially available has fewer reports of its properties after modifications and deserves more studies. Acid hydrolysis is a chemical modification that uses strong acids diluted, heated in temperature bellow gelatinization temperature, during a variable amount of time, resulting in a product denominated acid-thinned starch (ATS) (Biduski et al., 2016).

The characteristics of the ATS are the maintenance of its granular structure when viewed in the microscope, has no increased viscosity in high solids solutions when hot and forms a tender and chewable gel when cold (Zhang et al., 2017; Ulbrich, Lampl, & Flöter 2016). Industrial application of this acid-thinned starch is in the confectionary industry as a gelling agent especially in gum candies. There are very few reports in the literature on the production of gum candies with a starch source other than the traditional acid-thinned corn starch. Characteristics of alternative starch during and after cooking or the influence of other ingredients in the final quality of the candy are also sparse (Charoen, Savedboworn, Phuditcharnchnakun, & Khuntaweetap, 2015; Habilla & Cheng, 2015; Mutlu, Tontul, & Erbas; 2018).

Authors investigated the behavior of unmodified starches in the presence of different sugars but using one sugar at a time: corn (Sun, Xing, Qiu, & Xiong, 2014), wheat (Allan, Rajwa, & Mauer, 2018), wheat and cassava (Pourmohammadi, Abedi, Hashemi, & Torri, 2018). The main conclusions were increase in the gelatinization temperature and characteristics of the formed paste. In the confectionary industry sugars are used mostly in combination of sucrose and some type of syrup to control crystallization and to obtain the desired texture in the product. Thus, it is important to study the acid-thinned starch in the presence of sugar solutions that simulate the combinations used in the industry. The objective of this study was to obtain acid-thinned cassava starch, describe its characteristics and investigate the paste and technological properties in the presence of a mixture of sugars as used in candy industry (sucrose and glucose syrup).

2.2. MATERIAL AND METHODS

2.2.1. Materials

Unmodified cassava starch was Yoki®, sucrose was DoceSugar®, both locally commercially available and glucose syrup DE62 was Buffalo ® 1630 (Ingredion Brasil Ing Ind. Ltda) donated by DORI Alimentos SA (Rolândia, PR, Brazil).

2.2.2. Acid Hydrolysis of Cassava Starch

Acid-thinned cassava starch was prepared following the method of Zhang et al. (2017) with modifications. Starch slurry (40%, w/v) was prepared by mixing cassava starch with 0.1 M aqueous hydrochloric acid (HCl). The slurry was incubated in a water bath (Marconi MA 127/BO, Piracicaba, SP, Brazil) at 50 ºC, and allowed to react for 72 h (manual shaking at the beginning), the slurry was then adjusted to a pH of 7 using 0.1 M NaOH. Thereafter, the slurry was washed three times with distilled water, and the insoluble fraction was separated by centrifugation (Epperndorf AG Centrifuge 5804, Hamburg, Germany) 1500 x g for 10 min. Then the acid-thinned cassava starch was dried in an oven (Tecnal, TE-394/2, Piracicaba, Brazil) with air circulation at 50 °C for 20 h and ground in a Wiley mill (Basic IKA A11). Two batches were made with average of 90% yield.

2.2.3. Scanning electron microscopy

The scanning electron microscopy (SEM) micrographs were taken with FEI Quanta 200 microscope and images were obtained by XTM 2001 software (FEI Company, Netherlands) under a magnification of 5000 X. The samples were previously conditioned in a dissector with calcium chloride ($CaCl_2 \approx$ 0% RHE) for one week and later metalized with gold (99.6% purity) with a coating equipment (Sputter Coater SCD 050 BAL-TEC) at a coating rate of 0.51 Å/s for 98 s at a voltage of 40 mA and 5×10^{-1} mbar.

2.2.4. Light and polarized microscopy

Unmodified and acid-thinned cassava starches granules were analyzed by light microscopy (Olympus Optical Co., Ltd., Tokyo, Japan). Starch granules 100 mg were suspended in 900 mg of distilled water, a drop of starch suspension was spread on a microscope slide with a drop of glycerin. After 1 h at rest, the slide was then placed on the stage of a light microscope and analyzed for granule birefringence (using polarized light mode). A digital camera was attached to the microscope to capture the images, under a magnification of 400 X.

2.2.5. Particle size distribution and mean size

The particle size distribution of the unmodified and the acid-thinned cassava starches were determined with laser diffraction using a Mastersizer 2000 (Malvern Instruments Ltd., Malvern, Worcestershire, UK), for this analysis a small amount of the sample was dispersed in ethyl alcohol (99.5%). The measurement of the average granule size was determined based on the average diameter of a sphere of the same volume (diameter of De Brouckere D_{43}). All measurements were carried out twice.

2.2.6. X-ray diffraction

X-ray diffraction (XRD) patterns were obtained by using a X-ray diffraction (Shimadzu - XRD 7000, São Paulo, Brazil), with Cu radiation, sweep of 1 min^{-1} ranging from 3° to 50°, and a setting of 40 kV and 30 mA to show alterations in the crystallinity. Before analysis, the moisture content of the starches was equilibrated in a desiccator with 100% relative humidity. The relative crystallinity of the starches was determined following Nara and Komiya (1983) using Origin 8.0 software (Origin - version 8.0, Microcal Inc., Northampton, MA, USA). The graphs were placed between 2Θ angles of 5º and 35° and smoothed with the Adjacent Averaging tool. All measurements were carried out twice.

2.2.7. Water and sugar solution absorption index (AI)

Absorption index was according to Seibel and Beléia (2009) with modifications. A suspension of 1 g of unmodified and acid-thinned cassava starches in 30 mL of distilled water or sugar solution (SS): water, sucrose and glucose syrup (60:20:20) in previously tared centrifuge tubes. The suspension was stirred for 30 min on a horizontal shaker (Marconi MA830/A, Piracicaba, SP, Brazil) at 300 rpm at room temperature (about 25 ºC) and centrifuged (Epperndorf AG Centrifuge 5804, Hamburg, Germany) at 2.000 x g for 15 min. The supernatants were discarded, and the pellet in the tube was weighed. The IA is expressed in grams absorbed/g of the original sample. All measurements were carried out four times.

2.2.8. Swelling Power (SP) and Solubility (S%)

Swelling power and solubility were determined by using Leach, McCowen and Schoch (1959) with modifications. A suspension of starch slurry of 0.5 g in 30 mL of distilled water or SS, was made and heated in water-bath (Marconi MA830/A, Piracicaba, SP, Brazil) maintained at 90 °C for 30 min with constant stirring and cooled. The suspension was centrifuged (Epperndorf AG Centrifuge 5804, Hamburg, Germany) at 2.000 x g for 10 min and the supernatant collected in pre-weighed Petri dishes and evaporated at 105 °C for 4 h. The dried Petri dishes were weighed for calculation of solubility. The weight of wet sediment in centrifuge tube was noted to determine the swelling power. All measurements were carried out four times.

2.2.9. Thermal behavior (DSC)

The determination of the thermal behavior of unmodified and acid-thinned starches using DSC was as described by Franco, Cabral and Tavares (2002) with modifications. The measurements were carried out using TA60 - Shimadzu calorimeter (Shimadzu, São Paulo, Brazil). Three mg of starch sample and threefold the amount of distilled water or SS (9 µL) were added to a aluminum pan, hermetically sealed and stored for at least 14 h in a fridge prior to characterization. DSC measurements were performed with scanning rate of 5 ºC/min from 25 to 100 ºC. An empty aluminum capsule was used as a reference. All measurements were carried out four times.

2.2.10. Determination of the pasting properties

Pasting characteristics of unmodified and acid-thinned cassava starches were determined using a Rapid Visco Analyzer (RVA 4500, Perten, Macquarie Park, Australia). The starch slurries 10% w/w, with distilled water or SS (28 g total weight) were held at 50 ºC for 1 min, heated to 95 ºC at a rate of 6 ºC / min, and held at 95 ºC for 5 min, then cooled to 50 ºC at a rate of 6 ºC / min, and held at 50 ºC for 2 min. The measurements were carried out four times.

