UNIVERSIDADE ESTADUAL DE CAMPINAS
Faculdade de Engenharia de Alimentos

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GELIFICAÇÃO A FRIO DE ALGINATO E PECTINA COMO FERRAMENTA TECNOLÓGICA E SUSTENTÁVEL PARA A PRODUÇÃO DE BALAS DE GOMA

ALGINATE AND PECTIN COLD-SET GELATION AS A TECHNOLOGICAL AND SUSTAINABLE TOOL FOR JELLY CANDY MANUFACTURING

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Tese apresentada à Faculdade de Engenharia de Alimentos da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Doutor em Tecnologia de Alimentos

Thesis presented to the School of Food Engineering from the University of Campinas in partial fulfillment of the requirements for the degree of Doctor in Food Technology

Supervisora/Orientadora: PRISCILLA EFRAIM

ESTE EXEMPLAR CORRESPONDE À VERSÃO FINAL DA TESE DEFENDIDA POR MATHEUS HENRIQUE MARIZ DE AVELAR, E ORIENTADO PELA PROFA. DRA. PRISCILLA EFRAIM

CAMPINAS
2021

Ficha catalográfica

Universidade Estadual de Campinas
Biblioteca da Faculdade de Engenharia de Alimentos
Claudia Aparecida Romano - CRB 8/5816

Av32g

Avelar, Matheus Henrique Mariz de, 1992-
Gelificação a frio de alginato e pectina como ferramenta tecnológica e sustentável para a produção de balas de goma / Matheus Henrique Mariz de Avelar. – Campinas, SP : [s.n.], 2021.

Orientador: Priscilla Efraim.
Tese (doutorado) – Universidade Estadual de Campinas, Faculdade de Engenharia de Alimentos.

1. Alginatos. 2. Balas. 3. Compostos bioativos. 4. Gelificação a frio. 5. Pectina. 6. Sustentabilidade. I. Efraim, Priscilla. II. Universidade Estadual de Campinas. Faculdade de Engenharia de Alimentos. III. Título.

Informações para Biblioteca Digital

Título em outro idioma: Alginate and pectin cold-set gelation as a technological and sustainable tool for jelly candy manufacturing
Palavras-chave em inglês:
Alginates
Candy
Bioactive compounds
Cold-set gelation
Pectin
Sustainability
Área de concentração: Tecnologia de Alimentos
Titulação: Doutor em Tecnologia de Alimentos
Banca examinadora:
Priscilla Efraim [Orientador]
Carolina Siqueira Franco Picone
Ana Luiza Mattos Braga
Ana Lúcia Fadini
Helena Maria André Bolini
Data de defesa: 09-04-2021
Programa de Pós-Graduação: Tecnologia de Alimentos

Identificação e informações acadêmicas do(a) aluno(a)
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- Currículo Lattes do autor: http://lattes.cnpq.br/6152004648193258

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A ata de defesa com as respectivas assinaturas dos membros encontra-se no processo de vida acadêmica do aluno

“Se tudo é energia e se transforma, o amor que coloco aqui há de chegar aonde se faz necessário”

Tatiana Rocha

DEDICATÓRIA

Dedico esse trabalho aos meus pais, por todo o amor, apoio, esforço e dedicação para me proporcionar oportunidade de estudo e qualificação acadêmica.

AGRADECIMENTOS

A Deus, pela vida e saúde, pelos dons, pelas oportunidades e benções concedidas.

Aos meus pais e demais familiares pela educação, exemplo, suporte, esforço, amor e dedicação que tiveram comigo durante toda a minha vida pessoal e acadêmica.

À Mãe Tatiana de Iemanjá e à toda a família e egrégora espiritual do Terreiro de Umbanda Mãe de Deus por me ajudarem nos meus processos de cura, por me ajudarem a ter força para completar essa jornada e por me ensinarem o sentido da espiritualidade.

Ao Victor por toda companhia, apoio, incentivo e alegria.

À Syndel e Tiago pela amizade, carinho e companheirismo.

À profa. Dra. Priscilla Efraim pela orientação, atenção, paciência, dedicação e exemplo de profissionalismo, por todos os conhecimentos e oportunidades concedidas, por toda contribuição à minha capacitação profissional e realização deste sonho.

Ao Laboratório de Frutas, Hortaliças e Produtos Açucarados por me receber, me ensinar, me permitir crescer e por me oferecer estruturas para a realização deste e de todos os trabalhos de pesquisa.

Às técnicas Juliana e Leila por todo empenho e profissionalismo que as fazem ser os alicerces da área de frutas, hortaliças e produtos açucarados na Unicamp.

Aos meus colegas Ana Valéria, Bruna, Yuri e Luan pelo companheirismo e por toda a ajuda e prestatividade que sempre tiveram comigo.

Às alunas Marielle e Letícia pela oportunidade de fazer parte do início de suas jornadas científicas e acadêmicas e por todo apoio na realização das minhas pesquisas.

À Guilherme de Castilho Queiroz e ao CEREAL CHOCOTEC pela parceria, orientação e por todo seu apoio técnico durante a realização deste trabalho.

À Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) pelo apoio para a realização deste trabalho – Código de Financiamento 001.

Ao Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) pelos recursos concedidos para minha bolsa de estudos.

Ao Instituto Nacional da Propriedade Industrial pela patente concedida, e à INOVA por todo o suporte no processo de depósito de patente.

Aos membros da banca de defesa de tese pela disponibilidade e pela contribuição significativa para minha qualificação acadêmica e melhoria da qualidade deste trabalho.

A todos que de alguma forma colaboraram para a realização deste trabalho, muito obrigado!

RESUMO

A demanda por opções alimentares mais saudáveis e sustentáveis tem desafiado o setor industrial de balas a encontrar novos ingredientes e tecnologias para a fabricação de produtos mais conscientes do ponto de vista ambiental e com melhor composição nutricional. Neste contexto, este trabalho teve como objetivo avaliar o potencial tecnológico e sustentável do processo de gelificação a frio de misturas de alginato de sódio e pectina de alto teor de metoxilação, aqui denominado *cold-set gelation*, para a fabricação de balas de goma. A técnica de gelificação a frio foi aplicada em uma etapa de preparo da massa da bala realizada em temperatura ambiente, em substituição à etapa convencional de cozimento da calda. Inicialmente verificou-se a influência dos ingredientes (hidrocoloides, acidulantes e açúcares) na formação de géis com e sem polpa de fruta, e o seu efeito nas características tecnológicas e sensoriais das balas obtidas. Estruturas gelificadas mais firmes e coesas foram obtidas quando empregadas misturas poliméricas (1:1 de alginato: pectina) em concentrações acima de 10 g/kg para balas sem fruta e 20 g/kg para balas com polpa de fruta. As condições de secagem das balas de goma (temperaturas de 35-55 °C por 12-72 horas) foram estudadas e adequadas às formulações obtidas a frio, sendo definidas como as melhores condições de processo a 35 °C/ 72 horas de secagem. Balas de alginato e pectina apresentaram géis opacos e mais firmes em relação aos géis de balas de pectina. A gelificação a frio apresentou eficácia para conservação de componentes termosensíveis de polpas de frutas. Balas produzidas a frio com suco concentrado de morango apresentaram teores de ácido ascórbico e compostos fenólicos, respectivamente, 20 e 300% superiores em relação a balas de pectina obtidas pelo processamento convencional. O potencial sustentável do processo produtivo de balas a frio foi avaliado em escala piloto por meio das estimativas do consumo energético e do fator de emissão de gases de efeito estufa. Ao substituir a etapa de cozimento pelo preparo da massa da bala via gelificação a frio houve redução de quase 100 vezes no requerimento energético e de aproximadamente 300 vezes na taxa de emissão de CO_2, indicando a possibilidade de atribuição de autodeclarações ambientais (*carbon footprint*) nos rótulos dos produtos produzidos a frio. Estudos com consumidores indicaram efeito positivo dessas autodeclarações na aceitabilidade sensorial das balas. A estabilidade das formulações desenvolvidas neste trabalho foi avaliada durante 120 dias de armazenamento a 25°C. Neste período verificou-se a ocorrência de cristalização da sacarose, indicando necessidade de rebalanço entre sólidos açúcarados cristalizantes e anticristalizantes. O teor de compostos bioativos reduziu durante a estocagem, sugerindo a necessidade de estudos complementares em relação aos sistemas de embalagem. A aceitabilidade sensorial das balas estocadas não difeririu sensorialmente ($p<0.05$) em relação à das amostras recém processados, indicando que as alterações ocorridas no armazenamento não foram perceptíveis aos avaliadores. O processo de gelificação a frio se mostrou uma ferramenta com elevado potencial tecnológico e sustentável para a condução de processos de fabricação de balas de goma mais limpos e ambientalmente conscientes.

Palavras-chave: alginato, balas, compostos bioativos, gelificação a frio, pectina, sustentabilidade.

ABSTRACT

The demand for healthier and sustainable food options has been challenged the industrial sector of candies to find new ingredients and technologies for the manufacture of more environmentally conscious products with better nutritional composition. In this context, this study aimed to evaluate the technological and sustainable potential of the cold-set gelation process of mixtures of sodium alginate and high methoxylation pectin for the manufacture of jelly candies. The cold-set gelation technique was applied in a preparation step of the candy mass performed at room temperature, replacing the conventional syrup cooking step. Initially, the influence of ingredients (hydrocolloids, acidulants and sugars) on the formation of gels with and without fruit pulp, and their effect on the technological and sensory characteristics of the obtained candies were verified. Harder and more cohesive gelled structures were obtained when polymer blends (1:1 alginate: pectin) were employed at concentrations above 10 g/kg for candies without fruit and 20 g/kg for candies with fruit pulp. The drying conditions of the jelly candies (temperatures of 35-55 °C for 12-72 hours) were adapted to the cold-set products, being defined as the best process conditions 35 °C/ 72 drying hours. Alginate and pectin jellies showed opaque and harder gels compared to pectin candy gels. Cold-set gelation was an effective tool for the maintenance of thermosensitive compounds of fruit pulps. Cold-set candies produced with strawberry juice concentrate showed 20% more ascorbic acid and 300% more phenolic compounds than pectin candies obtained by the conventional manufacture processing. The sustainable potential of the cold-set manufacturing process was evaluated on a pilot processing scale by the estimates of energy requirement and greenhouse gases emission factor. The replacement of the syrup cooking step for the candy syrup mixing step by cold-set gelation allowed the reduction of almost 100 times in the energy requirement and about 300 times in the CO_2 emission rate, indicating the possibility of attributing environmental self-declarations (carbon footprint) on the labels of the cold-set products. Studies with consumers pointed out a positive effect of these self-declarations on the sensory acceptance of the jelly candies. The stability of the developed formulations was evaluated during 120 days of storage at 25 °C. The sucrose crystallization occurred during this period, indicating the need for adjust the crystallizing and anti-crystallizing sugar solids ratio. The bioactive compounds content decreased during storage, suggesting the need for further packaging studies. The sensorial acceptance of the stored candies did not differ sensorially ($p < 0.05$) in relation to that of fresh processed samples, indicating that the changes that occurred during the storage were not apparent to the evaluators. The cold-set gelation process presented itself as a tool with high technological and sustainable potential for the manufacturing of cleaner and more environmentally conscious jelly candies.

Keywords: alginate, bioactive compounds, candy, cold-set gelation, pectin, sustainability.

SUMÁRIO

INTRODUÇÃO GERAL

O Brasil apresenta destaque na produção e consumo de balas e confeitos no mundo. Com mais de 257 milhões de toneladas de balas e gomas de mascar produzidas no ano de 2019 (ABICAB, 2020), o país ocupa lugar entre os três maiores produtores mundiais de balas, confeitos e gomas de mascar, atrás apenas dos Estados Unidos e da Alemanha (MONTENEGRO & LUCCAS, 2014). O consumo interno brasileiro também é bastante expressivo. Anualmente no Brasil são consumidos cerca de 1,6 kg de confeitos de açúcar e gomas de mascar por habitante (PIVARO, 2019).

Nos últimos anos, a demanda do mercado consumidor por produtos fabricados de forma mais sustentável, bem como produzidos por empresas que praticam a responsabilidade ambiental e social é crescente (FOOD & BEVERAGE INSIDER, 2018). A "Sustentabilidade e Transparência" é uma das principais macrotendências de consumo que vem direcionando o mercado brasileiro de balas e confeitos. Essa macrotendência relaciona-se com linhas de produtos desenvolvidos com foco na valorização do agronegócio sustentável, no comércio justo e na redução do consumo energético e das emissões ambientais (QUEIROZ, 2014).

A busca por opções alimentares mais conscientes do ponto de vista ambiental desafia a indústria a encontrar alternativas tecnológicas para fabricação de alimentos. Nesse contexto, o processo de gelificação a frio por meio da aplicação de alginato de sódio com alto teor de ácido α-L-gulurônico (G) e pectina de alto teor de metoxilação (HM) surge como uma tecnologia alternativa com potencial sustentável para as indústrias de balas de gomas.

Soluções mistas de alginato de alginato de sódio de alto G e pectina HM podem criar estruturas gelificadas em temperatura ambiente quando acidificadas em uma faixa de pH entre 3,3-4,0 (GUO & KALETUNÇ, 2016). O mecanismo de gelificação se baseia na formação de zonas de junção entre os resíduos esterificados de ácido α-D-galacturônico da cadeia da pectina com os resíduos de ácidos α-L-gulurônicos da cadeia de alginato (WALKENSTRÖM et al. 2003), e as características do gel obtido são altamente dependentes do pH do meio, da quantidade, especificidade molecular e proporção entre os hidrocolóides utilizados (TOFT et al., 1986).

A aplicação do processo de gelificação a frio de alginato e pectina, denomidado neste trabalho como *cold-set gelation*, na fabricação de balas de goma pode contribuir para a obtenção de estruturas gelificadas com redução da demanda energética das linhas de processamento e diminuição das emissões ambientais das instalações industriais.

As balas de goma são um segmento significativo e crescente da indústria de confeitos e atualmente são o terceiro maior segmento de confeitos a base de açúcar, representando cerca de 21% do mercado mundial em termos de receita (BUSINESSWIRE, 2020). Na fabricação de balas de goma, os sistemas de cozimento das caldas e os sistemas de água quente e caldeira que fornecem energia para os processos aquecidos, estão entre as atividades mais intensivas em energia nas linhas industriais (AIGOURP, 2019).

Outra vantagem tecnológica da gelificação a frio está na sua aplicabilidade na fabricação de produtos com baixa estabilidade térmica (BOLDER et al., 2006). Neste sentido, formulações de balas com inclusão de polpas de frutas ou adição de componentes de interesse nutricional e funcional tendem a ser favorecidas.

As balas de goma são uma ampla classe de produtos cujas características são fortemente determinadas pelo teor de umidade final e pelo agente gelificante utilizado (EIRI BOARD, 2012). A combinação de alginato de sódio de alto G e pectina HM na produção de balas pode acarretar em alterações das características físicas e sensoriais observadas em produtos comerciais, devendo, portanto, ser analisadas cuidadosamente para que se possa obter produtos estáveis e com boa aceitabilidade sensorial.

Mediante o exposto, este trabalho apresenta estudos sobre a viabilidade do processo de gelificação a frio de alginato de sódio de alto G e pectina HM no desenvolvimento de balas de goma formuladas com e sem polpa de frutas. Foram avaliados os impactos do processamento a frio nas características físicas, físico-químicas e sensoriais dos produtos obtidos, bem como o potencial tecnológico para a manutenção de compostos bioativos termosensíveis durante o processamento e para a redução da demanda energética e de emissões de gases de efeito estufa no processo produtivo. O trabalho está apresentado em 5 capítulos, descritos a seguir:

Capítulo 1: Revisão Bibliográfica.

O capítulo apresenta uma breve revisão bibliográfica referente aos principais tópicos estudados ao longo da tese.

Capítulo 2: Alginate/Pectin cold-set gelation as a potential sustainable method for jelly candy production.

O capítulo apresenta um estudo sobre a viabilidade tecnológica do processo de gelificação a frio de misturas de alginato de sódio de alto G e pectina de alto teor de metoxilação na produção de balas de goma. Foram avaliados os efeitos de diferentes concentrações dos ingredientes (hidrocoloides, acidulante e açúcares) nas caracteristicas físico-químicas, sensoriais e na micro-estrutura dos produtos. Também foram determinados os melhores parâmetros de processo para a etapa de secagem das balas de goma produzidas a frio e foi avaliado em escala laboratorial o potencial de redução do consumo energético e de emissões de CO_2 propiciado pelo processo de produção de balas por gelificação a frio em relação ao processo convencional de fabricação de balas de goma.

Capítulo 3: Maintenance of Fruit Bioactive Compounds in Jelly Candy Manufacturing by Alginate/Pectin Cold-Set Gelation.

O capítulo apresenta um estudo sobre a viabilidade tecnológica do processo de gelificação a frio de misturas de alginato de sódio de alto G e pectina de alto teor de metoxilação na produção de balas de goma formuladas com adição de polpas de frutas. Foi verificada a influência das características físico-químicas das frutas na obtenção das balas de goma produzidas com alginato de sódio e pectina e foi avaliada a influência dos ingredientes (polpa de fruta, hidrocoloides e acidulante) nas características físico-químicas, sensoriais e na microestrutura dos produtos obtidos. Também foi realizado um estudo sobre o efeito do processo produtivo a frio na manutenção de compostos bioativos (vitamina C, compostos fenólicos totais e antocianinas totais) naturalmente encontrados no suco de morango utilizado na formulação das balas.

Capítulo 4: Sustainable performance of cold-set gelation in the confectionery manufacturing and its effects on perception of sensory quality of jelly candies.

O capítulo apresenta um estudo comparativo do potencial sustentável do processo de gelificação a frio na produção de balas de goma em relação ao método produtivo convencional. Foram mensurados, em escala piloto, o consumo energético e o fator de emissão de gases de efeito estufa da etapa de preparo da calda, comparando-se o processo a frio com o processo convencional que envolve calor (cozimento da calda). Também foi avaliada a influência de autodeclarações ambientais e de alegações de naturalidade e saudabilidade na aceitabilidade sensorial de balas de goma produzidas a frio com suco de morango concentrado.

Capítulo 5: Effect of cold-set gelation processing on the quality and retention of fruit bioactive compounds in jelly candies during storage.

O capítulo apresenta um estudo de estabilidade conduzido a 25 °C por 4 meses, de balas de goma produzidas a frio em duas versões: uma colorida e aromatizada artificialmente e outra formulada com polpa de morango. Foram avaliados mensamente parâmetros físico-químicos das balas (pH, atividade de água, textura instrumental, cor instrumental e sólidos totais) e o teor de compostos bioativos (vitamina C, compostos fenólicos totais, antocianinas totais) nas amostras de balas com morango. No final do período de estocagem, as balas foram avaliadas sensorialmente em comparação com amostras recém-processadas.

Os resultados apresentados neste trabalho estão protegidos pela patente de privilégio de inovação intitulada “Processo de obtenção de balas de goma”, de autoria de Efraim, P.; Avelar, M. H. M., número de registro BR1020180768174, depositada em 20/12/2018 no INPI - Instituto Nacional da Propriedade Industrial.

CAPÍTULO 1. REVISÃO BIBLIOGRÁFICA

CAPÍTULO 1. Revisão Bibliográfica

1. Balas: Aspectos Gerais

Balas são definidas pela legislação brasileira como produtos constituídos por açúcar e outros ingredientes que podem apresentar recheio, cobertura, formato e consistência variados (ANVISA, 2005). Conforme os ingredientes utilizados na formulação e as operações envolvidas no processo de fabricação, as balas podem ser classificadas como balas duras, balas moles (mastigáveis ou cristalizadas), balas de gomas ou caramelos de leite (SILVA, 2017). O Guia Alimentar para a População Brasileira, classifica as balas como "*Alimentos Ultraprocessados*" devido ao elevado teor de açúcares na composição e à presença de aditivos utilizados para dotar os produtos de propriedades sensoriais (MINISTÉRIO DA SAÚDE, 2014).

O Brasil ocupa lugar de destaque entre os três maiores produtores mundiais de balas, confeitos e gomas de mascar, atrás apenas dos Estados Unidos e da Alemanha (MONTENEGRO & LUCCAS, 2014). Em 2019, mais de 257 milhões de toneladas de balas e gomas de mascar foram produzidas no Brasil, sendo 86 milhões de toneladas exportadas e 181 milhões de toneladas consumidas internamente (ABICAB, 2020). De acordo com Pivaro (2019), o consumo brasileiro de balas é bastante expressivo. Estima-se que anualmente sejam consumidos cerca de 1,6 kg de confeitos de açúcar e gomas de mascar por habitante.

Nos últimos anos o mercado brasileiro de balas e confeitos tem sido fortemente direcionado pela crescente demanda do mercado consumidor por opções alimentares mais conscientes, nutritivas, naturais e sustentáveis (QUEIROZ et al., 2014). Nesse contexto, são numerosos os lançamentos de produtos isentos de aditivos artificiais (corantes e aromas sintéticos), produtos formulados com ingredientes naturais (inclusão de polpas de frutas processadas) e produtos adicionados de ingredientes funcionais (vitaminas, minerais e fibras) (FADINI & CRUZ, 2014; QUEIROZ & NABESHIMA, 2014).

Produtos com alegações de sustentabilidade também têm apresentado crescimento expressivo no mercado brasileiro. De acordo com Queiroz (2014), o segmento de balas e confeitos sustentáveis no Brasil é marcado pela forte valorização do consumidor pelo agronegócio sustentável e/ou orgânico, pelo comércio justo e solidário (*fair trade*), e pela produção com menores consumo energético e emissões para o meio ambiente (produtos com autodeclarações ambientais e especificação de *carbon footprint*).

Frente às tendências de saudabilidade e sustentabilidade, as indústrias de balas e confeitos têm recorrido ao uso de ingredientes alternativos e a novas tecnologias de processamento. A qualidade sensorial das novas formulações é uma preocupação constante, pois para que sejam aceitas pelo consumidor devem apresentar características sensoriais similares às versões convencionais.

1.1. Balas Duras

As balas duras são produtos obtidos a partir de uma solução concentrada de carboidratos com baixo teor de umidade (1–3%) que é resfriada a uma temperatura abaixo de sua temperatura de transição vítrea (Tg) de forma rápida o suficiente para que cristalização do açúcar não ocorra. As balas duras são produtos que se encontram em estado vítreo, constituídas por um fluido açucarado amorfo de alta viscosidade e baixa mobilidade molecular que apresenta características semelhantes às de um sólido (HARTEL et al., 2018a).

O processo de fabricação de balas duras inicia-se com o cozimento de soluções açucaradas a elevadas temperaturas até que um baixo conteúdo de água seja atingido. Em seguida a calda é colorida e aromatizada, e então formatada por meio do depósito em moldes ou por resfriamento até um estado altamente plástico que permite a moldagem no formato desejado. Ao ser resfriada à temperatura ambiente, a matriz açucarada da calda da bala endurece na forma de um corpo que, protegido do calor e da umidade, pode conservar sua qualidade por muitos anos (HARTEL, 2012; EDWARDS, 2008).

Balas duras são normalmente formuladas com proporções de sacarose e xarope de glicose que variam de 70:30 a 45:55, em base seca. As balas duras possuem atividade de água entre 0,25 a 0,40 e um teor de umidade médio entre 1-3%, embora produtos comerciais podem muitas vezes apresentar de 3 a 5% de umidade, dependendo da sua composição, condições e tempo de armazenato (ERGUN et al., 2010).

1.2. Balas Moles

Balas moles são produtos com composição semelhante à de balas duras, porém, se diferenciam dessas por apresentarem maior teor de umidade (6-10%), pela adição de gordura em sua composição e por serem submetidas a um tratamento mecânico (estiramento) após a etapa de cozimento, de forma a garantir a obtenção da textura característica deste tipo de produto (FADINI et al., 2003).

Devido à incorporação de ar durante a etapa de estiramento, as balas moles são classificadas como produtos aerados, e apresentam densidade média relativa de 1,0 g/mL. A utilização de gordura na formulação (entre 5-10%) tem como objetivo conferir maciez e diminuir a aderência da massa da bala nos equipamentos durante a fabricação e nos dentes durante a mastigação (HARTEL et al., 2018b).

De acordo com os ingredientes e as características de processo, as balas moles podem ser classificadas em balas moles mastigáveis e balas moles cristalizadas. As balas moles mastigáveis são formuladas com a adição de ingredientes que conferem à massa uma característica mastigável e de dissolução lenta. Já as balas moles cristalizadas são produzidas com a adição de ingredientes que induzem à cristalização do açúcar durante a etapa de estiramento. Tal cristalização altera as características de textura, reduzindo a pegajosidade da bala e conferindo uma textura mais firme e de dissolução mais rápida (FADINI et al., 2003).

As balas moles mastigáveis possuem baixo nível de cristalização, com cerca de 5-10% de cristais de açúcar na sua composição (HARTEL et al., 2018b). Nas balas moles cristalizadas, no entanto, a fração mássica de cristais pode chegar até 30% (SILVA, 2017). De forma geral, ambas os tipos de balas moles apresentam atividade de água entre 0,45 e 0,60 (ERGUN et al., 2010).

1.3. Balas de Gomas

Balas de goma são uma ampla classe de produtos elaborados a partir da mistura de xaropes de açúcares e um ou mais hidrocolóides, que são responsáveis por criar uma rede de gel que retém a solução açucarada e confere estrutura semi-sólida ao produto. São produzidas por cocção a temperaturas inferiores às empregadas para fabricação das outras categorias de balas, apresentanto, por essa razão, um maior conteúdo de umidade em comparação com as balas duras e moles (HARTEL et al., 2018c). As características físicas e sensoriais das balas de gomas são fortemente determinadas pelo seu teor de umidade final e pelo hidrocolóide utilizado (EIRI BOARD, 2012).

No segmento de confeitos gelificados, estão incluídos produtos como as jujubas, as gomas, as pastilhas e os populares produtos “gummy”. Sua textura, cor e brilho dependem da boa qualidade e dos tipos de matérias-primas utilizadas, das variáveis de formulação e de processamento (GARCIA, 2000).

As balas de goma são atualmente o terceiro maior segmento de confeitos a base de açúcar e representam cerca de 21% do mercado mundial em termos de receita (BUSINESSWIRE, 2020). A ampla variedade de produtos é obtida pela aplicação de diferentes hidrocolóides que podem ainda ser utilizados de maneira combinada para modificação de texturas e obtenção de confeitos com características diferenciadas.

O processo de fabricação de balas de gomas (Figura 1.) segue as etapas de cozimento dos açúcares com hidrocolóides; adição de corantes, aromatizantes e ácidos na calda; dosagem da calda em moldes de amido seco; secagem em estufa para remoção de umidade residual; desmoldagem, finalização (aplicação de coberturas de açúcar ou de agentes de brilho) e embalagem (EDWARDS, 2008).

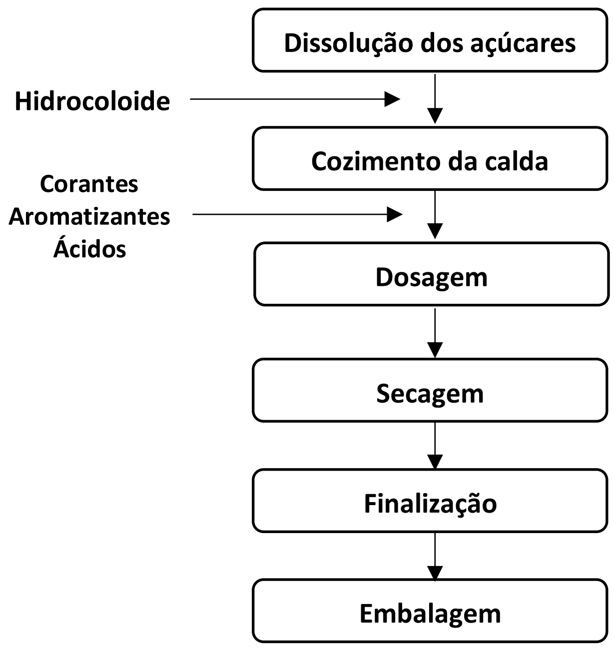

Figura 1. Diagrama de blocos do processo de fabricação de balas de goma.

Fonte: EDWARDS (2008).

Balas de goma são normalmente formuladas com cerca de 40-50% de sacarose e 50-60% de xarope de glicose em base seca. Devido ao alto teor de umidade residual das balas de goma em comparação com as demais categorias de balas (15-20% de umidade) e à composição, a sacarose deve permanecer completamente solubilizada no sistema e não sofrer cristalização ao longo de sua vida útil (HARTEL et al., 2018c). As balas de goma possuem uma faixa de atividade de água entre 0,5 e 0,7, portanto, tendem a perder umidade e endurecer se armazenadas em ambientes com baixa umidade relativa (ERGUN et al., 2010).

2. Processos de gelificação

O mecanismo de formação da rede de gel nas balas de goma é intrínseco ao hidrocoloide ou à combinação de hidrocoloides utilizada na formulação. As diferenças nas estruturas de ligação são responsáveis por variações nas características físicas observadas nas balas de goma disponíveis no mercado. A utilização de mistura de hidrocoloides pode fornecer uma variação ainda maior na textura do produto devido às complexas interações ocorrentes em géis mistos ou compostos (HARTEL et al., 2018c).

No Brasil, os principais tipos de balas de goma comercializados são as balas de gelatina (normalmente em formatos de personagens e finalizadas com uma cobertura de óleo para conferir brilho ao produto), balas de amido (envoltas tradicionalmente com açúcar cristalino ou com coberturas de drageamento macio de açúcar) e balas de pectina (processadas com ou sem polpa de fruta, recobertas com açúcar ou com chocolate na forma de confeitos finos ou bombons).

A seguir são descritos os mecanismos de gelificação dos principais hidrocoloides utilizados na fabricação de balas de gomas no Brasil.

2.1. Amido

O amido é um polissacarídeo que atua como a principal reserva energética das plantas. É composto por numerosas unidades de glicose e é encontrado dentro das células vegetais na forma de grânulos insolúveis em água de tamanho e morfologia altamente variáveis (GOREN et al., 2018). Estruturalmente, o amido consiste em dois polímeros: a amilose e a amilopectina.

A amilose é um polímero de cadeia linear com peso molecular médio de 10^6 Da, que consiste em moléculas de α-D-glicose unidas por ligações glicosídicas do tipo α-1,4. O número de unidades individuais varia dependendo da fonte de amido. A amilopectina é o componente do amido com maior cadeia e consiste em um polímero ramificado com peso molecular médio de 10^8 Da, composto não apenas de unidades de α-D-glicose unidas por ligações glicosídicas α-1,4, mas também por unidades de glicose unidas por ligações α-1,6 (pontos de ramificação). As frações ramificadas podem ter entre 20-30 unidades de glicose de comprimento unidas por ligações do tipo α-1,4 (HARTEL et al., 2018d).

O processo de formação do gel de amido se inicia com o aquecimento de uma suspensão de grânulos de amido em água. À medida que esta suspensão é aquecida, ela atinge o ponto de gelatinização do amido, que é a temperatura na qual o grânulo do amido começa a inchar. Conforme os grânulos de amido absorvem água, aumentam até atingirem seu tamanho máximo, quando começa a quebra de sua estrutura. Quando isso ocorre, os polímeros de amilose e amilopectina são liberados na solução e ficam livres para interagir entre si e criar redes associativas. Durante o resfriamento, essas interações aumentam e uma rede gelificada mais forte é formada (SHELDRAKE, 2010).

A produção de balas de goma de amido se inicia com a dissolução dos açúcares e dispersão do amido em água. Essa mistura é então cozida para promover a gelatinização do amido e a remoção parcial do conteúdo de água até que a calda apresente 20-25% de umidade. Após o cozimento são adicionados corantes e aromatizantes, e em sequência é feito o depósito da calda em moldes de amido seco (com umidade residual entre 6-9%). Nos moldes, conforme a temperatura da calda diminui, a gelificação do amido ocorre. Paralelamente a umidade residual das balas é removida. Os moldes de amido são acondicionados em câmaras a 49-65 °C durante 8-72 horas para que a secagem das balas ocorra e a umidade final de 15-20% seja atingida (MOORE, 2007; ERGUN et al., 2010; HARTEL et al., 2018c).

Balas de goma de amido são formuladas com 10-15% de amido em base seca. Água suficiente deve estar presente durante o processo de cozimento para garantir que a gelatinização ocorra, embora a quantidade necessária dependa do tipo de amido e do sistema de cocção (MOORE, 2007). Caldas cozidas em sistemas pressurizados necessitam de um teor mínimo de água de 18% enquanto caldas cozidas em tachos abertos devem ser preparadas com um maior conteúdo de água, chegando até 50% (HARTEL et al., 2018c).

Os principais amidos utilizados na fabricação de balas de goma são os amidos modificados por tratamento ácido e amidos com alto teor de amilose (MOORE, 2007). Os amidos com maior teor de amilose são mais propensos a gelificar devido à linearidade das cadeias de amilose, produzindo géis com maior firmeza (SHELDRAKE, 2010), no entanto, não podem ser empregados para a produção de balas em sistemas abertos pois requerem temperaturas mais altas para gelatinização (HARTEL et al., 2018c).

Os amidos modificados por tratamentos ácidos sofrem hidrólise durante o processo de modificação, o que diminui o tamanho das cadeias e reduz a viscosidade de suas pastas. Caldas de balas preparadas com esses amidos possuem um melhor escoamento e uma dosagem facilitada, reduzindo custos de energia para as industrias nos processos de bombeamento e depósito (HARTEL et al., 2018c).

2.2. Gelatina

A gelatina é um material proteico proveniente do tecido conjuntivo animal obtido por meio da hidrólise do colágeno em solução ácida (gelatina tipo A) ou básica (gelatina tipo B) seguida de extração com água quente. A gelatina é classificada conforme o seu processo de extração e força do gel, a qual é determinada instrumentalmente e expressa em '*Bloom*' (STEVENS, 2010). Para a fabricação de balas de goma geralmente são utilizadas gelatinas com bloom entre 200 e 275 (SUFFERLING, 2007), em quantidades entre 5-10% na formulação, para produzir géis firmes e elásticos (HARTEL et al., 2018c).

O gel da gelatina é uma rede de cadeias polipeptídicas com zonas de junção que são estabilizadas por ligações de hidrogênio. Quando estão em uma solução aquecida, as cadeias peptídicas da gelatina estão amplamente desorganizadas. Com o resfriamento, há a transição da conformação molecular enovelada para uma estrutura de hélice simples. A gelificação é a consequência de um retorno parcial das hélices simples à estrutura de hélice tripla do colágeno. Os géis de gelatina apresentam termoreversibilidade quando aquecidos em temperaturas acima de 37 °C, o que faz com que percam a estrutura e se dissolvam facilmente na boca (STEVENS, 2010).

O processo de fabricação de balas de goma de gelatina ocorre por meio do cozimento de uma calda de açúcares que posteriormente é misturada à uma solução de gelatina em água aquecida a temperaturas próximas de 80 °C. Após a mistura das soluções, a calda da bala deve apresentar um teor de sólidos solúveis final entre 76-78 °Brix. Corantes e aromatizantes são adicionados e na sequência é feita a dosagem da calda (em temperaturas entre 70-75 °C) em moldes de amido seco (com umidade residual entre 6,0-7,5%). Nos moldes a calda resfria e completa a gelificação da gelatina (SUFFERLING, 2007). Para a secagem, os moldes de amido são acondicionados em câmaras a 24-35°C durante 8-24 horas para que as balas sequem e atinjam médias de umidade entre 15 e 20% (HARTEL et al., 2018c).

2.3 Pectina

As pectinas são uma família de polissacarídeos complexos compostos majoritariamente por cadeias lineares de poliácidos α-D-galactopiranosilurônicos com vários conteúdos de ésteres metílicos (HARTEL et al., 2018d). As pectinas constituem a parede celular vegetal junto com a celulose, e são extraídas comercialmente da casca de frutas cítricas e do bagaço de maçã (GÜZEL et al., 2020).

A esterificação dos resíduos de ácido galacturônico com metanol ou ácido acético é uma característica estrutural muito importante das substâncias pécticas. O grau de esterificação (DE) é definido como a porcentagem de grupos carbonila esterificados com metanol. Se mais de 50% dos grupos são metilados, as pectinas são classificadas como de alto teor de metoxilação (HM). Se o DE for inferior a 50%, são classificadas como pectinas com baixo teor de metoxilação (LM) (SHARMA et al., 2006).

O processo de gelificação das pectinas HM requer baixo pH (entre 2,5 e 3,8), baixa atividade de água e conteúdo de sólidos solúveis entre 55% e 85%. Quanto maior o teor de sólidos solúveis, menor é a atividade de água, promovendo interações entre as moléculas de pectina, ao invés de interações entre pectina e solvente. O baixo pH reduz a dissociação dos grupos carboxila, diminuindo assim a repulsão eletrostática. Acredita-se que o mecanismo de gelificação se baseie na ligação de hidrogênio entre grupos carboxila não dissociados e grupos de álcool secundário, juntamente com interações hidrofóbicas entre grupos de éster metílico (BREJNHOLT, 2010).

A gelificação das pectinas LM ocorre na presença de cátions divalentes, geralmente cálcio, e se baseia na estrutura simétrica das cadeias de pectina que formam uma série de lacunas eletronegativas nas quais os cátions divalentes se associam formando dímeros de cadeias poligalacturônicas por interações iônicas com os grupos carboxílicos livres da pectina (BREJNHOLT, 2010). O mecanismo de gelificação das pectinas LM é conhecido por apresentar modelo de ligação de “caixa de ovo” devida à estrutura das zonas de junção (SHARMA et al., 2006).

As pectinas LM e HM são utilizadas em baixas concentrações (1-2%) na formulação de balas de goma e produzem um gel firme, com textura de corte e aparência translucida. Dentro da classe de pectinas HM há uma ampla variedade de opções comerciais com diferentes performances de gelificação. De forma geral, quanto maior o grau de esterificação das pectinas HM, maior é a sua velocidade de gelificação. Pectinas com DE acima de 70% gelificam entre 1-2 minutos, oferecendo dificuldade para aplicações em linhas de processamento de confeitos. As pectinas HM com DE de aproximadamente 60-68%, são intituladas “*slow-set*” devida sua gelificação menos acelerada (3-5 minutos) que contribui para uma dosagem de caldas de bala de goma mais facilitada. As pectinas HM tamponadas também podem favorecer a etapa de moldagem de balas pois são adicionadas de sais tampão (citrato de potássio ou citrato de sódio) com o objetivo de controlar a acidificação e retardar a formação do gel, embora possam também afetar propriedades texturais dos géis (HARTEL et al., 2018c).

O processo de fabricação de balas de goma de pectina se baseia no cozimento da calda a base de açúcares com a pectina até que se atinja o teor de sólidos solúveis totais de 76-78 °Brix. Em seguida, é feita a adição de corantes, aromas e ácidos e então a dosagem da calda final em moldes de amido seco (6-9% de umidade). Essa operação é acompanhada da redução da temperatura e consequente gelificação da pectina. Por fim, o produto passa por uma etapa de secagem em câmara a 49,0-65,5 °C durante 8-24 horas para que ocorra a redução da umidade da bala até valores entre 15 e 20% (SUFFERLING, 2007; HARTEL et al., 2018c).

3. Géis Mistos

Misturas de hidrocoloides apresentam um comportamento complexo, dependendo de como (ou se) as moléculas interagem entre si e de como o sistema é estruturado. Essas interações determinam se uma única fase mista ou se múltiplas fases distintas se formam. De forma geral, misturas de hidrocoloides apresentam características intermediárias em relação àquelas observadas individualmente. A maioria das misturas são inerentemente instáveis, tendendo à separação dos hidrocoloides em sua própria fase. Para a fabricação de balas de gomas mistas pode haver a necessidade de modificação das condições do processo para garantir a adequada gelificação da mistura (HARTEL et al., 2018c).

3.1. Alginato

O alginato é um polissacarídeo extraído de algas marinhas marrons constituído por cadeias lineares de resíduos de ácido α-L-gulurônico (G) e ácido ß-D-manurônico (M) conectados através de ligações do tipo 1-4. Os resíduos são dispostos em arranjos sequenciais de blocos homogêneos (MM ou GG) ou mistos (MG). A composição do arranjo varia conforme a fonte do alginato (SIEW et al., 2005).

Os alginatos são produzidos industrialmente como uma variedade de sais, sendo o alginato de sódio majoritariamente utilizado para aplicação em alimentos (HELGERUD et al., 2010). O alginato de sódio é utilizado em alimentos como agente espessante, gelificante, emulsificante, estabilizador e melhorador de textura. Vários produtos, como sorvetes, geleias, bebidas lácteas ácidas, molhos, macarrão instantâneo e cerveja são formulados com alginato de sódio (VASLIAUSKAS, 2020).

Os géis de alginato podem ser estruturados por diferentes ligações moleculares (VASLIAUSKAS, 2020). Entretanto, o processo de gelificação mais comum se dá por meio da ligação com íons divalentes, principalmente o cálcio (SIEW et al., 2005). Do ponto de vista químico, este mecanismo de formação de gel ocorre através de um processo de troca iônica. Para tanto, o alginato deve conter uma certa proporção de ácido gulurônico que deve estar agrupado em blocos. A zona de junção da rede de gel de alginato é formada quando um bloco G de uma molécula de alginato se liga a outro bloco G de outra molécula de alginato por intermédio dos cátions. Os blocos M e os blocos MG não participarão nas zonas de junção, mas formam os chamados segmentos elásticos na rede de gel. A interação entre o alginato e os íons de cálcio é comumente visualizada através do 'modelo de caixa de ovo', onde os íons de cálcio se encaixam no vazio estrutural na cadeia de alginato (HELGERUD et al., 2010).

A ligação específica do alginato com cátions multivalentes já foi descrita e avaliada em diversas pesquisas. Todavia, na literatura são escassos os trabalhos envolvendo a formação de géis de alginato por meio de gelificações ionotrópicas entre alginato e cátions monovalentes, criando junções intermoleculares do tipo "caixa de ovo" análogas àquelas formadas com cátions divalentes, bem como a formação de géis ácidos de alginato (KARAKASYAN et al., 2010).

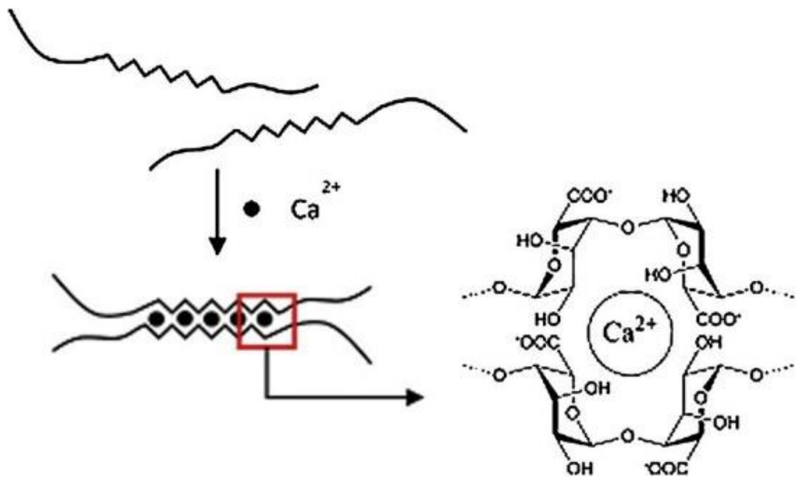

Figura 2. Modelo de gelificação "caixa de ovo" de alginato de sódio com íons Cálcio

Fonte: LI et al. (2017).

Os alginatos também podem formar géis ácidos em sistemas com pH abaixo do pKa de seus resíduos urônicos (pKa 3,4 e 3,6 para unidades M e G, respectivamente). O pH no entanto deve ser reduzido de forma controlada pois a adição direta de ácido ao alginato de sódio causa precipitação instantânea ao invés da formação de gel (KARAKASYAN et al., 2010). Presume-se que os géis ácidos de alginato sejam estabilizados por ligações de hidrogênio intermoleculares e se assemelham aos géis de alginato reticulados ionicamente no sentido de que os blocos de ácido gulurônico são os elementos principais para a formação da rede do gel e processos cooperativos parecem estar envolvidos na formação das zonas de junção (DRAGET et al., 2006).

As três principais diferenças entre os géis de alginato obtidos por acidificação e por gelificação ionotrópica estão no fatos de que os blocos de ácido manurônico, embora com menos eficiência em comparação com os blocos de ácido galacturônico, também suportam a formação de géis ácidos; os géis ácidos de alginato parecem ser de natureza equilibrada; e as maiores zonas de junção nos géis ácidos são de maior multiplicidade em relação às zonas de junção observadas nos géis reticulados ionicamente (DRAGET et al., 2006).

Ambos os géis de alginato obtidos com íons de cálcio ou por acidificação do sistema são termo-irreversíveis e irão se formar em uma ampla faixa de temperatura (HELGERUD et al., 2010).

3.2. Géis mistos de alginato e pectina

Quando utilizadas sozinhas, as pectinas HM são capazes de formar géis apenas em sistemas com alto teor de sólidos solúveis e em uma faixa estreita de baixo pH, enquanto as pectinas LM formam géis em sistemas com a presença de cátions divalentes, como cálcio. Ao introduzir alginato de sódio, é possível obter géis termo-reversíveis compostos de pectina e alginato em condições em que se tenha baixos teores de sólidos e dentro de uma faixa mais ampla de pH (HELGERUD et al., 2010).

O sistema de gelificação mista de alginato-pectina se baseia em um modelo sinérgico de zonas de junção em que blocos de resíduos esterificados de ácido α-D-galacturônico da cadeia da pectina interagem com blocos de resíduos de ácidos α-L-gulurônicos da cadeia de alginato. Esta interação ocorre quando os ácidos urônicos estão principalmente em sua forma protonada, e é estericamente favorecida porque ambos os tipos de blocos contêm ligações glicosídicas entre substituintes axiais (0-1 e 0-4) conferindo o mesmo conjunto de distâncias repetidas ao longo da cadeia de segmentos similares ordenados (TOFT et al., 1986).

A gelificação sinérgica de misturas de alginato de sódio e pectina ocorre em uma faixa de pH entre 3,3 e 4,0 dependendo da proporção entre alginato e pectina, da relação entre G e M do alginato e do grau de esterificação (DE) da pectina (GUO & KALETUNÇ, 2016). Os requisitos para a formação do gel e o fato de que os valores de pKa dos resíduos de ácido urônico nas moléculas de alginato e de pectina estão entre 3,4 e 3,7, indicam que as cadeias dos hidrocoloides devem estar parcialmente protonadas antes que a interação possa ocorrer e que a metilação é necessária apenas para reduzir repulsão eletrostática (WALKENSTRÖM et al. 2003).

As características dos géis de alginato e pectina são altamente dependentes da natureza dos hidrocolóides empregados assim como do pH do sistema. A literatura descreve que em sistemas com faixas de pH acima de 4 não há a formação de gel, e géis com máxima firmeza são obtidos quando preparados com alginatos com 70% de ácido α-L-gulurônico na composição e pectinas com 70% de ésteres metílicos, numa relação de 1:1 de alginato: pectina (TOFT et al., 1982).

Em contraste aos géis puros de alginato obtidos com íons de cálcio que são termicamente estáveis, os géis de alginato e pectina são termo-reversíveis (HELGERUD et al., 2010). Dependendo do pH do sistema, o ponto de fusão do gel pode variar entre 30 e 90 °C (TOFT et al., 1986). Géis mais fracos e com pontos de fusão mais baixos podem ser formados com alginatos ricos em ácido ß-D-manurônico e com pectinas de baixo DE (LM) (TOFT et al., 1982; WALKENSTRÖM et al. 2003).

Os géis mistos de alginato e pectina são normalmente preparados misturando os componentes em alta temperatura, acidificando a mistura e permitindo que a gelificação ocorra no resfriamento. Entretanto, alternativamente, as misturas mantidas em temperatura ambiente podem ser acidificadas diretamente ou por diálise, permitindo a obtenção de géis sem aplicação de calor (MORRIS & CHILVERS, 1984).

Para a acidificação dos sistemas os acidulantes lentos como a glucono-delta-lactona (GDL) são os mais indicados pela literatura para a obtenção de géis homogêneos de alginato-pectina via gelificação a frio (TOFT et al., 1986). O GDL é um éster cíclico neutro encontrado naturalmente no mel, na uva, na cerveja e em outras frutas. Industrialmente é produzida através da oxidação da D-glicose por microrganismos, se apresentando comercialmente como um pó branco cristalino, não tóxico, solúvel em água, com um leve sabor doce (CAVALLIERI, 2007; FOOD INGREDIENTS BRASIL, 2021). Quando dissolvido em água, o GDL se hidrolisa lentamente a ácido glucônico (Figura 3.) seguindo uma cinética de primeira ordem. A taxa de hidrólise é lenta, especialmente em temperatura ambiente ou de refrigeração (ZHOU et al., 2021). O ácido glucõnico se encontra sempre em equilíbrio com o GDL em solução aquosa e a velocidade da reação de hidólise depende da temperatura de processo e do pH do meio (CAVALLIERI, 2007).

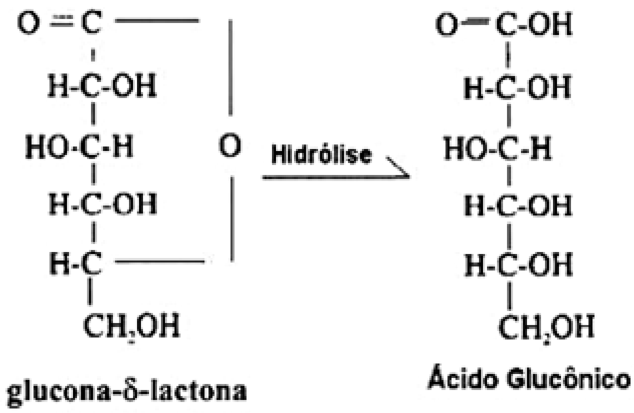

Figura 3. Modelo de gelificação “caixa de ovo” de alginato de sódio com íons Cálcio

Fonte: CAVALLIERI (2007).

A sinergia entre as móleculas de alginato de sódio e de pectina HM é uma das interações possíveis do alginato com outros hidrocolóides descritas pela literatura que apresentam valor comercial (HELGERUD et al., 2010).

O processo de gelificação das misturas de alginato e pectina quando realizado em temperatura ambiente apresenta um amplo potencial de aplicação nos setores industriais farmacêutico e alimentício, em vista da possibilidade de obtenção de estruturas gelificadas sem o consumo e aplicação de calor. As linhas de processamento tendem a ser beneficiadas com o menor consumo energético, reduzindo custos e diminuindo as taxas de emissões ambientais. Além disso, há a possibilidade de uma melhor manutenção de componentes termo sensíveis ao longo do processo, contribuindo para sua preservação e veiculação em preparações alimentícias ou em medicamentos. O alginato e a pectina, por serem hidrocoloides extraídos de matérias primas de origem vegetal, podem ainda contribuir para a substituição de agentes gelificantes de origem animal e desenvolvimento de alimentos e fármacos com foco nos segmentos crescentes de mercados vegetariano/vegano.

4. Referências

ABICAB. **Estatística Balas e Gomas**, 2020. Disponível em: <http://www.abicab.org.br/paginas/estatisticas/balas-gomas/>. Acesso em 23 de Novembro de 2020.

ANVISA. **Regulamento Técnico para balas, bombons e gomas de mascar** - RDC nº 265, de 22 de setembro de 2005, 2005. Disponível em: <http://portal.anvisa.gov.br/documents/394219/RDC_265_2005.pdf/>. Acesso em 23 de Novembro de 2020.

BREJNHOLT, S. M. Pectin. In: IMESON, A. (Ed.). **Food Stabilisers, Thickeners and Gelling Agents**. Blackwell Publishing, 2010, p. 237-265.

BUSINESSWIRE. **Correcting and Replacing Sugar Confectionery Market - Global Forecast and Opportunity Assessment by Technavio**, 2020. Disponível em: <https://www.businesswire.com/news/home/20170614006004/en/CORRECTING-REPLACING-Sugar-Confectionery-Market---Global>. Acesso em 23 de Novembro de 2020.

CAVALLIERI, A. L. F. **Gelificação a frio de proteínas do soro do leite: efeito da taxa de acidificação, pH final e adição de polissacarideos**. Campinas: Unicamp, 2007, 218 p.

DRAGET, K. I.; SKJÅK-BRÆK, G.; STOKKE, B. T. Similarities and differences between alginic acid gels and ionically crosslinked alginate gels. **Food Hydrocolloids**, v. 20, n. 2-3, p. 170–175, 2006.

EDWARDS, W. P. Gomas, productos gelificados y regaliz. In: EDWARDS, W. P. **La ciencia de las golosinas.** Zaragonza: Ed. Acribia, 2008, p. 121-135.

EIRI BOARD. **Hand Book of Confectionery with Formulations**. New Delhi: Engineers India Research Institute, 2012, 253 p.

ERGUN, R.; LIETHA, R.; HARTEL, R. W. Moisture and Shelf Life in Sugar Confections. **Critical Reviews in Food Science and Nutrition**, v. 50, n. 2, p. 162–192, 2010.

FADINI, A. L.; FACCHINI, F.; QUEIROZ, M. B.; ANJOS, V. D. A.; YOTSUYANAGI, K. Influência de diferentes ingredientes na textura de balas moles produzidas com e sem goma gelana. **Boletim do Centro de Pesquisa e Processamento de Alimentos**, v. 21, p. 131–140, 2003.

FADINI, A. L.; CRUZ, C. L. V. Controle e Adequação. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 73–115.

FOOD INGREDIENTS BRASIL. **Acidulantes**, 2021. Disponível em: <https://revista-fi.com.br/artigos/acidulantes/acidulantes>. Acesso em 23 de Novembro de 2020.

GARCIA, T. Analysis of gelatin-based confections. **The Manufacturing Confectioner**, v. 80, n. 6, p. 93-101, 2000.

GOREN, A.; ASHLOCK, D.; TETLOW, I. J. Starch formation inside plastids of higher plants. **Protoplasma**, v. 255, n. 6, p. 1855–1876, 2018.

GUO, J.; KALETUNÇ, G. Dissolution kinetics of pH responsive alginate-pectin hydrogel particles. **Food Research International**, v. 88, p. 129–139, 2016.

GÜZEL, M.; TEKTAŞ TAŞAN, N.; AKPINAR, Ö. Alternative pectin production methods and sources. **AGROFOR International Journal**, v. 5, n. 1, p. 38-45, 2020.

HARTEL, R. W. Hard Candy: from Hard Crack to the Glass Transition. **The Manufacturing Confectioner**, v. 92, n. 9, p. 70-80, 2012.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. Hard Candy. In: HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018a, p. 211-244.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. Aerated confections. In: HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018b, p. 301-328.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. Jellies, Gummies and Licorice. In: HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018c, p. 329-360.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. Starches, Proteins, Pectin, and Gums. In: HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018d, p. 125-150.

HELGERUD, T.; GÅSERØD, O.; FJÆREIDE, T.; ANDERSEN, P. O.; LARSEN, C. K. Alginates. In: IMESON, A. (Ed.). **Food Stabilisers, Thickeners and Gelling Agents.** Blackwell Publishing, 2010, p. 50-72.

KARAKASYAN, C.; LEGROS, M.; LACK, S.; BRUNEL, F.; MAINGAULT, P.; DUCOURET, G.; HOURDET, D. Cold Gelation of Alginates Induced by Monovalent Cations. **Biomacromolecules**, v. 11, n. 11, p. 2966–2975, 2010.

LI, J.; HE, J.; HUANG, Y. Role of alginate in antibacterial finishing of textiles. **International Journal of Biological Macromolecules**, v. 94, p. 466–473, 2017.

MINISTÉRIO DA SAÚDE. **Guia Alimentar para a população brasileira**, 2014. Disponível em: <https://bvsms.saude.gov.br/bvs/publicacoes/guia_alimentar_populacao_brasileira_2ed.pdf>. Acesso em 23 de Novembro de 2020.

MONTENEGRO, F. M.; LUCCAS, V. Os setores bakery & confectionery. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 18–31.

MOORE, C. O. Starch jelly candy. **The Manufacturing Confectioner**, v. 87, n. 10, p. 79-85, 2007.

MORRIS, V. J. & CHILVERS, G. R. Cold Setting Alginate-pectin Mixed Gels. **Journal of the Science of Food and Agriculture**, v. 35, n. 12, p. 1370-1376, 1984.

PIVARO, J. **Chocolates e Confeitos – Doces Indulgências**, 2019. Disponível em: <http://www.revistait.com.br/download/edicoes/IT-44-final-site.pdf/>. Acesso em 11 de outubro de 2020.

QUEIROZ, G. C. Sustentabilidade e Transparência. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 232-257.

QUEIROZ, M. B., & NABESHIMA, E. H. Naturalidade e Autenticidade. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 159–195.

QUEIROZ, G. C. et al. As macrotendências dos setores de *bakery & confectionery*. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 59-72.

SHARMA, B. R., NARESH, L., DHULDHOYA, N. C., MERCHANT, S. U., MERCHANT, U. C. An overview on pectins. **Times Food Processing Journal**, v. 23, n. 2, p. 44-51, 2006.

SHELDRAKE, P. Starch In: IMESON, A. (Ed.). **Food Stabilisers, Thickeners and Gelling Agents**. Blackwell Publishing, 2010, p. 293-324.

SIEW, C. K.; WILLIAMS, P. A.; YOUNG, N. W. G. New Insights into the Mechanism of Gelation of Alginate and Pectin: Charge Annihilation and Reversal Mechanism. **Biomacromolecules**, v. 6, n. 2, p. 963–969, 2005.

SILVA, L. B. **Effect of the use of polyols and açai (*Euterpe oleracea Mart.*) on the physicochemical, sensory and technological characteristics of chewy candies.** Campinas: Unicamp, 2017, 181 p.

STEVENS, P. Gelatine. In: IMESON, A. (Ed.). **Food Stabilisers, Thickeners and Gelling Agents**. Blackwell Publishing, 2010, p. 116-144.

SUFFERLING, K. Gelatin gummies and pectin jellies. **The Manufacturing Confectioner**, v. 87, n. 8, p. 43-50, 2007.

TOFT, K.; GRASDALEN, H.; SMIDSRØD, O. Synergistic Gelation of Alginates and Pectins. In: FISHMAN, M. L., JE, J. J. **Chemistry and Function of Pectins.** Washington: American Chemical Society, 1986, p. 117-132.

VASLIAUSKAS, R. **Sodium Alginate and applications: a review**, 2020. Disponível em: <https://www.elveflow.com/microfluidic-reviews/droplet-digital-microfluidics/sodium-alginate-and-applications-a-review>. Acesso em 31 de Dezembro de 2020.

WALKENSTRÖM, P.; KIDMAN, S.; HERMANSSON, A. M.; RASMUSSEN, P. B.; HOEGH, L. Microstructure and rheological behaviour of alginate/pectin mixed gels. **Food Hydrocolloids**, v. 17, n. 5, p. 593–603, 2003.

ZHOU, S.; JIN, T.; SHEEN, S.; ZHAO, G.; LIU, L.; JUNEJA, V.; YAM, K. Development of sodium chlorite and glucono delta-lactone incorporated PLA film for microbial inactivation on fresh tomato. **Food Research International**, 109067, 2020.

CAPÍTULO 2. ALGINATE/PECTIN COLD-SET GELATION AS A POTENTIAL SUSTAINABLE METHOD FOR JELLY CANDY PRODUCTION

Publication

Article published in **LWT – Food Science and Technology**, volume 123, 109119, Copyright Elsevier, February 2020. Doi:10.1016/j.lwt.2020.109119.

CAPÍTULO 2. Alginate/Pectin cold-set gelation as a potential sustainable method for jelly candy production

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Abstract

The reduction of environmental waste emissions and energy consumption in the confectionery industry is desirable. Therefore, this study evaluated the potential of alginate/pectin cold-set gelation technique in the jelly candy manufacturing process. The obtained products were evaluated by scanning electron microscopy and the parameters evaluated were the process energy requirements, sensory acceptance, and physicochemical characteristics (instrumental texture and color, moisture content, pH, and water activity). These parameters were compared to those of a standard pectin jelly candy. The gelling agents considerably influenced the physicochemical parameters of the candies. Alginate/pectin jellies showed a higher hardness value (16.2 N) and an opaque and lighter coloring compared to the pectin jelly candy (6.2 N). There was a dense and homogeneous network with a large amount of pores in cold-set candies, which differed from the sparse network with micelles and large pores in pectin jellies. The energy requirement of the cold-set process (0.013 kWh) was statistically lower than the conventional heating process (0.035 kWh). There was no significant difference ($p > 0.05$) between the alginate/pectin jellies and pectin candies for all sensory attributes evaluated, indicating that the cold-set gelation technique could be an alternative sustainable technology for the production of jelly candy.

Keywords: cold-setting gels; confectionery; hydrocolloids; sustainability.

1. Introduction

In recent years, the economic growth of the confectionery market has been driven by successful launches of healthy, fortified, functional, and sustainable products (Confectionery News, 2019).

The sustainability concept for the food industry unfolds at diverse opportunities along the production chain. In the confectionery sector, there has been a great focus on the sustainable, organic and “fair trade” production of the main raw materials and packaging used for products (Queiroz, 2014).

Another claim of sustainability in the industrial chain is the considerable reduction of energy consumption and environmental waste emissions (Queiroz, 2014). As the confectionery industry produces various products like candies, confections, and chocolates, this reduction should focus on the singularities of each production system. The candy line, in particular, has distinct processes according to the candy type, but all of them involve the syrup cooking step as a conventional critical point, due to the traditional equipment and systems that account for the highest energetic requirement of the confectionery manufacturing line (Aigroup, 2019).

Jellies and gummies are a significant and growing segment in the candy industry. They comprise a broad group of products whose characteristics are strongly determined by the gelling agent and the final moisture content (Coyle, 2007; DeMars & Ziegler, 2001; Eiri Board, 2012).

In jelly candy manufacturing, the gel structure is determined by the gelling agent, and it can occur by ionotropic gelation, cold-set gelation, or heat-set gelation (Saha & Bhattachaya, 2010). The most common hydrocolloids used in candy formulations are starch, pectin, agar, and gelatin. All of them require heating for candy gelation, which is usually done in the syrup cooking step (Edwards, 2008).

Other hydrocolloids are capable of gelation without heating. Cold-set gelation is a technology that has been extensively studied (De Moura et al., 2019; Brito-Oliveira, Bispo, Moraes, Campanella & Pinho, 2018; Lavoisier & Aguilera, 2019; Bilek & Özkan, 2018); however, its application in commercial candy production is unexplored.

Among the cold-set gelling agents, the combined use of sodium alginate and high methoxylation pectin is noteworthy. The mechanical properties of alginate/pectin gels depend on several factors and their gelling mechanism is not yet completely elucidated. When combined at pH 3.4-3.8, they form cohesive nets at room temperature (Walkenström, Hermansson, Rasmussen & Hoegh, 2003; Toft, Grasdalen & Smidsrød, 1986).

Cold-set gelation is a potential sustainable alternative for jelly candy industries to reduce the energy requirement for the structure of the candy gel. In this context, the aim of this study was to evaluate the performance of sodium alginate and pectin as gelling agents for jelly candies compared to a conventional hydrocolloid.

2. Material and methods

2.1. Material

The ingredients used in the preparation of the jelly candies were: sucrose (União, São Paulo, Brazil), glucose syrup (Excell 1040, Ingredion, Mogi Guaçu, Brazil), high methoxylation pectin (HM 121Slow, Degree of esterification 58%, CPKelco, Limeira, Brazil), sodium alginate (Algin I-3G-150 , viscosity 300 – 400 mPa·s, Kimica, Providencia, Chile), glucono-delta-lactone (GDL) (Art Alimentos, São Paulo, Brazil), sodium citrate (ACS, Synth, Diadema, Brazil), citric acid (ACS, Synth, Diadema, Brazil), pear flavor (HS-901-666-1, Givaudan, São Paulo, Brazil), and the food dye tartrazine yellow (CI 19140, Eskisa, São Paulo, Brazil).

2.2. Development of jelly candies

2.2.1 Definition of cold-set jelly candy manufacturing

The development of a cold-set jelly candy was based on the method of alginate/pectin gelation described by Walkenström et al. (2003), which consists of the dispersion of hydrocolloids in water with subsequent acidification to promote gelation. According to Toft et al. (1986), gels are harder at pH 3.4 and with a 1:1 (kg: kg) ratio of alginate: pectin.

As jelly candies are traditionally obtained from a mix of hydrocolloids and sugar solution, the cold-set candy process was proposed using the steps of (1) dissolving sucrose and glucose syrup in cold water, (2) dispersion of alginate and pectin in the sugar solution, (3) dissolution of GDL for acidification of the system and (4) the addition of food dye and flavor.

Then the obtained syrup follows the conventional jelly candy manufacturing steps of deposition in starch molds, drying, demolding, and finishing (Sufferling, 2007).

The mixing of the ingredients was performed with a digital mechanical bench agitator (Tecnal, model TE-039/1, Piracicaba, Brazil) at 380 rpm. The length of the mixing time during the candy manufacturing steps was fixed at 3.44, 0.78, 0.66, and 0.20 min for steps (1), (2), (3), and (4), respectively. The syrup was manually dosed with a funnel and dried in a forced air circulation drying oven (Tecnal, model TE-394/2, Piracicaba, Brazil) at 35 °C for 72 h.

2.2.2 Definition of the jelly candy formulation

A total of 18 candy formulations were tested. The final soluble solids content of the syrups was fixed at 71 °Brix and was evaluated as follows:

(a) The sucrose: glucose syrup ratio used in the base sugar syrup (1: 1 and 1: 2, kg: kg, dry basis);

(b) The percentage of polymer blend (alginate/pectin) required to promote gelation (10, 15 or 20 g/kg);

(c) The GDL content required for acidification of the system (10, 15 or 20 g/kg).

The varied contents were determined after preliminary tests. To evaluate the proposed formulations, a pectin jelly was produced to be used as a standard sample. It was prepared by the dissolution of sucrose (381.7 g/kg), glucose syrup (229.4 g/kg), sodium citrate (1.3 g/kg), citric acid (4 g/kg) and pectin (12 g/kg) in water (371.6 g/kg) and then heating at atmospheric pressure for 5.12 min until 71 °Brix. The pectin jelly was dosed into starch molds, dried in a forced air circulation drying oven (Tecnal, model TE-394/2, Piracicaba, Brazil) at 35 °C for 72 h and then demolded (Sufferling, 2007). The physical and physicochemical parameters of the candies were evaluated according to the methods described in section 2.4.

Table 1. Experimental proposal for definition of alginate/pectin jelly candy formulation.

Formulation	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F13	F14	F15	F16	F17	F18
Sucrose: Glucose syrup ratio (kg: kg, d.b.)	1:1									1:2								
Polymer blend (g/kg)*	10			15			20			10			15			20		
GDL** (g/kg)	10	15	20	10	15	20	10	15	20	10	15	20	10	15	20	10	15	20

F: formulation; d.b.: dry basis; * Polymer blend composed of an alginate: pectin ratio of 1: 1, kg: kg; **GDL: glucono-delta-lactone.

2.2.3. Definition of drying conditions

After evaluation, formulation 7 was selected and a drying study was carried out to determine the time and temperature parameters for the developed candy manufacturing process. A drying curve was performed over 72 h in a forced air circulation drying oven (Tecnal, model TE-394/2, Piracicaba, Brazil) at temperatures of 35, 45 and 55 °C, (temperatures commonly used in the drying step of jelly and gummies production) (Eiri Board, 2012; Sufferling, 2007; Moore, 2007). Samples were collected every 12 h for physical and physicochemical characterization according to the methods described in section 2.4.

2.3. Jelly candy processing

For a comparative study, two types of jelly candies were produced: an alginate/pectin jelly candy (APJ) and a pectin jelly candy (PJ), chosen as a reference candy in this study. Formulation 7 (item 2.2.2) was selected for the APJ, the production method followed the steps described in section 2.2.1 and the drying conditions were determined according to section 2.2.3. The PJ formulation and its production method are described in section 2.2.2. The APJ and PJ were flavored and colored with pear flavor and the food dye tartrazine yellow.

2.4. Physical and physicochemical determinations

The 18 jelly candy formulations produced in section 2.2.2 were characterized in relation to pH, according to AOAC Official Method 981.12 (AOAC, 2012) with a Potentiometer (Digimed, model DM-20, São Paulo, Brazil), and a hardness parameter, using a Texture Analyzer (TA-XT2i model, Surrey, England) according to Fadini et al. (2005) with modifications: the use of a cylindrical aluminum probe P/35, pre-test, test and post-test speeds of 2.0, 2.0 and 10.0 mm/s, respectively, and a penetration distance of 1 mm, in ten replicates.

The jellies of the drying study (section 2.2.3) were characterized in relation to pH and hardness (the same methods previously described); moisture content according to AOAC Official Method 920.151 (AOAC, 2012) in a vacuum oven, in triplicate; and water activity using a water activity analyzer (Aqualab, model 4TEV, Decagon Devices Inc., Pullman, USA) after equilibration at 25 °C, in triplicate.

The APJ and PJ samples (section 2.3) were characterized in relation to pH, moisture content and water activity, according to the previously described methods; instrumental color using a digital colorimeter (Hunter Lab UltraScan PRO, Washington DC, USA) in the CIELAB system (L*, a* and b*), in ten replicates; Texture Profile Analysis (TPA) using a Texture Analyzer (TA-XT2i model, Surrey, England) according to Delgado & Bañón (2014) with modifications. The samples were compressed twice using a D/40 acrylic disc, which allowed the samples to be deformed without penetration, and two consecutive cycles of 40% compression. The cross head moved at a constant speed of 1.0 mm/s with a trigger point of 0.01 N, in ten replicates.

2.5 *Scanning Electron Microscopy*

The structure of the APJ and PJ gels was evaluated using a scanning electron microscope (model TM-3000, Hitachi High Technologies, Tokyo, Japan) (Marfil, Anhê & Telis, 2012). The candy samples were placed directly in the sample holder. Images were taken in duplicate and processed by Image-Pro Plus v 7.01 software (Media Cybernetics, Inc.).

2.6 Sensory analysis

The APJ and PJ candies were sensorially evaluated in an acceptance test performed at the Food Sensory Analysis Laboratory of the Department of Food Technology - FEA/UNICAMP (approved by the Research Ethics Committee of the University of Campinas, under Certificate of Presentation for Ethical Assessment – CPEA 86627118.5.0000.5404). The 120 invited consumers analyzed the appearance, color, aroma, flavor, texture and general impression using a structured 9-point hedonistic scale ranked as follows: 9: I liked it extremely, 5: I did not like or dislike it, and 1: I disliked it extremely (Stone & Sidel, 2004).

2.7 Measurement of the energy requirement of the manufacturing processes

The energy requirements of the heating and cold-set candy manufacturing processes were evaluated by a bench-based estimation study. Considering the time of preparation of the cold-set candy syrup and the power of the bench agitator, the energy consumed was calculated using Equation 1 (Diaz, Redelsheimer & Dornfeld, 2011).

$$\text{Energy requirement (kWh)} = \frac{\text{time of the process (s) x power of the equipment (W)}}{3600\left(\frac{\text{s}}{\text{h}}\right)\text{x }1000\left(\frac{\text{W}}{\text{kW}}\right)} \quad \text{(Equation 1)}$$

The energy requirement for heating the candy syrup was estimated considering the volume and the internal calorific value of the gas burned during the cooking step, according Equation 2 (Eletrobrás, 2005). The gas used in the experiments was a liquefied petroleum gas consisting of 750 g/kg isobutane and 250 g/kg propane (isobutane internal calorific value: 9209 kJ/m³; propane internal calorific value: 117230 kJ/m³).

$$\text{Energy requirement (kWh)} = \text{Gas volume } (\text{m}^3) \text{ x Internal calorific value } \left(\frac{\text{kJ}}{\text{m}^3}\right) \text{x } 2{,}77 \text{ x } 10^{-4} \left(\frac{\text{kWh}}{\text{kJ}}\right) \text{ (Equation 2)}$$

Considering the mass loss by evaporation during the heating process, and the moisture loss of the candy syrups during the drying step, the weight yield of the heating and cold-set syrups was calculated using Equation 3, to adjust the estimated energy requirement of the processes (Equation 4), expressed by kWh/ g of candy.

$$\text{Weight yield} = \frac{\text{weight of candies after drying step (g)}}{\text{weight of candy syrup before cooking or cold−setting step (g)}} \text{ (Equation 3)}$$

$$\text{Energy requirement (kWh/ g of candy)} = \frac{\text{Energy requirement (kWh)}}{\text{weight yieald}} \text{ (Equation 4)}$$

2.8 Statistical Analysis

The Friedman's test and Nemenyi's test were used to analyze the results (at a 95% confidence interval) using the statistical software XLSTAT (Addinsoft, New York, NY, 2016).

3. Results and discussion

3.1. Tests of candy development

According to preliminary tests, the production of candies with less than 10 g/kg of polymer mixture was impossible due to the excessive softness of the gels and consequent collapse during the drying step. The soluble solids content of the sugar syrup should not be higher than 65 °Brix, due to the possibility of sucrose saturation and subsequent crystallization in the drying step.

The alginate/pectin candies produced with lower polymer content did not differ ($p > 0.05$) from the standard pectin candy. The highest hardness values were measured in candies with the most elevated concentrations of hydrocolloids (Table 2).

Table 2. Mean values of hardness (N) and pH of the 18 cold-set experimental proposed candy formulations.

Formulation	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F13	F14	F15	F16	F17	F18	SS
Hardness (N)*	60 ±37 abcd	59 ±40 abcd	60 ±16 abcd	57 ±13 abcd	65 ±15 abc	60 ±11 abc	78 ±15 a	67 ±26 abc	60 ±11 abc	49 ±10 cd	43 ±14 cd	46 ±13 cd	79 ±23 a	69 ±15 ab	52 ±11 bcd	74 ±17 a	57 ±17 abcd	71 ±14 ab	37 ±12 d
pH**	3.80 ±0.18 abcde	3.66 ±0.06 cdef	3.67 ±0.12 bcdef	3.92 ±0.03 ab	3.76 ±0.02 abcdef	3.60 ±0.01 def	3.97 ±0.01 a	3.83 ±0.02 abcd	3.73 ±0.01 acdef	3.87 ±0.06 abc	3.67 ±0.02 cdef	3.53 ±0.03 f	3.96 ±0.07 a	3.74 ±0.08 abcdef	3.73 ±0.12 abcdef	3.99 ±0.03 a	3.84 ±0.02 abcd	3.73 ±0.02 abcdef	3.53 ±0.01 ef

F, formulation; SS, standard sample. Mean values of 10 replicates (*) and triplicates (**). Mean values followed by different letters in the same column are significantly different ($p < 0.05$).

Jellies with a 1:2, kg: kg, ratio of sucrose: glucose syrup (Formulations 10-18) and 10 g/kg of polymer blend (Formulations 1-3; 10-12) had a high destructuration and adherence on the texture analyzer board. This was considered undesirable due to the possibility of adherence of the product in the teeth during mastication.

As expected, formulations with higher GDL concentrations presented lower pH values. In candies prepared with 1:1, kg: kg, of sucrose: glucose syrup, the instrumental hardness values grew as the GDL concentration increased. Similar results are described by Toft et al. (1986) in a gelation study of alginate/pectin model solutions. According to the authors, alginate/pectin gels are formed at pH below 3.8 and can be obtained in sugar-free systems. All the proposed formulations of this study presented pH values close to or slightly higher than the recommended pH value for gelation of the system.

For the sequential studies, formulation 7 was selected due to the high gel hardness and low adherence of the candy on the texture analyzer board during the compression test.

3.2 Determination of the drying conditions

The curves showing the mean values of hardness and moisture content at the different temperatures of the drying study are presented in Figures 1 and 2.

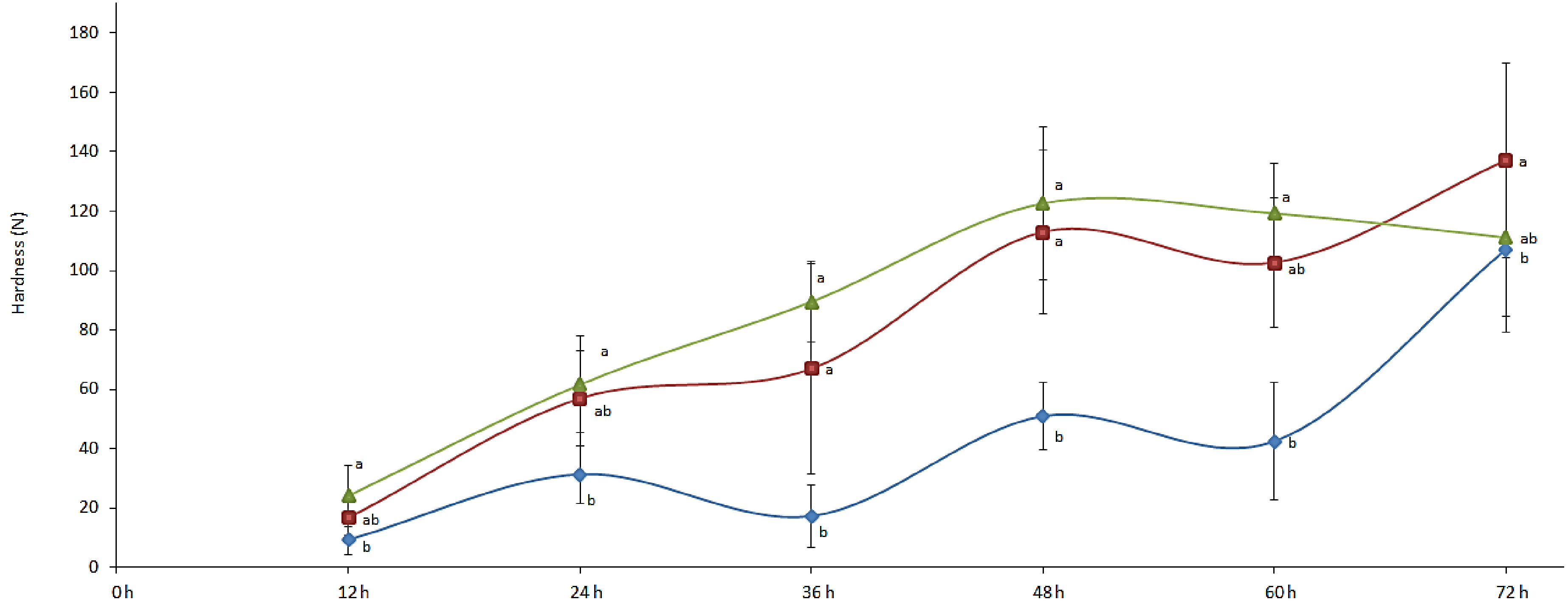


Figure 1. Mean values of hardness (N) during the drying process of cold-set jelly candy (formulation 7) at three different temperatures (●: 35 °C; ■: 45 °C; ▲: 55 °C). Mean values followed by the same letter are not significantly different ($p>0.05$) in respect to the drying temperature at the same evaluated drying time.

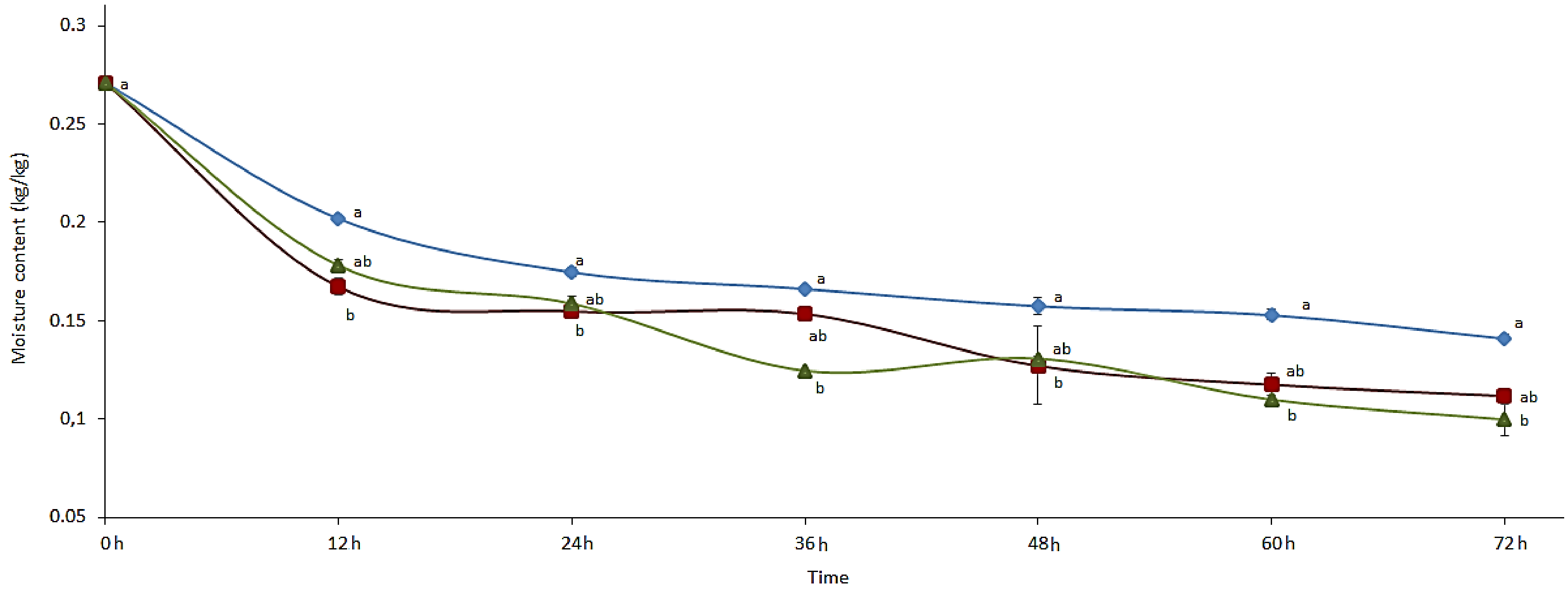


Figure 2. Mean values of moisture content (kg/kg) during the drying process of cold-set jelly candy (formulation 7) at three different temperatures (●: 35 °C; ■: 45 °C; ▲: 55 °C). Mean values followed by the same letter are not significantly different ($p>0.05$) in respect to the drying temperature at the same evaluated drying time.

During the drying process, temperature presented a significant difference ($p < 0.05$) in relation to the averages of hardness and moisture content. It was visually observed that candies dried at 45 and 55 °C had a crystallized layer on their inner surface, the thickness of which increased over the drying time.

Jelly candies traditionally have a moisture content of about 0.08-0.22 kg/kg (Ergun, Lietha & Hartel, 2010). Candy dehydration was faster at higher drying temperatures. At 45 °C, the moisture reduction was 1.2 times higher than at 35 °C, while at 55 °C, the decrease in moisture content was twice that at 35 °C. The water activity and pH curves are presented in Figures 3 and 4.

The average a_w presented significant differences ($p < 0.05$) at all times along the drying curve at the three temperatures evaluated. Similar to the moisture curves, the temperatures of 45 °C and 55 °C showed the lowest a_w values. For better stability, jelly candies should present a a_w range between 0.5-0.75 (Ergun et al., 2010), which was reached at all temperatures after 12 h of drying.

At the three temperatures tested, there was a sudden decline of pH values after the first 12 h of drying, followed by an increase after 24 h with a subsequent stabilization; except for the 45 °C temperature, which showed a considerable increase in pH at 48 h. The acidification behavior was related to the used acidulant. GDL is a D-gluconic acid cyclic ester commonly used as an acidifier in gelation systems because of its slow and controlled acidification that occurs when converted to gluconic acid in an aqueous system (Imeson, 2010; Søltoft-Jensen & Hansen, 2005; Xavier, Rauter & Queneau, 2010). In APJ candy production, GDL is ideal for the slow formation of the gel, giving time for the syrup to deposit in the drying molds.