2.2.11. Gel strength measurement

Gel strength of unmodified and acid-thinned cassava starches were measured by a TA.XT Plus Texture Analyzer (TA XT Plus Extended M eight, UK). The starch gel 10% w/w, with distilled water or SS, heated until complete dissolution of the starch and held for 5 minutes with constant stirring agitation in heating plates, then placed in 50 mL plastic cups and held in the fridge for 24 h before analysis. The procedure described by Cui, Fang, Zhou and Yang (2014) was used, with a cylindrical probe (P/0.5, 12.7 mm in diameter), which was programmed to move downwards for a compression ratio of 40% of the original height at a speed of 2 mm/s and a pre-test speed of 5 mm/s, a post-test speed of 5 mm/s as well as a trigger force of 4 g. The maximum force (N) required to compress the sample was recorded as gel strength. All measurements were carried out eight times.

2.2.12. Paste clarity

To determine paste clarity, it was used the method of Craig Maningat, Seib and Hoseney (1989) with modifications. Initially, 1% (w/v) starch slurry with distilled water or SS was prepared in test tubes and heated in a boiling water bath at 99º C (Marconi MA 127/BO, Piracicaba, SP, Brazil) for 1 h with constant stirring. The tubes were cooled and (% T) of gelatinized starch solutions were measured at 650 nm against distilled water or SS as a blank using a UV-visible spectrophotometer (model Libra S22, Biochrom, Cambridge United Kingdom). All measurements were carried out four times.

2.2.13. Statistical analysis

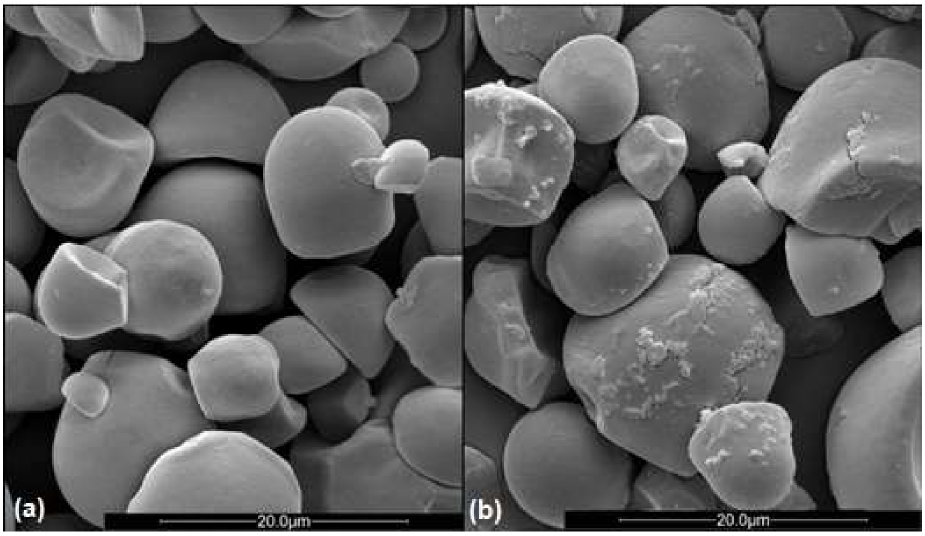
All numerical results are averages of at least two independent replicates, and values are represented as the mean ± standard deviation. Statistical significance analysis was by Statistica 7.0 software (Statsoft, Tulsa, USA) applying analysis of variance (ANOVA) and Tukey's test ($p \leq 0{,}05$).

2.3. RESULTS AND DISCUTION

2.3.1. Acid-thinned cassava starch characterization

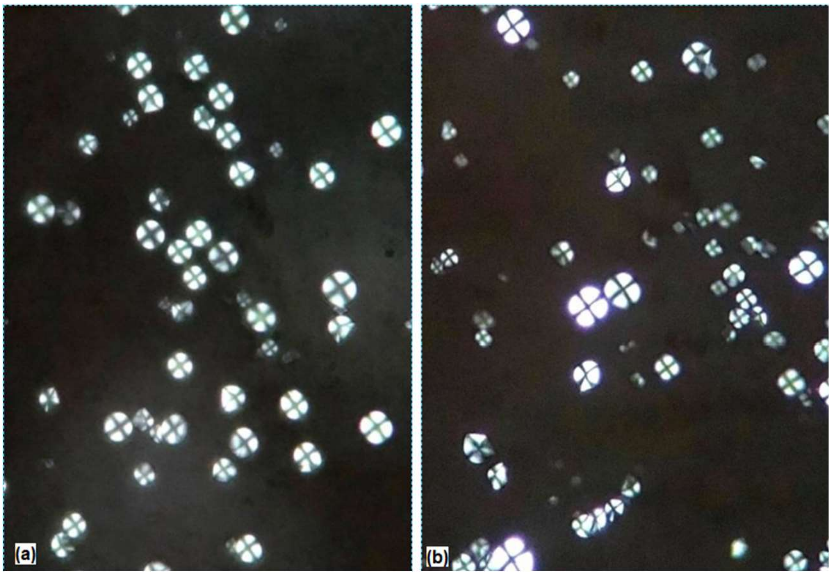
Cassava starch granules are of varied forms that may be described as spherical and oval with smooth or depressed surfaces and generally have a truncated end. The acid treatment with diluted hydrochloric acid did not alter granule form but showed some fissures and surface erosion when compared with the unmodified starch (Fig. 2.1). Ulbrich, Lampl and Flöter (2016) described similar alterations in SEM images in potato starch modified by 0.54 M HCl. The powdered material on the surface of granules is probably some of the hydrolyzed material not released from the surface during washings or discarded in the water after the acid treatment, that tend to adhere to the surface (LeCorre, Bras & Dufresne, 2012; Hernández-Jaimes et al., 2014).

Fig 2.1. Scan electron microscopy of unmodified (a) and acid-thinned (b) cassava starches granules under 5000 X increase.



In the polarized light microscopy, the granules had the Maltese cross intact like the unmodified granule and the birefringence was similar in the two samples (Fig. 2.2). According to Kumar et al. (2016) birefringence intensity depends on the granule size, relative crystallinity and on the microcrystals orientation from the hilum towards the surface. So, there were no apparent alterations when comparing unmodified and acid-thinned cassava starch granules when examined by polarized light microscopy.

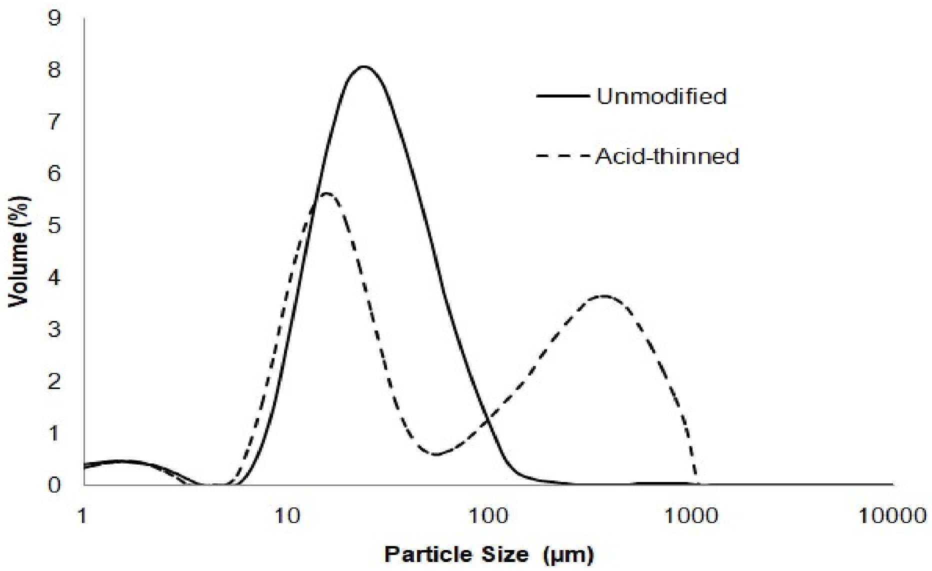
Fig 2.2. Polarized light microscopy of unmodified (a) and acid-thinned (b) cassava starches granules under 400 x increase.