The pH increase after 24 h may be related to the reduction of the moisture content that contributed to a partial reversion of the gluconic acids in GDL. After 72 h of drying, for all temperatures, the pH averages were above the range of 3.8 recommended for gel formation (Toft et al., 1986). However, all candies maintained the gel structure as evidenced by the instrumental hardness values.

The drying condition of 35 °C for 72 h was selected. Despite the longer drying time, the candies dried in these conditions presented better texture characteristics, the absence of a crystallized sugar layer on the inner surface and final products with low averages of water activity and moisture content, which contribute to a longer shelf-life.

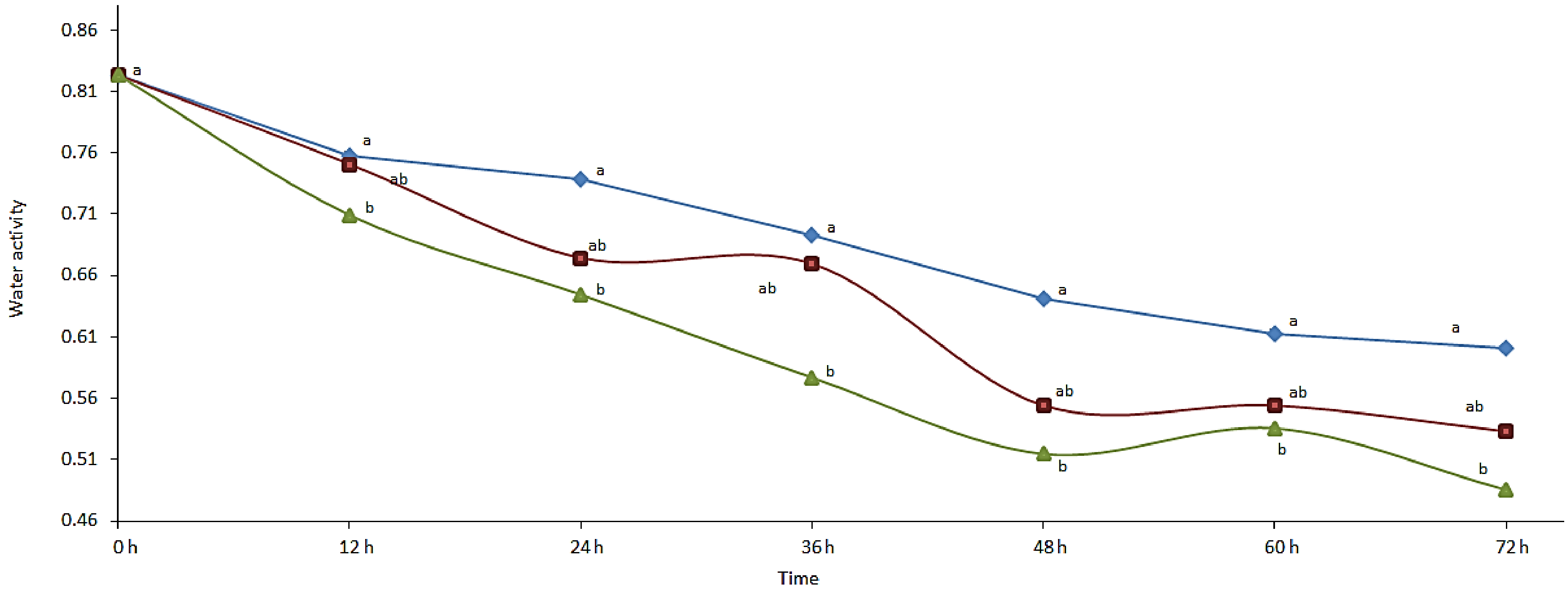


Figure 3. Mean values of water activity during the drying process of cold-set jelly candy (formulation 7) at three different temperatures (●: 35 °C; ■: 45 °C; ▲: 55 °C). Mean values followed by the same letter are not significantly different ($p>0.05$) in respect to the drying temperature at the same evaluated drying time.

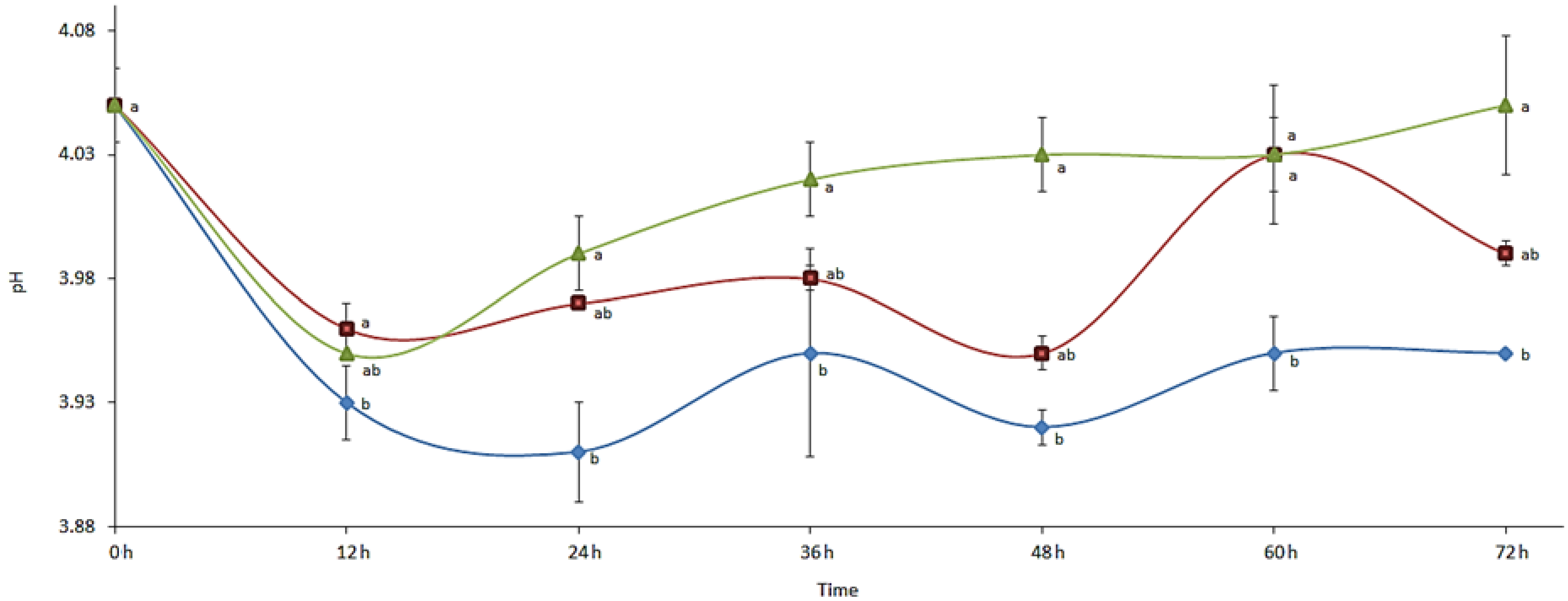


Figure 4. Mean values of pH during the drying process of cold-set jelly candy (formulation 7) at three different temperatures (●: 35 °C; ■: 45 °C; ▲: 55 °C). Mean values followed by the same letter are not significantly different ($p>0.05$) in respect to the drying temperature at the same evaluated drying time.

3.3. Candy production and Physical and physicochemical characterization

A new batch of formulation 7 was produced for a comparative study with a standard PJ candy. The syrup of the APJ candy consisted of water (237.1 g/kg), sucrose (336.6 g/kg), glucose syrup (396.3 g/kg), sodium alginate (10 g/kg), high methoxylation pectin (10 g/kg), GDL (10 g/kg), pear flavor (1.8 g/kg of prepared syrup) and the food dye tartrazine yellow (0.5 g/kg of prepared syrup). The formulation of PJ consisted of water (372.7 g/kg), sucrose (381 g/kg), glucose syrup (229 g/kg), high methoxylation pectin (12 g/kg), citric acid (4 g/kg), sodium citrate (1.3 g/kg), pear flavor (1.6 g/kg of prepared syrup) and the food dye tartrazine yellow (0.4 g/kg of prepared syrup). The results of the physicochemical characterization of the jelly candy samples are presented in Table 3.

Table 3. Physical and physicochemical parameters and sensorial attributes of the produced candies.

	Physical and physicochemical parameters												Sensorial atributes					
	Instrumental Texture						Instrumental Color			pH	Aw	Moisture Content (kg/kg)	Appearence	Color	Aroma	Flavor	Texture	Overall impression
	Hardness (N)	Springness	Cohesiveness	Gumminess	Chewiness	Resilience	L*	a*	b*									
PAJ	16.20 ±4.37*	0.49 ±0.06*	0.19 ±0.05*	2.85 ±0.60	1.42 ±0.27*	0.05 ±0.01*	64.02 ±0.90*	1.72 ±0.39*	56.36 ±1.55	3.95 ±0.01*	0.672 ±0.001*	0.15 ±0.01	6.6 ±1.7	7.0 ±1.8	5.0 ±1.0	5.3 ±2.0	4.5 ±1.9	5.3 ±1.7
PJ	6.24 ±0.50*	0.82 ±0.06*	0.48 ±0.03*	3.07 ±0.35	2.52 ±0.37*	0.15 ±0.01*	51.46 ±1.08*	3.80 ±0.90*	53.57 ±1.49	3.45 ±0.011*	0.583 ±0.005*	0.17 ±0.01	7.0 ±1.5	8.0 ±1.2	5.0 ±1.1	6.6 ±1.7	6.0 ±1.9	7.0 ±1.5
General average	11.22	0.65	0.33	2.96	1.97	0.10	57.74	2.76	54.96	3.70	0.627	0.16	7.0	7.5	5.0	6.0	5.0	6.0

Aw, water activity; PAJ, alginate/pectin jelly candy; PJ, pectin jelly candy. Mean values of 10 replicates of instrumental texture measurements and triplicates of instrumental color, pH. Aw and moisture content measurements. Mean values followed by (*) in the same line are significantly different ($p < 0.05$).

The samples showed a significant difference ($p < 0.05$) in relation to the texture parameters, except for gumminess. The APJ gel presented a harder texture with less elasticity, cohesiveness, chewiness, and resilience. When the alginate/pectin mix is used in jellies, the obtained gel is softer and less adhesive than other candy gels produced with carrageenan-konjac, gelatin/maize starch, and modified starch/non-starch polysaccharides (Habilla & Cheng, 2015; Kusumaningrum, Parnanto & Atmaka, 2016; Marfil et al., 2012).

The colorimetric parameter L* of the APJ candy was significantly higher ($p < 0.05$) than the PJ candy, showing a clear and opaque coloration visually observed in the product. The moisture content values of the two treatments did not differ ($p > 0.05$) and were adequate for the predicted range for this product category (Ergun et al., 2010). According to Hartel et al. (2018) jellies and licorices have a higher moisture content (0.16-0.20 kg/kg) while more complex gums have lower moisture content (0.07-0.08 kg/kg).

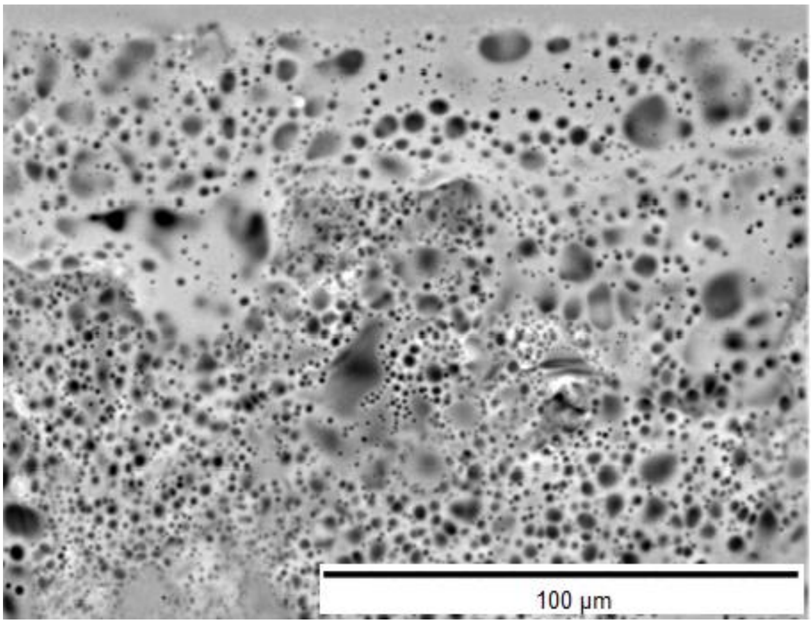
Both treatments presented a_w values in the recommended range of 0.5-0.75 (Ergun et al., 2010), however, the APJ water activity mean was significantly higher ($p < 0.05$) than the a_w value of PJ. Compared to monocomponent gels, sodium alginate/pectin systems have more hydrogen bonds between chains of macromolecules. Therefore, the water binding energy in the system and the bound water portion are increased and the rate of water removal in these gels is slower (Sokolovska, Kambulova & Overchuk, 2016). This factor could explain the higher a_w averages of the APJ candy.

The pH value of PJ was in the range of 3-3.5, which is indicated for gelation of high methoxylation pectin (Sufferling, 2007), while the pH value of the APJ was moderately higher than that recommended for alginate/pectin gelation (Toft et al., 1986).

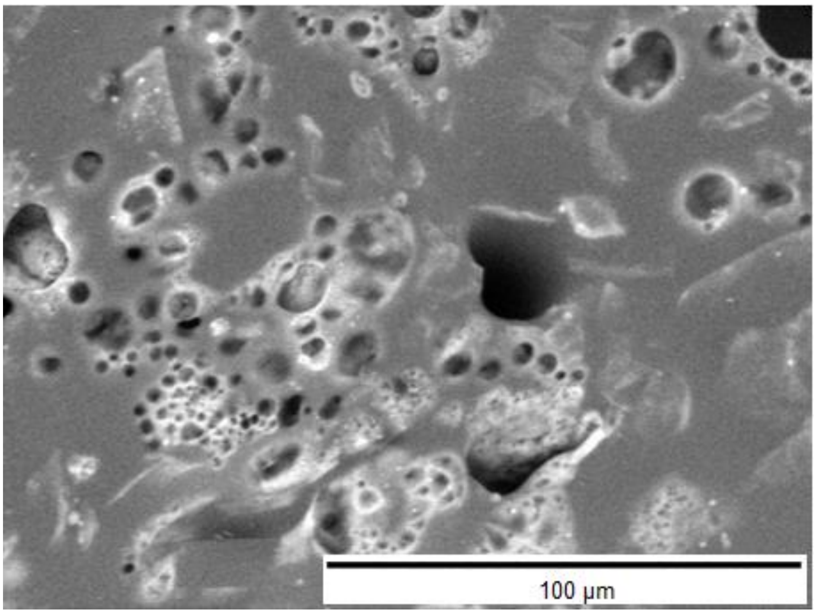
The microstructures of the APJ and PJ candies (Figure 5) had different characteristics in relation to candies produced with other hydrocolloids such as gelatin and starch (Otálora, de Jesús Barbosa, Perilla, Osorio & Nazareno, 2019; Marfil et al., 2012).

Alginate/pectin gels are formed by synergistic relationships between the α-D-galacturonic esterified molecules from pectin and α-L-guluronic acid residues from alginate that occur when the uronic acids are in their protonated form (Toft, 1983). In the literature, information on the microstructures of synergistic gels is scarce, however, in the microscopic images it was possible to verify a dense and homogeneous network structure with a large amount of pores, similar to that observed in the alginate/pectin gel model systems obtained by Walkenström et al. (2003).

The gel chain and density characteristics may justify the higher values of hardness and lower elasticity that were measured, as well as the visually observed opacity of the product.



(a)



(b)

Figure 5. Scanning electron microscopy of (a) alginate and pectin jelly candy at 100 µm and (b) pectin jelly candy at 100 µm.

In the PJ microscopy images, a sparse network structure with the presence of micelles and large pores was identified. The structure was similar to those observed in pure HM and low methoxylation (LM) pectin gels by Löfgren et al. (2002) and characterized as open networks with wires arranged in bundles or loose aggregates.

The concentration, pore size and structure of the polymers may influence the gels water retention capacity (Mohammadian & Madadlou, 2016). The sparse networks in the PJ samples may justify the higher moisture content and lower hardness values of the sample.

HM pectin gels are formed by interactions between molecules under conditions of low acidity and a_w, by means of hydrogen interactions between undissociated carboxyl groups and secondary alcohol groups, and hydrophobic interactions between methyl ester groups (Sharma, Naresh, Dhuldhova, Merchant & Merchant, 2006).

3.4. Sensory analysis

There was no significant difference ($p > 0.05$) between the candy samples for all sensory attributes evaluated (Table 3), indicating the sensory potential of the application of the cold-set gelation as a substitute technology to the conventional jelly candy process. The acceptance scores were located between the "indifferent" and "moderately liked" hedonic terms.

In the candy production sodium alginate formed a lighter and opaque gel, which resembles starch jelly candy and differs from agar, pectin, and gelatin candies.

3.5. Measurement of the energy requirement of the manufacturing processes

Table 4 presents the process variables of each candy manufacturing method. There was a significant difference ($p < 0.05$) between the energy consumption of the processes. Cold-set manufacturing had an energy requirement 2.7 times lower than the heating process, resulting in the use of 2.2 times less energy per gram of produced candy.

Table 4. Mean values of energy requirement and process variables of the cold-set and heating candy manufacturing processes.

Manufacturing Process	Process variable**									
	Sugar dissolving time (min)	Polymer blend dispersion time (min)	GDL dissolving time (min)	Flavoring time (min)	Cooking time (min)	Total syrup processing time (min)	Volume of burned gas (m^3)	Weight yield	Energy requirement (kWh)	Energy requirement by gram of candy (kWh/ g of candy)
Cold-set Manufacturing Process	3.44	0.78	0.66	0.20	-	4.59	-	0.64	0.013 ±0.001*	0.021 ±0.001*
Heating Manufacturing Process	-	-	-	-	5.12	5.12	0.001	0.74	0.035 ±0.002*	0.046 ±0.002*

GDL, glucono-delta-lactone. (**) Mean values of process variable of the manufacturing of 200g of candy syrup. Mean values followed by (*) in the same column are significantly different ($p < 0.05$).

In industrial jelly candy processing, the syrup cooking and drying steps correspond to the main energy requirements of the line, whereas the cooking step is responsible for the highest energy requirement of the whole line (Aigroup, 2019). The drying step of the cold-set process developed in this study used the same time/temperature conditions of the conventional process, so the difference in the energy demand was restricted to the syrup preparation step.

Considering the industrial machinery, the difference of energy requirements between the processes can reach very significant levels in the industrial line. The replacement of gas burning from the syrup cooking step with the use of electricity in the cold-set syrup mixing process could contribute not only for the industrial energy expenditure reduction, but also to reduce the environment gas emissions. The fossil energy resources (coal, oil, natural gas and secondary fuels), commonly used in heating industrial lines, have many disadvantages in terms of emission and human health. The levels of fossil fuels burning are attributed to the country where are consumed, however it is estimated that they correspond to 37% of global CO2 emissions (Chala, Abd Aziz & Hagos, 2018; Davis, Peters & Caldeira, 2011).

The electricity, particularly, can be generated from different ways according the resources and technologies of the country. When the production occurs in wind power stations, nuclear or hydroelectric power stations, the electricity cover sustainability concept in respect to the use of natural resources and the lower gas emissions. (Cardoso de Lima et al., 2018; Hadley & Short, 2001; Onat & Bayar, 2010).

The consumption of electricity generated from non-carbon intensive sources could aim the concept of "clean process" to the cold-set candy manufacturing. In this way, claims of sustainability such as environmental self-declaration and carbon foot print seals could be appointed to the cold-set jellies.

4. Conclusion

The production of jelly candies by cold-set gelation using alginate/pectin mixtures has great viability. The obtained candies presented values of physical and physicochemical parameters within the ranges recommended by the literature, which indicated stability for the products elaborated in this process. Sensorially, the alginate/pectin candies did not differ significantly in relation to the pectin candies, indicating cold-set manufacturing as a substitute alternative to the conventional candy production process. The developed process in this study had a lower energy consumption than the conventional heating candy manufacturing, assigning a sustainability potential for the cold-set candies in the confectionery market.

Acknowledgments

Conselho Nacional de Desenvolvimento Científico e Tecnológico - Brasil (CNPQ) for the fellowship to the first author, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, Innovation Agency of University of Campinas (Inova-Unicamp) and the Brazilian National Institute of Industrial Property for the patent filling BR 10 2018 076817, that contemplates and protects the results of this study.

5. References

Aigroup. Energy reduction factsheet: Saving energy in the confectionery manufacturing industry. (2019). http://cdn.aigroup.com.au/Environment/21_Food_Processing_Confectionery_Manufacturing_Energy_Reduction_Factsheet.pdf. Accessed 22, July, 2019.

AOAC. (2012). *Official Methods of Analysis of AOAC International*. 19th ed. Gaithersburg, MD: Association of Official Analytical Chemists.

Bilek, S. E., & Özkan, G. (2018). Encapsulation of zinc-chlorophyll derivatives in whey protein matrix by emulsion/cold-set gelation. *GIDA/ The Journal of Food Research, 43(1),* 174-183. doi: 10.153237/gida.321167.

Brito-Oliveira, T. C., Bispo, M., Moraes, I. C. F., Campanella, O. H., & Pinho, S. C. (2018). Cold-Set Gelation of Commercial Soy Protein Isolate: Effects of the Incorporation of Locust Bean Gum and Solid Lipid Microparticles on the Properties of Gels. *Food Biophysics, 13 (3)*, 226–239. doi:10.1007/s11483-018-9529-4.

Cardoso de Lima, G. S., Lopes, E. C., Motta, J. G., Asano, R., Valverde, M., Suyama, R., & Leite, P. T. (2018). Sustainable development enhanced in the decision process of electricity generation expansion planning. *Renewable Energy, 123*, 563–577. doi:10.1016/j.renene.2018.02.012.

Chala, G., Abd Aziz, A., & Hagos, F. (2018). Natural Gas Engine Technologies: Challenges and Energy Sustainability Issue. *Energies, 11(11),* 2934. doi:10.3390/en11112934.

Coyle, S. J. (2007). Cooking Equipment for Jelly Candy. *The Manufacturing Confectioner*, *99 (8*), 36-42.

Confectionery News. Organic candy: The future of confectionery, says new report. (2019). https://www.confectionerynews.com/Article/2007/08/08/Organic-candy-the-future-of-confectionery-says-new-report. Accessed 22, July, 2019.

Davis, S. J., Peters, G. P., & Caldeira, K. (2011). The supply chain of CO2 emissions. *Proceedings of the National Academy of Sciences, 108(45),* 18554–18559. doi:10.1073/pnas.1107409108.

Delgado, P., & Bañón, S. (2014). Determining the minimum drying time of gummy confections based on their mechanical properties. *CyTA - Journal of Food, 13(3),* 329–335. doi:10.1080/19476337.2014.974676.

DeMars, L. L., & Ziegler, G. R. (2001). Texture and structure of gelatin/pectin-based gummy confections. *Food Hydrocolloids, 15(4-6),* 643–653. doi:10.1016/s0268-005x(01)00044-3.

De Moura, S. C. S. R., Berling, C. L., Garcia, A. O., Queiroz, M. B., Alvim, I. D., & Hubinger, M. D. (2018). Release of anthocyanins from the hibiscus extract encapsulated by ionic gelation and application of microparticles in jelly candy. *Food Research International, 121,* 542-552. doi:10.1016/j.foodres.2018.12.010.

Diaz N., Redelsheimer E., & Dornfeld D. (2011) Energy Consumption Characterization and Reduction Strategies for Milling Machine Tool Use. In: Hesselbach J., & Herrmann C. (Eds) *Glocalized Solutions for Sustainability in Manufacturing* (pp. 263-267). Berlin, Heidelberg: Springer.

Edwards, W. P. (2008). Gomas, productos gelificados y regaliz (Gums, jelly products and licorice) [In Spanish]. In: Edwards, W. P. *La ciencia de las golosinas* (pp. 121-135). Zaragonza: Ed. Acribia.

Eletrobrás. (2005). *Eficiência Energética no Uso de Vapor* (*Energy Efficiency in Steam Use*) [In Portuguese]. Rio de Janeiro: Eletrobrás, 196 p.

Ergun, R., Lietha, R., & Hartel, R. W. (2010). Moisture and Shelf Life in Sugar Confections. *Critical Reviews in Food Science and Nutrition, 50(2),* 162–192. doi:10.1080/10408390802248833.

Eiri Board. (2012). *Hand Book of Confectionery with Formulations*. New Delhi: Engineers India Research Institute, 253 p.

Fadini, A. L., Jardim, D. C. P., Queiroz, M. B., Bertin, A. P., Efraim, P., & Mori, E. E. M. (2005). Características sensoriais e de textura de chicles drageados diet produzidos com diferentes tipos de polióis (*Sensory and texture characteristics of diet panned chewing gum produced with different types of polyols*) [In Portuguese]. *Brazilian Journal of Food Technology, 8*, 113-119.

Habilla, C., & Cheng, L. H. (2015). Quality of jelly candy made of acid-thinned starch added with different non-starch polysaccharides. *Journal of Food Research and Technology, 3,* 14-22.

Hadley, S. W., & Short, W. (2001). Electricity sector analysis in the clean energy futures study. *Energy Policy, 29 (14),* 1285–1298. doi:10.1016/s0301-4215(01)00073-8.

Hartel, R. W., Elbe, J H. V., & Hofberger, R. (2018). *Confectionery Science and Technology*. Berlin: Springer International Publishing, 542 p. 10.1007/978-3-319-61742-8.

Imeson, A. (2010). *Food Stabilisers, Thickeners and Gelling Agents*. Oxford: Blackwell Publishing Ltd, 352 p.

Kusumaningrum, A., Parnanto, N. H. R., & Atmaka, W. (2016). Study of the effects of carrageenan-konjac variation concentrations as gelling agent on the physical, chemical and sensory characteristics of yellow pumpkins (*Cucurbita maxima*) jelly candy. *Jurnal Teknosains Pangan*, *1*, 1-11.

Lavoisier, A., & Aguilera, J. M. (2019). Starch gelatinization inside a whey protein gel formed by cold gelation. *Journal of Food Engineering, 256,* 18-27. doi:10.1016/j.jfoodeng.2019.03.013.

Löfgren, C., Walkenström, P., & Hermansson, A. M. (2002). Microstructure and Rheological Behavior of Pure and Mixed Pectin Gels. *Biomacromolecules, 3(6),* 1144–1153. doi:10.1021/bm020044v.

Marfil, P. H. M., Anhê, A. C. B. M., & Telis, V. R. N. (2012). Texture and Microstructure of Gelatin/Corn Starch-Based Gummy Confections. *Food Biophysics*, *7(3),* 236–243. doi:10.1007/s11483-012-9262-3.

Mohammadian, M., & Madadlou, A. (2016). Cold-set hydrogels made of whey protein nanofibrils with different divalent cations. *International Journal of Biological Macromolecules*, *89*, 499–506. doi:10.1016/j.ijbiomac.2016.05.009.

Moore, C. O. (2007). Starch jelly candy. *The Manufacturing Confectioner*, *87(10),* 79-85.

Onat, N., & Bayar, H. (2010). The sustainability indicators of power production systems. *Renewable and Sustainable Energy Reviews, 14(9*), 3108–3115. doi:10.1016/j.rser.2010.07.022.

Otálora, M. C., de Jesús Barbosa, H., Perilla, J. E., Osorio, C., & Nazareno, M. A. (2018). Encapsulated betalains (*Opuntia ficus-indica*) as natural colorants. Case study: Gummy candies. *LWT - Food Science and Technology, 103,* 222-227. doi:10.1016/j.lwt.2018.12.074.

Queiroz, G. C. (2014). Sustentabilidade e Transparência (*Sustainability and Transparency*) [In Portuguese]. In: Queiroz, G. C., Rego, R. A., & Jardim, D. C. P. (Eds.). *Brasil Bakery* & *Confectionery Trends 2020.* (pp. 232-257). Campinas: ITAL.

Saha, D., & Bhattacharya, S. (2010). Hydrocolloids as thickening and gelling agents in food: a critical review. *Journal of Food Science and Technology, 47(6),* 587–597. doi:10.1007/s13197-010-0162-6.

Sharma, B. R., Naresh, L., Dhuldhoya, N. C., Merchant, S. U., Merchant, U. C. (2006). An overview on pectins. *Times Food Processing Journal, 23 (2),* 44-51.

Søltoft-Jensen, J., & Hansen, F. (2005). New Chemical and Biochemical Hurdles. In: Sun, D. W. (Ed.) *Emerging Technologies for Food Processing* (pp. 387-416). London: Elsevier. doi:10.1016/b978-012676757-5/50017-7.

Sokolovska, I., Kambulova, J., & Overchuk, N. (2016). Study of the water binding in the gel systems of pectin and sodium alginate. *Eastern-European Journal of Enterprise Technologies, 2(11),* 4-11.

Stone, H., & Sidel, J. L. (2004). *Sensory Evaluation Practices. 3rd ed*. Amsterdam: Elsevier, 377 p.

Sufferling, K. (2007). Gelatin gummies and pectin jellies. *The Manufacturing Confectioner, 87(8),* 43-50.

Toft, K. (1983). Gel Formation in Alginate-Pectin Systems Using Slow Acidifier. *European Science Fundation Workshop on Specific Interactions in Polysaccharide Systems*, Uppsala, Sweden, 26-27.

Toft, K., Grasdalen, H., & Smidsrød, O. (1986). Synergistic Gelation of Alginates and Pectins. In: Fishman, M. L., & Je, J. J., *Chemistry and Function of Pectins* (pp. 117–132). Washington: American Chemical Society. doi:10.1021/bk-1986-0310.ch010.

Xavier, N. M., Rauter, A. P., Queneau, Y. (2010) Carbohydrate-Based Lactones: Synthesis and Applications. In: Rauter A., Vogel P., Queneau Y. *Carbohydrates in Sustainable Development II. Topics in Current Chemistry vol 295* (pp. 19-62). Berlin: Springer.

Walkenström, P., Kidman, S., Hermansson, A. M., Rasmussen, P. B., & Hoegh, L. (2003). Microstructure and rheological behaviour of alginate/pectin mixed gels. *Food Hydrocolloids, 17(5),* 593–603. doi:10.1016/s0268-005x(02)00119-4.

CAPÍTULO 3. MAINTENANCE OF FRUIT BIOACTIVE COMPOUNDS IN JELLY CANDY MANUFACTURING BY ALGINATE/PECTIN COLD-SET GELATION

Publication

Article published in **Journal of Food Processing and Technology**, Volume 11, Issue 4, April 2020. Doi: 10.35248/2157-7110.20.11.826

CAPÍTULO 3. Maintenance of Fruit Bioactive Compounds in Jelly Candy Manufacturing by Alginate/Pectin Cold-Set Gelation

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Abstract

Enhancing the conservation of nutrients and bioactive compounds during the fruit processing is desirable. Therefore, this study evaluated the potential of the alginate/pectin cold-set gelation technique in the manufacturing of jelly candies formulated with fruit pulps (blackberry, guava, mango, strawberry and orange). A compared study between strawberry cold-set jellies (SAP) and a standard strawberry pectin jelly candy (SP) was carried out. The candies were evaluated by scanning electron microscopy and sensory acceptance, and were characterized in relation to the physicochemical characteristics (instrumental texture and color, moisture content, pH, and water activity) and bioactive compounds content (ascorbic acid, total phenolic and total anthocyanin compounds). The physicochemical characteristics of the different fruits did not influence the cold-set gelation process, which indicates the applicability of the process in a wide variety of fruits jelly candy formulations. SAP showed lower moisture content and water activity value than SP. Microscopic images showed a dense and homogeneous network with a large amount of pores in cold-set jellies, differing from the sparse and micellar network of pectin candies. The bioactive compounds contents of SPA (734.08 mg ascorbic acid/100 g and 254.4 mg gallic acid/ 100 g) were significantly higher ($p<0.05$) than the compounds of jellies obtained by the conventional process (597.4 mg ascorbic acid/100 g and 76.7 mg gallic acid/100 g). There was no significant difference ($p <0.05$) between the candies in relation to any of the evaluated sensory attributes, indicating cold-set gelation as a potential technology for fruit jelly candy manufacturing with a high content of natural bioactive compounds of the fruit.

Keywords: candy; cold-setting gels; confectionery; functional foods; hydrocolloids; phytonutrients.

1. Introduction

The industrial manufacturing of candies elaborated with fruit and vegetable ingredients has been set as a great alternative for obtaining products with claims of healthiness and naturalness in the confectionery market. Candies produced from fruit can differ from conventional products by their sensory quality, absence of synthetic dyes and aromas and partial reduction of the sugar content [1-4].

In recent years the candy market has been stimulated by the growing consumer demand for healthier products and sustainability claims on their labels. In this context the cleaner food production, with reduced energy consumption and waste emissions for the environment has gained prominence [5,6].

Jellies and gummies are a significant segment of the candy market. The main ingredients of these products are sucrose and other sugar syrups added by hydrocolloids. Their technological characteristics vary according to the gelling agent used in the processing and the final moisture content [7-9].

Among the jelly candy manufacturing steps, the syrup cooking represents the highest energy demand of the industrial line [10]. In this context, the use of cold-set gelation technique in the candy gel structuring showed potential to reduce the energy consumption during the candy manufacturing process by the dispense of the syrup cooking step [11].

Sodium alginate and high methoxylation pectin are hydrocolloids with a specific capacity of cold-set gelation. When combined and acidified to pH 3.4-3.8, provide the formation of cohesive networks of gel at room temperature by biomolecular mechanisms not totally elucidated [12,13].

The alginate and pectin cold-set gelation has also a high technological potential to maintain natural compounds and sensory characteristics of fruit pulps in candy formulations. The low processing temperatures can enable the conservation of the thermosensitive nutrients and functional components of the fruits. In this context, the aim of this study was to evaluate the performance of sodium alginate and high methoxylation pectin cold-set gelation in the production of jelly candies with fruit pulp and compare the obtained products with jellies produced by the conventional process.

2. Material and methods

2.1. Material

The ingredients used in the jelly candy manufacturing were: sucrose (União, São Paulo, Brazil), glucose syrup (Excell 1040, Ingredion, Mogi Guaçu, Brazil), frozen fruit pasteurized (blackberry, guava, orange, mango and strawberry) (Brasfrut, Feira de Santana, Brazil), strawberry juice concentrate (30 °Brix, Loop, Piracicaba, Brazil), high methoxylation pectin (HM 121Slow, Degree of esterification 58%, CPKelco, Limeira, Brazil), sodium alginate (Algin I-3G-150, viscosity 300 – 400 mPa·s, Kimica, Providencia, Chile), glucono-delta-lactone (GDL) (Art Alimentos, São Paulo, Brazil) and citric acid (ACS, Synth, Diadema, Brazil).

2.2. Development of jelly candies

2.2.1 Cold-set jelly candy manufacturing

The cold-set jelly candy manufacturing process was defined from modifications in the process of obtaining pure alginate/pectin gels [11,13], following the steps: (1) dissolution of sucrose, glucose syrup and fruit pulp in water, (2) dispersion of hydrocolloids (alginate and pectin) in the solution of sugars and fruit pulp, (3) dissolution of glucono-delta-lactone (GDL) to acidify the system, (4) deposition of the final candy syrup in starch molds and (5) drying in an oven at 35 °C/72 h. The ingredients were mixed with a digital mechanical bench agitator (Tecnal, model TE-039/1, Piracicaba, Brazil) at 380 rpm. The syrup was manually dosed with a funnel and the candies were dried in a forced air circulation drying oven (Tecnal, model TE-394/2, Piracicaba, Brazil).

2.2.2 Definition of the jelly candy formulation

To define the candy formulation, 9 treatments were tested, with variation of:

(a) The percentage of polymer blend (alginate/pectin) required to promote gelation (20, 40 or 60 g/kg);

(b) The GDL content required for acidification of the system (5,10, 20 or 30 g/kg).

The contents were determined after preliminary tests. The polymer blend was fixed at 1:1 (kg: kg) ratio of alginate: pectin, due to harder gels are obtained with these contents [12]. The sucrose: glucose syrup ratio was fixed at 2: 1 (kg: kg, d.b) according to the better results of Avelar & Efraim [11]. The pulp content of the formulations was fixed at 120 g/ Kg (w.b) and the final soluble solids content of the candy syrups was fixed at 71 ° Brix.

The alginate and pectin cold-set gelation depends on the pH of the system, so the nine treatments were formulated with five different fruit pulps with different pH ranges: blackberry, guava, orange, strawberry and mango. These fruits were selected due to their different sensory and nutritional characteristics (color, flavor and bioactive compounds). The soluble solids content of each fruit pulp was considered on dry basis as non-crystallizable sugar solids (glucose syrup) in the balance of sugar ratio.

Table 1. Experimental proposal for definition of fruit alginate/pectin jelly candy formulation.

Ingredients	Formulation								
	F1	F2	F3	F4	F5	F6	F7	F8	F9
Polymer blend (g/kg)*	20		40			60			
GDL** (g/kg)	5	10	5	10	20	5	10	20	30

F: formulation; * Polymer blend composed of an alginate: pectin ratio of 1: 1, kg: kg; **GDL: glucono-delta-lactone.

2.2.3. Drying conditions

After the tests with the different fruits, a strawberry candy formulation (F5) was selected to conduct a drying study to determine the time and temperature parameters for the cold-set candy manufacturing process. Strawberry was selected due its great acceptability and the widely use of strawberry flavor in confectionery products.

A drying curve was performed during 72 h in a forced air circulation drying oven (Tecnal, model TE-394/2, Piracicaba, Brazil) at temperatures of 35, 45 and 55 °C, temperatures commonly used in the jelly candies production) [9, 14, 15]. Samples were collected each 12 h for physical and physicochemical characterization.

2.2.4. Definition of the fruit solids content in the formulation

A reformulation study was carried out with the purpose of increasing the final fruit solids content of the developed candy. Strawberry pulp and juice concentrate were used to test formulations with 0.1, 0.2, 0.3 and 0.4 (kg/kg) of strawberry on wet basis. The formulation used as reference was the selected in the tests for jelly candy development. The final soluble solids content of the candy syrups was fixed at 71 °Brix and the strawberry solids content was considered as non-crystallizing solids, replacing glucose syrup solids in the sugar ratio of each candy syrup.

2.3. Jelly candy processing

The strawberry alginate and pectin cold-set jelly candies (SAP) were compared with strawberry pectin jelly candies (SP). The SAP formulation was defined in the tests for increasing the fruit solid content. The SAP processing followed the steps previously described while the drying conditions used were those determined in drying study. The SP samples were prepared by the dissolution of sucrose, glucose syrup, citric acid and pectin in strawberry juice concentrate, heating at atmospheric pressure until 71 ° Brix, dosing in starch molds, drying in a forced air circulation drying oven at 35 °C/72 h and demoulding [14].

2.4. Physical and physicochemical characterization

The fruit pulps and the strawberry juice concentrate were characterized in relation to pH according to AOAC Official Method 981.12 [16] using potentiometer (Digimed, model DM-20, São Paulo, Brazil), titratable acidity according to AOAC Official Method 981.15 [16], moisture content in a vacuum oven according to AOAC Official Method 920.151 [16], water activity using water activity analyzer (Aqualab, model 4TEV, Decagon Devices Inc., Pullman, USA) after equilibrium at 25 °C, and instrumental color using a digital colorimeter (Hunter Lab UltraScan PRO, Washington DC, USA) in the CIELAB system (L *, a * and b *), in triplicate.

The jelly candies produced in the tests for definition of formulation were evaluated in relation to pH [16] and hardness parameter, using a Texture Analyzer (TA-XT2i model, Surrey, England), with a cylindrical aluminum probe P/35, pre-test, test and post-test speeds of 2.0, 2.0 and 10.0 mm/s, respectively, penetration distance 1mm, in ten replicates [17].

The strawberry candies submitted to the drying study were characterized in relation to pH, moisture content, hardness and water activity [16, 17].

The SAP and SP samples were characterized in relation to pH and moisture content [16], water activity, instrumental color and texture profile analysis “TPA” using a Texture Analyzer (TA-XT2i model, Surrey, England) [18]. The samples were compressed twice using a D/40 acrylic disk, which allowed the sample to be deformed without penetration, 2 consecutive cycles of 40% compression, cross head moved at constant speed of 1.0 mm/s with triger point 0, 01 N., in ten replicates. The microstructure of the SAP and SP gels was evaluated by Scanning Electron Microscopy, using a table-type microscope (model TM-3000, Hitachi High Technologies America, Inc., Japan) [19].

2.5 *Bioactive compounds content*

SAP and SP candies and the strawberry juice concentrate were evaluated in relation to the total phenolic compounds content using FolinCiocalteu reagent and absorbance measuring at 765 nm using a spectrophotometer (model Cirrus 80, Femto, São Paulo, Brazil) [20].

The ascorbic acid content was determined by the titratable method [21], and the total anthocyanin content was evaluated by the pH differential spectroscopic method, using two buffer solutions: 0.025 M potassium chloride (pH 1.0) and a 0.4 M sodium acetate (pH 4.5). The extraction was performed with ethanol as solvent: 0.1 M HCl (85: 15%, v: v) and the absorbance measured in a spectrophotometer (model Cirrus 80, Femto, São Paulo, Brazil), at 510 and 700 nm. The absorbance of the diluted sample (A) was calculated by the Equation 1.

$$A = (A_{510} - A_{700})_{pH\ 1.0} - (A_{510} - A_{700})_{pH\ 4.5} \qquad \text{(Equation 1)}$$

The total anthocyanin content was calculated by the Equation 2.

$$Total\ anthocyanin\ content\ \left(\frac{mg}{100g}\right) = \frac{A\ x\ M\ x\ DF\ x\ 1000}{(\varepsilon\ x\ \lambda\ x\ m)} \qquad \text{(Equation 2)}$$

Where “A” was the previously calculated absorbance (Equation 1), M is the molecular weight of cyanidin-3-glucoside (449.2 g/ mol), DF is the dilution factor, ε is the molar absorptivity coefficient (29600 M-1cm-1), λ is the cuvette optical pathlength (1 cm) and m is the weight of the sample (g) [22].

2.6 Sensory analysis

The strawberry jellies (SPA and SP) were evaluated sensorially in relation to the appearance, color, aroma, flavor and texture attributes by 120 evaluators in an acceptance test performed at the Food Sensory Analysis Laboratory of the Department of Food Technology - FEA / UNICAMP (approved by the Committee of Research Ethics at the State University of Campinas, with Certificate of Presentation for Ethical Assessment - CPEA 86627118.5.0000.5404), using a structured 9-point hedonic scale ranked 9: I liked it extremely and 1: I disliked it extremely [23].

2.7 Statistical Analysis

Analysis of Variance (ANOVA), Tukey's test, Friedman's test and Nemenyi's test were applied on the results at a 95% of confidence interval using XLSTAT statistical software (Addinsoft, New York, NY, 2016).

3. Results and discussion

3.1. Physical and physicochemical characterization of the fruits

The results of the physicochemical characterization of the fruit ingredients are presented in Table 2.

Table 2. Physical and physicochemical parameters of the fruit pulps and strawberry juice concentrate.

Fruit pulp	Physical and physicochemical parameters							
	Aw	Instrumental Color			Moisture Content (kg/kg)	pH	Soluble solids content (°Brix)	Titratable acidity (g citric acid/100g)
		L*	a*	b*				
Blackberry	0.9922 ± 0.0003 b	9.45 ± 0.70 d	33.41 ± 0.81 a	16.20 ± 1.09 a	9.26 ± 0.01 b	3.29 ± 0.01 d	8.20 ± 0.16 c	1.014 ± 0.015 b
Guava	0.9940 ± 0.0004 ab	43.94 ± 1.82 c	35.76 ± 2.07 a	33.25 ± 2.91 b	9.06 ± 0.92 c	4.08 ± 0.01 b	8.33 ± 0.05 c	0.504 ± 0.015 d
Mango	0.9949 ± 0.0003 a	55.34 ± 0.92 b	19.40 ± 0.26 c	72.69 ± 1.24 a	8.63 ± 0.03 d	4.27 ± 0.01 a	13.10 ± 0.08 b	0.402 ± 0.003 e
Orange	0.9771 ± 0.0018 c	67.28 ± 2.96 a	10.32 ± 2.07 d	69.40 ± 3.23 a	8.35 ± 0.03 e	4.07 ± 0.01 b	18.80 ± 0.09 a	1.151 ± 0.040 a
Strawberry	0.9943 ± 0.0000 ab	52.21 ± 4.58 b	25.34 ± 2.25 b	27.68 ± 3.30 b	9.42 ± 0.02 a	3.51 ± 0.01 c	7.40 ± 0.01 d	0.878 ± 0.016 c
Strawberry juice concentrate	0.9621 ± 0.0001	- 18.82 ± 0.00	20.66 ± 0.14	12.24 ± 0.46	6.85 ± 0.02	3.26 ± 0.01	30.00 ± 0.05	2.650 ± 0.034

Aw, water activity. Mean values of 10 replicates of instrumental texture measurements and triplicates of instrumental color, pH. Aw, titratable acidity and moisture content measurements. Mean values followed by (*) in the same line are significantly different ($p < 0.05$).

The average values for water activity were located slightly out of the 0.98 range indicated for fruit pulps [24]. In general, the physicochemical parameters of the fruit pulps presented mean values closed to the ranges reported by the literature [25-29]. Considering the indicated values for the physical and physicochemical parameters of strawberry pulp, the strawberry juice concentrate presented averages within the expected range.

3.2 Development of the candy formulations

The nine formulations proposed in Table 1 were defined in preliminary tests. According to these initial experiments, it was not possible to obtain adequate gelled structures in formulations with less than 20 g/kg of polymeric mixture. Smaller contents provided weak structures that break during the drying step. The solution of sugars and fruit pulp should have total soluble solids content until 65 °Brix, due to the occurrence of saturation and crystallization of sucrose in syrups with higher soluble solids content.

The values of hardness of the nine evaluated formulations are presented in Table 3. The gelation occurred successfully at all the formulations with the five evaluated fruit pulps. The highest hardness averages were obtained in treatments produced with 60 g/kg of polymeric mixture.

Table 3. Mean values of hardness (N) and pH of the 9 cold-set experimental proposed fruit candy formulations.

	Hardness (N)*									pH**								
Fruit candies	F1	F2	F3	F4	F5	F6	F7	F8	F9	F1	F2	F3	F4	F5	F6	F7	F8	F9
Blackberry	47 ±19 c	58 ±27 c	91 ±22 bc	99 ±22 bc	88 ±22 bc	185 ±40 a	179 ±25 a	161 ±33 a	139 ±27 ab	4.12 ±0.05 abc	3.93 ±0.06 bc	4.08 ±0.05 abc	4.09 ±0.01 abc	3.90 ±0.02 bc	4.29 ±0.05 ab	4.13 ±0.02 ab	3.96 ±0.03 ab	3.83 ±0.05 c
Guava	59 ±22 c	63 ±17 c	168 ±32 ab	165 ±41 ab	136 ±21 bc	216 ±39 a	203 ±30 a	208 ±36 a	194 ±28 a	4.20 ±0.04 ab	3.96 ±0.01 b	4.35 ±0.08 a	4.14 ±0.06 ab	3.93 ±0.07 b	4.32 ±0.03 a	4.13 ±0.05 ab	4.02 ±0.03 ab	3.90 ±0.11 b
Mango	92 ±24 d	88 ±23 cd	157 ±26 bc	152 ±16 cd	137 ±16 cd	219 ±23 ab	246 ±37 a	224 ±29 ab	245 ±38 a	4.19 ±0.00 ab	4.01 ±0.06 abc	4.09 ±0.27 abc	4.11 ±0.05 abc	3.94 ±0.03 bc	4.35 ±0.06 a	4.18 ±0.01 ab	3.95 ±0.01 bc	3.87 ±0.02 c
Orange	55 ±19 c	64 ±15 c	88 ±19 c	91 ±16 bc	79 ±7 c	167 ±24 a	160 ±22 a	154 ±30 a	143 ±26 ab	4.15 ±0.02 ab	3.95 ±0.05 abc	4.25 ±0.05 a	4.06 ±0.01 abc	3.83 ±0.02 bc	4.26 ±0.01 a	4.13 ±0.03 abc	3.93 ±0.04 abc	3.81 ±0.01 c
Strawberry	121 ±25 cd	108 ±23 d	147 ±21 bcd	122 ±38 cd	107 ±25 d	241 ±32 a	229 ±28 a	188 ±19 ab	160 ±23 abc	4.17 ±0.01 abc	3.90 ±0.01 abcd	4.27 ±0.02 a	4.04 ±0.00 abcd	3.82 ±0.05 bcd	4.25 ±0.03 ab	3.57 ±0.04 d	3.90 ±0.00 abcd	3.78 ±0.02 cd

F, formulation. Mean values of 10 replicates (*) and triplicates (**). Mean values followed by different letters in the same column are significantly different ($p < 0.05$).

The physical chemical characteristic of the fruits (pH and acidity) showed a low influence in the gel formation process, despite the alginate/pectin cold-set gelation mechanism occurs on specific pH conditions. Almost all candy formulation presented pH values outside the 3.4-3.8 range considered ideal for gelation of alginate-pectin complexes [12,13].

As expected, formulations with higher GDL content showed the lowest pH values. The same results were observed in the study of model jelly candy processing by alginate/pectin cold-set gelation with no added fruit ingredients [11].

According to the results, the strawberry formulation 5 was selected to conduct the next study, due to the great gel hardness and to the pH mean closed to the recommended range for alginate/pectin gelation.

3.3 Determination of the drying parameters

The curves generated for the physical and physicochemical parameters in the drying study are shown in Figures 1, 2, 3 and 4.

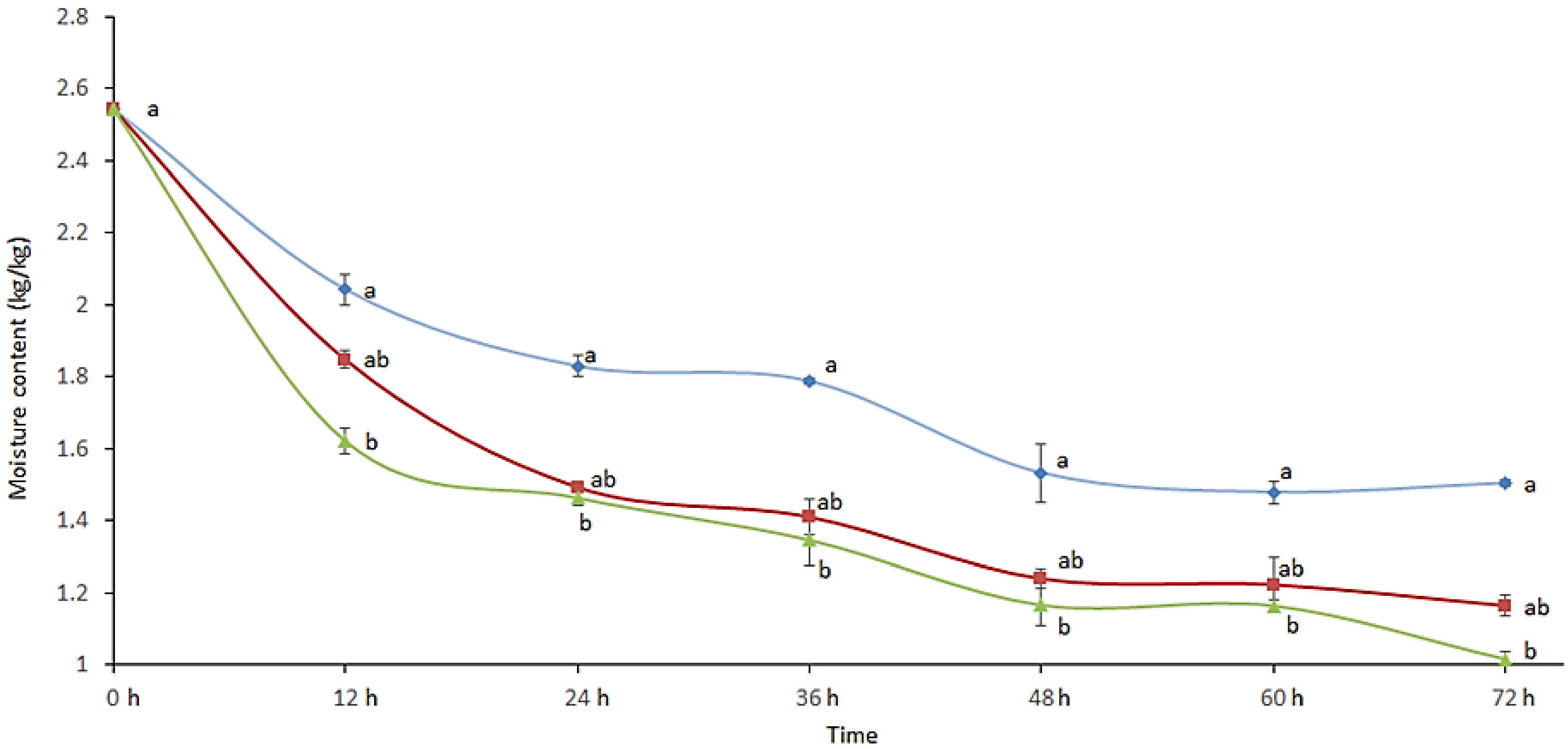


Figure 1. Mean values of moisture content (kg/kg) during the drying process of strawberry cold-set jelly candy (formulation 5) at three different temperatures (●: 35 °C; ■: 45 °C; ▲: 55 °C). Mean values followed by the same letter are not significantly different ($p>0.05$) in respect to the drying temperature at the same evaluated drying time.

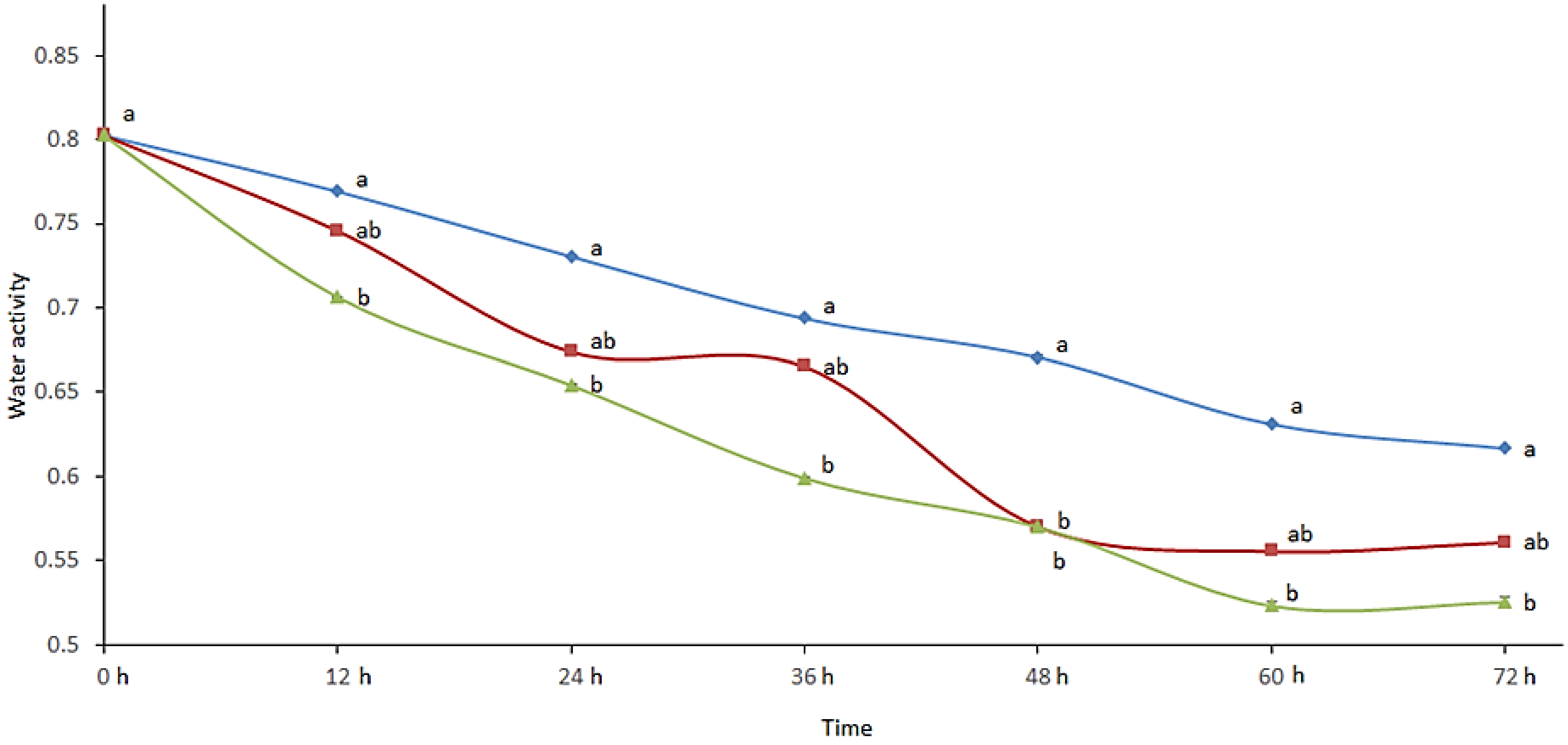


Figure 2. Mean values of water activity during the drying process of strawberry cold-set jelly candy (formulation 5) at three different temperatures (●: 35 °C; ■: 45 °C; ▲: 55 °C). Mean values followed by the same letter are not significantly different (p>0.05) in respect to the drying temperature at the same evaluated drying time.

There was significant difference ($p < 0.05$) between the averages of all physical-chemical parameters at the three evaluated temperatures. As expected, the speed of the dehydration process was higher as higher the drying temperature. Visually it was observed that candies dried at 45 and 55 °C presented a crystallized layer on the surface whose thickness increased over the drying time. It indicates that the drying at these temperatures promotes a higher and faster dehydration causing the sucrose crystallization on the product surface.

Jelly candies must have an average moisture content of 0.08-0.22 kg/kg and water activity between 0.5-0.75 for better stability [30], which were reached for all drying temperature after 12 hours of drying.

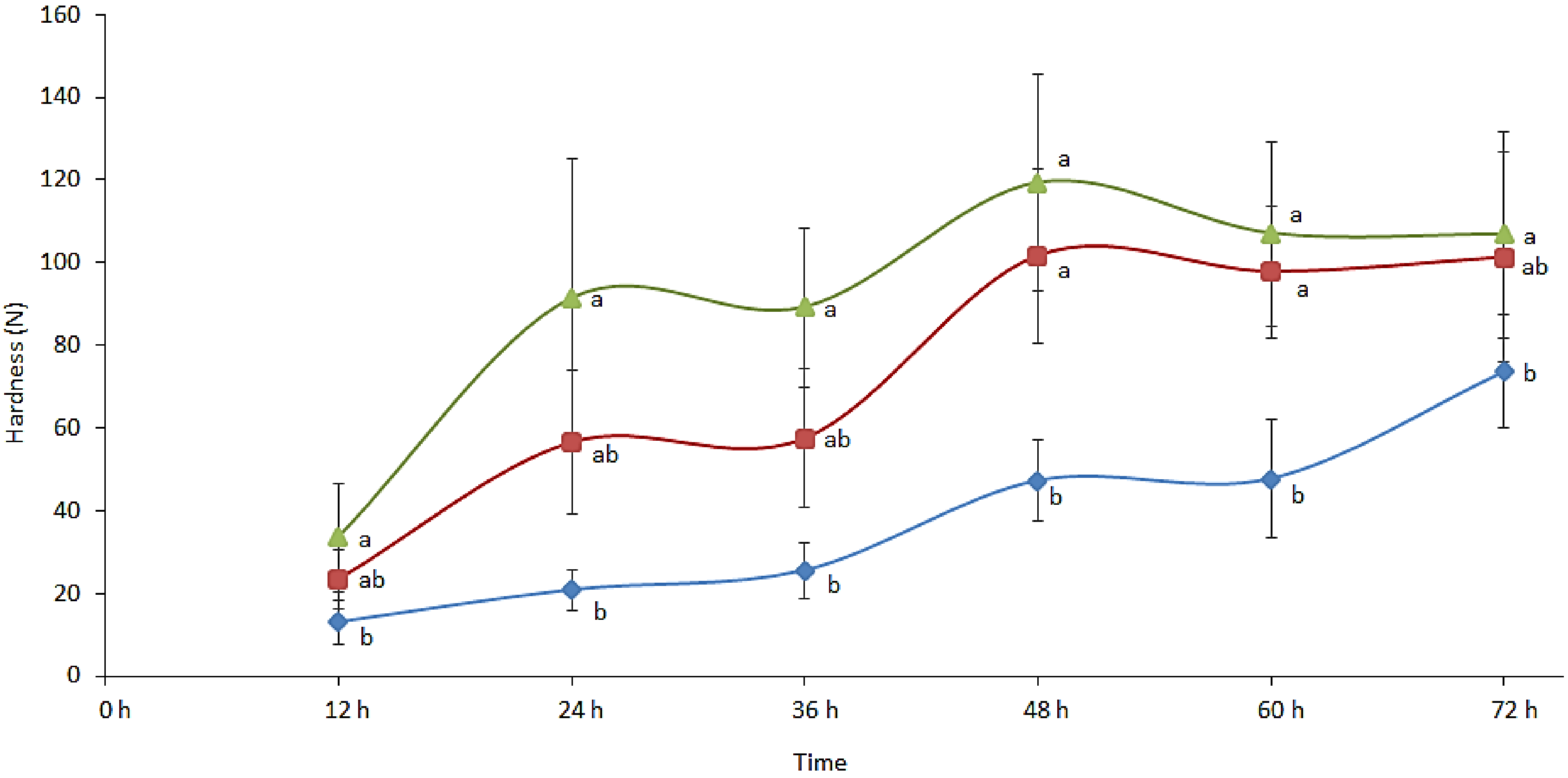


Figure 3. Mean values of hardness (N) during the drying process of strawberry cold-set jelly candy (formulation 5) at three different temperatures (●: 35 °C; ■: 45 °C; ▲: 55 °C). Mean values followed by the same letter are not significantly different ($p>0.05$) in respect to the drying temperature at the same evaluated drying time.

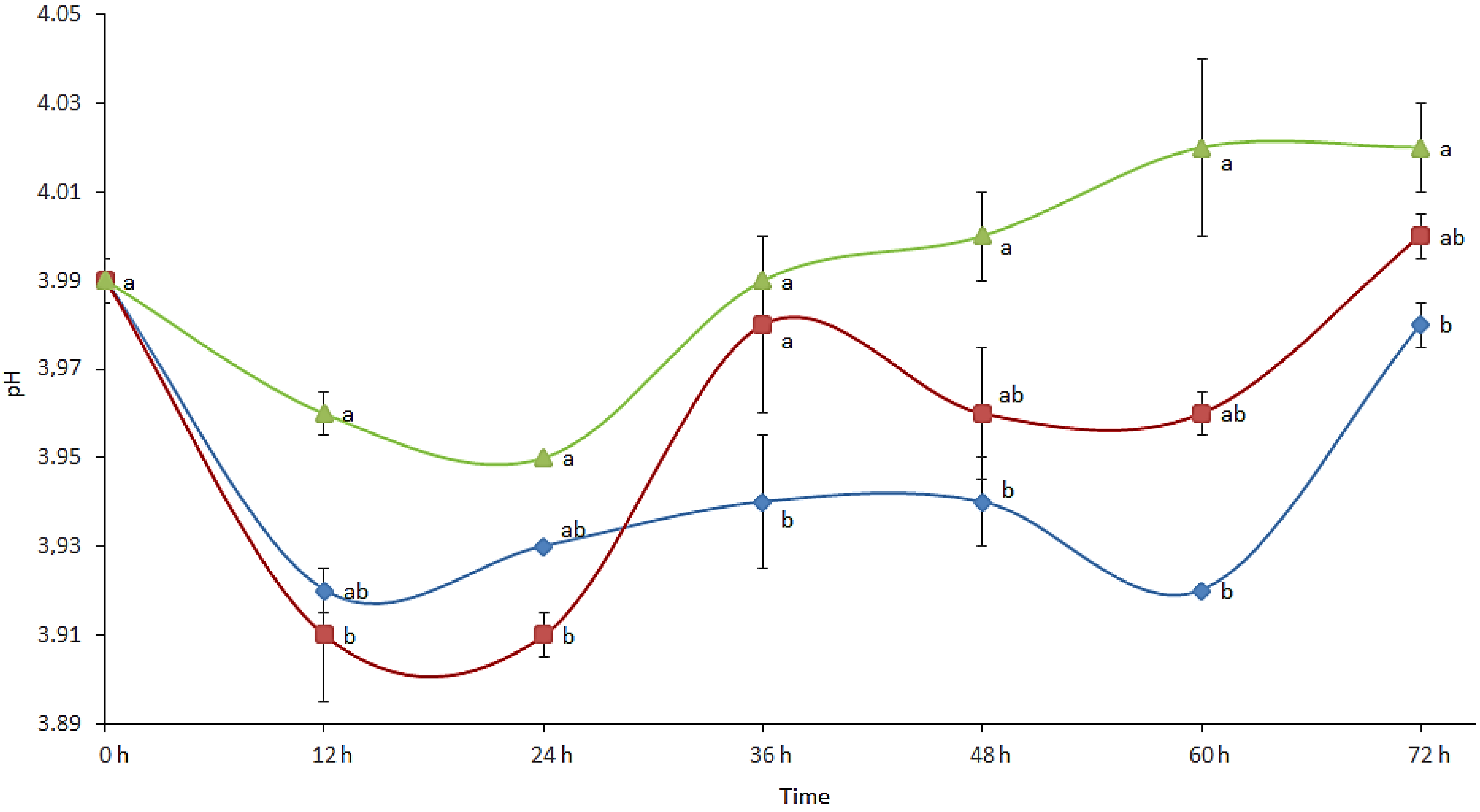


Figure 4. Mean values of pH during the drying process of strawberry cold-set jelly candy (formulation 5) at three different temperatures (●: 35 °C; ■: 45 °C; ▲: 55 °C). Mean values followed by the same letter are not significantly different ($p>0.05$) in respect to the drying temperature at the same evaluated drying time.

The pH means oscillated during the drying process at the three evaluated temperatures, with falls at 12 and 36 h and pecks after 24 and 60 h. The changes on the pH are related to the slow acidification comportment of GDL, which cyclic ester structure is gradually converted into gluconic acid in an aqueous medium [31-33]. For the manufacturing of fruit cold-set jelly candies, GDL is an optimal acidulant due to the slow formation of the gel, which makes possible dosing the syrup in the drying molds in a timely manner [11].

The drying condition of 35 °C/72 h was selected due the better texture characteristics, absence of a layer of crystallized sucrose on the surface and the adequate values of Aw and moisture content presented by the candies.

3.4 Reformulation tests to increase the fruit content

After selecting the polymeric mixture and GDL contents and the drying conditions of the process, reformulation tests were carried out to evaluate the possibility of increasing the fruit solids content in the candy and, in this way, obtain a product with high appeals of naturalness and healthiness.

The soluble solids of the strawberry pulp and juice concentrate were considered as non-crystallizable solids (glucose syrup) in the balance of the sugar ratio. The polymeric mixture and GDL contents were fixed at the concentrations selected in the tests for jelly candy development.

In the reformulation tests, the moisture content of the pulp was a limiting factor for increasing the fruit content in the formulation due to the standardization of the final soluble solids content of the candy syrup (71 °Brix). For this reason, 200 g/kg of strawberry pulp (w.b) was the highest content reached in the candy syrup formulation, which corresponds to 8.1g/Kg (db) of strawberry solids in the candy after the drying step. Using strawberry concentrate juice, it was possible to perform tests ranging from 100, 200, 300 and up to 400 g/kg in the syrup formulation.

The gelation occurred successfully at all the tested formulations. The candy syrup produced with 400 g/kg of strawberry juice concentrate was selected due to the highest strawberry solids content reached in the tests.

The final strawberry alginate/pectin jelly candy syrup (SPA) consisted of strawberry juice concentrate (400 g/kg), sucrose (440 g/kg), glucose syrup (110 g/kg), sodium alginate (20 g/kg), high methoxyylation pectin (20 g/kg), glucono-delta-lactone (10 g/kg). The formulation of strawberry pectin jelly (SP) consisted of strawberry juice concentrate (395 g/kg), sucrose (465 g/kg), glucose syrup (120 g/kg), high methoxyylation pectin (14 g/kg) and citric acid (6 g/kg).

3.5. Physical, chemical and physical-chemical characterization of the developed candies.

3.5.1 Physical and physical-chemical characterization

The results of the physical and physical-chemical characterization of the strawberry jelly candies are presented in Table 4.

Table 4. Physical and physicochemical parameters and bioactive compounds contents of strawberry jelly candies and strawberry juice concentrate.

	Physical and physicochemical parameters												Chemical parameters		
	Instrumental Texture						Instrumental Color			pH	Aw	Moisture Content (kg/kg)	AA (mg ascorbic acid g $^{-1}$)	TPC (mg gallic acid g^{-1})	TAC (mg cyanidin-3-glycoside g^{-1})
	Hardness (N)	Springness	Cohesiveness	Gumminess	Chewiness	Resilience	L*	a*	b*						
SAP	7.672 ±1.154	0.206 ±0.077 *	0.031 ±0.000	0.234 ±0.037	0.049 ±0.025 *	0.007 ±0.002 *	7.506 ±0.231 *	0.730 ±0.409	0.660 ±0.190 *	3.646 ±0.317	0.5686 ±0.001 *	1.14 ±0.13 *	734.083 ± 13.10*	254.44 ± 35.64*	0.0515 ± 0.0201
SP	4.576 ±3.080	0.064 ±0.029 *	0.026 ±0.012	0.188 ±0.202	0.012 ±0.011 *	0.015 ±0.013 *	-12.273 ±0.789 *	2.533 ±1.121	-0.383 ±0.112 *	3.263 ±0.011	0.6016 ±0.0035 *	1.51 ±0.01 *	597.376 ± 84.08*	76.66 ± 10.00**	0.0560 ± 0.0000
SJC	-	-	-	-	-	-	-	-	-	-	-	-	1575.34 ± 00.00	660.00 ± 31.50	0.5121 ± 0.0804
General average	6.124	0.135	0.028	0.211	0.030	0.011	-2.383	1.631	0.138	3.454	0.5851	13.280	-	-	-

Aw, water activity; AA, ascorbic acid content; TPC, total phenolic compounds content; TAC, total anthocyanin content; SAP, strawberry alginate/pectin jelly candy; SP, strawberry pectin jelly candy; SJC, strawberry juice concentrate. Mean values of 10 replicates of instrumental texture measurements and triplicates of instrumental color, pH. Aw and moisture content measurements. Mean values followed by (*) in the same line are significantly different ($p < 0.05$).

A lighter and more opaque red color was observed in the SAP samples, which was confirmed by the instrumental color analysis. The mean value of SPA luminance (L*) was significantly lower ($p < 0.05$) than those of SP while the SPA chromaticity index b* were significantly higher than those of SP.

There was no significant difference ($p < 0.05$) between the hardness, gumminess and cohesiveness. The SAP gel presented a texture with more elasticity, chewiness and less resilience, as observed in cold-set model jellies produced with alginate and pectin [11].

Both treatments showed moisture content and water activity values closed to the recommended ranges for gummies and jellies (0.08-0.22 kg/kg of moisture content and water activity between 0.5-0.75) [30]. However, the SP candies differ significantly ($p<0.05$) by the highest values for these parameters.

3.5.2 Chemical characterization

According to the average values for the bioactive compounds contents of processed strawberry pulp reported by the literature (Ascorbic acid content: 44-71 mg ascorbic acid/ 100g frozen pulp; total anthocyanin content: 0.5-3.79 mg cyanidin-3-glycoside/ 100 g frozen strawberry; total phenolic compounds: 250 mg ellagic acid/ 100g frozen strawberry) [22,34,35] the strawberry juice concentrate presented mean values below the expected range for total anthocyanin and total phenolic compounds contents.

The juice concentrate processing occurs by heating treatment to remove the moisture content and increase soluble solids content. The process conditions (temperature and time) and storage probably caused changes on the fruit pulp´s final content of the thermosensitive nutrients and bioactive compounds.

The alginate/pectin candies showed higher mean values ($p < 0.05$) for the ascorbic acid and total phenolic compounds contents. Ascorbic acid is a water-soluble vitamin essential for the health with antioxidant action, whose stability in food processing is subject to oxygenation and high temperature and water activity conditions [36]. Phenolic compounds have antioxidant and coloring properties and have a strong influence on the sensory quality and nutritional value of strawberries. They are susceptible to degradation in process conditions involving high temperatures, light, oxygen, enzymes, metal ions and possible associations with other organic components [37,38]. The differences between the levels of ascorbic acid and phenolic compounds in the candy samples indicate that the cold-set process allows a better conservation of these bioactive compounds in the final product.

The total anthocyanin contents showed no significant difference ($p<0.05$) between the candy samples. Anthocyanins are the most common fruit flavonoids. They have antioxidant activity and are related to red-blue pigmentation. In strawberry, anthocyanins are quantitatively the most important type of polyphenols. The pelargonidin- and cyanidin- glycosides or acylated forms are the major anthocyanin representative compounds in strawberry. The retention and stability of anthocyanins after food manufacturing is mainly determined by the processing temperature, but it is also influenced by other factors such as pH, the presence of oxygen, light, enzymes and metal ions [39, 40].

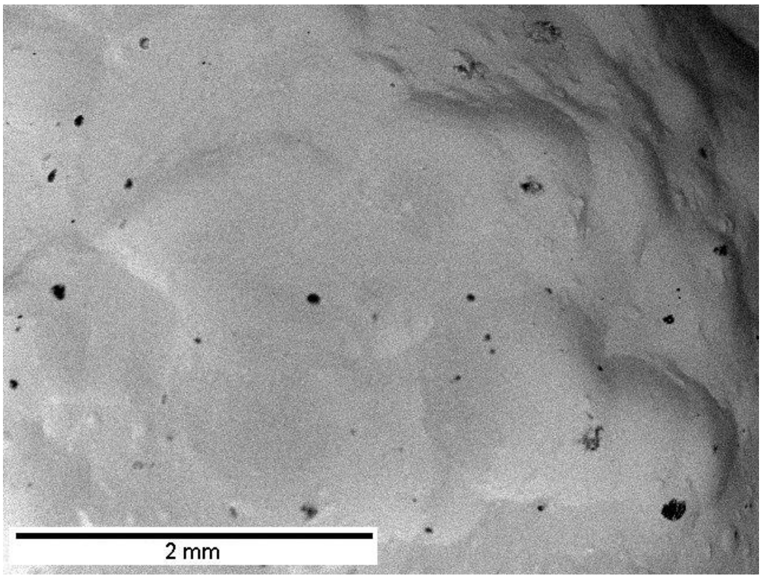
It was expected that the conventional heating process would imply in a higher degradation of the total anthocyanin content compared to the cold-set process. The similar anthocyanin contents of the samples can be justified by the high concentrations of sugar in the candy formulations, which may have a protective effect on the stability of anthocyanins during the syrup cooking, reducing the mobility of water and energy of activation of the degradation reaction [41]. Considering the anthocyanin content and the fruit solids of the strawberry juice concentrate, there was a loss of anthocyanin in the both manufacturing processes, indicating that another common parameter of the both processes (as oxygenation or pH) may have conducted to these levels.

The developed strawberry cold-set candy had higher fruit solids and total phenolic compounds contents than candies produced with fruit ingredients in other studies reported by the literature, such as fruit jellies elaborated with apple/blackberry puree and enriched with grape skin powders [42] and no-added sucrose chewy candies incorporated with differently processed açaí [43]. The high levels of fruit and phenolic compounds contents of SPA enhance claims of naturalness and healthiness to the developed product.

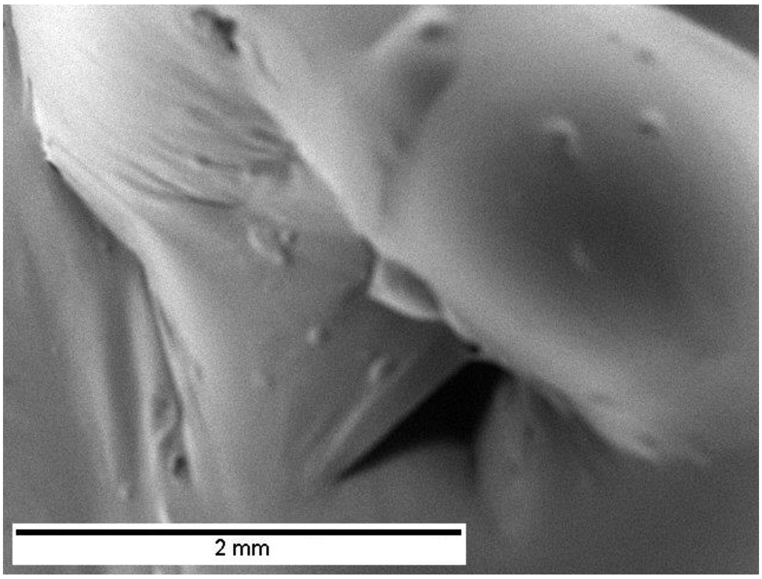
The results of the chemical determinations indicate the viability of the alginate/ pectin candy manufacturing process to the conservation and retention of bioactive compounds from fruit ingredients used in the formulation. SPA had retention of 93.53% of total phenolic compounds while SP allowed retention of 31.16%. The cold-set jelly candy process also has the potential of reduce energy consumption in the jelly candy industrial lines due to the elimination of the syrup cooking step. According results of a comparative bench study of energy requirement by Avelar & Efraim [11], the energy demand of the cold-set process (0.013 kWh) is statistically lower than the conventional heating process (0.035 kWh). In this way, the cold-set fruit jelly processing can also get claims of sustainability.

3.5.3 Microstructure

The scanning electron microscopy images of the candies are shown in figure 5.



(a)



(b)

Figure 5. Scanning electron microscopy of (a) strawberry alginate and pectin jelly candy at 2 mm and (b) strawberry pectin jelly candy at 2 mm.

The strawberry alginate/pectin candies presented a microstructure characterized by a dense and homogeneous surface with the presence of pores along the network, similar to the microstructure observed in pure alginate and pectin gels [13] and model alginate/pectin candies produced by cold-set gelation [11]. These microstructural aspects can justify the instrumental color values and the visual opacity observed in the candy.

The strawberry pectin candies showed a non-homogeneous structure characterized by aggregates of micelles and the presence of large and sparse pores. Pure pectin gels are described in the literature as open networks with wires arranged in loose bundles or aggregates [11, 44].

In general, in general, the SPA microstructure observed in the scanning analysis differ from those reported in jellies and gummies produced with others conventional gelling agents [45, 46].

3.6 Sensory acceptance

The results of the sensory acceptance test are shown in Table 5.

	Sensorial atributes					
	Appearence	Color	Aroma	Flavor	Texture	Overall impression
SAP	6.0 ±1.7	6.0 ±1.6	6.0 ±1.2	6.0 ±1.9	4.0 ±2.0	6.0 ±1.7
SP	6.0 ±1.9	7.0 ±1.5	6.0 ±1.4	6.0 ±1.7	4.0 ±2.3	5.5 ±1.8
General average	6.0	6.5	6.0	6.0	4.0	5.7

Table 5. Sensorial attributes of the produced candies

SAP, strawberry alginate/pectin jelly candy; SP, strawberry pectin jelly candy. Mean values followed by (*) in the same line are significantly different ($p < 0.05$).

SPA and PJ showed low acceptance in relation to the texture parameter, with mean values located around the term “slightly disliked.” Compared to cold-set model candies without fruit pulp, the jellies produced from strawberry juice concentrate showed lower instrumental hardness values and lower sensory acceptance for texture [11]. These results indicate that high fruit contents in the candy formulation can modify the final candy gel texture and decrease its acceptability.

The evaluated strawberry jelly candies showed no significant difference ($p < 0.05$) in relation to all the evaluated sensory parameters, which indicates viability in replacing the conventional candy production process with the cold-set gelation process without decreasing the sensory acceptance.

4. Conclusion

Fruit jelly candies were successfully produced by the alginate/pectin cold-set gelation technique with maintenance of bioactive compounds from the fruit ingredients used in the formulation. The ascorbic acid and total phenolic compounds contents of the strawberry alginate/pectin candies were significantly higher ($p<0.05$) than those of strawberry pectin jellies. The mean values of the physical and physical-chemical parameters of the produced candies located in the range for this product category. Sensorially, there was no significant differences ($p<0.05$) between any of the evaluated attributes, indicating the potential for replacing the conventional jelly candy processing by the cold-set gelation process. It is worth noting that the cold-set manufacturing process also has the potential to reduce energy consumption in industrial jelly candy processing lines due to the elimination of the syrup cooking step. In this way, claims of healthiness and sustainability could be attributed to the cold-set products.

Acknowledgments

Conselho Nacional de Desenvolvimento Científico e Tecnológico - Brasil (CNPQ) for the fellowship to the first author, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, Innovation Agency of University of Campinas (Inova-Unicamp) and the Brazilian National Institute of Industrial Property for the patent filling BR 10 2018 076817, that contemplates and protects the results of this study.

5. References

1. Avelar MHM, Silva LB, Azevedo FB, Efraim P. A byproduct of uvaia (Eugenia pyriformis) processing as a natural source for coloring sugar hard-panning confections. Journal of Food Process Engineering. 2019; 42:7: 1-8. doi:10.1111/jfpe.13250.

2. Mongia G. Fruit ingredients in confectionery applications. The Manufacturing Confectioner. 2014; 94:8: 73-82.

3. Mutlu C, Tontul SA, Erbas M. Production of a minimally processed jelly candy for children using honey instead of sugar. LWT - Food Science and Technology. 2018; 93: 499–505. doi:10.1016/j.lwt.2018.03.064.

4. Silva LB, Queiroz MB, Fadini AL, Fonseca RCC, Germer SPM, et al. Chewy candy as a model system to study the influence of polyols and fruit pulp (Açai) on texture and sensorial properties. LWT–Food Science and Technology. 2016; 65: 268–274. doi:10.1016/j.lwt.2015.08.006.

5. Confectionery News. Organic candy: The future of confectionery, says new report. (2019). https://www.confectionerynews.com/Article/2007/08/08/Organic-candy-the-future-of-confectionery-says-new-report.

6. Queiroz GC. Sustentabilidade e Transparência (Sustainability and Transparency) [In Portuguese]. In: Queiroz GC, Rego RA, Jardim DCP. (Eds.). Brasil Bakery & Confectionery Trends 2020. 2014; 232-257. Campinas: ITAL.

7. Coyle SJ. Cooking Equipment for Jelly Candy. The Manufacturing Confectioner. 2007: 99:8: 36-42.

8. DeMars LL, Ziegler GR. Texture and structure of gelatin/pectin-based gummy confections. Food Hydrocolloids. 2001; 15:4-6: 643–653. doi:10.1016/s0268-005x(01)00044-3.

9. Eiri Board. Hand Book of Confectionery with Formulations. New Delhi: Engineers India Research Institute. 2012.

10. Aigroup. Energy reduction factsheet: Saving energy in the confectionery manufacturing industry. (2019). http://cdn.aigroup.com.au/Environment/21_Food_Processing_Confectionery_Manufacturing_Energy_Reduction_Factsheet.pdf.