Unmodified starch had a medium size of 31±2.8 μm, and according to the literature review of Zhu (2015), the size of cassava starch may vary from 2 to 32 μm. The acid-thinned cassava starch had the average diameter of 166.8±39.4 μm, and this significant increase in granule size may be confirmed by the granule size distribution (Fig. 2.3). Superficial areas (m^2/g) were in the average 11.2±0.2 and 14.4±3.1, for the unmodified and acid-thinned starch with a significant difference between averages. The values for surface areas may indicate the agglomeration of different sizes of granules due to, possibly starch granules agglomeration during the analysis, that expanded the determined area, since they were measured as individual larger granules.

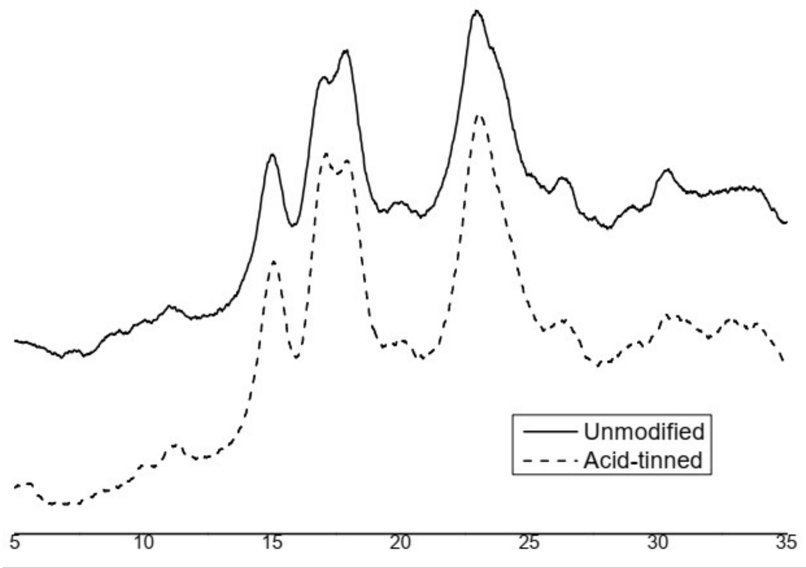
Similar effect occurred with corn starch treated with sulfuric acid 3.16 M for 2 h at 57.5 ºC in the report of Hernández-Jaimes et al. (2014), that observed an increase in particle size distribution and confirmed agglomeration after the hydrolyzed material was sonicated and the granules separated, decreasing the average size of particles. The higher the span the more heterogeneous or higher polydispersity is associated with the granule size distribution (Hijo et al., 2015). Span value was 2.0±0.1 for unmodified starch and 13.6±6.9 for the acid-thinned starch confirming that the acid-thinned starch is more heterogeneous in size and had a bimodal distribution.

Fig 2.3. Cassava starch granule size distribution before and after acid hydrolysis.



Unmodified and acid-thinned starches had relative crystallinity of 15,69±0.3 and 18,77±0.5%, there was a significant difference between the samples. The higher peaks for both samples were at 2θ = 15º, 17º e 23º (Fig. 2.4) characteristic of type A crystals (Jiang et al., 2018). Zhu (2015) described in his review, values between 15.3 and up to 49% in relative crystallinity for cassava starch with crystal patterns of type A and C_a, a mixture of A and B with higher proportion for type A. Beninca et al. (2013) found higher values of relative crystallinity of untreated cassava starch (22,65%), cassava starch treated with HCl 0.15 mol L−1 at 30 ºC (29,79%) and cassava starch treated with HCl 0.15 mol L−1 at 50 ºC (33.10%).

Fig 2.4. X ray diffraction of cassava starch before and after modification.



For waxy corn starch, Jiang et al. (2018) observed increased in crystallinity from 24.48% to 25.96% and then decreased to 25.20% with the increase of hydrochloric acid concentration (0.25 to 1.5 M), they described that acid initially acts making the amorphous region shorter, causes chains rearrangement forming a more stable crystalline structure with increased crystallinity. As the concentration of acid continues to increase, the crystalline area begins to be attacked.

2.3.2. Paste and technological properties of the acid-thinned cassava starch in sugar solution (SS)

To simulate an actual application of the acid-thinned starch in gum candy a solution of water, sucrose and glucose syrup (60:20:20) was used in determining absorption index, swelling power and solubility (90 ºC), DSC, RVA, gel strength and paste clarity. The acid-thinned cassava starch had higher absorption, but lower swelling power than the unmodified associated to higher solubility in water, all characteristics desirable for candy application (Table 2.1).

Table 2.1– Results for absorption index (AI), swelling power (SP) and solubility (S) at 90ºC of unmodified and acid-thinned starch (in water) and acid-thinned SS (in sugar solution).

Samples	AI (g/g)	SP (g/g)	S (%)
Unmodified	0.94±0,03[c]	8.42±0,68[a]	12.17±4,69[b]
Acid-thinned	1.29±0.12[b]	0.80±0.15[c]	34.11±5.74[a]
Acid-thinned SS	1.85±0,07[a]	1.35±0,30[b]	-

Results are average (n=4) ± stand deviation *SS= Sugar solution: water:sucrose:glucose syrup (60:20:20).

Ali & Hasnain (2014) also found similar behavior for swelling power and solubility (at 90ºC measured in water). Higher SP values for native sorghum starch, lower SP values for acid-thinned sorghum starch (hydrolysate with 0.1 M HCl), and for solubility, higher values for acid-thinned sorghum starch compared to native starch. Those results were attributed to the hydrolysis of the glycosidic links along the molecules resulting in lower swelling capacity, but at the same time a higher solubility due to the formation of lower molecular weight soluble fractions. There were no works that evaluated AI and SP of acid-thinned starches in sugar solution. The acid-thinned cassava starch in SS, had an increase in AI and SP, due to the higher density of the SS (1.14 g/cm^3) in comparison to water density. Both are important functions for the application of the acid-thinned starch.

Unmodified starch had lower peak gelatinization temperature in the DSC compared to the acid-thinned starch, measured both in water or sugar solution. Initial peak gelatinization temperature was different for all the samples, the same occurring for the final peak temperature, both being the highest for sugar solution (Table 2.2). Ulbrich, Beresnewa-Seekamp, Walthe, & Flöter (2016) using acid-thinned corn starch modified with (0.72 M HCl) for 4 and 24 h of hydrolysis detected increase in the peak temperature of gelatinization and attributed to the rearrangement of glycosidic chains that hamper water penetration in the granules. Another explanation for the increase in gelatinization temperatures for acid-thinned cassava starch, may be related to complexation of starch granules detected in the results of particle size, surface area, span and starch granule size distribution. Enthalpy was not different for the unmodified and acid-thinned starch in water, or in the sugar solution, but the variation of values was high.

Table 2.2 - Thermal properties measured by differential scanning calorimetry of unmodified and acid-thinned starch (in water) and acid-thinned SS (in sugar solution).