11. Avelar MHM, Efraim P. Alginate/pectin cold-set gelation as a potential sustainable method for jelly candy production. LWT–Food Science and Technology. 2020; 123. doi:10.1016/j.lwt.2020.109119.

12. Toft K, Grasdalen H, Smidsrød O. Synergistic Gelation of Alginates and Pectins. In: Fishman ML, Je JJ. Chemistry and Function of Pectins. 1986; 117–132. Washington: American Chemical Society. doi:10.1021/bk-1986-0310.ch010.

13. Walkenström P, Kidman S, Hermansson AM, Rasmussen PB, Hoegh L. Microstructure and rheological behaviour of alginate/pectin mixed gels. Food Hydrocolloids. 2003; 17:5: 593–603. doi:10.1016/s0268-005x(02)00119-4.

14. Sufferling K. Gelatin gummies and pectin jellies. The Manufacturing Confectioner. 2007; 87:8: 43-50.
15. Moore CO. Starch jelly candy. The Manufacturing Confectioner. 2007; 87:10: 79-85.
16. AOAC. Official Methods of Analysis of AOAC International. 19th ed. Gaithersburg, MD: Association of Official Analytical Chemists, 2012.
17. Fadini AL, Jardim DCP, Queiroz MB, Bertin AP, Efraim P, et al. Características sensoriais e de textura de chicles drageados diet produzidos com diferentes tipos de polióis (Sensory and texture characteristics of diet panned chewing gum produced with different types of polyols) [In Portuguese]. Brazilian Journal of Food Technology. 2005; 8: 113-119.
18. Delgado P, Bañón S. Determining the minimum drying time of gummy confections based on their mechanical properties. CyTA - Journal of Food. 2014; 13:3: 329–335. doi:10.1080/19476337.2014.974676.
19. Marfil PHM, Anhê ACBM, Telis VRN. Texture and Microstructure of Gelatin/Corn Starch-Based Gummy Confections. Food Biophysics. 2012; 7:3: 236–243. doi:10.1007/s11483-012-9262-3.
20. Singleton VL, Othofer R, Lamuela-Raventos, RM. Analysis of total phenols and others oxidation substrates and antioxidants by folin-ciocauteau reagent. Methods in Enzimology. 1999; 299: 152-178. doi:10.1016/S0076-6879(99)99017-1.
21. Cheftel H, Pigeaud ML. Estimation of Ascorbic Acid (Vitamin C) by Titration. Nature. 1936; 138:3497: 799–799. doi:10.1038/138799b0.
22. Tonutare T, Moor UL, Szajdak L. Strawberry anthocyanin determination by pH differential spectroscopic method – how to get true results? Acta Scientiarum Polonorum Hortorum Cultus. 2014; 13:3: 35-47.
23. Stone H, Sidel JL. Sensory Evaluation Practices. 3rd ed. Amsterdam: Elsevier. 2004.
24. Sandulachi, E. Water activity concept and its role in food preservation. (2012). http://www.utm.md/meridian/2012/MI_4_2012/8_Art_Sandulachi_E_Water.pdf.
25. Alamar PD, Caramês ETS, Poppi RJ, Pallone JAL. Quality evaluation of frozen guava and yellow passion fruit pulps by NIR spectroscopy and chemometrics. Food Research International. 2016; 85: 209–214. doi:10.1016/j.foodres.2016.04.027.
26. De Souza VR, Pereira PAP, da Silva TLT, de Oliveira Lima LC, Pio R et al. Determination of the bioactive compounds, antioxidant activity and chemical composition of Brazilian blackberry, red raspberry, strawberry, blueberry and sweet cherry fruits. Food Chemistry, 2014; 156: 362–368. doi:10.1016/j.foodchem.2014.01.125.

27. Gonçalves GAS, Resende NS, Carvalho EEN, de Resende JV, Vilas Boas EVB. Physicochemical and volatile profile alterations in pasteurized and frozen strawberry pulp during storage. Journal of Food Processing and Preservation. 2017; 42:1: e13317,1-11. doi:10.1111/jfpp.13317

28. Leahu A, Damian C, Oroian M, Ropciuc S. Physico-chemical parameters of fruit juices-evolution during storage. Lucrări Ştiinţifice-Seria Zootehnie. 2013; 59: 213-217.

29. Pelegrine DH, Silva FC, Gasparetto CA. Rheological Behavior of Pineapple and Mango Pulps. LWT - Food Science and Technology. 2002; 35:8: 645–648. doi:10.1006/fstl.2002.0920.

30. Ergun R, Lietha R, Hartel RW. Moisture and Shelf Life in Sugar Confections. Critical Reviews in Food Science and Nutrition. 2010; 50:2: 162–192. doi:10.1080/10408390802248833.

31. Imeson, A. Food Stabilisers, Thickeners and Gelling Agents. Oxford: Blackwell Publishing Ltd. 2010.

32. Søltoft-Jensen J, Hansen F. New Chemical and Biochemical Hurdles. In: Sun, D. W. (Ed.) Emerging Technologies for Food Processing. 2005; 387-416). London: Elsevier. doi:10.1016/b978-012676757-5/50017-7.

33. Xavier NM, Rauter AP, Queneau Y. (2010) Carbohydrate-Based Lactones: Synthesis and Applications. In: Rauter A, Vogel P, Queneau Y. Carbohydrates in Sustainable Development II. Topics in Current Chemistry Berlin: Springer. 2010; 2985: 19-62.

34. Asami DK, Hong YJ, Barrett DM, Mitchell AE. Comparison of the total phenolic and ascorbic acid contents of freeze-dried and air-dried marionberry, strawberry, and corn grown using conventional, organic, and sustainable agricultural practices. Journal of Agricultural and Food Chemistry. 2003; 51: 1237-1241. doi: 10.1021/jf020635c.

35. Freire JM, Abreu CMP, Rocha DA, Corrêa AD, Marques NR. Quantificação de compostos fenólicos e ácido ascórbico em frutos e polpas congeladas de acerola, caju, goiaba e morango (Quantification of phenolic compounds and ascorbic acid in frozen fruits and pulps of acerola, cashew, guava and strawberry) [In Portuguese]. Ciência Rural. 2013; 43:12: 2291-2296. doi:10.1590/S0103-84782013005000132.

36. Uddin M, Hawlader MN, Ding L, Mujumdar A. Degradation of ascorbic acid in dried guava during storage. Journal of Food Engineering. 2002; 51:1: 21–26. doi:10.1016/s0260-8774(01)00031-0.

37. Tulipani S, Mezzetti B, Capocasa F, Bompadre S, Beekwilder J, et al. Antioxidants, Phenolic Compounds, and Nutritional Quality of Different Strawberry Genotypes. Journal of Agricultural and Food Chemistry. 2008; 56:3: 696–704. doi:10.1021/jf0719959.
38. Volf I, Ignat I, Neamtu M, Popa V. Thermal stability, antioxidant activity, and photo-oxidation of natural polyphenols. Chemical Papers. 2014; 68:1: 1-9. doi:10.2478/s11696-013-0417-6.
39. Patras A, Brunton NP, O'Donnell C, Tiwari BK. Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation. Trends in Food Science & Technology. 2010; 21:1: 3–11. doi:10.1016/j.tifs.2009.07.004.
40. Rein M. Copigmentation reactions and color stability of berry anthocyanins. Helsinki: University of Helsinki. 2005; 10-14.
41. Tsai PJ, Hsieh YY, Huang TC. Effect of Sugar on Anthocyanin Degradation and Water Mobility in a Roselle Anthocyanin Model System Using17O NMR. Journal of Agricultural and Food Chemistry. 2004; 52:10: 3097–3099. doi:10.1021/jf0306587.
42. Cappa C, Lavelli V, Mariotti M. Fruit candies enriched with grape skin powders: physicochemical properties. LWT - Food Science and Technology. 2015; 62:1: 569–575. doi:10.1016/j.lwt.2014.07.039.
43. Da Silva LB, Annetta FE, Alves AB, Queiroz MB, Fadini AL, et al. Effect of differently processed açai (Euterpe oleracea Mart.) on the retention of phenolics and anthocyanins in chewy candies. International Journal of Food Science & Technology. 2016; 51:12: 2603–2612. doi:10.1111/ijfs.13245.
44. Löfgren C, Walkenström P, Hermansson, AM. Microstructure and Rheological Behavior of Pure and Mixed Pectin Gels. Biomacromolecules. 2002; 3:6: 1144–1153. doi:10.1021/bm020044v.
45. De Moura SCSR, Berling CL, Garcia AO, Queiroz MB, Alvim ID, et al. Release of anthocyanins from the hibiscus extract encapsulated by ionic gelation and application of microparticles in jelly candy. Food Research International. 2018; 121: 542-552. doi:10.1016/j.foodres.2018.12.010.
46. Otálora MC, de Jesús Barbosa H, Perilla JE, Osorio C, Nazareno MA. Encapsulated betalains (Opuntia ficus-indica) as natural colorants. Case study: Gummy candies. LWT - Food Science and Technology. 2018; 103: 222-227. doi:10.1016/j.lwt.2018.12.074.

CAPÍTULO 4. SUSTAINABLE PERFORMANCE OF COLD-SET GELATION IN THE CONFECTIONERY MANUFACTURING AND ITS EFFECTS ON PERCEPTION OF SENSORY QUALITY OF JELLY CANDIES

Publication

Article published in **Cleaner Engineering and Technology,** Volume 1, 100005, Copyright Elsevier, December 2020. https://doi.org/10.1016/j.clet.2020.100005.

CAPÍTULO 4. Sustainable performance of cold-set gelation in the confectionery manufacturing and its effects on perception of sensory quality of jelly candies

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Highlights

- Cold-set jellies had an ingredient cost 0.2 times higher than pectin jellies.
- Cold-set jellies had a processing energy demand 99 times lower than pectin jellies.
- Cold-set jellies processing had 300 times less CO_2 emissions than pectin jellies.
- Sustainable claims had positive impact on sensory acceptance of cold-set jellies.
- Consumers informed high interest but low knowledge about sustainability labeling.

Abstract

Finding new technologies for enhance the sustainable confectionery production is desirable. In this context the cold-set gelation emerges as potential tool for the jelly candy industry. This study evaluated sustainability aspects of alginate/pectin cold-set gelation technique in the jelly candy manufacturing process and its impacts in sensory quality of the obtained products. The energy requirement and the CO_2 emissions of cold-set jelly candy processing were measured, comparing to the conventional jelly candy manufacturing process. The produced candies were evaluated in relation to the bioactive compounds content (ascorbic acid, total phenolic and total anthocyanin compounds) and sensorially evaluated in acceptance tests wherein healthy and environmental sustainability labeling were put to the test. A questionnaire of purchase behavior was also applied to voluntary consumers. The results indicated the cold-set processing had lower energy demand (99 times lower) and gas emission (300 times lower) compared to the conventional manufacturing. Cold-set jellies showed about 3.3 times more phenolic compounds and 1.22 times more acid ascorbic content than pectin jellies. The consumer informed high interest and willing to pay more in jelly candy with sustainability labeling, however they showed low knowledge and frequency of consumption of these products. Results from the sensory acceptance test showed no significant difference ($p < 0.05$) between the candies regarding the attributes, but when sustainable claims were labeled it was verified an increasing in the sensory acceptance for appearance, texture and overall impression of the cold-set candies, suggesting the sustainable marketing potential of cold-set jelly candy manufacturing processing.

Keywords: candy; cold-setting gels; CO_2 emissions; confectionery; energy requirement; sensory analysis.

1. Introduction

Jellies and gummies are a popular and significant growing class of confections in the candy market [1]. They comprise a broad group of products elaborated from mixture of sugar syrups and hydrocolloids (gelling agent), such as gelatin, starch and pectin [2]. Their technological and organoleptic characteristics vary according to the hydrocolloid used and the final moisture content of the confection [3].

In recent years the candy market has been stimulated by confectionery launches with claims of healthiness, functionality, fortified formulation and sustainability on their labels [4]. The growing interest of consumers for adequate the diet has been increased the demand for find more conscious, convenient, nutritious and natural food options [5].

The candy industry has been found in the segment of gummies and jellies with fruit ingredients a great market strategy for attend claims of healthiness and naturalness. Fruit jelly candies stand out for their sensory quality, reformulation with less sugar content and no adding synthetic dyes and flavors [6].

For sustainability claims there has been a great focus of candy industry on sustainable manufacturing processes such as organic, “fair trade” and other production methods that aim reducing energy consumption and waste emissions for the environment along all food processing chain and packaging [7].

Claimed launches requires the regulation of labels to current legislation and technical standards. Formulations with natural ingredients and improved nutritional composing must follow the food labeling guidelines [8]. For environmental claims, the incorporation of environmental auditing or third party certification obtaining are necessary for implement environmental labeling on their products [9]. In this context the International Standards Organization (ISO) certification packaging is constantly requested [10].

The self-declared environmental claims are the most numerous sustainable labels worldwide. They are a cheap and easily applicable option to show environmental information for the consumer and they are based on self-declarations by manufacturer or retailers [10]. Eco-labels, energy labels, green stickers, carbon labels and product labels are examples of the diversity of environmental labels [11].

There is a growing segment of consumers disposed to pay more for green products as energy-efficient products and carbon reduction potentials [12]. In this context new technologies and strategies aiming to enhance the environmental management of confectionery processing industry have been extendedly evaluated and reported by the scientific literature. Among the recently appointed alternatives, the cold-set gelation technology applied to jelly candy manufacturing is noteworthy [13].

Cold-set gelation is the technique of obtaining gels by combining certain hydrocolloids under specific conditions with no heating. This technique present applicability in industrial processing of products with low thermal stability [14]. Sodium alginate and high methoxylation pectin are two gelling agents with specific capacity of cold-set gelation. When mixed in a medium at pH 3.4-3.8, these hydrocolloids can structure cohesive nets at room temperature [15].

Recent studies have been suggested the sodium alginate/high methoxylation pectin cold-set gelation as a potential sustainable technology able to replace the conventional jelly candy manufacturing process due its promising lower energy requirement [13] and its low processing temperatures which enable the maintenance of thermosensitive compounds of fruit ingredients and obtaining fruit candies with higher nutritional value [16].

The conventional manufacturing of jellies and gummies differ slightly according to the gelling agent, but in general all they follow the same steps of (i) ingredient mixing (for dissolving all sweeteners and solubilize hydrocolloid); (ii) cooking (for reduce water content and induce gelation); (iii) cooling the syrup and adding food additives (colors, flavors and acids); (iv) syrup dosing in dried starch powder molds (in starch mogul systems); (v) Curing or stoving (drying of molded candies in curing rooms for remove the excess moisture, cool and solidify the candies); (vi) finishing (covering the candies with oil or sugar coating) [3].

Several machinery systems can be used for the cooking step such as batch kettle cooking, vacuum cooking, swept surface heat exchanger, and coil cooking [3]. According to Aigroup [17], cooking systems and the hot water and boiler systems, which provides energy for the cooking equipment, are among the most energy intensive activities in confectionery manufacturing lines beside cool rooms, cooling towers and conveying systems.

Hot water and boiler systems in too many countries are operated with fossil energy resources (coal, oil, natural gas and secondary fuels), which presents environmental disadvantages such as high carbon footprint [18]. The fossil fuels burning levels vary according the country consume, but it is estimated they provide about 37% of the total global CO_2 emissions [19].

The industrial production of jellies and gummies correspond to about 25% of the energy consumption of all the confectionery sector, consuming more than 294 GWh of primary energy and emitting 60,000 t CO_2 emissions a year [20].

Aiming the reduction of energy requirement and environmental emissions from jelly candy production the cold-set gelation stands out as an alternative for the cooking step. According Avelar & Efraim [13] alginate/pectin cold-set gelation enables obtaining sweet gelled structures, with no heating requirement following the steps of (i) ingredient mixing; (ii) direct syrup dosing in dried starch molds; (iii) curing or stoving; and (iv) finishing. In cold-setting manufacturing the machineries of the conventional cooking step are replaced for electric-moved mixing equipment and heat generation systems are not required, reducing energy demand and environmental emissions of the candy manufacturing line.

The researches published to date have been evaluated the cold-set processing only on laboratory scale [16]. Its sustainability potential, however, still needs be analyzed on higher scales for better estimate the environment impacts to industrial lines.

The possibility of obtaining environmental claims by this new technology and attributing to the developed products also must be evaluated, as well as its effect on the sensorial consumer acceptance. Considering the studies about sensory perception of environmental labeled candies and consume behavior are too scarce in the literature, these data can be an important source to guide the industrial confectionery sector.

In this context, the aim of this study was to evaluate the sustainable performance of sodium alginate/ high methoxylation cold-set gelation technique as a tool for jelly candy processing compared to the conventional manufacturing process in transposed processing scale lines, and verify the impact of sustainable claims on the label of the produced candies in its sensory acceptance.

2. Material and methods

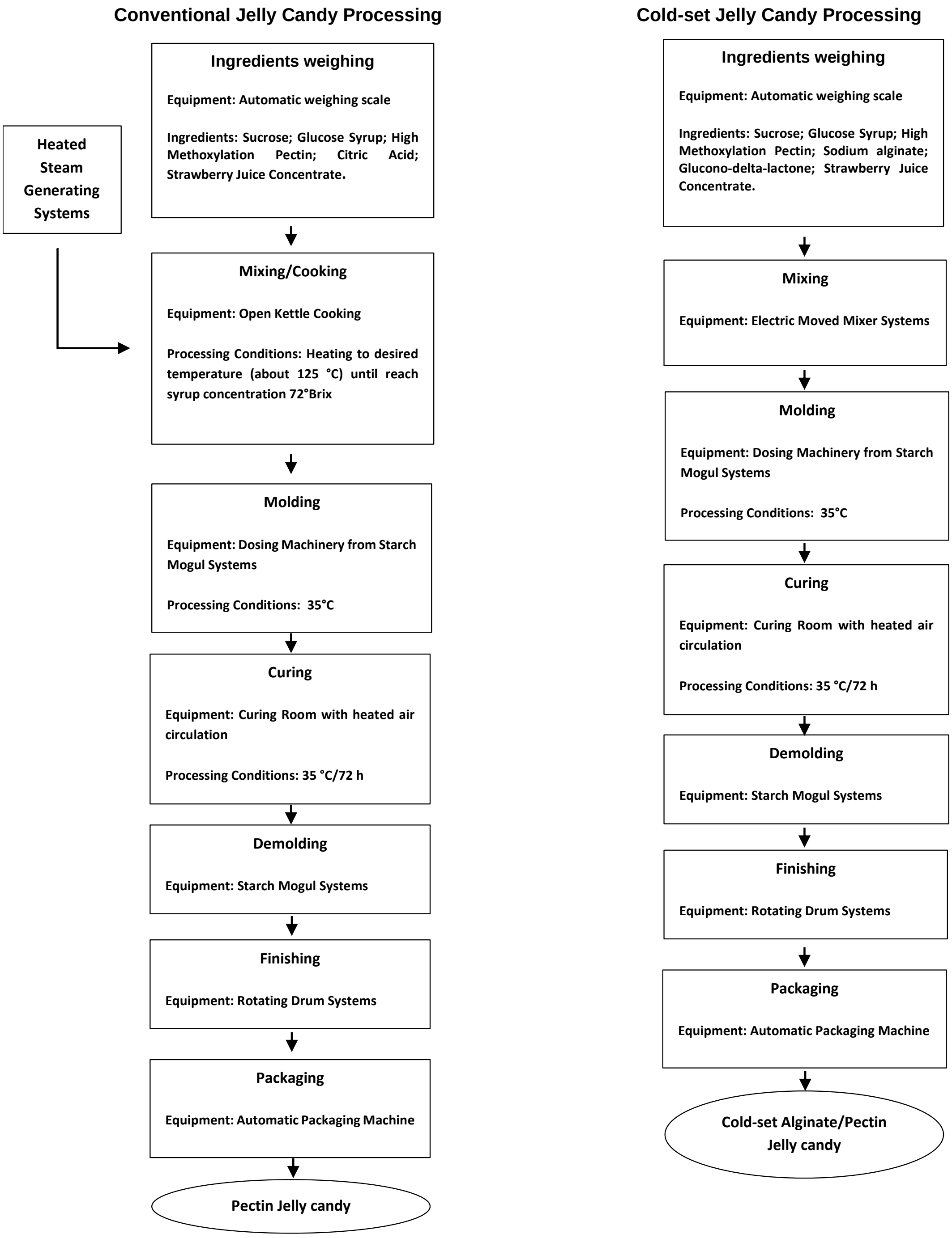
2.1. Material

Ingredients used for jelly candy production: citric acid (ACS, Synth, Diadema, Brazil), high methoxylation pectin (HM 121Slow, Degree of esterification 58%, CPKelco, Limeira, Brazil), glucono-delta-lactone (GDL) (Art Alimentos, São Paulo, Brazil), glucose syrup (Excell 1040, Ingredion, Mogi Guaçu, Brazil), sodium alginate (Algin I-3G-150, viscosity 300 – 400 mPa·s, Kimica, Providencia, Chile), strawberry juice concentrate (30 °Brix, Loop, Piracicaba, Brazil), sucrose (refined sugar, União, São Paulo, Brazil).

2.2. Definition of boundaries of the study

The flowcharts of conventional pectin jelly candy processing (HCP), described by Hartel [3], and alginate/pectin cold-set jelly candy processing (CSCP), developed by Avelar & Efraim [13], are presented in Figure 1. Comparing the two processes it is identified they share the same steps of ingredient weighting, syrup dosing, curing, demolding, finishing and packaging (with same machinery and processing conditions).

Three mainly differences, however, can be appointed: (i) Ingredients of formulation (cold-set jellies requires both sodium alginate and pectin as gelling agents and glucone-delta-lactone as acidulant instead citric acid); (ii) Heat requirement for operating cooking machinery in pectin jellies processing; and (iii) quality of final products (as previously described different hydrocolloids provide candy gels with distinct properties).



Source: Avelar & Efraim [13]; Hartel [3].

Figure 1. Flowchart of conventional pectin jelly candy processing and cold-set jelly candy manufacturing.

Considering the contrasting points between the manufacturing processes, the boundaries of this present study were delimited as the following points:

(i) Ingredients: Analysis of economic impact of replacement the recipe of pectin jelly candy for alginate/pectin cold-set jelly candy;

(ii) Candy syrup preparing step: Analysis of the sustainable potential of cold-set candy syrup mixing step compared to conventional cooking step by the measurement of energy requirement and CO_2 emissions;

(iii) Final products: Analysis of the quality of cold-set jellies, the potential of healthiness and environmental sustainability claiming and its effects on sensory acceptance.

2.3. Economic analysis of jelly candy formulation

A strawberry cold-set jelly candy (CSC) and a strawberry pectin jelly candy (HC) formulated by Avelar et al. [16] (Table 1.) were suggested for conduction of this study, aiming to obtain natural confections with high content of bioactive compounds and due to the great acceptability and widely use of strawberry flavor in confectionery products.

Table 1. Strawberry jelly candies formulations.

Ingredients	Quantity (g/kg)	
	Strawberry cold-set jelly candy	Strawberry pectin jelly candy
Sucrose	440	465
Glucose syrup	110	120
Strawberry juice concentrate	400	395
Sodium alginate	20	-
High methoxylation pectin	20	14
Glucono-delta-lactone	10	-
Citric acid	-	6

Source: Avelar et al. [16].

The price quote of each ingredient in 2019 year was inquired directly to the producing or reselling companies [21] and the total cost of the candy recipe was calculated considering the ingredients percentage in the formulations. The final cost was adjusted to the processing yield factors (calculated in item 2.4.2), for be expressed in price (US$)/kg of produced candy.

2.4. Sustainability analysis of cold-set jelly candy processing

2.4.1 Jelly candy manufacturing processes definition

CSCP followed the steps: (i) dissolution of sucrose and glucose syrup in strawberry juice concentrate, (ii) dispersion of gelling agents (alginate and pectin) in the solution of sugars and fruit juice, (iii) dissolution of glucono-delta-lactone (GDL) to acidify the system, (iv) dosing of final candy syrup in starch molds and (v) drying in a forced air circulation drying oven (Tecnal, model TE-394/2, Piracicaba, Brazil) at 35 °C/72 h [16].

HCP was performed by dissolution of the ingredients and cooking at atmospheric pressure until 71 °Brix, dosing the final candy syrup into starch molds, and drying in the same forced air circulation drying oven at 35 °C for 72 h [22]. Two batches of each candy sample at different scales were produced for a comparing evaluation of energy requirement of the processes: a bench-scaled batch and a pilot plant scale batch.

The bench scaled CSCP was performed with a digital mechanical bench agitator (Tecnal, model TE-039/1, Piracicaba, Brazil) at 380 rpm. The length time of mixing steps was fixed at 3.44, 0.78, and 0.86 min for steps (i), (ii), and (iii), respectively. The bench scaled HCP was carried out in a gas burning bench cooker with cooking time fixed at about 5.12 min (until 71 °Brix was reached). The burned gas was a liquefied petroleum gas consisting of 750 g/kg isobutane and 250 g/kg propane. The CSC and HC syrups were manually dosed with a funnel and the candies were dried in a forced air circulation drying oven (Tecnal, model TE-394/2, Piracicaba, Brazil).

Both plant scale candy processes were performed at the Fruit, Vegetable and Confectionery plant pilot of the University of Campinas (School of Food Engineering, UNICAMP, São Paulo, Brazil) with a jacketed pot (Geiger, model UMM SK12, Pinhais, Brazil) at 1750 rpm. The jacket pot rotor was used for ingredients mixing in CSCP with no steam applying. The length of the mixing time steps was fixed at 1.00, 0.66, and 1.50 min for steps (i), (ii), and (iii), respectively.

The HCP was performed at 2.50 min with steam pressure 1.00 kgf/cm³. The steam generating boiler (Domel, model VSVG.310, São Paulo, Brazil) was operated with 3 kgf/cm³ steam pressure, gas consumption per hour: 22.73 kg/h, and LPG gas as burning fuel.

2.4.2 Measurement of the energy requirement and CO_2 emissions of candy syrup processing steps

The direct differences of requirements and emission between CSCP and HCP are related to the syrup preparing step, for that reason the comparing study was bounded to this step. The energy requirements of CSCP in both processing scale were measured considering the time of candy syrup preparation and the power of the equipment (bench agitator power: 180 W, jacket pot power: 2 kW) according to Equation 1 [23].

$$\text{Energy requirement (kWh)} = \frac{\text{time of the process (s) x power of the equipment (W)}}{3600\left(\frac{\text{s}}{\text{h}}\right)\text{x } 1000\left(\frac{\text{W}}{\text{kW}}\right)} \quad \text{(Equation 1)}$$

The energy requirement of both scaled HCP was calculated according to Equation 2 [24], considering the volume and the internal calorific value of the gas burned during the heating of the candy syrup (*bench scale*: isobutane internal calorific value: 9,209 kJ/m³, propane internal calorific value: 117,230 kJ/m³; *pilot scale*: liquefied petroleum gas: 11,000 kcal/kg) [25].

$$\text{Energy requirement (MJ)} = \text{Gas volume } (\text{m}^3) \text{ x Internal calorific value } \left(\frac{\text{MJ}}{\text{m}^3}\right) \text{(Equation 2)}$$

The weight yield of each jelly candy process was calculated considering the mass loss by evaporation during the cooking step and moisture loss during drying step (Equation 3). The energy requirement of the processes was adjusted to the weight yield and expressed by MJ/kg of produced candy.

$$\text{Weight yield} = \frac{\text{weight of candies after drying step (kg)}}{\text{weight of candy syrup before cooking or cold−setting step (kg)}} \quad \text{(Equation 3)}$$

For CSCP the estimation of carbon dioxide emissions was performed considering the average annual CO_2 emission factor for Brazilian electricity [26], while for HCP it was calculated considering the Brazilian CO_2 emission factor for direct burning [27].

2.4.3 Measurement of indirect requirements of energy and resources

The indirect requirement of resources related to boiler consumption of energy, water and fuel for steam production in HCP was calculated. The electric energy demanding was estimated using Equation 1 (item 2.4.2) considering HCP time (2.50 min) and power of the boiler (232.6 kW). The fuel consumption was determined by the hourly consumption rate (22.73 kg LPG gas/h) and processing time.

The water requirement was calculated by the hourly steam production factor with water supply at 20°C (311 kg steam/h) during the time of operation. The CO_2 emissions were estimated by the sum of direct emissions from fuel combustion and indirect emissions from electricity consumption according methods described in item 2.4.2.

2.5. Evaluation of the quality of jelly candies

2.5.1 Bioactive compounds content

The bioactive compounds content of the produced candies was evaluated in order to verify the possibility of attributing claims of healthiness on the label of the obtained products. The ascorbic acid content was analyzed by the titratable method according to Cheftel & Pigeaud [28]. The phenolic compounds content was measured using Folin Ciocalteu reagent, with a spectrophotometer (model Cirrus 80, Femto, São Paulo, Brazil) at 765 nm [29].

The total anthocyanin content was determined by pH differential spectroscopic method according to Tonutare et al. [30]. Two buffer solutions were used: 0.025 M potassium chloride (pH 1.0) and a 0.4 M sodium acetate (pH 4.5). Ethanol solvent 0.1 M HCl (85: 15%, v: v) was used to the extraction. The measurements were carried out on the same spectrophotometer as mentioned above at 510 and 700 nm. The absorbance of the diluted sample (A) was calculated by Equation 4 and the total anthocyanin content by the Equation 5.

$$A = (A_{510} - A_{700})_{pH\ 1.0} - (A_{510} - A_{700})_{pH\ 4.5} \qquad \text{(Equation 4)}$$

$$Total\ anthocyanin\ content\ \left(\frac{mg}{100g}\right) = \frac{A\ x\ M\ x\ DF\ x\ 1000}{(\varepsilon\ x\ \lambda\ x\ m)} \qquad \text{(Equation 5)}$$

In the Equation 5, "A" is previously calculated absorbance, "M" is the molecular weight of cyanidin-3-glucoside (449.2 g/mol), DF is the dilution factor, ε is the molar absorptivity coefficient (29,600 L mol^{-1} cm^{-1}), λ is the cuvette optical pathlength (1 cm) and m is the weight of the sample (g) [30].

2.5.2 Sensory analysis

A sensory analysis test was carried out at the Food Sensory Analysis Laboratory of the Department of Food Technology - FEA / UNICAMP (Certificate of Presentation for Ethical Assessment - CPEA 86627118.5.0000.5404). The candies were evaluated in an acceptance test by 120 evaluators in relation to the attributes appearance, color, aroma, flavor, texture and overall impression, using a structured 9-point hedonic scale ranked 9: I liked it extremely and 1: I disliked it extremely [31].

The sensory test was divided into three sessions for evaluating the impact of labels on sensory acceptance and purchase intention. In the first session the evaluators performed a blind test, in which samples of CSC and HC were served with no information. Before the second session they received a card with explanations about products with sustainability claims: self-declared environmental label, naturalness (identification of natural ingredients) and healthiness (identification of high nutrients content). Then, they answered a questionnaire on consumer awareness for the product, elaborated according to Silva et al. [32] with modifications.

In the second session the consumers evaluated once again CSC and HC, but this time the samples were identified with designation of environmental sustainability (energy requirement and CO_2 emission) according to results obtained in item 2.4.2.

In the third session the candy samples were labeled with the same environmental sustainability information from second session, but this time the labeling was added by healthiness claims (bioactive compound content) according to values measured in item 2.5.1.

2.6 Statistical Analysis

The data were submitted to Analysis of Variance (ANOVA), Tukey's test, Friedman's test and Nemenyi's test at 5% significance level using XLSTAT statistical software

(Addinsoft, New York, NY, 2016). The questionnaire reliability was determined with Cronbach's alpha coefficient [33].

3. Results and Discussion

3.1. Economic analysis of jelly candy formulation

The price of raw materials and the cost of jelly candy formulations are presented in table 2. Considering the manufacturing processes yields the CSC price per kg was 0.20 times higher than HC price.

Table 2. Cost analysis of jelly candy formulation

Ingredients	**Price (US$/kg)**	**Food Brand**	**Source**
Sucrose	1.30	-	USDA/ERS*
Glucose syrup	0.79	-	USDA/ERS*
Strawberry juice concentrate	4.09	Loop	Direct quote**
Sodium alginate	44.09	Master Sense	Direct quote**
High methoxylation pectin	22.05	Cargill	Direct quote**
Glucono-delta-lactone	3.90	Art Alimentos	Direct quote**
Citric acid	0.65	Ensign	Direct quote**
Formulation	**Price (US$/kg of candy syrup)**	-	-
Cold-set jelly candy formulation	3.65	-	-
Pectin jelly candy formulation	2.62	-	-
Jelly candies	**Price (US$/kg of produced candy)**	-	-
Strawberry Cold-set jelly candy	2.34	-	-
Strawberry Pectin jelly candy	1.94	-	-

* Average of world refined sugar price and wholesale price for glucose syrup in 2019 according the Economic Research Service of United States Department of Agriculture [33]; ** Direct quote made with the producing company or reseller companies.

Despite the cost, CSCP still must be considered due its promising environmental impacts. Once sustainability claims are allowed to label CSC, the final higher market price may be supported by environmental marketing strategic. In addition, it´s important to highlight that gummy and jellies produced with other hydrocolloids may have recipe costs equal or even higher than CSC due to price and required quantity of gelling agent. Gums and drops produced with arabic gum, for example, can reach very higher charges due cost, volatility prices, and high hydrocolloid usage level (20-50%) in the recipes [3].

3.2. Direct and indirect energy requirement and CO_2 emissions

The processes presented energy requirement with significant difference ($p < 0.05$) on both evaluated scales (Figure 2). HCP had an energy demand/volume of produced candy two times higher than CSCP on lab bench scale, and 97 times higher on pilot plant scale.

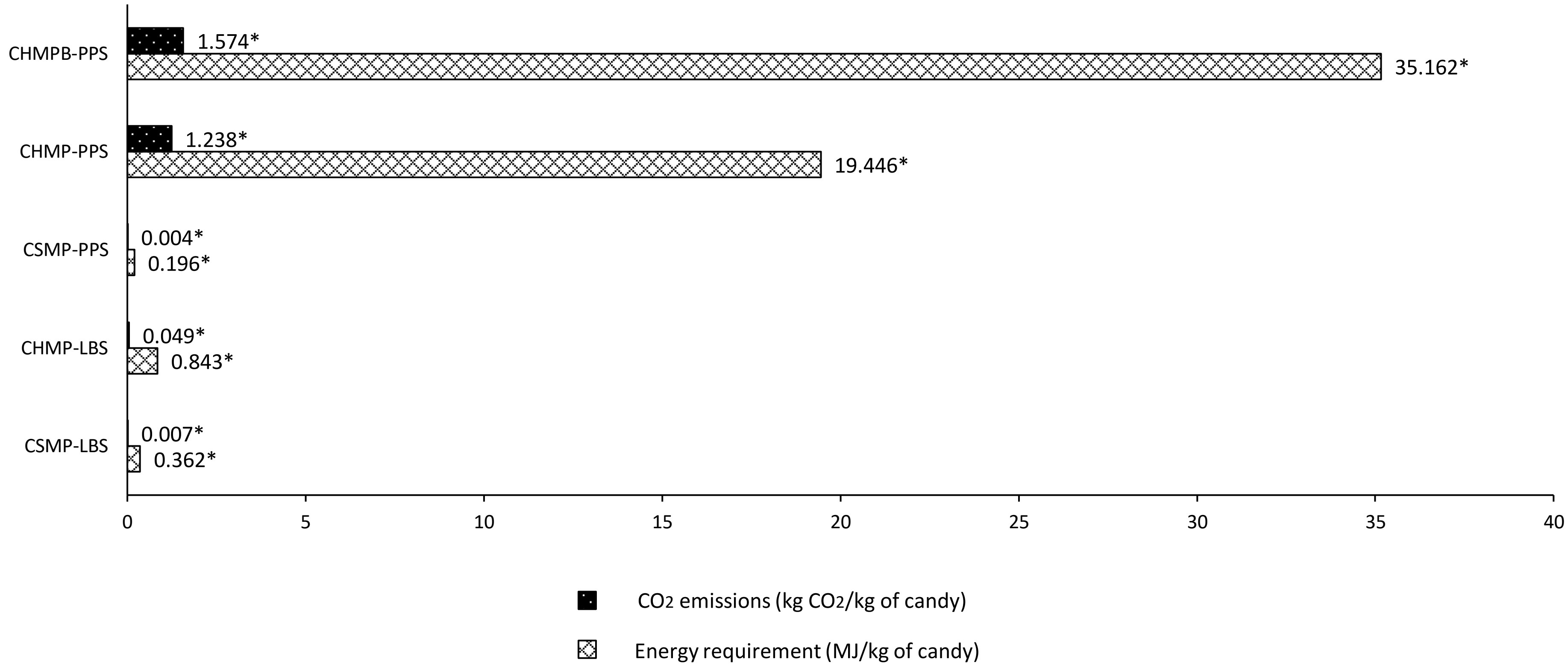
For HCP the boiler demanded 0.426 kg fuel, 5.837 L water and 15.716 MJ electric energy for kg of produced candy. Considering these rates, the total energy requirement of pilot plant scaled HCP was 179 times higher than CSCP.

Changing steam-powered cooking process for electric-powered mixing step makes boiler systems not necessary, implying in cost saving for industrial installation and operation. Furthermore, as only electric energy is required in cold-setting processing line, the environmental emissions are indirect and reduced, as well as resource consumption.

The volume of CO_2 emission of pilot plant scaled CSCP was 309 times lower than HCP and 393 times lower than HCP when considered the emissions from boiler operating. The appointed reduction of environmental emissions is very promising and desirable due the significant share of jellies in candy market.

Gums and jellies are the third-largest segment of sweet products, corresponding to about 20.64% of the global sugar confectionery market in terms of revenue [34]. Brazil follows United States and Germany in the ranking of world largest confectionery manufacturer, with 2019 production of more than 257,000 t of candies [35].

The global warming potential estimated by Nilsson et al. [36] for sugar confectionery products is about 3.92 kg CO_2-eq/kg of product. Considering the rates of reduction in CO_2 emissions between CSCP and HCP the cold-set gelation may contribute positively for environmental impact in the global confectionery industry chain.



Mean values of CO2 emissions/energy requirement of different manufacturing processes at the same evaluated scale followed by (*) are significantly different ($p < 0.05$)

Figure 2. Energy Requirement and Environmental Emissions of Candy Manufacturing Processes (CSMP: Cold-set Manufacturing Process; CHMP: Conventional Heating Manufacturing Process; CHMPB: Conventional Heating Manufacturing Process considering Steam Boiler Activity) in different Processing Scales (LBS: Lab Bench Scale; PPS: Pilot-Plant Scale)

The search for lower environmental impact in the confectionery industry by the energy saving and CO_2 emission reducing have also been reported by many other studies in the literature. Miah [37], for example, developed methodological tools based on heat integration and Life Cycle Assessment (LCA), evaluating a heat integration framework with combined direct and indirect heat exchange from zonal to multiple zones, and incorporating heat pump technology to enhance low grade heat recovery. It was concluded that heat integration can reduce factory energy consumption by 4.04–6.05% while the energy reduction by the heat pump technology is by up to 29.2%, despite the complexity design impose and long economic paybacks.

Jou et al. [38] studied the complete replacement of natural gas by the recovered waste tail gas emitted from petrochemical processes and verified a save 5.8×10^6 m^3 of natural gas consumption of furnace, which implies to reducing 3.5×10^4 t of CO_2 emission annually.

The energy demand and CO_2 emissions quantified in this study indicate the possibility of appointing environmental self-declared claims such as “reduced energy consumption and carbon footprint” in the CSC label.

3.3 Evaluation of the quality of jelly candies

3.3.1 Bioactive Compounds Content

CSC presented higher averages ($p<0.05$) for total phenolic compounds and ascorbic acid content proving CSCP efficiency for maintenance of thermosensitive compounds of fruit ingredients during candy manufacturing [16].

Ascorbic acid (vitamin C) is an important water-soluble vitamin with physiological, anticarcinogenic and antioxidant functions [39] which stability is influenced by the presence of oxygen, high temperature and high or low water activity [40]. The Food and Agriculture Organization/World Health Organization (FAO/WHO) indicates 45 mg of vitamin C per day as recommended nutrient intake for adults [41]. The Food and Drug Administration (FDA) suggested a higher daily intake (90 mg/day for adults) [42], and requires the food must contain 20 percent or more of the reference daily intake of the substance necessary to achieve the claimed effect for the regulation of health claim “high content” on the label [43].

Considering the candies serving sizes indicated by FDA as 15 g of candy [44], the CSC serving offers an ascorbic acid content 1.22 times the daily intake recommended by FDA, which makes it possible to appoint claims of healthiness on the candy label.

Table 3. Bioactive compounds contents of strawberry jelly candies.

AA, ascorbic acid content; TPC, total phenolic compounds content; TAC, total anthocyanin content. Mean values followed by (*) in the same column are significantly different (p < 0.05).

Samples	Chemical parameters		
	AA (mg ascorbic acid g $^{-1}$)	TPC (mg gallic acid g^{-1})	TAC (mg cyanidin-3- glycoside g^{-1})
Strawberry cold-set jelly candy	734.083 ± 13.10*	254.44 ± 35.64*	0.0515 ± 0.0201
Strawberry pectin jelly candy	597.376 ± 84.08*	76.66 ± 10.00*	0.0560 ± 0.0000

Source: Avelar et al. [16].

Polyphenolics are a wide group of organic compounds with great interest in nutrition and human health due to their antioxidant properties and protection effects against certain cancers and diseases [45]. In food processing, they are subjected to degradation to oxygen, light, high temperatures, enzymes, metal ions and possible associations with other organic components [46].