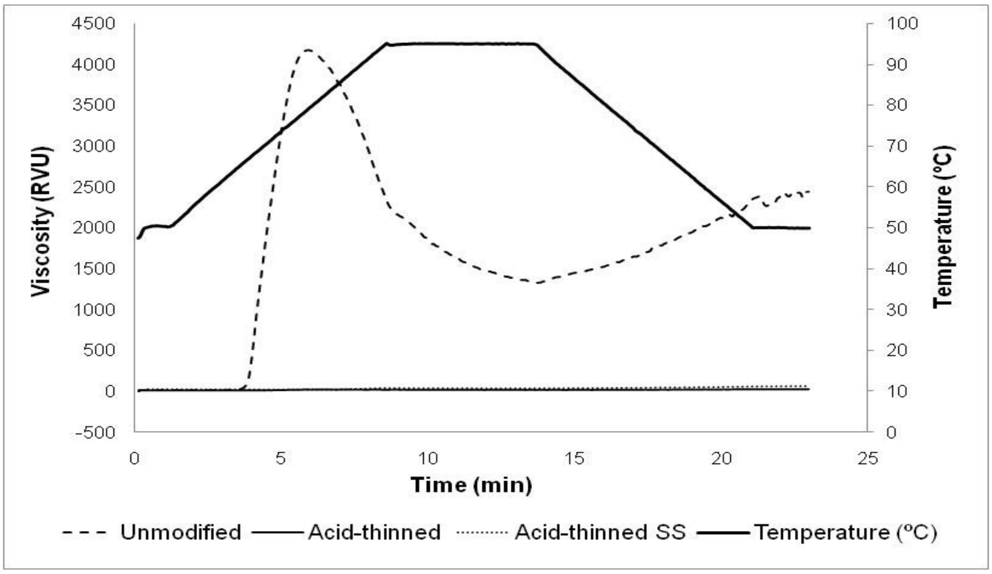
Samples	T_p	T_o	T_c	ΔH J/g
Unmodified	77.1±3.1^b	74.7±1.4^c	77.9±2,1^c	0.67±0.4^{ab}
Acid-thinned	81.7±1,8^a	78.4±2.9^b	82.2±2.7^b	1.15±0.8^a
Acid-thinned SS	84.8±3.1^a	83.2±2.6^a	86.5±3.8^a	0.34±0.2^b

The results are means (n = 4) ± standard deviation Tp = peak temperature; To = "onset" initial peak temperature; Tc = "endset" final peak temperature; ΔH = enthalpy variation; * SS = sugar solution: water: sucrose: glucose syrup (60:20:20)

There were no data in the literature for thermal properties of acid-thinned starch in sugar solution but the in the report of Allan, Rajwa, & Mauer (2018) the addition of 19 different sugars or polyols increased the gelatinization temperature of native wheat starch especially for sugars with 12 carbons. Enthalpy was higher for only three of the 79 sugars solutions or polyols compared to water gelatinization in the study and there was no relationship between gelatinization temperature and enthalpy. It is possible that sugar may form intermolecular associations with the starch since they are similar chemical molecules. Another explanation is that in the sugar solution there is a lower amount of available water that may hamper the gelatinization. Increase, decrease and no alteration of enthalpy have been reported during gelatinization of starch in the presence of sugar solutions (Li, Li & Gao, 2015; Pourmohammadi, Abedi, Hashemi, & Torri, 2018; Ahmad & Williams, 1999).

RVA viscosity with unmodified starch at 10% was typical while acid-thinned starch had no detected viscosity in water or sugar solution (Fig. 2.5). These results are related to the lower swelling power of the acid-thinned cassava starch (table 2.1), since the starch was not able to absorb water and swell, then it did not develop detectable viscosity in RVA. Zhang et al. (2017) found the same behavior for acid-thinned waxy corn starch. It was suggested that this may be attributed to the hydrolysis of starch polymers and that lower molecular chains have lower viscosity (Wang & Copeland, 2015; Zhang et al., 2017).

Fig. 2.5 - Pasting profiles (10%) of unmodified, acid-thinned (in water) and acid-thinned SS (in sugar solution: water, sucrose and glucose syrup - 60:20:20).



Gel strength of all samples were different, unmodified starch had the highest force (0.259±0.05 N), followed by the acid-thinned starch gelled in the sugar solution (0.131±0.03 N) and the lowest for the acid-thinned starch gelled in water (0.080±0.01 N), demonstrating that the sugars are important in contributing to the gel strength of acid-thinned starches. Sorghum starch acid hydrolyzed had comparative values for gel strength at 8%, (0.18 N) for the unmodified and (0.12 N) for the acid-thinned (Ali & Hasnain, 2014). Gel starch is formed by the association or reorganization of leached amylose chains through hydrogen bonding, for the retention of water between the chains of the starch network and the swollen granules that are embedded on the continuous amylose matrix. The acid-thinned starches have reduced gel strength, probably because with treatment, breakdown occurs in some intermolecular links in the chains of amylose and amylopectin (Ali & Hasnain, 2014; Gunaratne, Ranaweera & Corke; 2007).

Unmodified starch had light transmission of (68.0±1.8 %T) while the acid-thinned starch gelled in water had a lower value (18.7±1.5 %T), possibly because the soluble fraction is higher in this starch. Gelling in the sugar solution increased light transmission (50.8±3.4 %T), a result attractive for the application of the starch especially in the productions of confectionary products that have the addition of food coloring agents and translucent properties are desirable.

2.4. CONCLUSION

Acid hydrolysis did not alter granule morphology but there was a tendency for the starch granules to agglomerate. The paste and technological properties were changed after acid hydrolysis. Acid-thinned starches had an increase in relative crystallinity, lower swelling power, higher solubility, gelatinization peak temperature was higher but had no detected viscosity in the RVA. Gel strength and paste clarity was higher for the samples made with sugar solution. All these results are in accord to requirements for acid-thinned starches and provide desirable functional properties for application in confectionary products, especially in gum candy.

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CAPÍTULO 3 - GUMMY CANDIES PRODUCED WITH ACID-THINNED CASSAVA STARCH

Gummy candies produced with acid-thinned cassava starch

HIGHLIGHTS

- The type and/or amount of starch influenced physical and sensory characteristics of the candies.
- The use of acid-thinned cassava starch in the production of gummy candies is promising.
- Gummy candies produced with acid-thinned cassava starch at 12% are equally preferred as standard corn starch gummy candies at 8%.

ABSTRACT

In the production of gummy candies, acid-thinned starch acts as the gelling agent that contributes to the structure and final texture of the candy where softness and chewiness are desirable. The objective of this work was to apply acid-thinned cassava starch in the formulation of gummy candies and compare them by physical and sensory analysis with control candies produced with acid-thinned corn starch. The gummy candies were produced with 8% of acid-thinned corn starch and 12 and 16% of acid-thinned cassava starch. Results of moisture, pH, water activity and adsorption curves were similar for all formulations. The different starch sources and/or amount influenced in resulting color and texture profile, hardness and chewiness were similar for candies with 12% cassava starch and 8% corn starch. The higher content of cassava starch (16%) led to gummy candy with almost twice hardness and chewiness. In the Flash Profile assessors noticed the same color and texture differences found in the physical analyses. For the Preference-Ranking test, there was no difference between gummy candies with corn starch (8%) and cassava starch (12%), which were the preferred ones. It was possible to obtain gummy candies with acid-thinned cassava starch at 12% and it is promising, as it generated gummy candies equally preferred in comparison with the candy control.

Key words: Physical Analyses. Texture Profile. Flash Profile. Preference-Ranking.

3.1. INTRODUCTION

Cassava is an important source of starch, for example, in Africa, cassava crop is an incentive for rural development, poverty reduction, economic growth and food security. There is also acknowledgment of cassava crop in conditions of climate change adaptation strategies, especially in countries that regularly have periods of drought. According to biannual report on global food markets from FAO, the world balance production of cassava is 277.1 million tonnes of fresh root (FAO, 2018).

Starch is the second most abundant natural polysaccharide stored in plants, the first being cellulose. It is one of the main sources of energy for humans, as well as a valuable material for the food industry (Ren, Zhang, Zhang, & Guo, 2015). However modified starches are now mostly used, and the main reason is the differentiated functional properties of such starches, like increased stability under different processing conditions. Within the confectionery area, a specific example of starch modification can be highlighted for use in soft candies and/or gummy candies, starches that are required to provide a soft texture (Luallen, 2018).

For application in the gummy candy industry, a chemical modification is necessary, the acid hydrolysis of native starch. The acids generally used in this process are hydrochloric or sulfuric acids diluted to a certain extent and used for variable periods of time and heated below the gelatinization temperature, the final starch is named acid-thinned starch (ATS) (Wang & Copeland, 2015). There are several studies on acid modification of native starch, and most research use corn starch, waxy (Zhang et al. 2017) or regular corn starch (Jiang et al. 2018). The commercially available industrial acid-thinned starch is also corn starch. There might be an interest to in investigating other sources of starch, which can generate products with different characteristics, or which have a similar application.

Soft or gummy candies are usually composed of solutions rich in sucrose and glucose syrup, together with gelling agents, such as pectin, starch or gelatin (Marfil, Anhê &Telis, 2012; Delgado & Bañón, 2015). They are complex gel systems in which various associations occur among the ingredients in a matrix (Pocan, Ilhan & Oztop, 2019). In gummy candies, the texture depends mainly on the formation of the gel network that is strongly affected by the nature of the gelling agent used in the formulation (Marfil, Anhê & Telis, 2012; Pocan, Ilhan & Oztop, 2019). The ATS contributes to the final structure of the gummy candies while simultaneously giving softness and chewiness, characteristics desirable in soft candies (Delgado & Bañón, 2015).

For a complete evaluation of a product, it is important to carry out physical and sensory analyses. Instrumental methods such as texture analyzers help to understand the physical character of a food (Bridges, Smythe & Reddrick, 2017). The Flash Profile is a descriptive sensory methodology that is being studied in the academic area and used in industries. This methodology is considered faster than traditional methods and brings reliable results on the sensory profile of a product (Liu, Bredie, Sherman, Harbertsone, & Heymann, 2018). The objective of this work was to apply acid-thinned cassava starch in the formulation of gummy candies and compare them by physical and sensory analysis with control candies produced with acid-thinned corn starch.

3.2. MATERIAL AND METHODS

3.2.1. Materials

Unmodified cassava starch Yoki®, sucrose DoceSucar®, orange flavor essence Arcolor®, orange colorant Mix® and citric acid Fmaia locally commercially available, acid-thinned corn starch Candymil ®, glucose syrup BUFFALO® 1630 -, both are Ingredion® donated by DORI Alimentos SA (Rolândia, PR, Brazil).

3.2.2. Acid Hydrolysis of Cassava Starch

Acid-thinned cassava starch was prepared following the method of Zhang et al. (2017) with modifications. Starch slurry (40%, w/w) was prepared by mixing cassava starch (80 g) with 0.1 M aqueous hydrochloric acid (HCl). The slurry was incubated in a water bath (Marconi MA 127/BO, Piracicaba, SP, Brazil) at 50 ºC, and allowed to react for 72 h, the slurry was then adjusted to a pH 7 using 0.1M NaOH. Thereafter, the slurry was washed three times with distilled water, and the insoluble fraction was separated by centrifugation (Epperndorf AG Centrifuge 5804, Hamburg, Germany) 1500 x g for 10 min. Then the acid-thinned cassava starch was dried in an oven (Tecnal, TE-394/2, Piracicaba, Brazil) with air circulation at 50 ºC for 20 h and ground in a Wiley mill (Basic IKA A11) with 90% yield.

3.2.3. Gummy candies production

Three artificially orange-flavored gummy candies formulations were prepared: one with 8% commercial acid-thinned corn starch (control) and two with concentrations of 12 and 16% acid-thinned cassava starch (Table 3.1). Acid-thinned starch, sugar and glucose syrup suspension was cooked until a clear paste was evident. Then was cooked with continuous stirring until a soluble solid content of 65 ºBrix measured hot in a digital pocket refractometer (Atago PAL-BX/RI, Ribeirão Preto, Brazil). The heating was turned off, and citric acid, orange flavor and orange colorant were added. The formulations were deposited with the aid of a 7.5 mL measuring spoon, in silicone forms dusted with unmodified cassava starch and oven-dried at 45 ºC for 72 h. The candies were kept in plastic bags and in vacuum-sealed jars for up to three weeks. All analyses were done in two different batches.

Table 3.1 - Formulation of gummy candies with acid-thinned corn starch (control) or acid-thinned cassava starch.

Ingredients	CO8 = Corn 8%		CA12 = Cassava 12%		CA16 = Cassava 16%	
	%	**Content**	**%**	**Content**	**%**	**Content**
Water (g)	58	136	54	127	49	117
Acid-thinned starch (g)	8	19	12	28	16	38
Glucose syrup (g)	17	40	17	40	17	40
Sugar (g)	17	40	17	40	17	40
Citric acid (g)	0.5	1.1	0.5	1.1	0.5	1.1
Orange flavor (µL)	-	240	-	240	-	240
Orange colorant (µL)	-	120	-	120	-	120

3.2.4. Physical analysis of gummy candies

The moisture was determined using a Karl Fischer automatic titrator (Schott, Titroline KF). Samples with 0.5 g of finely grounded candies were added into the KF titrimetric chamber containing low-water methanol/formamide mixture 2:3 as the solvent. After the complete dissolution, Karl Fischer reagent (pyridine-free, containing iodine, sulfur dioxide and imidazole dissolved in methanol) was pumped to the chamber until all the water of solution was titrated. The titration was finished when only free iodine remained causing ionic conduction, detected by the double platinum pin electrode. The instrument was calibrated determining the average titer strength of the KF titrant against 30 µL distilled water, until the standard deviation of the average was less than 1%. Moisture measurements were carried out four times.

The pH measurements were determined in a One-hand pH/temperature measuring instrument (Testo 205, Lenzkirch, Germany). The water activity (Aw) was measured using an Aqualab 4 TEV digital hygrometer (Decagon, Pullman, USA) at 25 ºC. Measurements of pH and Aw were carried out four times. A colorimeter Konica Minolta® CR-400 (Tokyo, Japan) with D65 illuminant was used to determine the color parameters (L*, a*, b*) according to the CIELab system. The H* hue was calculated (arc tang (b*/a*)). In total, eight measurements were made for each sample.

Samples were subjected to texture profile analysis (TPA), using a TA-XT Plus texture analyzer (Stable Micro Systems, Surrey, England) with a 35 mm diameter cylindrical aluminum probe. Measurements were conducted at a pre-test speed of 1.0 mm/s, post-test of 10.0 mm/s and test at 2.0 mm/s with a compression rate of 50%, the average size of the candies was 10 mm high by 25 mm length. From the TPA curve, texture characteristics such as hardness, chewiness, adhesiveness and springiness were determined. Eight measurements were made for each sample.

The results of the analysis of moisture, pH, Aw, color and texture are the mean±standard deviation, and are averages of at least two independent replicates. Statistical significance analysis was performed using Statistica 7.0 software (Statsoft, Tulsa, USA) and applying analysis of variance (ANOVA) with Tukey's test ($p \leq 0,05$).

The adsorption isotherms were collected in an Aw and isotherm generator (Aqualab model VSA 1102, Pullman, WA). Adsorption curves were constructed, followed by desorption curves at 25 ºC. Finally, three mathematical models were applied to fit the curve: the double log polynomial (DLP) model, the Brunauer, Emmet, and Teller (BET) model, and the Guggenheim, Anderson, de Boer (GAB) model. The data adjustment used the equipment's own software (SorpTrac Data Analysis Tool 1.14), and the coefficient of determination (R^2) was calculated.

3.2.5. Sensory analysis

This study was authorized by the Ethics Committee of Universidade Estadual de Londrina (Certificate of Ethical Evaluation Presentation 36840214.0.0000.5231). All assessors were gummy candies consumers, and before the trials, they answered a self-administered questionnaire on socio-demographic data and consumption habits. Tests were conducted in a sensory analysis laboratory, in individual booths, under white light. Sensory analyses used a complete randomized block design. The samples were presented with a code with three randomized digits and assessors were required to clean the palate with water between samples.