The regulation for polyphenols consumption is challenged to the variety of substances and their contents in foods, shelf stability and proven scientific evidences of the health effects. For these reasons FDA have no regulatory recommendations yet for phenolic claims to food labels [45]. According to literature the phenolic compounds daily intake is estimated between 150 mg and 1 g/day [47]. CSC presented 3.3 times more phenolic compounds than HC. According to polyphenolic averages of the foods richest in antioxidant listed by Pérez-Jiménez et al. [48], CSC have a high phenolic content per candy gram. The possibility of appointment of health claims on the label, however, must be better evaluated according to legislation.

Anthocyanins are the main phenolic compounds in strawberry fruit [49], which stability during food processing is influenced by oxygen, pH, enzymes, light and metal ions presence [50]. There was no significant difference (p<0.05) between the total anthocyanin content of the jellies, probably due to the high sugar content of HC recipe, which exercised protective effect on degradation reaction during HCP heating [16].

3.3.2 First Sensory Analysis: blind test

The results of the blinded sensory acceptance session are presented in Table 4. There was only significant difference ($p<0.05$) between the samples for the texture parameter, wherein CSC showed higher average value. The acceptance scores for all sensory evaluated parameters were located between the term "indifferent" (mean 5.0) and I liked it moderately (mean 7.0), similar to the obtained for Avelar & Efraim [13] in the acceptance evaluation of cold-set model candies with no fruit pulp ingredients. According to the authors cold-set jellies and pectin jellies showed no sensory difference ($p<0.05$) between any of the sensory attributes in the blind sensory test.

Table 4. Sensory attributes of the produced candies at blind and informed sessions.

Sensory atributes	**Sensory test**	Average score	
		Strawberry cold-set jelly candy	strawberry pectin jelly candy
Appereance	Blind sensory test	5.8 ±1.7 b	5.7 ±1.9 a
	Sensory test with suitability information	6.6 ±1.5 a*	5.8 ±1.7 a*
	Sensory test with healthiness and suitability information	6.7 ±1.7 a*	5.9 ±1.9 a*
Color	Blind sensory test	6.0 ±1.7 a	6.8 ±1.5 a
	Sensory test with suitability information	6.3 ±1.7 a	6.7 ±1.5 a
	Sensory test with healthiness and suitability information	6.4 ±1.7 a	6.8 ±1.5 a
Aroma	Blind sensory test	6.1 ±1.4 a	6.1 ±1.5 a
	Sensory test with suitability information	5.9 ±1.3 a	5.8 ±1.3 ab
	Sensory test with healthiness and suitability information	6.0 ±1.3 a	5.7 ±1.3 b
Flavor	Blind sensory test	6.4 ±1.9 a	6.6 ±1.7 a
	Sensory test with suitability information	6.5 ±1.8 a	6.4 ±1.9 a
	Sensory test with healthiness and suitability information	6.7 ±1.7 a	6.3 ±1.8 a
Texture	Blind sensory test	5.0 ±2.2 b*	4.7 ±2.3 a*
	Sensory test with suitability information	5.7 ±2.0 a*	4.9 ±2.2 a*
	Sensory test with healthiness and suitability information	6.1 ±1.9 a*	4.8 ±2.1 a*
Overall impression	Blind sensory test	5.9 ±1.7 b	5.8 ±1.8 a
	Sensory test with suitability information	6.4 ±1.6 a*	5.8 ±1.6 a*
	Sensory test with healthiness and suitability information	6.6 ±1.6 a*	5.8 ±1.5 a*

Mean values followed by (*) in the same line are significantly different ($p < 0.05$) in relation to the same sensorial attribute at the same sensory test session. Mean values of different sensory test sessions followed by the same letter in the same column are not significantly different ($p>0.05$) in relation to the same sensorial attribute.

3.3.3 Purchase Intention questionnaire

The questionnaire was applied between the first and second sensory sessions. The questionnaire reliability was determined with Cronbach's alpha coefficient and the obtained value was α =0.80. The consumers, which 33% were male and 67% were female aged from 18 to 34 years, answered about seals and their purchase intention in 16 questions as follows:

(i) Do you know any of these seals or labels or information used in packaging of candies and food in general? (Product with self-declared environmental claim; Product with carbon footprint certification; Product with identification of natural ingredients; Product with identification of high nutrients content)

(ii) Have you ever consumed candies with any of these labels (Product with self-declared environmental claim; Product with carbon footprint certification; Product with identification of natural ingredients; Product with identification of high nutrients content).

According to consumers answer, the frequency of consumption is lower than the knowledge about candy with claims on packaging for all evaluated seals, labels and information (Figure 3). Healthiness and naturalness claims were indicated as better known and more consumed than sustainable claims.

According to Ertz et al. [10], although the growing environmental labeling and exposing of consumer to pro-sustainable behavior, other factors such as price, brand, quality are still considered more important in consumer purchase. The limited knowledge of the consumer about specificities of environmental declarations, the difficulty to process sustainable claim and the multiple formats of environmental declarations used for comparable products are other limiting factors to the effectiveness of environmental labeling [51].

Healthiness claims are highly valued by consumers, however, the information on the labels receives varying attention according to the product, context and consumer interest. It is also indicated there are difficulties in assessing health claims for several reasons, such as terminology, presence of too much information, difficult in interpretation and the attempt to make diet-planning calculations [52].

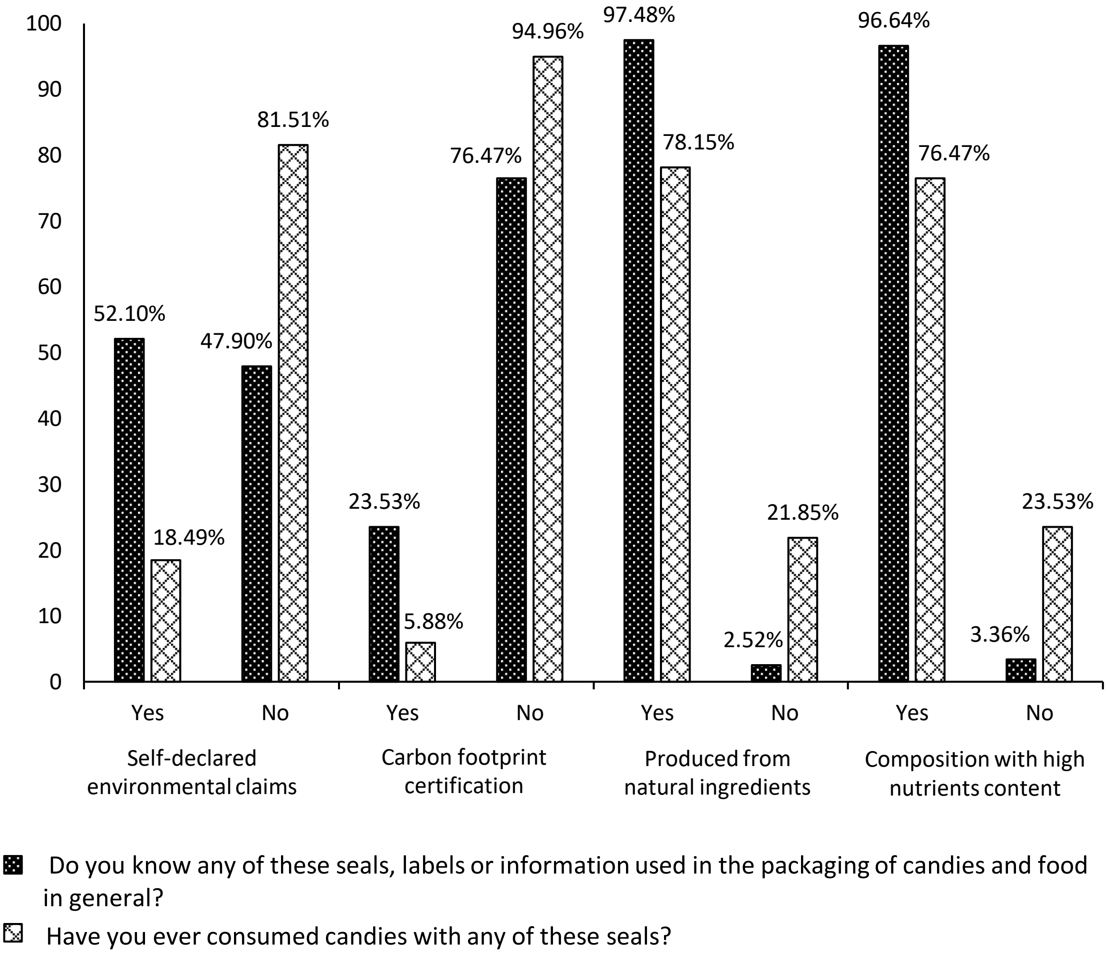


Figure 3. Knowledge and frequency of consumption of candy with seals, labels or information on the packaging

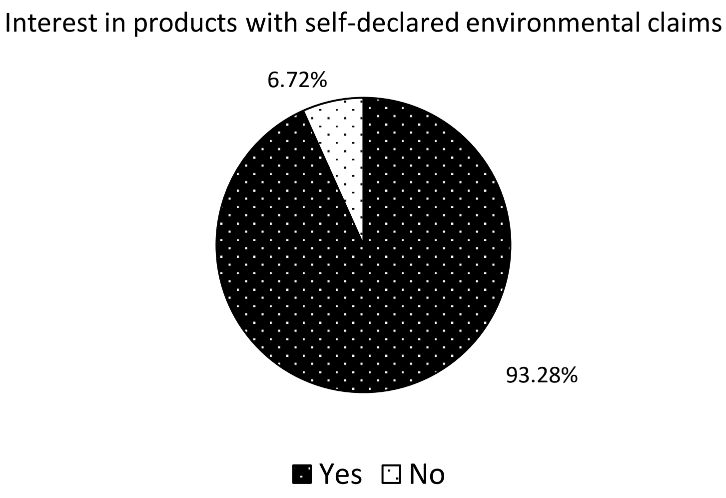
(iii) Are you interested in products with self-declared environmental claim?

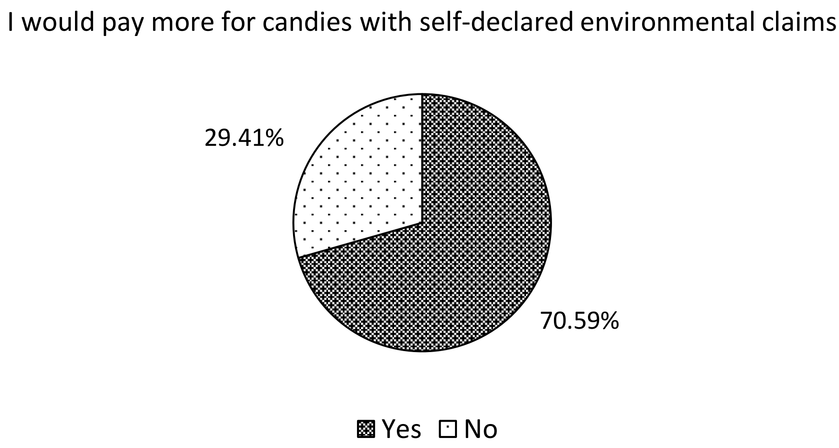
(iv) How often do you consume any candy with self-declared environmental claim?

(v) Would you pay more for a candy with self-declared environmental claim?

Most consumers showed interest in products with self-declared environmental claims (Figure 4), however, more than 73% of them reported they have never consumed environmental labeled candies. When asked if they knew of any seal, label or information about self-declared environmental claims, almost half of consumers respond they did not (Figure 3). The underinformed consumer combined with low market supply may justify the low consumption reported.

Over 70% of evaluators informed they would pay more for candies with sustainable environmental labelling. Other studies also pointed to consumer´s high willingness to pay more for environmentally friendly products [10], and reported that more sustainable products are also considered to be more expensive [53].





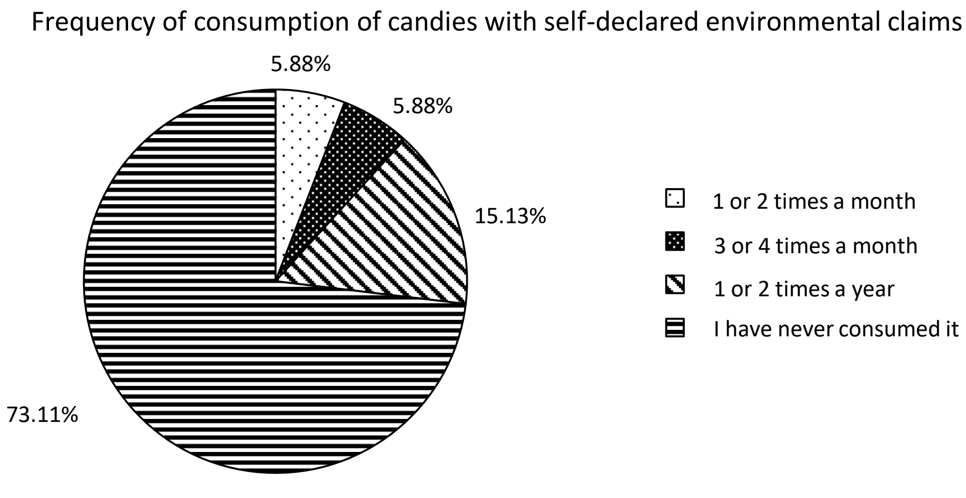
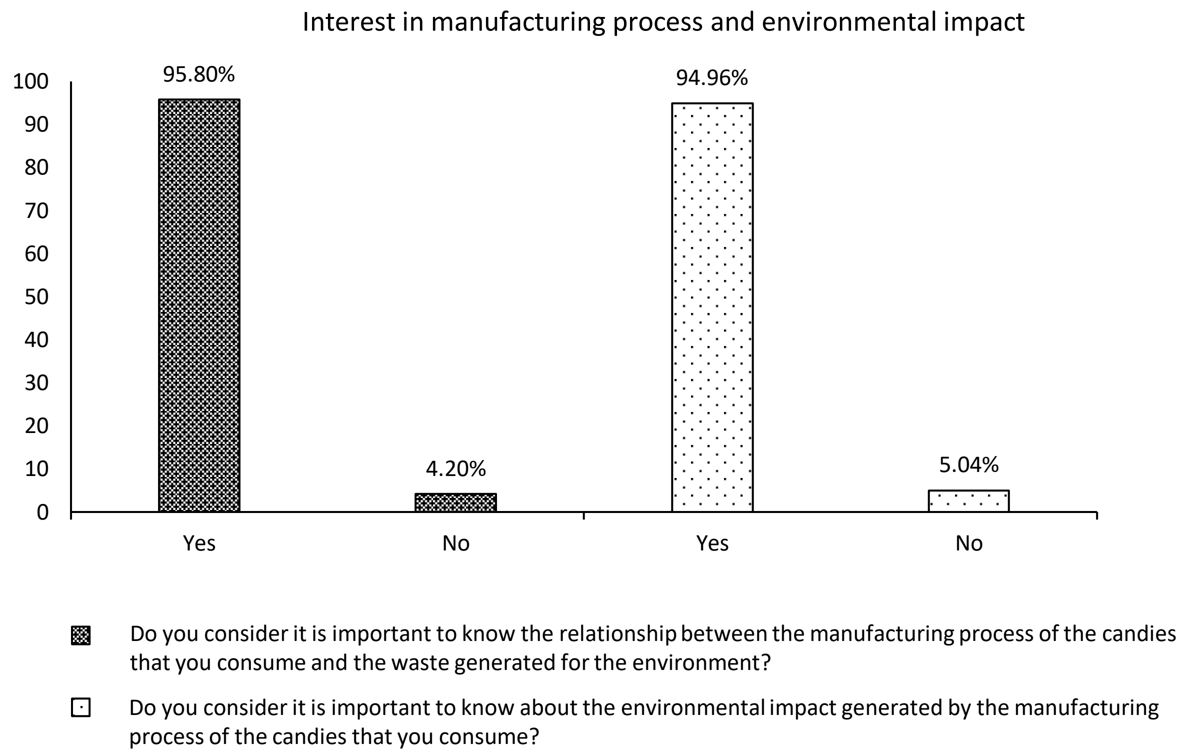


Figure 4. Interest, willingness to pay and frequency of consumption of products with self-declared environmental claims

(vi) Do you consider important to know the relationship between manufacturing process, energy consumption and environmental waste of the candies you consume?

(vii) Do you consider important to know about the environmental impact generated by the manufacturing process of candies you consume?

The interest between candy manufacturing process and its environmental impacts and generated waste was indicated by most of consumers (about 95%) (Figure 5). The environmental impact of food production and distribution and the food choices has been recognized by consumers and many studies have reported a growing interest in sustainable production and consumption in agriculture and food chain [54].



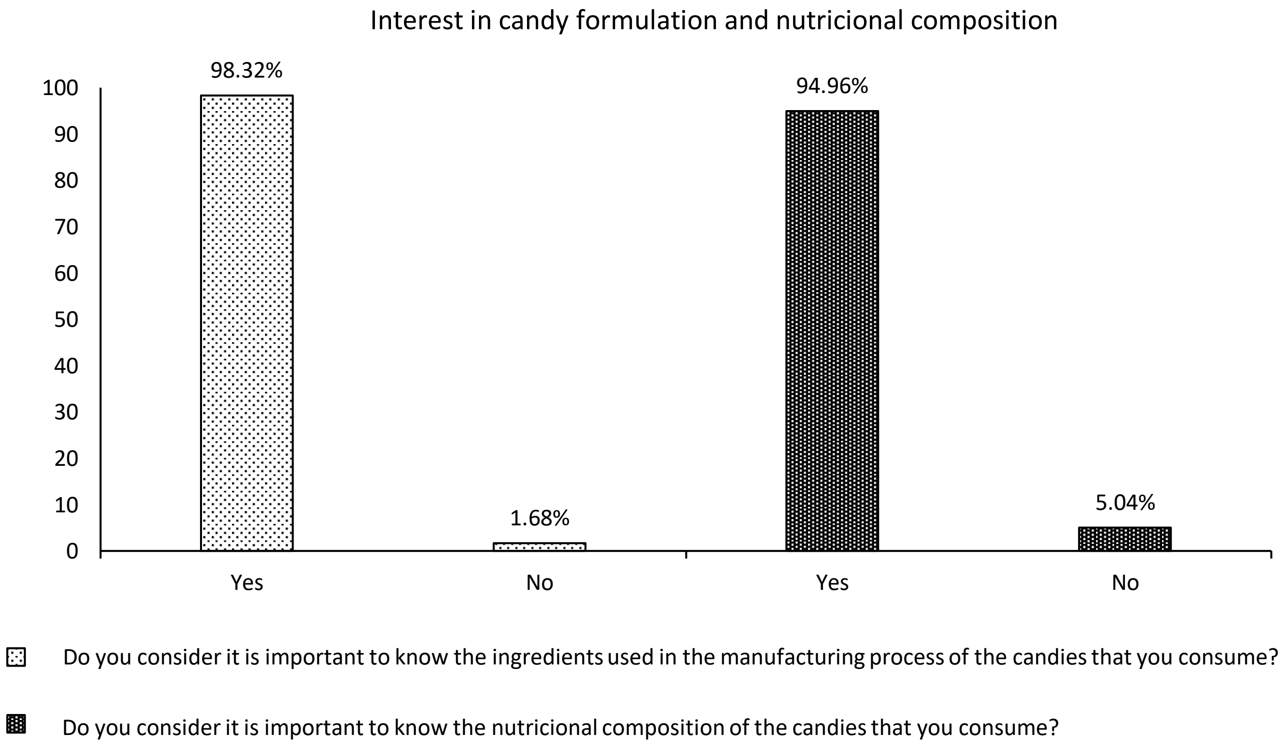


Figure 5. Interest in candy formulation and nutritional composition and manufacturing process and environmental impact

(viii) Are you interested in carbon footprint certified products?

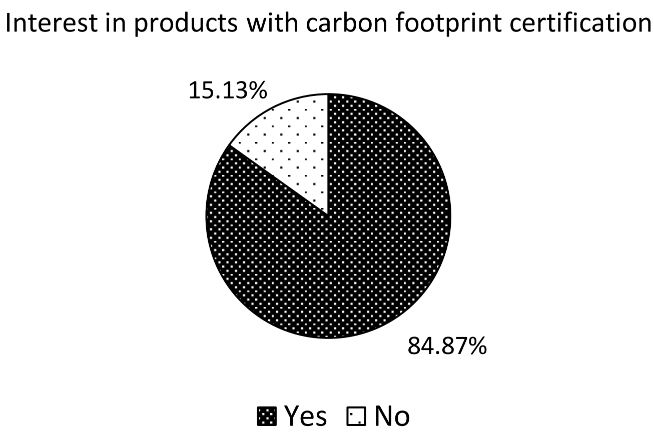
(ix) How often do you consume any type of carbon footprint certified candy?

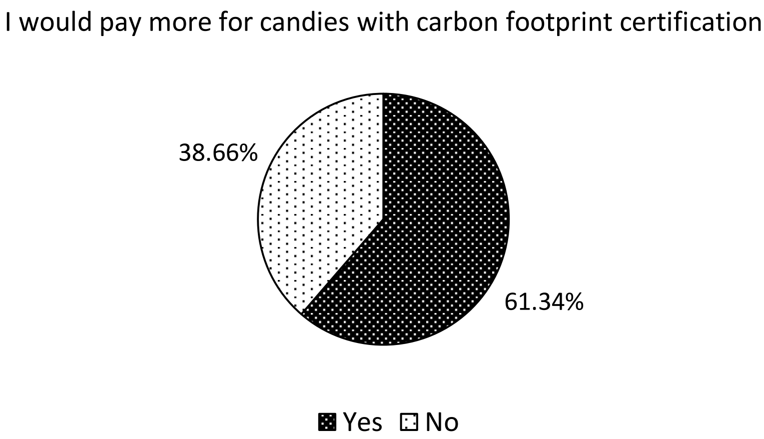
(x) Would you pay more for a certified carbon footprint candy?

The majority of consumers (about 76%) informed they didn´t know about carbon footprint certification (Figure 3) and almost 92% of them never consumed candies with these labeling (Figure 6). However, the majority of evaluators showed interest and willingness to pay more for these labelled products.

The carbon footprint corresponds to greenhouse gas emissions during the life cycle of a product or service (from production, use/consumption to disposal) and it is calculated according to the greenhouse gases considered and the boundaries of the calculation (considered production stages with different possibilities of combinations of direct and indirect emissions according to the definitions of life cycle assessment) [55]. Carbon footprinting is not universally used and some countries adopt alternative methods to assess greenhouse gas emission [56].

According to executive and business trends studies, sustainable production of the main raw materials (organic, fair trade production) and packaging, and local supply of materials are considered the most important environmental tools adopted by the concept of sustainability in the confectionery sector, while the reduction of energy and gas emissions receive a lesser degree of importance [7].





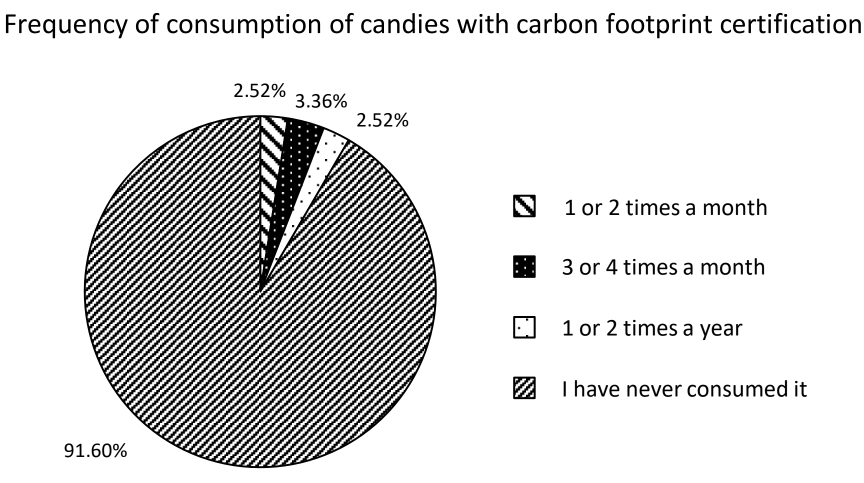


Figure 6. Interest, willingness to pay and frequency of consumption of candies with carbon footprint certification

(xi) Do you consider important to know about ingredients used to make the candies you consume?

(xii) Do you consider important to know about nutritional composition of the candies you consume?

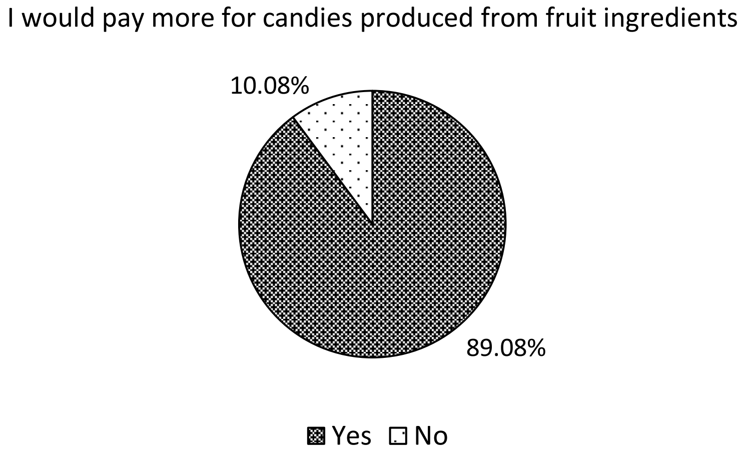
When asked about formulation of candies and their nutritional facts most consumers reported interest (Figure 5) and most confirmed they knew about nutritional seal, label or information (Figure 3).

(xiii) How often do you consume any kind of candy with the claim “contains pulp/fruit juice in the formulation”?

(xiv) Would you pay more for a candy made from fruit pulp?

Almost 90% of consumers would pay more for candies produced from fruit ingredients and more than half of them showed high or moderate consumption of these products (Figure 7).

Health perception is partly related to the process of assessing and understanding health claims, which are designed to provide useful information from manufacturers to consumers about concerning functions and benefits of the products or components [52]. Confectionery products with fruit ingredients are a growing segment of food market and supply consumers´ desire for healthier, more authentic and natural foods. The consumer perceives fruits as ingredients with nutritional and functional value and, in this way, fruit flavored and colored candies are seen as higher quality products [57].



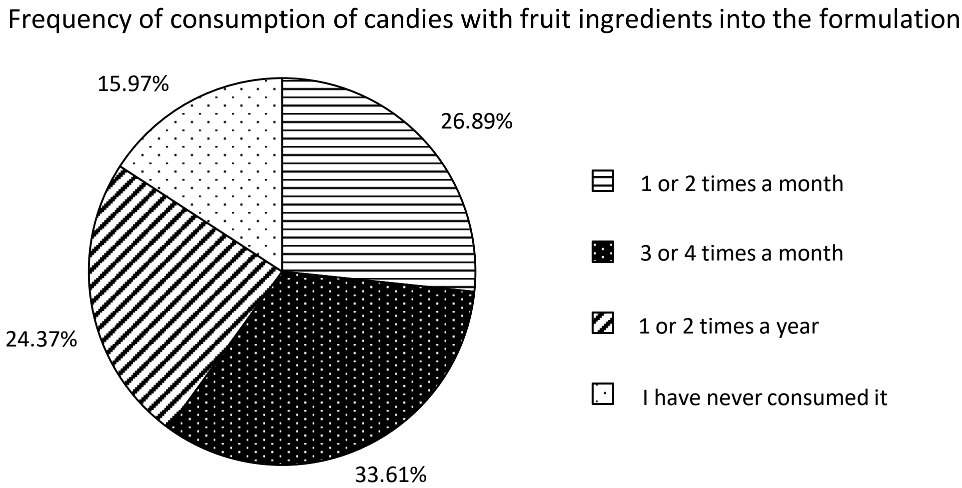


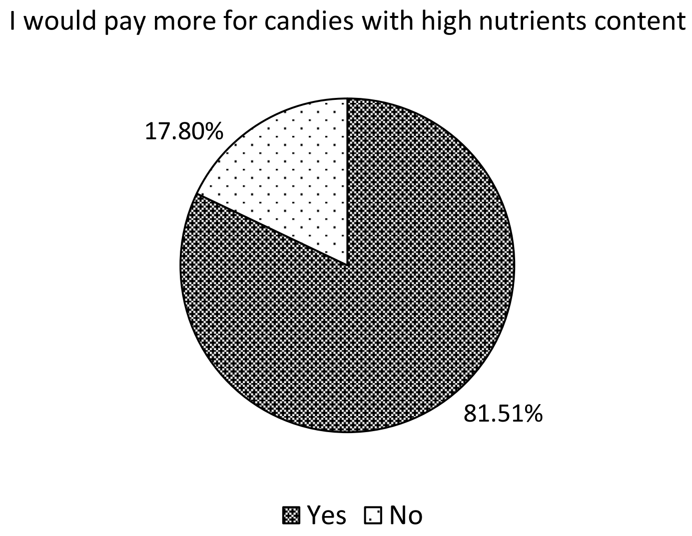
Figure 7. Willingness to pay and frequency of consumption of candies with fruit ingredients

(xv) How often do you consume any kind of high nutrient candy?

(xvi) Would you pay more for high nutrient candy?

More than 80% of consumers have shown willingness to pay more for candies with better nutritional composition. According to Ran et al. [58] many studies have shown that consumers are willing to pay more for products with nutritional information and many of them believe that nutrition labels help to interpret nutrition claims in the front of the packaging.

When asked about their frequency of consumption of candies with any high nutrient content, about half of them reported high or moderate consumption of products with these claims (Figure 8).



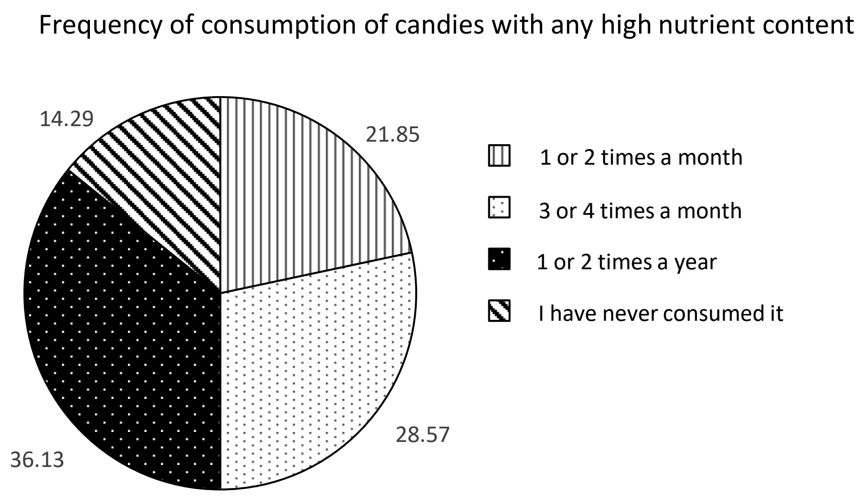


Figure 8. Willingness to pay and frequency of consumption of candies with high nutrients content

3.3.4 Second sensory analysis session: test with samples identified with designation of environmental sustainability

In the second session consumers assessed the same candy samples, but this time they were identified with designation of environmental sustainability. According to results of item 3.2, CSC was labeled with the information "the manufacturing process of this jelly candy consumed 99% less energy and generated 300 times lower carbon dioxide emission for the environment than the conventional candy manufacturing process", while HC was identified with the information "this jelly candy was produced by the conventional manufacturing process".

After sample identification, there was a significant difference ($p<0.05$) between the samples for texture, appearance and overall impression parameters, wherein HC showed the lower scores (Table 4).

The average score given to aroma parameter of HC in second session was significantly lower ($p<0.05$) in relation to the average score of the blind test. CSC with designation of environmental sustainability showed higher values for appearance, texture and overall impression in relation to the scores reached in blind test, which means were relocated more next to term I liked it moderately (average score 7.0).

Factors such as positive attitudes, quality of life and environment are appointed by consumers of sustainable products as determinant in their purchase behavior and decision [51]. The observed changes when sustainability claims were attributed to the candy labels confirmed the interest of consumers in the environmental confectionery segment indicated in the questionnaire.

HC scores showed no significant difference ($p<0.05$) between the sessions. The results highlight the influence of claims and labeling on sensory evaluation and reinforce the market potential of CSCP due to the increased acceptance of CSC.

Other studies have been reported the relation of environmental claims and food acceptance. In the confectionery sector, Silva et al. [32] verified the impact of sustainability labeling in sensory perception and purchase intention of chocolate consumers and concluded that acceptance scores increased, with no significant differences ($p<0.05$), when sustainable labeling (organic and Rainforest Alliance certifications, and designation of origin) were informed, however, they observed for the same samples the sustainability claim can positively influence the consumer, inducing an initial interest to consumption of chocolates with sustainability labeling, but the continuous consumption depends more on the sensory expectations.

3.3.5 Third sensory analysis session: test with samples identified with environmental sustainability designation and health claims

In the third session, samples were identified with designation of environmental sustainability and healthiness (according to the results of item 3.2 and 3.3.1) in order to verify the influence of health factors in the acceptance of sustainable labelled products. HC was identified with the information "this jelly candy was produced by the conventional manufacturing process", while CSC was labeled with the information "the manufacturing process of this jelly candy consumed less energy and emitted less carbon dioxide to the environment than the conventional candy manufacturing process. This manufacturing process has also conserved the nutrients in the strawberry pulp used as an ingredient of the candy, so this jelly candy has 22% more vitamin C and three times more total phenolic compounds than a jelly candy produced by the conventional method".

CSC score increased from the second to the third session when health claims were added to its sustainability designation, however, there was no significant difference ($p<0.05$) between the sessions. A significant drop was verified for the acceptance of HC aroma, while the others sensory attributes did not present significant statistical changes.

Despite the increase of CSC acceptance scores, there was no significant difference between the second and third sessions. However, the statistically distinction to the first session was maintained for appearance, texture and global impression parameters. These results confirmed the health influence on consumer perception of food quality. Some studies have already reported health concerns and economic factors, in general, as the main drivers in the consumer´s food choice, followed by environmental issues [59].

4. Conclusion

Despite the possibility of slightly higher ingredient costs the cold-set gelation technique using alginate/pectin mixtures showed great sustainable potential for the jelly candy processing industry due to the lower energy consumption and CO_2 emissions than the conventional candy manufacturing in both evaluated scales. In addition, the bioactive compounds content (ascorbic acid and total phenolic content) of the strawberry juice concentrate used as raw material were better maintained in cold-set jellies than in the pectin jellies.

The results of the questionnaire informed the consumer is very interested and willing to pay for products labelled with environmental and health claims. However, the knowledge about the sustainable claims and the consumption of this product segment are very low, which indicates the importance of the industry offering more options and helping the consumer to better understand sustainable food labelling.

A positive influence on consumer acceptance was observed when environmental sustainability and health labels were informed, increasing the sensory scores of the cold-set candy. This study confirmed the feasibility and market potential of cold-set jelly candy manufacturing against the growing food trend of environmental sustainability and healthiness.

Acknowledgments

We thank Cereal Chocotec/ITAL, Conselho Nacional de Desenvolvimento Científico e Tecnológico - Brasil (CNPQ) for the fellowship to the first author, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, Innovation Agency of University of Campinas (Inova-Unicamp) and the Brazilian National Institute of Industrial Property for the patent filling BR 10 2018 076817, that contemplates and protects the results of this study.

5. References

1. Eiri Board, Hand Book of Confectionery with Formulations, Engineers India Research Institute, New Delhi, 2012.
2. S.J. Coyle, Cooking Equipment for Jelly Candy, The Manufacturing Confectioner. 99 (2007) 36-42.
3. R.W. Hartel, Jellies, Gummies and Licorices, in: R.W. Hartel, J.H.V. Elbe, R. Hofberger, Confectionery Science and Technology, Cham: Springer International Publishing, 2018, pp. 329-360. doi:10.1007/978-3-319-61742-8.
4. Confectionery News, Organic candy: The future of confectionery, says new report. https://www.confectionerynews.com/Article/2007/08/08/Organic-candy-the-future-of-confectionery-says-new-report, 2019 (accessed 02 April 2020).
5. F.M. Montenegro, V. Luccas, Macro trends in the bakery and confectionery sectors [*In Portuguese*], in: G.C. Queiroz, R.A. Rego, D.C.P. Jardim (Eds.), Brasil Bakery & Confectionery Trends 2020, ITAL, Campinas, 2014, pp. 59-71.

6. G. Mongia, Fruit ingredients in confectionery applications, The Manufacturing Confectioner. 94 (2014), 73-82.

7. G.C. Queiroz, Sustainability and Transparency [*In Portuguese*], in: G.C. Queiroz, R.A. Rego, D.C.P. Jardim (Eds.), Brasil Bakery & Confectionery Trends 2020, ITAL, Campinas, 2014, pp. 232-257.

8. FDA. Food and Drug Administration, Guidance for Industry: Food Labeling Guide. https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-food-labeling-guide , 2013 (accessed 03 April 2020).

9. P. Castka, C.J. Corbett, Management Systems Standards: Diffusion, Impact and Governance of ISO 9000, ISO 14000, and Other Management Standards, Foundations and Trends in Technology, Information and Operations Management. 7 (2015), 161–379. doi:10.1561/0200000042.

10. M. Ertz, J. François, F. Durif, How Consumers React to Environmental Information: An Experimental Study, Journal of International Consumer Marketing. 29 (2017) 162–178. doi:10.1080/08961530.2016.1273813.

11. ISO 14021, Environmental labels and declarations Self-declared environmental claims (Type II environmental labelling). http://www.iso.org/iso/catalogue_detail?csnumber=23146, 2012 (accessed 03 April 2020).

12. J. Kaenzig, R. Wüstenhagen, The Effect of Life Cycle Cost Information on Consumer Investment Decisions Regarding Eco-Innovation, Journal of Industrial Ecology. 14 (2009) 121–136. doi:10.1111/j.1530-9290.2009.00195.x.

13. M.H.M. Avelar, P. Efraim, Alginate/pectin cold-set gelation as a potential sustainable method for jelly candy production, LWT–Food Science and Technology. 123 (2020). doi:10.1016/j.lwt.2020.109119.

14. S.G. Bolder, H. Hendrickx, L. Sagis, E. Van der Linden, Ca2+-induced cold set gelation of whey protein isolate fibrils, Applied Rheology. 16 (2006) 258–264. Doi: ttps://doi.org/10.1515/arh-2006-0018.

15. P. Walkenström, S. Kidman, A.M. Hermansson, P.B. Rasmussen, L. Hoegh, Microstructure and rheological behaviour of alginate/pectin mixed gels, Food Hydrocolloids. 17 (2003) 593–603. doi:10.1016/s0268-005x(02)00119-4.

16. M.H.M. Avelar, L.N. Lima, P. Efraim, Maintenance of Fruit Bioactive Compounds in Jelly Candy Manufacturing by Alginate/Pectin Cold-Set Gelation, Journal of Food Processing and Technology. 11 (2020) 1-11. doi: 10.35248/2157-7110.20.11.826.

17. Aigroup, Energy reduction factsheet: Saving energy in the confectionery manufacturing industry. http://cdn.aigroup.com.au/Environment/21_Food_Processing_Confectionery_Manufacturing_Energy_Reduction_Factsheet.pdf, 2019 (accessed 03 April 2020).
18. G. Chala, A. Abd Aziz, F. Hagos, Natural Gas Engine Technologies: Challenges and Energy Sustainability Issue, Energies. 11 (2018) 2934. doi:10.3390/en11112934.
19. S.J. Davis, G.P. Peters, K. Caldeira, The supply chain of CO2 emissions, Proceedings of the National Academy of Sciences. 108 (2011) 18554–18559. doi:10.1073/pnas.1107409108.
20. J. Wojdalski, J. Grochowicz, B. Dróżdż, K. Bartoszewska, P. Zdanowska, A. Kupczyk, A. Ekielski, I. Florczak, A. Hasny, G. Wójcik, Energy efficiency of a confectionery plant – Case study, Journal of Food Engineering. 146, (2015) 182–191. doi:10.1016/j.jfoodeng.2014.08.019.
21. USDA, Sugar and Sweeteners Yearbook Tables. https://www.ers.usda.gov/data-products/sugar-and-sweeteners-yearbook-tables/, 2020 (acessed 20 August 2020).
22. K. Sufferling, Gelatin gummies and pectin jellies, The Manufacturing Confectioner. 87 (2007) 43-50.
23. N. Diaz, E. Redelsheimer, D. Dornfeld, Energy Consumption Characterization and Reduction Strategies for Milling Machine Tool Use, in: J. Hesselbach, C. Herrmann (Eds), Glocalized Solutions for Sustainability in Manufacturing, Heidelberg: Springer., Berlin, 2011, pp. 263-267.
24. Eletrobrás, Energy Efficiency in Steam Use [*In Portuguese*], Eletrobrás, Rio de Janeiro, 196 p., 2005.
25. Petrobrás, Liquefied petroleum gas [*In Portuguese*].http://sites.petrobras.com.br/minisite/assistenciatecnica/public/downloads/manual-tecnico-gas-liquefeito-petrobras-assistencia-tecnica-petrobras.pdf, 2013 (accessed 07 April 2020).
26. MCTIC. Ministry of Science, Technology, Innovations and Communications, Dispatch analysis method [*In Portuguese*]. .https://www.mctic.gov.br/mctic/opencms/ciencia/SEPED/clima/textogeral/emissao_despacho.html, 2018 (accessed 07 April 2020).
27. MCTIC. Ministry of Science, Technology, Innovations and Communications. Annual estimates of greenhouse gas emissions in Brazil [*In Portuguese*].

http://sirene.mctic.gov.br/portal/export/sites/sirene/backend/galeria/arquivos/2018/10/11/Estimativas_2ed.pdf, 2014 (Accessed 07 April 2020).