For the Flash Profile test, eighteen consumers (14 females and 4 males) were recruited. Most participants (72%) aged between 25 and 35 years old and 28% under 25 years old, 83% graduate students and 17% undergraduate; they were candies and sweets regular consumers, with 61% consuming 1 to 3 times a week. The test was applied according to Terhaag and Benassi (2010), the three candies were simultaneously served, and the assessors were requested to record attributes considering the similarities and differences among samples regarding appearance, aroma, flavor and texture (lightly squeezing the candy with the fingers and mouthfeel perceptions).

The assessor was then interviewed, and an individual score sheet and a corresponding list of attributes definition was defined for each assessor. Once again gummy candies were simultaneously presented, and the assessors ordered the samples by the increased intensity of each attribute. The data were analyzed by the Generalized Procrustes Analysis, using the software Senstools version 2.3.28 (OP & P Product Research, Utrecht, Netherlands). Data were provided as 18 individual matrices (one per assessor) with three lines (samples) and a different number of columns ranging from 7 to 11 (attributes). The criterion for choosing the most relevant attributes was the high correlation value ($r \geq |0.80|$) with dimensions 1 and 2 of the sample configuration for each assessor.

To determine which gummy candy formulation (CO8, CA12 and CA16) was preferred by the assessors a Preference-Ranking test was performed. Whereby each assessor was asked to evaluate the samples, considering overall preference. They were asked to rank samples based on their preferences, from 1 being ‘most preferred’ to 3 being ‘least preferred’. Additionally, the assessors were asked to justify their choices. Overall differences among ranked samples was analyzed using Friedman test, the minimum significant value (at the level of 1%) for difference was obtained from Newel and MacFarlane (1987).

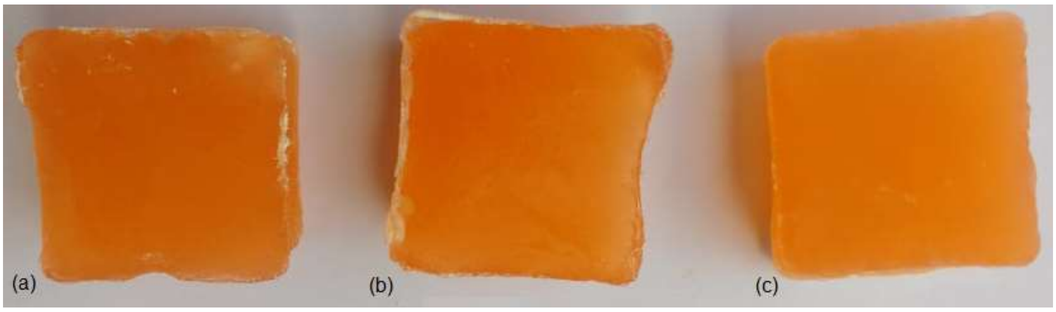
3.3. RESULTS AND DISCUSSIONS

3.3.1. Physical characterization of gummy candies

Industrially produced gummy candies are made with acid-thinned corn starch, considered the standard formulation, but after the acid hydrolysis of the cassava starch, it was possible to produce gummy candies formulated with this acid-thinned cassava starch (Fig. 3.1). Preliminary tests were carried out to define the final formulations of the gummy candies, based on the study by Habilla, Sim, Aziah, and

Cheng (2011), who used 6.9% acid-thinned corn starch and konjac or psyllium powder in gummy candy formulations. The tests started with 6% starch in the formulations, but with that percentage, the candies became too soft, and it was not possible to remove them from the molds after drying. It was necessary to use a higher percentage of starch so that the gummy candies could be released from the molds. Thus, the percentages of 8% for acid-thinned corn starch, 12 and 16% for acid-thinned cassava starch were defined.

Fig 3.1. Samples of gummy candies made with acid-thinned starch, (a) corn – 8% (b) cassava – 12% and (c) cassava – 16%.



There was no difference in moisture, pH or Aw among the three formulations of gummy candies (Table 3.2), that had mean values of 16.4±0.5, 2.6±0.2 and 0.65±0.02, respectively. The values of moisture and Aw are within the considered standard for gummy candies, which should be 15 to 20 g/100 g and from 0.5 to 0.75, respectively. Gummy candies must be stored to maintain these parameters as they tend to lose moisture and harden if stored in a dry place (Ergun, Lietha & Hartel, 2010). In pear-flavored gummy candies produced with alginate and pectin, Avelar and Efraim (2020) reported similar values of moisture (15 to 17 g / 100 g), higher pH (3.4 to 3.9) and similar values for Aw (0.58 to 0.67).

Table 3.2 -Results of the physical analyses of the gummy candies.

Reviews	CO8	CA12	CA16
Moisture (g / 100g)	17.0±1.4[a]	15.9±1.0[a]	16.3±0.7[a]
pH	2.4±0.3[a]	2.6±0.3[a]	2.7±0.4[a]
Aw	0.63±0.04[a]	0.65±0.03[a]	0.67±0.03[a]
Color			
L*	49±2[a]	46±1[b]	45±3[b]
H*	58±4[a]	54±4[b]	51±5[b]
Texture			
Hardness (N)	118±9[b]	124±14[b]	252±32[a]
Chewiness(N)	46±4[b]	50±10[b]	95±14[a]
Adhesiveness (N)	0.15±0.02[b]	23.5±5.4[a]	0.25±0.06[b]
Springness	0.66±0.04[c]	0.84±0.03[a]	0.75±0.04[b]

Gummy candies produced with acid-thinned starch: CO8 - corn 8%, CA12 -cassava 12% and CA16 cassava 16%. Moisture, pH and Aw were measured four times, duplicated for each batch, and color and texture were measured eight times, quadruplicate for each batch. Different letters in the same line indicate significant differences between samples by Tukey test ($p \leq 0.05$).

The candies were characterized as orange in color and intermediate brightness, gummy candies with 8% corn starch different for being lighter (higher value of L*) and more yellowish (higher value of H*) than gummy candies CA12 and CA16 produced with cassava starch. Similar values for hardness and chewiness were observed for the candies with 12% cassava starch and corn starch (8%), but the use of higher percentages of cassava starch (16%) led to gummy candy with almost twice the hardness and chewiness. Gummy candy with 12% cassava starch differed from those candies in that it was more adhesive and elastic.

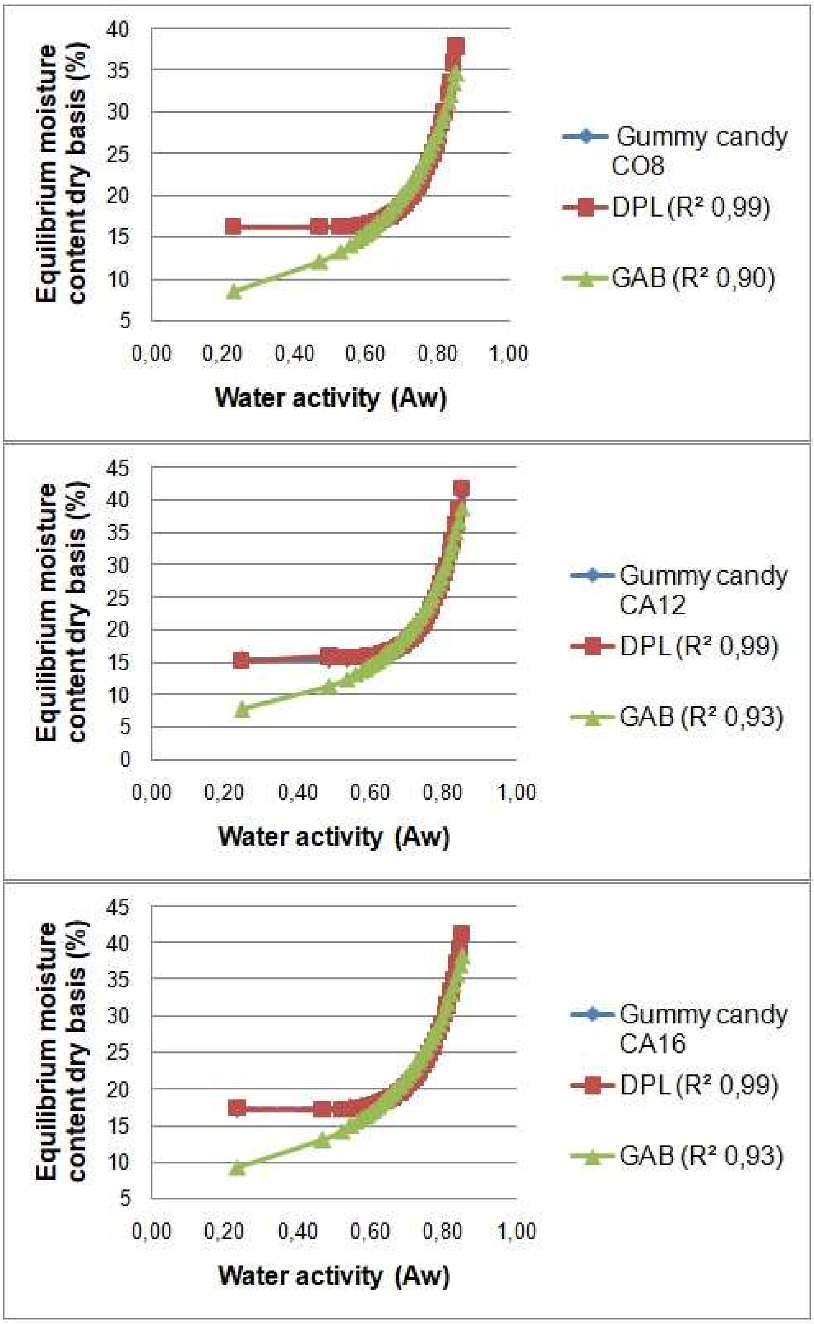
No data were found for gummy candies produced only with acid-thinned starch as the gelling agent. In candies produced with alginate and/or pectin, which are also polysaccharides but used in lower concentrations (2%), Avelar and Efraim (2020) had comparable values for springiness (0.49 - 0.82), lower hardness (6.24 -16.20 N), and chewiness (1.42 – 2.52), they used a cylindrical probe D/40 and compression rate of 40% for TPA analysis. Marfil, Anhê and Telis (2012), for candies (20 mm length and 31 mm diameter) produced with a mixture of gelatin and acid-thinned corn starch, using an acrylic probe (49.2 mm in diameter) and a 40% compression rate, found lower hardness (1.10 to 42.69 N), adhesiveness (0.35 to 2.08 N) similar to gummy candies CO8 and CA16 and higher values for springiness (0.94 to 0.98). Although the compression ratio is similar, these differences in results may be attributed to the different probes, conditions used, the different size of the candies, and they may also be due to the gelling agents used in the formulations of the candies, which directly influences the final texture.

Adsorptions curves for all samples at equilibrium had average values of Aw between 0.23 and 0.85, which corresponds to variations of moisture in dry basis between 8 and 39% (Fig. 3.2). The moisture contents of the gummy candies remained relatively stable up to values of 0.60-0.70 Aw, which is characteristic of sugary products (Ergun, Lietha & Hartel, 2010). As the relative moisture increased and Aw of the samples were higher than 0.70, there was a tendency to absorb ambient water. The average Aw values of the gummy candies were 0.65, which means that samples are already at the limit Aw for stability. In this case, it is recommended storage in packages that do not allow the exchange of humidity with the environment before consumption to prevent unwanted changes.

The adsorption curves of gummy candies are similar to type III isotherms obtained by Avelar, Silva, Azevedo, and Efraim (2019) for hard sugar-panned confections, which were made with fruit/vegetable-based concentrate and uvaia (*Eugenia pyriformis*) by-product. Additionally, in isotherms obtained by Witczak, Witczak, Socha, Stepien, and Grzesik (2016) for candied orange peel with sucrose and/or glucose/fructose-based syrups also had type III isotherms, despite being different products, this behavior is characteristic of products with a high content of low molecular weight sugars. Type III isotherm curves have a low and gradual increase in moisture content up to approximately 0.6 to 0.8 Aw, followed by a rapid and sharp increase in moisture content (Barbosa-Cánovas, Fontana Jr, Schmidt, & Labuza, 2007).

According to R^2, the model that best fitted the curves was the Double Log Polynomial Model (DLP). The Guggenheim, Anderson and Boer (GAB) model, despite having a relatively high R^2 value (from 90 onwards), the adsorption curve of GAB does not adjust at the same points as the sample curve.

Fig 3.2. Adsorption isotherms curves of gummy candies produced with acid-thinned starch (CO8 = corn 8%, CA12 = cassava 12% and CA16 = cassava 16%).



3.3.2. Sensory Evaluation of Gummy Candies

The Flash Profile resulted in a two-dimensional solution with a high explanation (95.2% of the variability) (Fig. 3.3). The panel's consensus can be confirmed by the low residue (4.8%) of the solution as well as by the low individual residual variance value of the assessors (between 0.02 and 0.70) (data not shown). As a comparison, Rezende, Benassi, Vissotto, Augusto, and Grossmann (2015), applying the Flash Profile under similar conditions (3 samples and 18 assessors), the first two dimensions accounted for 89% of the data variance.

The consensus plot shows the adequate separation of the samples in the first two dimensions (Fig 3.3). The number of attributes raised by the assessors was between 7 and 11, with an average of 9 attributes. The attributes best correlated (r ≥ |0.80|) with dimensions 1 and 2 for each assessor are described in Table 3.3, the most cited attributes were orange color, brightness, opacity, orange flavor, sweet flavor, acid flavor, softness, hardness and adhesiveness.

Fig 3.3. Two-dimensional consensus plot for gummy candies produced with acid-thinned starch (CO8 = corn – 8%, CA12 = cassava 12% and CA16 = cassava 16%).

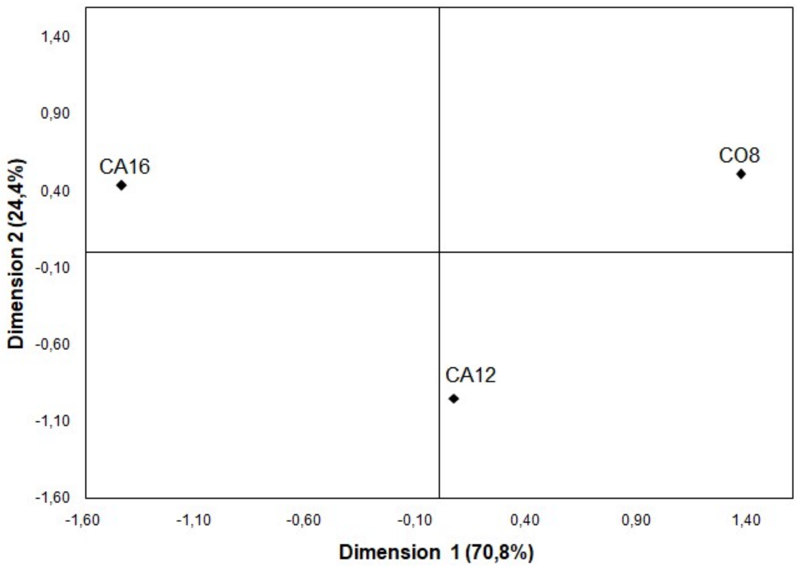


Table 3.3 - Attributes best correlated (r ≥ |0.80|) with dimensions 1 and 2 for each assessor.