28. H. Cheftel, M.L. Pigeaud, Estimation of Ascorbic Acid (Vitamin C) by Titration, Nature. 138 (1936) 799–799. doi:10.1038/138799b0.
29. V.L. Singleton, R. Othofer, R.M. Lamuela-Raventos, Analysis of total phenols and others oxidation substrates and antioxidants by folin-ciocalteau reagent, Methods in Enzimology. 299 (1999) 152-178. doi:10.1016/S0076-6879(99)99017-1.
30. T. Tonutare, U.L. Moor, L. Szajdak, Strawberry anthocyanin determination by pH differential spectroscopic method – how to get true results? Acta Scientiarum Polonorum Hortorum Cultus. 13 (2014) 35-47.
31. H. Stone, J.L. Sidel, Sensory Evaluation Practices, 3rd ed, Elsevier, Amsterdam, 2004, 377 p.
32. A.R.A. Silva, A.S. Bioto, P. Efraim, G.C. Queiroz, Impact of sustainability labeling in the perception of sensory quality and purchase intention of chocolate consumers, Journal of Cleaner Production. 141 (2017) 11–21. doi:10.1016/j.jclepro.2016.09.024.
33. A. Matthiensen, Use of Cronbach's Alpha Coefficient in Questionnaire Assessments *[In Portuguese]*. https://www.infoteca.cnptia.embrapa.br/bitstream/doc/936813/1/DOC482011ID112.pdf, 2011 (accessed 07 April 2020).
34. Businesswire, Correcting and Replacing Sugar Confectionery Market - Global Forecast and Opportunity Assessment by Technavio https://www.businesswire.com/news/home/20170614006004/en/CORRECTING-REPLACING-Sugar-Confectionery-Market---Global, 2020 (accessed 18 August 2020).
35. Abicab, Candies & Gums: Production, Apparent Consumption, Export and Import in Volume [*In Portuguese*]. http://clientes.focoimg.com.br/abicab/storage/app/public/editor/15918888235ee24bb72f99f.pdf, 2020 (accessed 20 August 2020).
36. K. Nilsson, V. Sund, B. Floren, The environmental impact of the consumption of sweets, crisps and soft drinks, Nordic Council of Ministers, Copenhagen, 2011.
37. J. Miah, From factory to supply chain: reducing environmental impacts of confectionery manufacturing using heat integration and life cycle assessment, University of Surrey, Guildford, 2018.

38. C.-J.G. Jou, C.-R. Wu, C.-L. Lee, Reduction of energy cost and CO2 emission for the furnace using energy recovered from waste tail-gas, Energy. 35 (2010), 1232–1236. doi:10.1016/j.energy.2009.11.002.

39. K.A. Naidu, Vitamin C in human health and disease is still a mystery? An overview, Nutrition Journal. 2 (2003). doi:10.1186/1475-2891-2-7.

40. M. Uddin, M.N.A. Hawlader, L. Ding, A. Mujumdar, Degradation of ascorbic acid in dried guava during storage, Journal of Food Engineering. 51 (2002), 21–26. doi:10.1016/s0260-8774(01)00031-0.

41. FAO. Food and Agriculture Organization, Human Vitamin and Mineral Requirements. http://www.fao.org/3/a-y2809e.pdf, 2001 (accessed 03 April 2020).

42. FDA. Food and Drug Administration, Frequently Asked Questions for Industry on Nutrition Facts Labeling Requirements. https://www.fda.gov/media/99069/download, 2020 (accessed 03 April 2020).

43. FDA. Food and Drug Administration, Guidance for Industry: Evidence-Based Review System for the Scientific Evaluation of Health Claims. https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-evidence-based-review-system-scientific-evaluation-health-claims, 2009 (accessed 03 April 2020).

44. FDA. Food and Drug Administration, Food Labeling: Serving Sizes of Foods That Can Reasonably Be Consumed at One Eating Occasion; Dual-Column Labeling; Updating, Modifying, and Establishing Certain Reference Amounts Customarily Consumed; Serving Size for Breath Mints; and Technical Amendments: Guidance for Industry Small Entity Compliance Guide. https://www.fda.gov/media/111144/download, 2018 (accessed 03 April 2020).

45. H. Cory, S. Passarelli, J. Szeto, M. Tamez, J. Mattei, The Role of Polyphenols in Human Health and Food Systems: A Mini-Review, Frontiers in Nutrition, 5 (2018) 1-9. doi:10.3389/fnut.2018.00087.

46. I. Volf, I. Ignat, M. Neamtu, V. Popa, Thermal stability, antioxidant activity, and photo-oxidation of natural polyphenols, Chemical Papers. 68 (2014) 1-9. doi:10.2478/s11696-013-0417-6.

47. A. Tresserra-Rimbau, A. Medina-Remón, J. Pérez-Jiménez, M.A. Martínez-González, M.I. Covas, D. Corella, J. Salas-Salvadó, E. Gómez-Gracia, J. Lapetra, F. Arós, M. Fiol, E. Ros, L. Serra-Majem, X. Pintó, M.A. Muñoz, G.T. Saez, V. Ruiz-Gutiérrez, J. Warnberg, R. Estruch, R.M. Lamuela-Raventós, Dietary intake and major food sources of polyphenols in a Spanish population at high cardiovascular risk: The PREDIMED study, Nutrition,

Metabolism and Cardiovascular Diseases. 23 (2013) 953–959. doi:10.1016/j.numecd.2012.10.008.

48. J. Pérez-Jiménez, V. Neveu, F. Vos, A. Scalbert, Identification of the 100 richest dietary sources of polyphenols: an application of the Phenol-Explorer database, European Journal of Clinical Nutrition. 64 (2010) S112–S120. doi:10.1038/ejcn.2010.221.
49. S. Tulipani, B. Mezzetti, F. Capocasa, S. Bompadre, J. Beekwilder, C.H.R. de Vos, E. Capanoglu, A. Bovy, M. Battino, Antioxidants, Phenolic Compounds, and Nutritional Quality of Different Strawberry Genotypes, Journal of Agricultural and Food Chemistry. 56 (2008) 696–704. doi:10.1021/jf0719959.
50. A. Patras, N.P. Brunton, C. O'Donnell, B.K. Tiwari, Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation, Trends in Food Science & Technology. 21 (2010) 3–11. doi:10.1016/j.tifs.2009.07.004.
51. C. Leire, Å. Thidell, Product-related environmental information to guide consumer purchases – a review and analysis of research on perceptions, understanding and use among Nordic consumers, Journal of Cleaner Production. 13 (2005) 1061–1070. doi:10.1016/j.jclepro.2004.12.004.
52. G. Nocella, O. Kennedy, Food health claims – What consumers understand, Food Policy. 37 (2012) 571–580. doi:10.1016/j.foodpol.2012.06.001.
53. J. Aschemann-Witzel, Consumer perception and trends about health and sustainability: trade-offs and synergies of two pivotal issues, Current Opinion in Food Science. 3 (2015) 6–10. doi:10.1016/j.cofs.2014.08.002.
54. I. Vermeir, W. Verbeke, Sustainable Food Consumption: Exploring the Consumer "Attitude – Behavioral Intention" Gap, Journal of Agricultural and Environmental Ethics. 19 (2006) 169–194. doi:10.1007/s10806-005-5485-3.
55. A.M. Leach, K.A. Emery, J. Gephart, K.F. Davis, J.W. Erisman, A. Leip, M.L. Pace, P. D´Odorico, J. Carr, L.C. Noll, E. Castner, J.N. Galloway, Environmental impact food labels combining carbon, nitrogen, and water footprints, Food Policy. 61 (2016) 213–223. doi:10.1016/j.foodpol.2016.03.006.
56. C. Pattara, C. Russo, V. Antrodicchia, A. Cichelli, Carbon footprint as an instrument for enhancing food quality: overview of the wine, olive oil and cereals sectors, Journal of the Science of Food and Agriculture. 97 (2016) 396–410. doi:10.1002/jsfa.7911.
57. M.B. Queiroz, E.H. Nabeshima, Naturalness and Authenticity [*In Portuguese*], in: G.C. Queiroz, R.A. Rego, D.C.P. Jardim (Eds.), Brasil Bakery & Confectionery Trends 2020, ITAL, Campinas, 2014, pp. 159-195.

58. T. Ran, C. Yue, A. Rihn, Does Nutrition Information Contribute to Grocery Shoppers' Willingness to Pay? Journal of Food Products Marketing, 23 (2016) 591–608. doi:10.1080/10454446.2015.1048027.

59. H. Hartikainen, T. Roininen, J.-M. Katajajuuri, H. Pulkkinen, Finnish consumer perceptions of carbon footprints and carbon labelling of food products, Journal of Cleaner Production. 73 (2014) 285–293. doi:10.1016/j.jclepro.2013.09.018.

CAPÍTULO 5. EFFECT OF COLD-SET GELATION PROCESSING ON THE QUALITY AND RETENTION OF FRUIT BIOACTIVE COMPOUNDS IN JELLY CANDY DURING STORAGE

Submission

Article submitted to **Journal of Food Processing and Preservation**, on November 2020.

CAPÍTULO 5. Effect of cold-set gelation processing on the quality and retention of fruit bioactive compounds in jelly candies during storage.

Running Title: Quality of cold-set jelly candies during storage.

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Abstract

Cold-set gelation has been reported as an effective technology for sustainable manufacturing of jelly candy with improved nutritional composition. The stability of cold-set sweets, however, still must be evaluated. In this study, flavored and fruit cold-set jellies were stored during four months at 25°C. Its physicochemical parameters and bioactive compounds contents were monthly evaluated, with pectin jelly candies adopted as standard samples. On the last month stored jellies were sensorially compared to fresh samples. All treatments showed no significant changes ($p<0.05$) for moisture content during storage. There was an increasing on water activity averages and the occurrence of sucrose crystallization on all samples, changing its texture profile. The bioactive compounds content of cold-set jellies decreased over the months, which may be related to its porous microstructure. Stored cold-set jellies showed sensory acceptance scores with no significant difference ($p<0.05$) to fresh processed candies indicating that low sensory changes occurred during storage.

Keywords: candy; cold-setting gels; confectionery; functional foods; hydrocolloids; stability.

Practical application

The cold-set jelly candy manufacturing is an innovative processing technology for obtaining confectionery products with claims of health and sustainability. The evaluation of the physicochemical and sensory parameters during storage indicated a similar stability of cold-set products compared to conventional pectin jelly candies. The results presented in this study will help better understand the stability behavior of cold-set candies and guide the confectionery industry to define the best packaging and storing conditions and improve the maintenance of the quality during the shelf life.

1. Introduction

In recent years the confectionery industry has been investing in the improvement of candy processing and packaging technologies as well as in the development and launch of new products for supplying the growing consumer´s demand for healthier and more natural and sustainable food options (Avelar, Silva, Azevedo, & Efraim, 2019; Montenegro & Luccas, 2014).

For the confectionery class of jellies and gummies, current studies have been reporting the use of cold-set gelation technique in jelly candy manufacturing as a sustainable strategic for production of candies with improved functional composition. According to the researches, when polymeric mixtures of sodium alginate / high methoxylation pectin are acidified with glucone-delta-lactone in high sugar solution medium, it can structure confectionery gels at room temperature and obtaining jelly candies with lower energy requirement (Avelar & Efraim, 2020).

In the conventional jelly candy manufacturing the syrup cooking step comprises some of the highest energy requirements of the whole processing line. Its replacement for cold-set gelation implies to changes of industrial machinery and consequently to significant reduction of energy consumption and environmental emissions (Avelar, Queiroz & Efraim, 2020). Moreover, considering the thermo sensibility of bioactive compounds and nutrients, the cold-set processing enables a better maintenance of nutritional and functional composition of jellies formulated with fruit ingredients due its manufacturing temperatures are lower than that of cooking step (Avelar, Lima & Efraim, 2020).

Confectionery products are microbiologically stable and have long shelf lives compared to other food due to their high sugar content and low water activity ranges (Ergun, Lietha & Hartel, 2010; Subramaniam, 2016). Despite of the noteworthy performance of cold-set gelation to the jelly candy manufacturing is already known, the stability of the obtained products still needs to be evaluated for better understand the relationship between this new processing technology and the quality of the jellies during storage. In this context, the aim of this study was to evaluate the physical, physicochemical, and chemical behavior and the sensory quality of jelly candies produced by sodium alginate/ high methoxylation pectin cold-set gelation technique during their storage, compared to a pectin jelly candy chosen as standard sample.

2. Material and methods

2.1. Material

Sucrose (União, São Paulo, Brazil), glucose syrup (Excell 1040, Ingredion, Mogi Guaçu, Brazil), sodium citrate (ACS, Synth, Diadema, Brazil), citric acid (ACS, Synth, Diadema, Brazil), glucono-delta-lactone (GDL) (Art Alimentos, São Paulo, Brazil), sodium alginate (Algin I-3G-150, Guluronic acid content 60% viscosity 300 – 400 mPa·s, Kimica, Providencia, Chile), high methoxylation pectin (HM 121Slow, degree of esterification 58%, CPKelco, Limeira, Brazil), frozen pasteurized strawberry pulp (Brasfrut, Feira de Santana, Brazil), pear flavor (HS-901-666-1, Givaudan, São Paulo, Brazil), food dye tartrazine yellow (CI 19140, Eskisa, São Paulo, Brazil) and mineral oil (Lugol, Ideal, Nova Lima, Brazil).

2.2. Definition of jelly candy formulas

Four candy formulations were defined for the comparative storage study: a cold-set jelly candy (FCJ) and a pectin candy (FPJ), both artificially colored and flavored; and a fruit cold-set jelly candy (SCJ) and a fruit pectin candy (SPJ). Pectin jellies were selected as standard samples and strawberry pulp was chosen to formulate the fruit jellies due to the widely use and acceptance of the strawberry flavor in confectionery products. The formulations were defined according to the better results obtained by Avelar & Efraim (2020) and Avelar, Lima & Efraim (2020) and are described in Table 1.

Table 1. Pectin jelly candy and cold-set jelly candy syrup formulations used to evaluate the shelf-life of flavored and strawberry jelly candies.

Ingredients	Quantity (g/ kg)			
	Flavored cold-set jelly candy	Flavored pectin jelly candy	Strawberry cold-set jelly candy	Strawberry pectin jelly candy
Water	237.1	372.7	109	203.3
Sucrose	336.6	381	331.2	413.3
Glucose syrup	396.3	229	390.8	261.8
Strawberry Pulp	-	-	109	109.5
Sodium alginate	10	-	20	-
High methoxylation pectin	10	12	20	12.1
Glucono-delta-lactone	10	-	20	-
Citric acid	-	4	-	-
Sodium citrate	-	1.3	-	-
Pear flavor*	1.8	1.6	-	-
Food dye tartrazine yellow*	0.5	0.4	-	-

* Quantity (g/kg of prepared candy syrup)

Source: (Avelar & Efraim, 2020; Avelar, Lima & Efraim, 2020).

2.3. Jelly candy processing

The cold-set jelly candy processing was performed according to Avelar & Efraim (2020) following the steps: (1) dissolving sugars, (2) dispersion of hydrocolloids in the sugar solution, (3) dissolution of acidulant (GDL), (4) addition of food dye and flavor, (5) dosing the candy syrup in starch molds and (6) drying in an oven at 35 °C/72 h. For fruit cold-set jelly candy manufacturing the fruit pulp was dissolved with the sugars in water in the first step and no food dye and flavor were added (Avelar, Lima & Efraim, 2020).

The pectin jellies and the fruit pectin jellies were manufactured according to Sufferling (2007). The ingredients were mixed and cooked at atmospheric pressure until 71 °Brix, food dye and flavor were added after cooking when required. The candy syrups were dosed into starch molds, dried in a forced air circulation drying oven at 35 °C for 72 h and demolded.

The ingredients of cold-set jellies were mixed with a digital mechanical bench agitator (Tecnal, model TE-039/1, Piracicaba, Brazil) at 380 rpm during 5.08 min. The cold-set and pectin candy syrups were manually dosed with a funnel and the candy drying was performed in a forced air circulation drying oven (Tecnal, model TE-394/2, Piracicaba, Brazil) at 35 °C for 72 h. After demoulding, all the candy treatments were finished with a mineral oil coating and then packed in double-layer packaging bags consisting of one laminated layer and one polyethylene layer.

2.4. Physical and physicochemical characterization of the strawberry pulp

The frozen pasteurized strawberry pulp used for the fruit jelly candy processing was submitted to physical and physicochemical characterization in triplicate. The parameters evaluated were: moisture content in a vacuum oven, according to the method 920.151 (AOAC, 2012); pH with a potentiometer (Digimed, model DM-20, São Paulo, Brazil), according to method 981.12 (AOAC, 2012); water activity with a water activity analyzer (Aqualab, model 4TEV, Decagon Devices Inc., Pullman, USA) after equilibration at 25 °C; titratable acidity according to the method 981.15 (AOAC, 2012) and instrumental color expressed in the CIELAB system (L*, a* and b*) using a digital colorimeter (Hunter Lab UltraScan PRO, Washington DC, USA).

2.5. Evaluation of jelly candies stability

The four candy formulations were submitted to comparative stability studies. The fruit cold-set candy was compared to the fruit pectin jelly candy while the flavored cold-set candy was compared to the flavored pectin candy. The packed candies were stored in BOD at 25 ºC for four months. Sensory evaluation was performed at the final fourth month comparing the stored products with fresh produced samples. Candies were monthly collected for physical, physicochemical and chemical characterization as described below.

2.5.1. Physical and physicochemical characterization of jelly candies

The jelly candies were monthly evaluated in relation to moisture content, water activity, pH and instrumental color using the same methods previously described in item 2.4. The chromatic properties were expressed in the CIELAB system (L*, a* and b*) and the Saturation (C*, chroma) and hue angle (h) were determined according the Equations 1 and 2 (Minolta, 1998).

$$C^* = (a^{*2} + b^{*2})^{1/2} \quad \text{(Equation 1)}$$

$$h = \arctan\left(\frac{b^*}{a^*}\right) \qquad \text{(Equation 2)}$$

The instrumental hardness was measured using a Texture Analyzer (TA-XT2i model, Surrey, England) with cylindrical aluminum probe P/35, penetration distance of 1 mm. The speeds of pre-test, test and post-test were 2.0, 2.0 and 10.0 mm/s, respectively (Fadini et al., 2005). The candy samples were standardized in a 2 gram "drop" shape with 1.5 x 1.5, cm x cm, width x height. Ten replicates of each treatment were used in the analysis.

2.5.2. Determination of bioactive compounds content of the fruit jelly candies

The frozen strawberry pulp and the fruit cold-set and pectin jellies were evaluated according to the total phenolic compounds content with FolinCiocalteu reagent using a spectrophotometer (model Cirrus 80, Femto, São Paulo, Brazil) at 765 nm (Singleton et al., 1999), ascorbic acid content by the titratable method (Cheftel & Pigeaud, 1936) and total anthocyanin content by pH differential spectroscopic at 510 and 700 nm with 0.025 M potassium chloride (pH 1.0) and a 0.4 M sodium acetate (pH 4.5) as buffer solutions and extraction with ethanol solvent 0.1 M HCl (85: 15%, v: v) (Tonutare, Moor, & Szajdak, 2014). The Equation 3 was applied for calculate the absorbance of the diluted sample (A) and the total anthocyanin content was determined using the Equation 4.

$$A = (A_{510} - A_{700})_{pH\ 1.0} - (A_{510} - A_{700})_{pH\ 4.5} \qquad \text{(Equation 3)}$$

$$Total\ anthocyanin\ content\ \left(\frac{mg}{100g}\right) = \frac{A\ x\ M\ x\ DF\ x\ 1000}{(\mathcal{E}\ x\ \lambda\ x\ m)} \qquad \text{(Equation 4)}$$

In the Equation 4, “A” is the absorbance of the diluted sample, M is the molecular weight of cyanidin-3-glucoside (449.2 g/ mol), DF is the dilution factor, ε is the molar absorptivity coefficient (29600 M-1cm-1), λ is the cuvette optical pathlength (1 cm) and m is the weight of the sample (g) (Tonutare et al., 2014).

2.5.3. Sensory evaluation of jelly candies

A sensory acceptance test was carried out for the evaluation of the influence of storing on the jelly candy sensory quality. A blind test with 120 volunteer evaluators was performed at the Food Sensory Analysis Laboratory of the Department of Food Technology - FEA / UNICAMP (previously approved by the Committee of Research Ethics at the State University of Campinas, with Certificate of Presentation for Ethical Assessment - CPEA 86627118.5.0000.5404) using a structured 9-point hedonic scale (ranked 9: I liked it extremely and 1: I disliked it extremely). The four months stored candies were compared to fresh processed samples in relation to the scores of sensory acceptance of the attributes appearance, color, aroma, flavor, texture and overall impression (Stone & Sidel, 2004).

2.6. Statistical Analysis

The data were submitted to Shapiro-Wilk test (for checking if they there was normal distribution) and Bartlett test (for checking variance homogeneity). Analysis of variance (ANOVA) or Kruskal-Wallis rank-sum test was used to assess significant differences between the groups and multiple mean comparisons were analyzed by Tukey's test (for data sets with equal variances) and Nemenyi´s test (for data sets with unequal variances). The statistical analysis was performed using the software R (R, Inc., Boston, MA, USA) version 4.0.2.

3. Results and discussion

3.1. Physical, physicochemical and chemical characterization of the frozen strawberry pulp

The results of the characterization of the frozen strawberry pulp used as ingredients for the fruit jelly candies processing are presented in Table 2. The mean values of the physicochemical properties were within the range indicated by the literature (Gonçalves et al., 2017; Sandulachi, 2012). The total content anthocyanin was located in the expected rate of 0.50-3.79 mg cyanidin-3-glycoside/ 100 g frozen strawberry suggested by Tonutare et al. (2014), while the total phenolic compounds content was slightly above the expected range of 250 mg ellagic acid/ 100g frozen strawberry indicated by Asami et al. (2003).

Table 2. Physical and physicochemical parameters and bioactive compounds contents of frozen strawberry pulp.

Physical and physicochemical parameters							
Water Activity	Instrumental Color			Moisture Content (kg/kg)	pH	Soluble solids content (°Brix)	Titratable acidity (g citric acid/100g)
	L*	a*	b*				
0.9943 ± 0.0001	52.21 ± 4.58	25.34 ± 2.25	27.68 ± 3.30	9.42 ± 0.02	3.51 ± 0.01	7.40 ± 0.01	0.878 ± 0.016

Chemical parameters		
Ascorbic Acid Content (mg ascorbic acid g^{-1})	Total Phenolic Compounds Content (mg gallic acid g^{-1})	Total Anthocyanin Content (mg cyanidin-3- glycoside g^{-1})
20.28 ± 0.12	292.385 ±19.164	1.067 ± 0.790

Source: (Avelar, Lima & Efraim, 2020).

Mean values of 10 replicates of instrumental texture measurements and triplicates of instrumental color, pH. Aw, titratable acidity and moisture content measurements.

3.2. Evaluation of jelly candies stability

3.2.1 Physical and physicochemical parameters

The curves showing the mean values of moisture content and water activity at storage of the different treatments of jelly candy are presented in Figures 1 and 2.

Despite the soluble solids content of all candy syrups was standardized in 71 °Brix and the drying conditions for all candy treatments were fixed in 35 °C/ 72 h, the moisture means of the candy samples after processing variated from 0.15 to 0.17 kg/kg, but with no significant difference ($p<0.05$). This variance may be related to any failure on the manual syrup dosing. Candies dosed with different wight can compromise the homogeneity of the drying step and imply in final products with different water contents.

All candy samples showed no significant difference ($p < 0.05$) in relation to moisture content along the storage, appointing efficiency of the packaging as moisture barrier. The mean values of the four treatments at all evaluated times were located in the predicted range of 0.08-0.22 kg/kg for gummies and jellies (Ergun et al., 2010; Hartel, Elbe, & Hofberger, 2018).

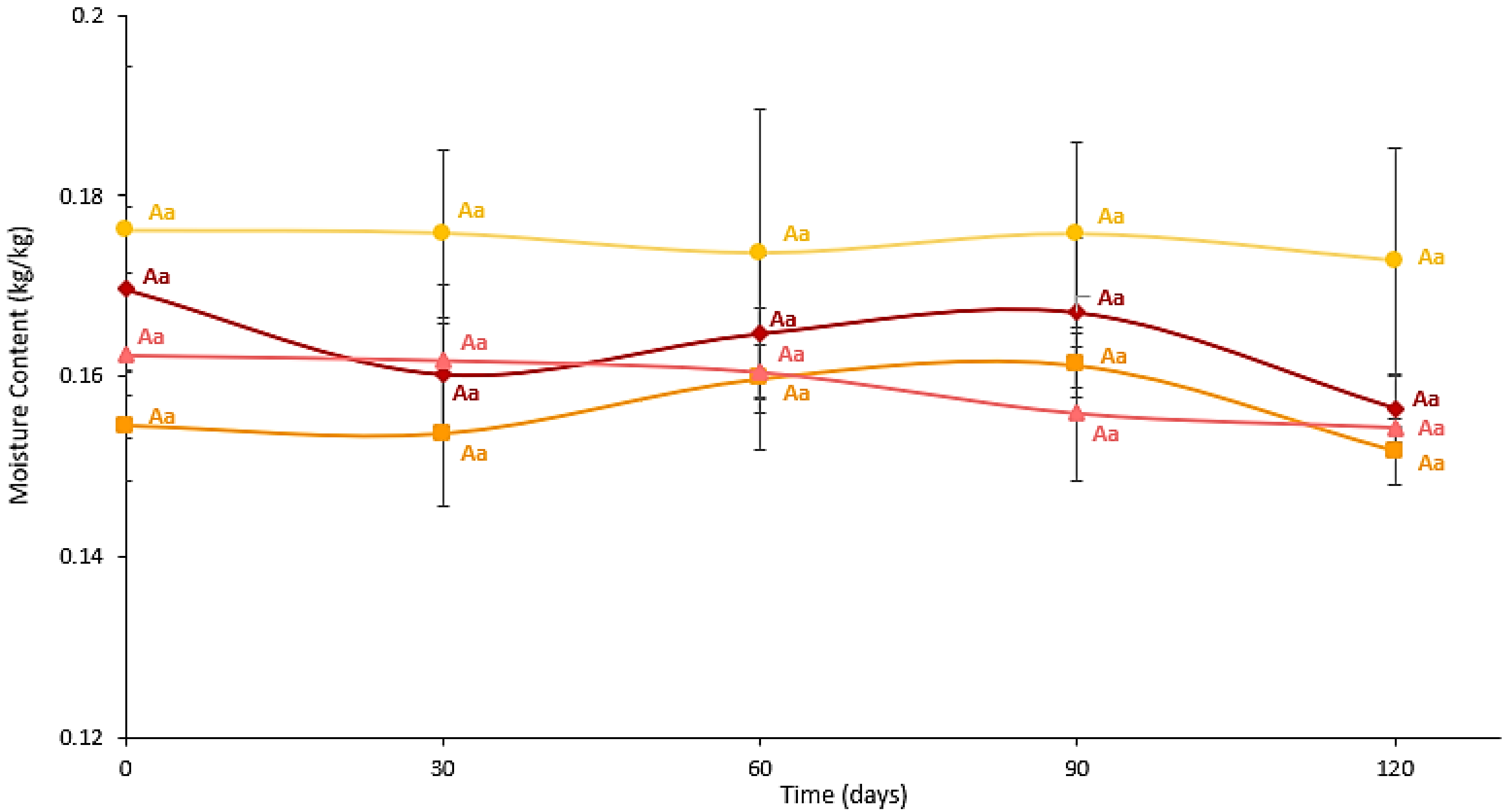

Figure 1. Mean values of moisture content (kg/kg) during the storage of jelly candies (■: Flavored cold-set jelly candy; ●: Flavored pectin jelly candy; ♦: Strawberry cold-set jelly candy; ▲: Strawberry pectin jelly candy) at 25 °C. Mean values of the same treatment followed by the same capital letter are not significantly different ($p>0.05$) in respect to the time of storage. Mean values of different treatments in the same time of storage followed by the same small letter are not significantly different ($p>0.05$).

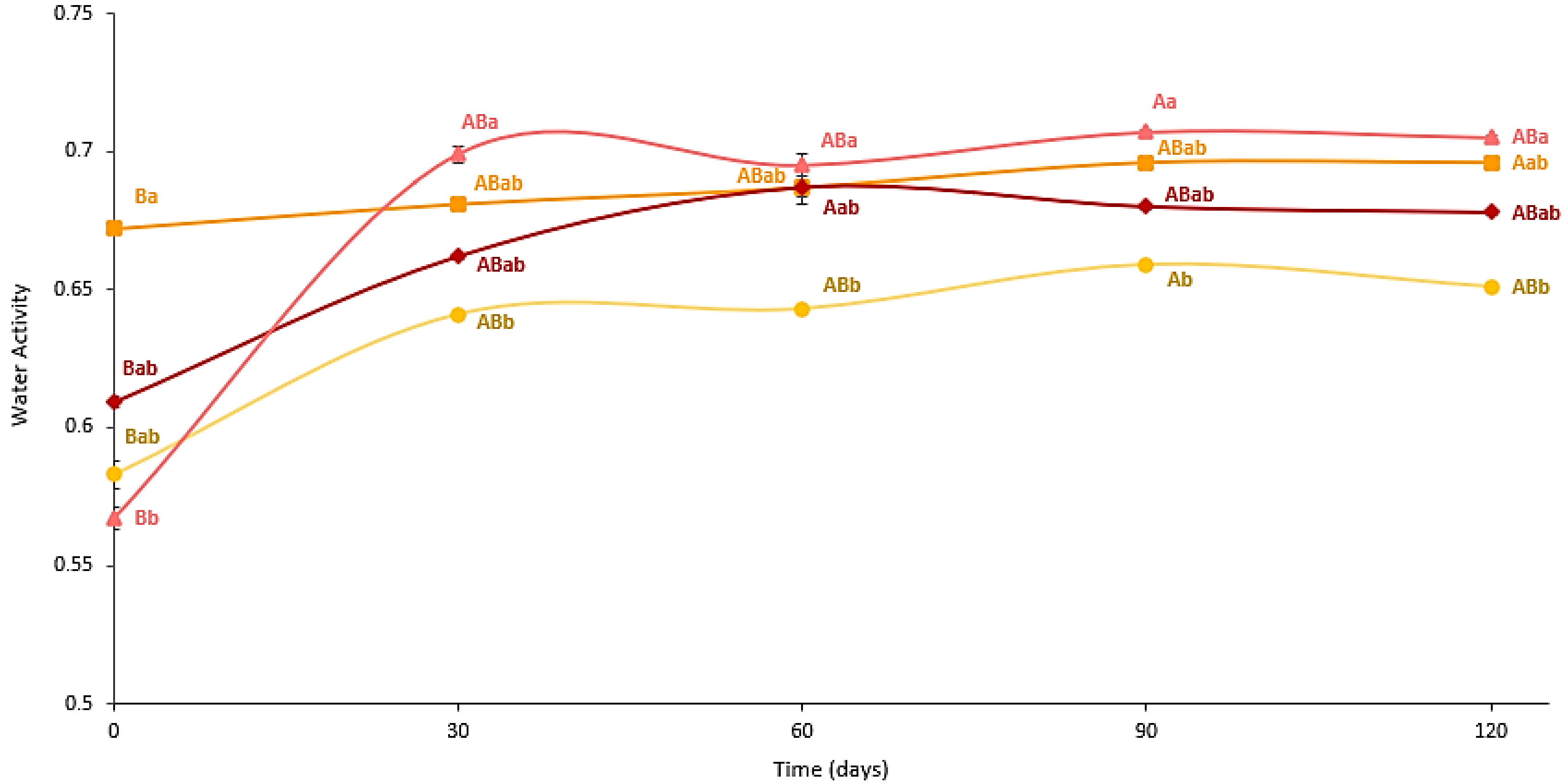

Figure 2. Mean values of water activity during the storage of jelly candies (■: Flavored cold-set jelly candy; ●: Flavored pectin jelly candy; ♦: Strawberry cold-set jelly candy; ▲: Strawberry pectin jelly candy) at 25 °C. Mean values of the same treatment followed by the same capital letter are not significantly different ($p>0.05$) in respect to the time of storage. Mean values of different treatments in the same time of storage followed by the same small letter are not significantly different ($p>0.05$).

At all evaluated times the a_w mean values of all the four candy treatments were located between 0.5-0.75, recommended range for better stability of jelly candies (Ergun et al., 2010). However, there was an increasing on the water activity averages along the storage (Figure 2) for all candy samples. According to Hartel et al. (2018) typically, the microbial growth is not an issue in jelly candies. But, is recommended that the water activity range should not be higher than 0.65–0.68 unless a microbial inhibitor is added to the formulation to prevent the yeast and mold growing.

Changes in a_w as in the moisture content may affect the stability, texture and other sensory properties of confections (Ergun et al., 2010). The packaging used in this study acted as a successful barrier to the moisture migration from the medium, preventing water absorption/desorption by the candies. So, the water activity behavior of the samples may be influenced by other factors such the internal packaging conditions (air composition and air relative humidity) or the sucrose crystallization process, which was visually verified inside the samples.

The sucrose crystallization mechanism is based in the steps of nucleation and growth. During the crystal growing kinetics the concentration of the remaining liquid phase decreases until the phase equilibrium. So, less water molecules get linked to the crystallized state, more free water is available on the system and, consequently, the water activity range is higher (Da Silva et al., 2016; Hartel, Ergun & Vogel, 2010; Laos, Kirs, Pall & Martverk, 2011).

The time of 120 days was determined as the final time of storage in this study due to the occurrence of grained structures in the jelly candies. For FPJ, SCJ and SPJ the sucrose crystallization was observed by growing grained layers below the surface of the candies while for FCJ it was observed as granules homogeneously distributed inside the jelly.

According to Subramaniam (2016), changes in texture of gummy products can occur along the time, becoming hard as long a surface crust develops on the sweets due to the loss of moisture, or becoming soft as a result of the absorption of moisture under high ambient humidity.

Despite of the graining processes, SCJ and SPJ showed no significant differences in relation to the hardness averages over time (Figure 3), indicating the composition of strawberry pulp as a determining factor on texture controlling of the fruit jellies. Fruit fibers and other components can inhibit the sucrose crystal growing due to modifications in the thermodynamic driving force (effect on solubility concentration) or due to specific effects on the crystal structure which prevents the diffusion and incorporation of sucrose molecules into the lattice (Hartel et al., 2010).

The occurrence of sucrose crystallization in all candy treatments may be related to many factors. The first one is the candy formulation. According to Hartel et al (2018), gummy and jelly candies have the potential to grain over time if they were formulated with improper sucrose: glucose syrup ratio and if all sucrose crystals were not initially dissolved in the syrup. The common sugar ratio for gelled confectionery products is 40-50% of sucrose to 60-50% of glucose syrup, in dry basis. If higher sucrose contents are used, the sucrose supersaturation and consequent crystal formation are induced. In this case, to preventing the graining it is important to reduce the sucrose content and increase the concentration of other ungraining agents such as glucose syrup or invert sugar. The jellies candies produced in this study were formulated with 1:1 of sucrose: glucose syrup ratio, in dry basis. In this case it´s suggested to change the sugar ratio to 60% glucose syrup: 40% sucrose, to better prevent the sucrose graining. Checking the complete sucrose dissolution in water by refractometry analysis, as it was made in this study, is also another great tool for ensure there´s not remaining unsolved sugar crystals.

Another factor to be considered is the syrup stirring. The agitation of the sugars solution in the presence of growing crystals can contribute to enhance the crystal growth rate. Increased agitation intensifies the mass transfer by convection, bringing molecules more quickly to the growing interface. However, once any mass transfer limitation has been completely alleviated, further increases in agitation have little effect on the crystal growth (Hartel et al., 2010). In this study the cold-set candy syrups were prepared by stirring at 380 rpm/ 5.08 min. A slower agitation may contribute to prevent the sucrose graining and also the aeration of the candy syrup, decreasing the occurrence of remaining bubbles in the gelled structure.

The last factor is the drying equipment used in both manufacturing processes. For lab-scaled candy processing it is common to use forced air circulation drying oven in the drying step (also called curing or stoving). However, the effects on candy dehydration can differ from those obtained by industrial machinery. According Hartel et al. (2018) curing rooms are used by confectionery factories for remove the excess moisture and let the candy cools and solidifies. Molded jellies trays are dried by uniform air flow at appropriate speed, temperature and relative humidity. Despite the controlled time and temperature conditions, in this study the drying oven did not keep constant the relative humidity of the air. Besides, if the air flow was too strong, the dehydration must had occurred too fast, inducing sucrose crystals generation.

At all times of storage, the pH averages of the cold-set jellies (Figure 4.) were located close to the range of 3.4-3.8 recommended for cold-set gelation of sodium alginate and high methoxylation pectin mixtures (Toft, Grasdalen, & Smidsrød, 1986). The pH values of

FPJ were close to 3-3.5, indicated range for high methoxylation pectin gelation (Sufferling, 2007), at all evaluated times. There were changes in the pH values of the strawberry cold-set and pectin candies during storage, which may be related to the degradation of strawberry organic compounds, such as ascorbic acid.

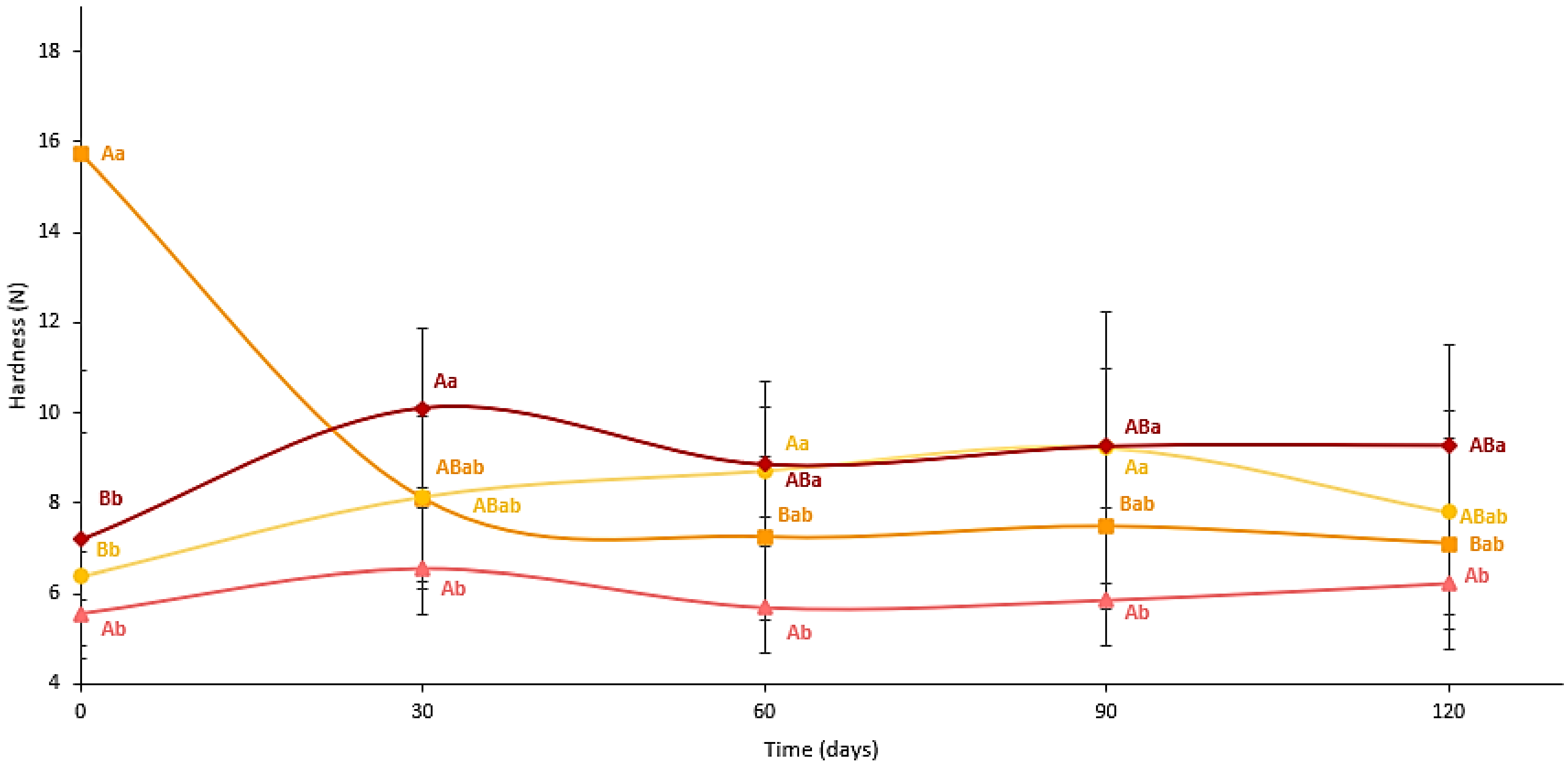

Figure 3. Mean values of Hardness during the storage of jelly candies (■: Flavored cold-set jelly candy; ●: Flavored pectin jelly candy; ♦: Strawberry cold-set jelly candy; ▲: Strawberry pectin jelly candy) at 25 °C. Mean values of the same treatment followed by the same capital letter are not significantly different (p>0.05) in respect to the time of storage. Mean values of different treatments in the same time of storage followed by the same small letter are not significantly different (p>0.05).