Assessors	Dimension 1	Dimension 2
1	orange color (1); brightness (1); acidity (-1); orange flavor (1); hardness (-1), chewiness (1); adhesiveness (-1)	orange scent (-0.89)
2	orange color (1); grip (1)	opacity (-0.89); homogeneity of the surface powder (-0.89); sweet aroma (-0.84); sweet taste (-0.84); orange flavor (-0.84); citrus flavor (0.89), flour flavor (0.89); soft (-0.84); chewy (-0.84)
3	orange color (-1); homogeneous appearance (-1); orange flavor (-1); hardness (-1); stickiness (1); sweetness (-1); orange flavor (-1)	opacity (0.89); homogeneity / lumps (0.84)
4	orange color (1); brightness (1); superficial smooth texture (-1); hardness (-1); adhesion (-1)	orange flavor (-0.84); acid flavor (-0.84)
5	orange color (1); brightness (1); sticky aspect (1); firmness (-1); grip (1)	orange flavor (-0.84); sweet taste (0.84)

6	sweet aroma (-1); acid flavor (1); orange flavor (1); flour texture in the mouth (-1); gumminess (1); adhesive (1)	orange color (0.89); brightness (0.89); sweet taste (0.89); hardness (-0.89)
7	orange color (1); brightness (1); firmness (-1); adhesion (1); orange flavor (1); acid flavor (-1); sweetness (1)	elasticity (-0.84)
8	color (1); softness (1); sticky (-1); acid taste (1); orange taste (1); sweetness (1)	brightness (-0.84)
9	color (1); brightness (1), thickness (1); orange flavor (1); softness (1); orange flavor (1)	stickiness (-0.89)
10	orange color (1); thickness (1); porous surface (-1); opacity (-1); sweet taste (1); acid taste (1)	orange flavor (-0.84); orange flavor (-0.84); hardness (0.84); adhesiveness (-0.84)
11	orange flavor (1); orange flavor (1); sweet taste (-1)	orange color (-0.89); surface homogeneity (-0.98); acid flavor (-0.84); resistance (0.84); chewability (0.84); adhesiveness (0.84)
12	orange color (-1); shape / height (1); transparency (1); orange flavor (1)	chewiness (-0.89); adhesion (-0.89); hardness (-0.89); acidity (-0.89)
13	sweet aroma (1); stickiness (-1)	orange color (-0.89); brightness (0.89); straight shape (0.89); sweet taste (0.84); orange flavor (0.84); hardness (0.84)
14	orange color (1); opacity (-1); sticky (-1); firmness (-1); softness (1); sweet taste (-1); acidity (1)	orange flavor (-0.84)
15	orange color (1); surface powder (-1); opacity (-1); firmness (-1); ease in dissolving (1); sweet taste (1); powder flavor (-1)	sticky (-0.89); orange flavor (-0.84)
16	orange color (1); opacity (-1); surface starch (-1); softness / touching (1); softness in the bite (1); starch flavor (-1); acidity (-1)	sticky (-0.89); orange flavor (-0.89); sweet (0.89)
17	orange color (-1); opacity (-1); superficial white powder (-1), smooth surface uniformity (1); hardness (-1)	sugary aroma (-0.84); orange flavor (-0.84); orange flavor (-0.84); acidic taste (-0.84); sweet taste (0.84); gumminess (-0.89)
18	opacity (-1); brightness (1); shear (-1)	orange color (0.84); chewing firmness (0.84); adhesiveness (-0.84); citrus flavor (0.89); sweetness (0.84); sour taste (0.89)

Dimension 1 (70.8% of the variance) was positively correlated with the attributes orange color, brightness, orange flavor, and softness/ease of chewing and negatively correlated with opacity and hardness, attributes associated with the perception of the presence of starch (taste of starch/powder, starch/superficial powder and texture of flour in the mouth) (Table 3.3). Dimension 2 (24.4%) was positively correlated with the sweet taste attribute and negatively correlated with the sensation of stickiness (adherence/stickiness/sticky) and with the orange aroma and flavor and acid flavor attributes (Table 3.3).

Thus, the CO8 candy (located in the upper right part of the plot) was described as having a greater intensity of orange color and brightness and as being softer and easier to chew and with a greater flavor of orange (Table 3.3, Fig. 3.3). The description matches with the highest observed L* and H* values (Table 3.2). In contrast, the CA16 candy with 16% cassava starch (located in the upper left part of the plot) can be described as opaquer, with a flavor more associated with starch and harder (Table 3.3, Fig. 3.3); this candy had already been highlighted for its greater hardness and chewiness in the texture profile (Table 3.2). The CA12 candy (located in the lower central part of the plot) was described as having intermediate characteristics between the CO8 and CA16 candies, but it differed by its greater adhesiveness (Table 3.3, Fig. 3.3), which was also observed in the instrumental analysis (Table 3.2).

After obtaining the description of the candies, the preference of the gummy candies was evaluated, and the CO8 and CA12 candies were both preferred by the assessors (102 and 106 points in the sum of ranking values, respectively). When asked to describe the reason for the preference, most assessors reported that they preferred the gummy candies CO8 and CA12 by texture (softer) and taste (sweeter and with more orange flavor). The CA16 gummy candies (152 points) were the least preferred (minimum difference value of 32 at the level of 1%), and among the reasons cited were being harder and/or drier and presenting less orange flavor.

Despite the proportion of citric acid and artificial orange flavoring (Table 3.1) being the same in the 3 formulations, the CA16 gummy candies were sensory perceived as the formulation with less orange flavor (in the Flash Profile and in the Preference-Ranking test). This fact can be explained by the higher proportion of starch used and by a possible interaction of flavoring with starch. Piccone, Rastelli, and Pittia (2011) studied the release of strawberry aroma (by gas chromatography and using an electronic nose) in candies with different gelling agents (gelatin, aerated gelatin, gummy gelatin, gelatin and starch, extruded starch and pectin). The authors observed that there was a lower rate of release of the volatiles in the candies with starch and gelatin, due to the greater rigidity and firmness and they conclude that composition, type of biopolymers and physical properties affect the retention of the aroma compounds and the results of this study could be useful to understand the mechanism involved in the breakdown of the candies and the related flavor release. Probably due to the higher starch content, the perception of the artificial orange flavor of the CA16 gummy candy was changed.

3.4. CONCLUSION

Gummy candies with acid-thinned cassava starch were comparable to candies produced with traditional acid-thinned corn starch. With the results of the physical and sensory analyses of the candies, it was possible to observe the similarities and differences among the formulations. All gummy candies had the same moisture content, pH, Aw and similar adsorption curves. The differences in the type and/or amount of starch influenced the texture of the candies, the brightness and the orange flavor perceived by the assessors. In view of what has been exposed, the production of the gummy candy with acid-thinned cassava starch at 12% in the formulation is promising, as it generated gummy candy with desirable physical properties and equally preferred in comparison with candies produced with acid-thinned corn starch in Preference-Ranking test.

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CAPÍTULO 4 - CONSIDERAÇÕES FINAIS

4.1. CONSIDERAÇÕES FINAIS

A hidrólise ácida não alterou a morfologia dos grânulos do amido ácido-modificado, mas alterou as propriedades de pasta e tecnológicas, sendo essas, propriedades adequadas para a aplicação deste amido em balas de goma. Foi obtido balas de goma com o amido de mandioca ácido-modificado comparáveis com balas de goma produzidas com o tradicional amido de milho ácido-modificado. Pode-se afirmar que o tipo e/ou quantidade de amido influência nas características físicas e sensoriais das balas observadas nas análises instrumentais e pelos avaliadores na análise sensorial.

Apesar de todos estes experimentos, são necessários mais estudos sobre a hidrólise ácida do amido de mandioca visando a redução do tempo total de hidrólise, que foi de 72 h, avaliar as propriedades dos amidos ácido-modificados, para investigar qual ou quais são as características mais importante na aplicação deste amido e o porquê foi necessário utilizar uma porcentagem maior de amido de mandioca ácido-modificado em comparação ao amido de milho ácido-modificado na formulação das balas de goma, bem como as melhores condições de armazenamento e embalagem, tendo em vista a estabilidade e a vida de prateleira das balas de goma.