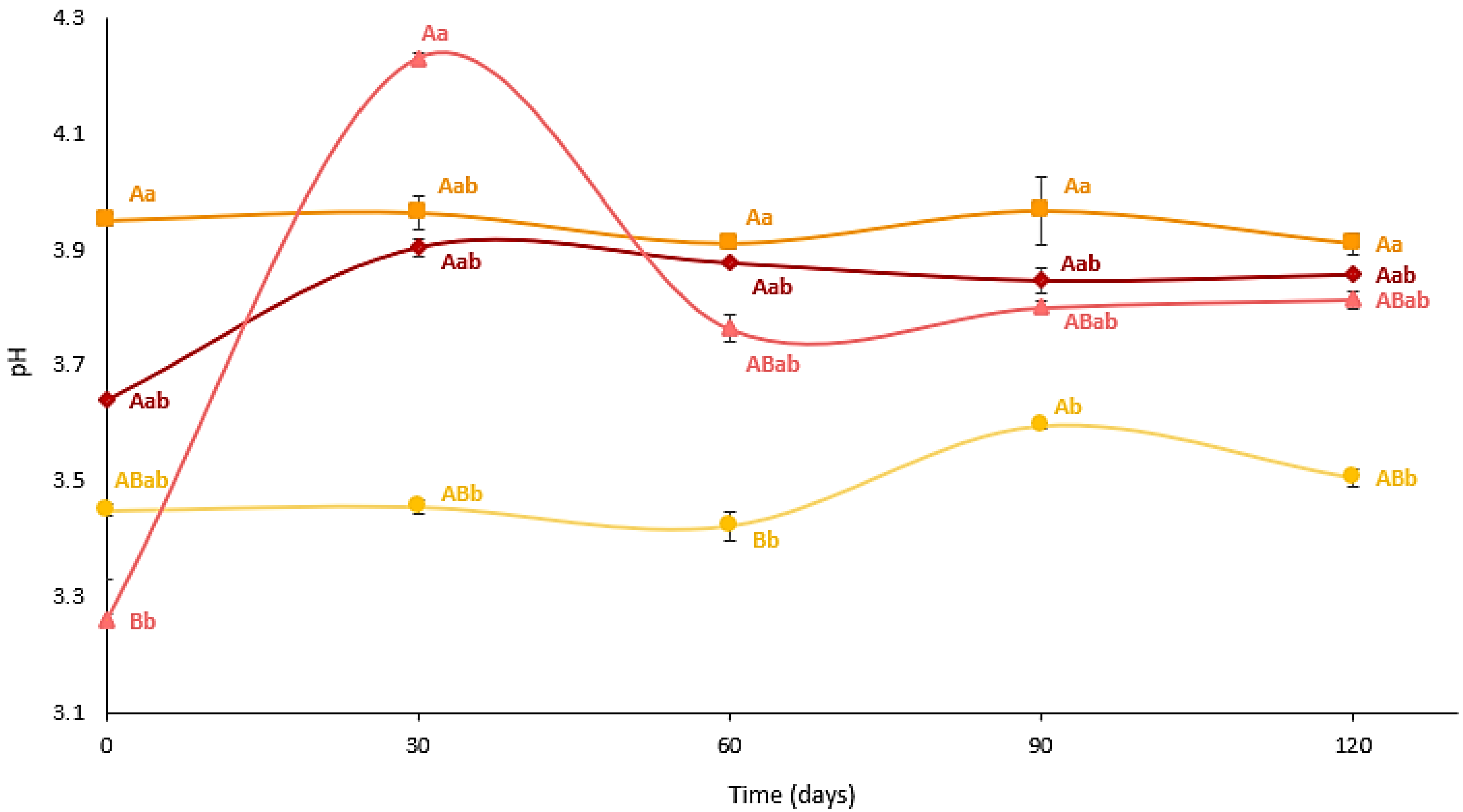

Figure 4. Mean values of pH during the storage of jelly candies (■: Flavored cold-set jelly candy; ●: Flavored pectin jelly candy; ♦: Strawberry cold-set jelly candy; ▲: Strawberry pectin jelly candy) at 25 °C. Mean values of the same treatment followed by the same capital letter are not significantly different (p>0.05) in respect to the time of storage. Mean values of different treatments in the same time of storage followed by the same small letter are not significantly different (p>0.05).

The results of instrumental colorimetric analysis are presented in Table 3. The jellies produced by cold-set gelation were visually clearer and opaquer than pectin jellies as described in the literature (Avelar & Efraim, 2020; Avelar, Lima & Efraim, 2020). During storage the cold-set samples maintained these characteristics, according to the higher values of L* and lower averages of a*.

The colorimetric analysis indicated color stability in candies produced with synthetic dye. The colorimetric parameter b* and Chroma C* of FCJ and FPJ samples showed no statistical difference ($p < 0.05$) between the periods of storage while the parameter a* had little significant changes.

Comparing the color of the jellies produced with strawberry pulp, SPJ was more red, intense and darker than SCJ at all evaluated times, which was verified by the higher a* values and lower averages of L* and hº. The saturation of these samples, however, kept statistically similar over storage.

Table 3. Colorimetric Parameters of jelly candies produced by cold-set gelation and conventional processing during storage.

Times (days)	Colorimetric Parameters																			
	L*				a*				b*				C*				h			
	FCJ	FPJ	SCJ	SPJ	FCJ	FPJ	SCJ	SPJ	FCJ	FPJ	SCJ	SPJ	FCJ	FPJ	SCJ	SPJ	FCJ	FPJ	SCJ	SPJ
0	64.03 ±0.90 Aa	51.46 ±1.08 Ac	57.73 ±2.15 Ab	30.37 ±0.53 Abd	1.73 ±0.40 Ad	3.83 ±0.90 ABc	14.08 ±0.48 Ab	20.98 ±0.45 Aa	56.36 ±1.55 Aa	53.57 ±1.50 Aa	13.63 ±0.25 Cb	16.55 ±0.55 ABb	56.39 ±1.55 Aa	53.72 ±1.44 Aa	19.60 ±0.52 Bc	26.72 ±0.54 Ab	1.54 ±0.01 Ba	1.50 ±0.02 ABb	0.77 ±0.01 Cc	0.68 ±0.02 Bd
30	63.74 ±0.99 Aa	47.71 ±1,91 Bb	51.37 ±1.02 BCab	29.76 ±3.97 Abc	1.39 ±0.16 Ad	5.41 ±0.78 Ac	12.09 ±0.27 Bb	16.52 ±0.63 Ba	55.92 ±0.85 Aa	53.55 ±5.90 Aa	13.13 ±0.20 Cb	17.33 ±0.46 Ab	55.93 ±0.85 Aa	53.82 ±5.95 Aa	17.85 ±0.25 Cb	23.94 ±0.75 Bb	1.54 ±0.01 Ba	1.47 ±0.01 BCb	0.83 ±0.01 BCc	0.81 ±0.01 Ac
60	57.01 ±0.80 Ca	51.34 ±1.17 Ab	48.55 ±0.48 Cc	33.93 ±0.37 Abd	0.34 ±0.14 Bd	5.46 ±0.12 Ac	11.78 ±0.26 Bb	13.98 ±0.37 Ca	51.93 ±2.24 Aa	54.68 ±0.85 Aa	13.95 ±0.42 BCb	11.76 ±0.08 Db	51.93 ±2.25 Aa	54.94 ±0.84 Aa	18.26 ±0.49 BCb	18.27 ±0.23 Db	1.56 ±0.01 Aa	1.47 ±0.01 BCb	0.87 ±0.01 Bc	0.70 ±0.02 Bd
90	61.19 ±1.84 ABa	54.50 ±0.47 Ab	52.13 ±0.66 Bb	29.15 ±1.99 Bc	0.51 ±0.04 Bc	2.89 ±0.09 Bb	13.77 ±1.10 Aa	14.47 ±0.35 Ca	52.92 ±1.50 Ab	56.70 ±1.80 Aa	16.63 ±0.20 Ac	14.29 ±0.96 Cc	52.93 ±1.50 Ab	56.77 ±1.80 Aa	21.60 ±0.56 Ac	20.34 ±0.91 Cc	1.56 ±0.01 Aa	1.52 ±0.01 Aa	0.88 ±0.04 ABb	0.77 ±0.02 Ac
120	59.94 ±0.56 BCa	45.23 ±0.84 Bc	49.49 ±1.57 BCb	35.29 ±1.40 Ad	1.71 ±0.32 Ad	4.88 ±0.78 Ac	11.02 ±0.56 Bb	14.5 ±0.63 Ca	54.31 ±1.90 Aa	44.19 ±1.02 Bb	14.98 ±0.69 Bc	14.93 ±0.61 BCc	54.33 ±1.90 Aa	44.46 ±1.08 Bb	18.60 ±0.86 BCc	20.82 ±0.86 Cc	1.54 ±0.01 Ba	1.46 ±0.02 Db	0.94 ±0.01 Ac	0.80 ±0.01 Ad

FCJ, flavored cold-set jelly candy; FPJ, flavored pectin jelly candy; SCJ, strawberry cold-set jelly candy; SPJ, strawberry pectin jelly candy; L*, Lightness; a*, colour index (green to red); b*, colour index (blue to yellow); C*, Chroma; h, hue angle. Candy samples with mean values followed by the same capital letter in the same column are not significantly different ($p>0.05$) in respect to the time of storage. Mean values of different candy treatments in the same time of storage followed by the same small letter are not significantly different ($p>0.05$).

3.2.2 Chemical parameters

The mean values of the bioactive compound contents presented by the strawberry cold-set jelly candy and pectin jelly candies during storage are showed in Table 4.

The SCJ samples presented higher ascorbic acid content than SPJ after processing (time 0), assenting to the literature reports. According to Avelar et al. (2020) the cold-set gelation is an efficient technology for jelly candy manufacturing with maintenance of the content of thermosensitive bioactive compounds due to the low processing temperatures.

After 30 days of storage, however, the ascorbic acid content of both samples decreased and got statistically similar ($p < 0.05$) and after 60 days of storage there was no significant measured levels for any treatment. The degradation of ascorbic acid during processing or storage is catalyzed by the presence of oxidases, traces of certain metals and the increasing of temperature and pH rates (Bauernfeind & Pinkert, 1970; Naidu, 2003; Uddin et al., 2002). The decreasing behavior of ascorbic acid may be related to the increasing observed on the pH average of SPJ and the remaining oxygen present inside the packaging of both samples.

There was no significant difference between the total phenolic compounds of SCJ and SPJ after processing. These results differed from the study of Avelar et al. (2020) about cold-set and pectin jellies formulated with high fruit content. According to the authors, jelly candies produced with high levels of strawberry juice concentrate by cold-set gelation presented three times more phenolic compound content than pectin jellies formulated with the same fruit ingredient. The total anthocyanin content of the cold-set and pectin jellies with strawberry juice concentrate, however, showed no significant difference ($p<0.05$), as occurred with SCJ and SPJ in this present study. Avelar et al. (2020) pointed out that the high sucrose content of the pectin candy formula can preserve the anthocyanin compounds during the cooking step, equalizing the anthocyanin content to the cold-set processed jellies.

Table 4. Bioactive compounds content of strawberry jelly candies produced by cold-set gelation and conventional processing during storage.

Times (days)	Bioactive Compounds					
	AA (mg ascorbic acid g^{-1})		TPC (mg gallic acid g^{-1})		TAC (mg cyanidin-3- glycoside g^{-1})	
	SCJ	SPJ	SCJ	SPJ	SCJ	SPJ
0	2.174 ±0.001 a*	1.087 ±0.181 a*	26.10 ±1.16 a	25.97 ±2.40 a	0.228 ±0.038 a	0.3123 ±0.057 a
30	1.087 ±0.001 b	1.081 ±0.001 a	25.48 ±5.22 a	24.48 ±3.32 a	0.190 ±0.001 ab*	0.2659 ±0.0126 ab*
60	-	-	26.23 ±0.01 a	25.35 ±4.64 a	0.180 ±0.032 ab*	0.2655 ±0.0126 ab*
90	-	-	25.48 ±5.22 a	25.48 ±3.23 a	0.0590 ±0.007 b*	0.2085 ±0.0214 ab*
120	-	-	12.68 ±2.82 b*	23.37 ±1.91 a*	0.091 ±0.012 ab*	0.1517 ±0.006 b*

SCJ, strawberry cold-set jelly candy; SPJ, strawberry pectin jelly candy; AA, ascorbic acid content; TPC, total phenolic compounds content; TAC, total anthocyanin content. Candy samples with mean values followed by (*) in the same line are significantly different ($p < 0.05$). Mean values followed by different letters in the same column are significantly different ($p < 0.05$).

In this study, the anthocyanin content of both samples decreased significantly during storage, while only the phenolic compounds content of SCJ reduced statistically ($p<0.5$) on the last month. The degradation of these bioactive compounds during processing and storage are related to exposure to oxygen, light, enzymes, high pH and temperature ranges, presence of metal ions, organic acids and other components (Friedman & Jürgens, 2000; Moser et al., 2017; Patras et al., 2010; Tulipani et al., 2008).

The microstructural differences between the candy gels are an important point to be considered. The jelly candies produced by cold-set gelation have a dense and homogeneous microstructure with the presence of a large amount of pores, while pectin jellies are characterized by a sparce microstructure with micelles aggregates and large pores (Avelar & Efraim, 2020; Avelar, Lima & Efraim, 2020). The porous network of SCJ possibly impacted on the stability of the fruit bioactive compounds content.

A possible technological strategy for enhancing the maintenance of bioactive compounds in cold-set jellies during storage is the adequation of the candy finishing step to its microstructural properties. Jelly candies are usually finished with coatings composed by special glazing agents or sugar crystals in order to reduce sticking, and improve appearance, providing the reduction of candy compression and collapse during packaging and acting as barrier against humidity and surrounding air. A complete coating of the surface is important in achieving a high level of storage stability against moisture absorption (Subramaniam, 2016). The jellies produced in this study were finished by application of oil coating on the candy surface. Maybe the sugar crystals coating should be a better option to cover the cold-set candies due its porous gelled microstructure. The sucrose crystals layer could contribute to prevent the exposition to the remaining air inside the packaging, which must have affected the stability of the fruit bioactive compounds.

Other factor to be considered is the oxygenation of the candy syrup during the mixing step of the cold-set jelly candy manufacturing due to the incorporation of air from the medium by the mechanical stirrer moving. The oxygen molecules incorporated and dispersed in the gel matrix possibility may have supported the degradation reactions during storage. A better evaluation of the impact of this step, therefore, still makes necessary for improvement of the fruit cold-set jelly candy manufacturing process.

The mean values of bioactive compounds recovery along the storage are presented in Figure 5. After 30 days the samples showed significant difference only for the recovery levels of ascorbic acid content. Despite the decreasing behavior over the time and the statistical differences between the candies, the mean values of relative remaining quantity of total phenolic compound and total anthocyanin contents did not differ on the first two months of storage.

Comparing to other studies about the manufacturing of natural candies with fruit ingredients, SCJ and SPJ formulations showed low fruit solids content which impacted on its low bioactive compound contents and recovery levels over storage. Chewy candies processed with spray-dried and freeze-dried açai powder by Da Silva et al. (2016), for example, showed higher contents of total anthocyanin and phenolic compounds, and higher recovery levels of these bioactive compounds after 6 months of storage (phenolic compounds recovery between 71-78 percent; anthocyanin recovery between 85-99 percent). The authors suggested that the selection of the type of processed fruit as an ingredient in confectionery products is an essential to obtaining candies with great stability of colour and retention of bioactive compounds after processing and along the storage and indicated a better performance in the retention of bioactive compounds when freeze-dried açai was used to the chewy candy production.

Tea hard candies added with chokeberry extract and freeze-dried black raspberry powder produced by Bunce (2007) also presented higher anthocyanin, total phenolic and ascorbic acid contents than the averages observed in this present study, with also higher recovery after 30 weeks of storage. The author indicated the low water activity of the hard candies limited the mobility of the bioactive compounds, enhancing the recovery of the functional compounds on the candy shelf life.

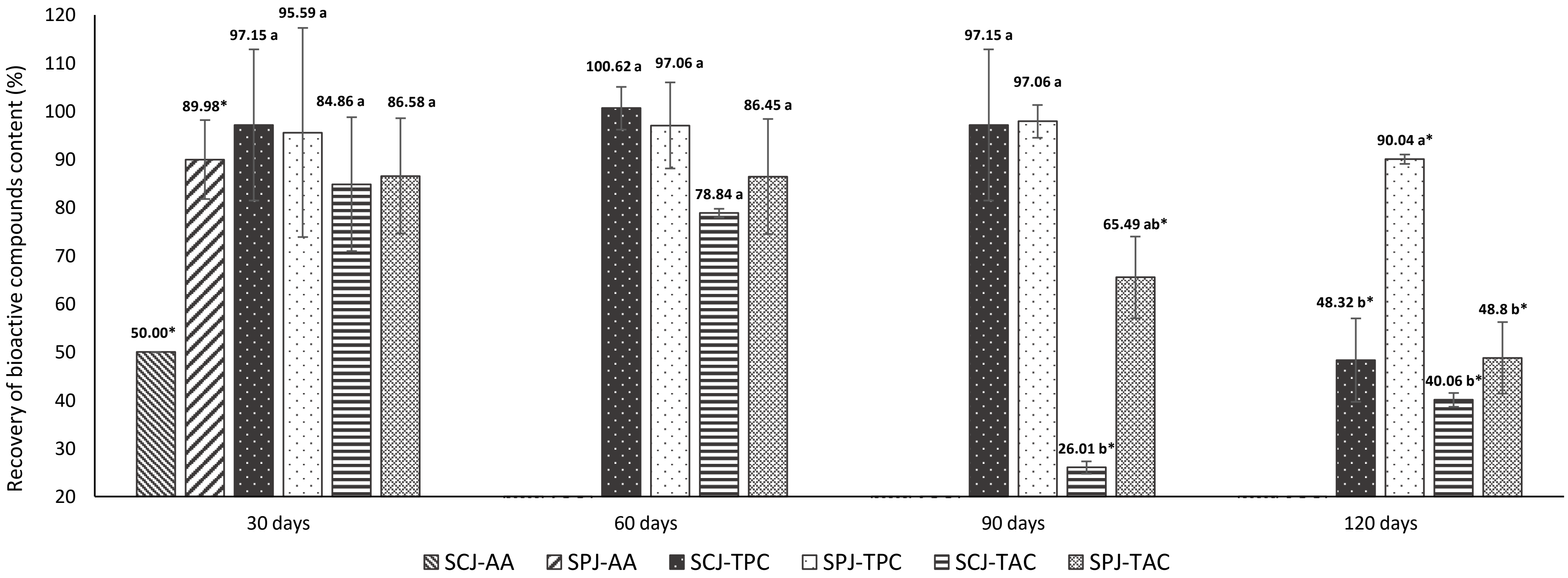

Figure 5. Remaining relative content of bioactive compounds in strawberry jelly candies produced by different processing (SCJ: Strawberry cold-set jelly candy; SPJ: Strawberry pectin candy; AA: Ascorbic Acid; TPC: Total phenolic compounds content; TAC: Total anthocyanin content) during storage at 25 °C. Mean values of the same treatment followed by the same letter are not significantly different ($p>0.05$) in respect to the time of storage. Mean values of different treatments followed by (*) are significantly different ($p>0.05$).

3.2.3 Sensory quality

The results of the sensory acceptance test are presented in Table 5. The stored candies showed acceptance scores with no significant difference ($p<0.05$) in relation to the acceptance scores of its after-processed samples. These results suggest the changes occurred during storage were not sensorially perceptible to the consumers, and the sensory quality of the samples was relatively stable.

The acceptance scores for appearance, aroma and color of SPJ and SCJ samples were lower than those received by pectin and cold-set jelly candies produced with high strawberry juice concentrate content by Avelar et al. (2020) suggesting the low strawberry solids content and possibly the quality of the frozen pasteurized pulp used in this present study as relevant factors to the sensory profile of the evaluated jellies.

Table 5. Sensorial acceptance of the produced candies after storage.

Sensorial atributes	Samples	Candy treatments			
		Flavored cold-set jelly candy	Flavored pectin jelly candy	Strawberry cold-set jelly candy	strawberry pectin jelly candy
Appearence	Fresh sample	6.6 ±1.7 Aa	7.0 ±1.5 Aa	4.3 ±2.0 Aa	4.6 ±1.9 Aa
	Four months stored sample	6.2 ±1.8 Aa	7.0 ±1.4 Aa	4.6 ±1.8 Aa	5.6 ±2.1 Aa
Color	Fresh sample	7.0 ±1.8 Aa	8.0 ±1.2 Aa	4.8 ±2.0 Aa	4.6 ±1.8 Aa
	Four months stored sample	6.6 ±1.7 Aa	6.7 ±1.5 Aa	4.3 ±1.9 Aa	5.3 ±2.0 Aa
Aroma	Fresh sample	5.0 ±1.0 Aa	5.0 ±1.1 Aa	5.0 ±1.1 Aa	5.3 ±1.1 Aa
	Four months stored sample	5.4 ±1.1 Aa	5.4 ±1.1 Aa	5.6 ±1.3 Aa	6.2 ±1.2 Aa
Flavor	Fresh sample	5.3 ±2.0 Aa	6.6 ±1.7 Aa	5.3 ±2.3 Aa	6.6 ±2.1 Aa
	Four months stored sample	5.2 ±2.3 Aa	6.3 ±1.8 Aa	5.2 ±2.1 Aa	6.0 ±1.9 Aa
Texture	Fresh sample	4.5 ±1.9 Aa	6.0 ±1.9 Aa	5.3 ±1.9 Aa	6.3 ±1.7 Aa
	Four months stored sample	4.4 ±2.2 Aa	5.9 ±2.0 Aa	4.9 ±1.8 Aa	5.6 ±1.9 Aa
Overall impression	Fresh sample	5.3 ±1.7 Aa	7.0 ±1.5 Aa	4.6 ±1.8 Aa	6.2 ±1.7 Aa
	Four months stored sample	5.1 ±1.9 Aa	6.3 ±1.6 Aa	5.1 ±1.7 Aa	5.8 ±1.6 Aa

Sensory acceptance scores to the sensorial attributes of the same treatment followed by different capital letter are significantly different ($p < 0.05$) in relation to the time of storage. Mean values in the same line followed by different small letter are significantly different ($p < 0.05$) in relation to the candy treatment.

4. Conclusion

Under the conditions applied in this study, jelly candies produced by cold-set gelation showed low and stable values of water activity and moisture content over storage, suggesting safety of cold-set products to microbial growth and deterioration. The occurrence of sucrose crystallization was visually verified in the internal structure of all candy samples, impacting on its texture profile over time. Jellies produced with strawberry pulp, however, showed no significant different ($p<0.05$) between hardness averages during storage, appointing fruit ingredients as a determining factor on texture controlling of fruit candies.

Despite of the color and texture changing over the months, the sensory acceptance scores of fresh and stored cold-set jellies showed no significant difference ($p<0.05$), indicating stability of sensory attributes of stored cold-set candies.

The bioactive compounds contents in SCJ decreased significantly over time, which may be related to the porous microstructure of cold-set gels and the uncontrolled internal conditions of the packaging used in this study. The cold-set gelation processing has been appointed as a potential and innovative technology for sustainable production of jelly candies with health appeals. In this way, packaging studies become necessary for find better alternatives to enhance the fruit bioactive compounds stability during shelf-life of cold-set products.

Acknowledgments

Conselho Nacional de Desenvolvimento Científico e Tecnológico - Brasil (CNPQ) for the fellowship to the first author, Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, Innovation Agency of University of Campinas (Inova-Unicamp) and the Brazilian National Institute of Industrial Property for the patent filling BR 10 2018 076817, that contemplates and protects the results of this study.

5. References

AOAC. (2012). *Official Methods of Analysis of AOAC International (19th ed)*. Gaithersburg, MD: Association of Official Analytical Chemists.

Asami, D. K., Hong, Y. J., Barrett, D. M., & Mitchell, A. E. (2003) Comparison of the total phenolic and ascorbic acid contents of freeze-dried and air-dried marionberry, strawberry, and corn grown using conventional, organic, and sustainable agricultural practices. *Journal of Agricultural and Food Chemistry, 51*, 1237-1241. doi: 10.1021/jf020635c.

Avelar, M. H. M., Silva, L. B., Azevedo, F. B., & Efraim, P. (2019). A byproduct of uvaia (*Eugenia pyriformis*) processing as a natural source for coloring sugar hard-panning confections. *Journal of Food Process Engineering, 42(7), 1-8*. doi:10.1111/jfpe.13250.

Avelar, M. H. M., & Efraim, P. (2020). Alginate/pectin cold-set gelation as a potential sustainable method for jelly candy production. *LWT–Food Science and Technology, 123,* doi:10.1016/j.lwt.2020.109119.

Avelar, M. H. M., Lima, L. N., & Efraim, P. (2020) Maintenance of Fruit Bioactive Compounds in Jelly Candy Manufacturing by Alginate/Pectin Cold-Set Gelation. *Journal of Food Processing Technology, 11(826)*. doi: 10.35248/2157-7110.20.11.826.

Avelar, M. H. M., Queiroz, G. C., & Efraim, P. (2020) Sustainable performance of cold-set gelation in the confectionery manufacturing and its effects on perception of sensory quality of jelly candies. *Cleaner Engineering and Technology*. https://doi.org/10.1016/j.clet.2020.100005.

Bauernfeind, J. C., & Pinkert, D. M. (1970). Food Processing with Added Ascorbic Acid. *Advances in Food Research, 18*, 219–315. doi:10.1016/s0065-2628(08)60371-7.

Bunce, M. G. (2007). *Anthocyanin and tea extract enriched hard candy to increase visual appeal and total phenolics.* Ohio State University. https://etd.ohiolink.edu/!etd.send_file?accession=osu1406642018&disposition=inline.

Cheftel, H., & Pigeaud, M. L. (1936). Estimation of Ascorbic Acid (Vitamin C) by Titration. *Nature, 138(3497),* 799–799. doi:10.1038/138799b0.

Da Silva, L. B., Annetta, F. E., Alves, A. B., Queiroz, M. B., Fadini, A. L., da Silva, M. G., & Efraim, P. (2016). Effect of differently processed açai (*Euterpe oleracea Mart*.) on the retention of phenolics and anthocyanins in chewy candies. *International Journal of Food Science & Technology, 51(12),* 2603–2612. doi:10.1111/ijfs.13245.

Ergun, R., Lietha, R., & Hartel, R. W. (2010). Moisture and Shelf Life in Sugar Confections. *Critical Reviews in Food Science and Nutrition, 50(2),* 162–192. doi:10.1080/10408390802248833.

Fadini, A. L., Jardim, D. C. P., Queiroz, M. B., Bertin, A. P., Efraim, P., et al. (2005). Características sensoriais e de textura de chicles drageados diet produzidos com diferentes tipos de polióis (*Sensory and texture characteristics of diet panned chewing gum produced with different types of polyols*) [In Portuguese]. *Brazilian Journal of Food Technology, 8,* 113-119.

Friedman, M., & Jürgens, H. S. (2000). Effect of pH on the Stability of Plant Phenolic Compounds. *Journal of Agricultural and Food Chemistry, 48(6),* 2101–2110. doi:10.1021/jf990489j.

Gonçalves, G. A. S., Resende, N. S., Carvalho, E. E. N., de Resende, J. V., & Vilas Boas, E. V. de B. (2017). Physicochemical and volatile profile alterations in pasteurized and frozen strawberry pulp during storage. *Journal of Food Processing and Preservation, 42(1),* e13317. doi:10.1111/jfpp.13317.

Hartel, R. W., Elbe, J H. V., & Hofberger, R. (2018). *Confectionery Science and Technology*. Berlin: Springer International Publishing, 542 p. 10.1007/978-3-319-61742-8.

Hartel, R. W., Ergun, R., & Vogel, S. (2010). Phase/State Transitions of Confectionery Sweeteners: Thermodynamic and Kinetic Aspects. *Comprehensive Reviews in Food Science and Food Safety, 10(1),* 17–32. doi:10.1111/j.1541-4337.2010.0.

Laos, K., Kirs, E., Pall, R., & Martverk, K. (2011). The Crystallization Behaviour of Estonian Honeys. *Agronomy Research, 9 (Special Issue II),* 427–432.

Minolta, K. (1998). *Precise Color Communication: Color Control from Perception to Instrumentation*. Japan: Konica Minolta, Inc., Chapters 1, 4.

Montenegro, F. M., & Luccas, V. (2014). As macrotendências dos setores de bakery e confectionery (*Macro trends in the bakery and confectionery sectors*) [In Portuguese]. In: Queiroz, G. C., Rego, R. A., & Jardim, D. C. P. (Eds.). *Brasil Bakery* & *Confectionery Trends 2020.* (pp. 59-71). Campinas: ITAL.

Moser, P., Telis, V. R. N., de Andrade Neves, N., García-Romero, E., Gómez-Alonso, S., & Hermosín-Gutiérrez, I. (2017). Storage stability of phenolic compounds in powdered BRS Violeta grape juice microencapsulated with protein and maltodextrin blends. *Food Chemistry, 214*, 308–318. doi:10.1016/j.foodchem.2016.07.081.

Naidu, K. A. (2003). Vitamin C in human health and disease is still a mystery? An overview. *Nutrition Journal, 2(7).* doi:10.1186/1475-2891-2-7.

Patras, A., Brunton, N. P., O'Donnell, C., & Tiwari, B. K. (2010). Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation. *Trends in Food Science & Technology, 21(1),* 3–11. doi:10.1016/j.tifs.2009.07.004.

Sandulachi, E. (2012). Water activity concept and its role in food preservation. Retrieved from http://www.utm.md/meridian/2012/MI_4_2012/8_Art_Sandulachi_E_Water.pdf.

Singleton, V. L., Othofer, R., & Lamuela-Raventos, R. M. (1999). Analysis of total phenols and others oxidation substrates and antioxidants by folin-ciocauteau reagent. *Methods in Enzimology*, *299, 152-178.* doi:10.1016/S0076-6879(99)99017-1.

Stone, H., & Sidel, J. L. (2004). *Sensory Evaluation Practices (3rd ed)*. Amsterdam: Elsevier, 377 p.

Subramaniam, P. (2016). The Stability and Shelf Life of Confectionery Products. In: Subramaniam, P. *The Stability and Shelf Life of Food* (pp. 545–573). doi:10.1016/b978-0-08-100435-7.00019-8.

Sufferling, K. (2007). Gelatin gummies and pectin jellies. *The Manufacturing Confectioner, 87(8),* 43-50.

Toft, K., Grasdalen, H., & Smidsrød, O. (1986). Synergistic Gelation of Alginates and Pectins. In: Fishman, M. L., & Je, J. J., *Chemistry and Function of Pectins* (pp. 117–132). Washington: American Chemical Society. doi:10.1021/bk-1986-0310.ch010.

Tonutare, T., Moor, U. L., & Szajdak, L. (2014). Strawberry anthocyanin determination by pH differential spectroscopic method – how to get true results? *Acta Scientiarum Polonorum Hortorum Cultus, 13(3),* 35-47.

Tulipani, S., Mezzetti, B., Capocasa, F., Bompadre, S., Beekwilder, J., et al. (2008). Antioxidants, Phenolic Compounds, and Nutritional Quality of Different Strawberry Genotypes. *Journal of Agricultural and Food Chemistry, 56(3),* 696–704. doi:10.1021/jf0719959.

Uddin, M., Hawlader, M. N., Ding, L., & Mujumdar, A. (2002). Degradation of ascorbic acid in dried guava during storage. *Journal of Food Engineering, 51(1)*, 21–26. doi:10.1016/s0260-8774(01)00031-0.

DISCUSSÃO GERAL

A gelificação a frio de misturas de alginato de sódio e pectina de alto teor de metoxilação é um processo ainda pouco estudado e empregado industrialmente. Neste trabalho verificou-se a viabilidade da sua aplicação no processo de produção de balas de goma, em substituição à etapa convencional de cozimento da calda. Os produtos obtidos pelo processamento a frio apresentaram características físicas diferentes das observadas em balas de goma de pectina. No entanto, não apresentaram diferença significativa ($p<0.05$) em relação à aceitabilidade sensorial, o que indica um potencial sensorial para substituição de produtos comerciais por balas produzidas a frio.

Os géis mistos de alginato e pectina possuem uma estrutura microscópica composta por uma rede densa e homogênea com grande quantidade de poros, que determina fortemente as características físicas das balas (textura firme e pouco elástica, geís de aparência clara e opaca) e exerce grande influência no comportamento dos produtos ao longo da vida de prateleira.

Os estudos de formulação realizados neste trabalho avaliaram a influência dos ingredientes (hidrocoloides, acidulante e açúcares) nas características físicas e físico-químicas das balas. Estruturas gelificadas mais firmes e coesas foram obtidas quando formuladas com mais de 10 g/kg de misturas poliméricas compostas de 1:1 de alginato: pectina. Quando há a inclusão de polpa de fruta no sistema o teor mínimo de mistura polimérica aumenta para 20 kg/kg. Em ambos os casos, quanto maior o teor de mistura polimérica, maior é a dureza do gel e também maior é a viscosidade da calda, o que dificulta a sua dosagem. A avaliação das propriedades reológicas poderia auxiliar na compreensão da influência dos ingredientes e do tempo de preparo sobre as características de escoamento da calda. Essas informações são fundamentais para auxiliar o setor industrial na adaptação dos sistemas de bombeamento e depósito das caldas para a fabricação de balas a frio.

A característica de acidificação lenta da glucona delta-lactona (GDL) foi essencial para a aplicação do processo de gelificação de alginato e pectina na fabricação de balas, no sentido de permitir uma formação lenta da rede de gel e proporcionar tempo hábil para a dosagem da calda nos moldes. Nos tratamentos avaliados, maiores concentrações de GDL implicaram em balas com menores valores de pH e, consequentemente, com maiores médias no parâmetro de dureza instrumental.

A produção de balas com relação de 1:2 kg:kg de sacarose: xarope de glicose, em base seca, foi inviabilizada devido à excessiva maciez e pegajosidade dos produtos. Apesar da proporção de 1:1 de sacarose:xarope de glicose ter sido indicada neste trabalho como uma melhor relação de sólidos açucarados, os resultados dos estudos de estabilidade indicaram a necessidade de um reajuste no balanço de açúcares em vista da ocorrência da cristalização da sacarose durante o armazenamento. Estudos de formulação de balas a frio com polióis e demais substitutos de açúcares também se fazem necessários em vista da atual demanda por redução de açúcar em produtos industrializados.

A inclusão de polpas de frutas na formulação de balas de gomas de alginato e pectina se mostrou possível, e os resultados dos estudos de estabilidade indicaram forte efeito dos sólidos de frutas no controle da textura e do processo de cristalização da sacarose nas balas. As características físico-químicas das frutas apresentaram pouca influencia durante o processo de formação da rede de gel, apesar do mecanismo ser dependente de uma faixa de pH específico. A possibilidade de inclusão de frutas possibilita a fabricação de balas de goma mais naturais, livre de aditivos e com a utilização de matérias-primas regionais.

A incorporação de altos teores de fruta nas balas, no entanto, é limitada pela alta umidade das polpas. Em altas concentrações, o elevado conteúdo de água das polpas dificulta a formulação de caldas de bala com maior teor de sólidos solúveis, o que acaba aumentando o tempo necessário para secagem do produto. Como alternativa há a possibilidade de aplicação de sucos concentrados, como foi feito neste estudo, ou de frutas nas formas desidratadas ou liofilizadas. O alto teor de sólidos de fruta, entretanto, pode provocar mudanças indesejáveis nas características de textura das balas e comprometer a sua estabilidade e aceitabilidade sensorial. As amostras produzidas com suco concentrado de morango, por exemplo, apresentaram valores de dureza instrumental mais baixos e menor aceitação sensorial para o atributo textura.

A temperatura de 35 °C foi indicada como a melhor condição de processo para a secagem das balas de goma de alginato-pectina no equipamento utilizado (estufa de secagem com circulação e renovação de ar). Temperaturas mais altas conduziram a uma desidratação mais rápida; entretanto, induziram o processo de cristalização da sacarose, comprometendo a textura dos produtos. Neste estudo, as caldas das balas foram produzidas com 72 °Brix e secas por 72 horas. Esse tempo de secagem é considerado relativamente longo em relação ao tempo utilizado para balas de gelatina e pectina (HARTEL et al., 2018c) e, portanto, bastante expressivo do ponto de vista energético.

As curvas de secagem indicaram que após 12 horas foi possível obter balas com teor de umidade entre 15 e 20%, valores dentro da faixa recomendada para a estabilidade dessa categoria de produto. Nesse tempo, entretanto, as amostras ainda apresentavam valores altos de atividade de água (acima de 0,75) e não apresentaram textura adequada.

A literatura descreve que géis de alginato/pectina com máxima firmeza são obtidos quando produzidos com alginatos de sódio com 70% de ácido α-L-gulurônico e pectinas HM com grau de esterificação (DE) de 70% (TOFT et al., 1986). Apesar da possibilidade de obtenção de géis mais firmes em menor tempo de secagem, o uso dos hidrocoloides com estas especificações pode dificultar a aplicação da tecnologia de gelificação a frio para a produção de balas, pois pectinas HM com DE maior ou igual a 70% possuem alta velocidade de gelificação, que as torna incompatíveis com os sistemas industriais de dosagem das caldas de balas (HARTEL et al., 2018c). O aumento do teor de sólidos solúveis da calda da bala ou a aplicação de tecnologias de secagem alternativas, como as micro ondas ou ultra som, podem ser alternativas mais eficazes para a redução do tempo de secagem.

A gelificação a frio se apresentou como um processo eficiente para a conservação de nutrientes e compostos bioativos termo-sensíveis provenientes de ingredientes de frutas. A adição direta de vitaminas e outros nutrientes na formulação das balas também tende a ser favorecida, permitindo menor perda ao longo do processo, reduzindo custos para as indústrias.

A redução significativa ($p<0.05$) do teor de ácido ascórbico e de antocianinas ao longo do armazenamento indica a necessidade de estudar materiais e condições de embalagem e estocagem para a manutenção do teor de compostos bioativos no armazenamento e a extensão da vida útil das balas.

O processo de fabricação de balas de goma a frio também apresentou potencial sustentável devido à redução significativa ($p<0.05$) do consumo energético no preparo da calda da bala e das emissões diretas e indiretas de gases de efeito estufa relacionadas a essa etapa. A substituição do processo de cozimento a vapor pela etapa de mistura elétrica pode dispensar a necessidade de caldeiras na linha de produção, o que também implica em uma menor demanda industrial por recursos (água e combustível para a caldeira), e na redução de custos para a instalação da linha de processamento e para as operações industrial. Os estudos realizados em planta piloto indicaram uma redução de quase 100 vezes na energia consumida no preparo da calda e de aproximadamente 300 vezes nas emissões de CO_2. Estima-se que estes valores podem alcançar níveis ainda mais significativos nas linhas industriais.

Dependendo das concentrações dos hidrocolóides utilizados na formulação das balas, a gelificação a frio pode acarretar em um custo de matérias-primas ligeiramente superior aos de outros produtos convencionais. No entanto, o potencial sustentável e tecnológico desse processo pode oferecer a possibilidade de atribuição de alegações de sustentabilidade, saudabilidade, nutrição e funcionalidade nos produtos obtidos, o que pode ajudar a sustentar o preço final do produto no mercado.

Os participantes dos testes sensoriais informaram ter um alto interesse em produtos com alegações sustentáveis e estarem dispostos a pagar mais por esses produtos, apesar da maior parte deles (73%) nunca ter consumido balas com algum rótulo ambiental. A maioria dos avaliadores (76%) também informou não conhecer a certificação de pegada de carbono e praticamente todos (92%) nunca consumiram balas com essa rotulagem. As alegações de redução de carbono quando apresentadas junto às amostras nos testes sensoriais conduziram ao aumento significativo ($p<0.05$) da aceitabilidade sensorial do produto. Esses resultados indicam que a linha de balas sustentáveis é um segmento de mercado a ser explorado no Brasil. Neste contexto, a tecnologia de gelificação a frio de alginato e pectina surge como uma ferramenta tecnológica promissora para a obtenção de opções alimentares mais conscientes do ponto de vista ambiental.

Além de balas de goma, estima-se que a gelificação de alginato e pectina possa ser aplicada na fabricação de outros produtos alimentícios gelificados como geleias, recheios de bombom, sobremesas lácteas e preparados prontos para consumo no lar ou no segmento de *food service*. As aplicações, no entanto, precisam ser melhor avaliadas.

CONCLUSÃO GERAL

O processo de gelificação a frio de misturas de alginato de sódio e pectina de alto teor de metoxilação se mostrou ser uma tecnologia viável para a produção de balas de goma, conferindo caráter sustentável ao processo e permitindo uma melhor manutenção de nutrientes e componentes bioativos termo sensíveis quando presentes na formulação das balas. O consumo energético e as emissões de CO_2 da etapa de preparo da calda foram significativamente inferiores às do processo convencional de cozimento da calda, permitindo a atribuição de autodeclarações ambientais de pegada de carbono nos rótulos dos produtos obtidos. Verificou-se que a rotulagem sustentável exerce um efeito positivo na aceitabilidade das balas, elevando as médias de aceitação dos seus parâmetros sensoriais. Além disso, os avaliadores indicaram um alto interesse em consumir balas com alegações sustentáveis e alta disposição a pagar mais por esses produtos. Os estudos de estabilidade indicaram a necessidade de ajuste no balanço de sólidos açucarados cristalizáveis e não cristalizáveis para inibir o processo de cristalização da sacarose durante a vida de prateleira dos produtos. O processo de gelificação a frio de alginato e pectina possui potencial tecnológico para aplicação em outros produtos alimentícios, se apresentando como uma ferramenta tecnológica promissora para a fabricação sustentável de alimentos.

SUGESTÃO PARA TRABALHOS FUTUROS

- Promover estudos de reformulação adequando o balanço de sólidos açucarados cristalizáveis e não cristalizáveis das balas conforme solubilidade dos açúcares em sistemas multicomponentes, visando prevenir a ocorrência de cristalização da sacarose durante o armazenamento;
- Promover estudos para a obtenção balas mais firmes em menor tempo de secagem;
- Estudar o desenvolvimento de formulações de balas de goma de alginato/pectina em versões *diet* com diferentes substitutos de açúcares e adequar às condições de processo caso necessário;
- Promover um estudo de estabilidade das novas formulações para determinação de sistemas de embalagens e armazenamento adequados aos produtos;
- Estudar a viabilidade da produção de outros alimentos como geleias, recheios de bombom e sobremesas por meio da tecnologia de gelificação a frio de alginato de sódio e pectina de alto teor de metoxilação.

REFERÊNCIAS BIBLIOGRÁFICAS

ABICAB. **Estatística Balas e Gomas**, 2020. Disponível em: <http://www.abicab.org.br/paginas/estatisticas/balas-gomas/>. Acesso em 23 de Novembro de 2020.

AIGROUP. **Energy reduction factsheet: Saving energy in the confectionery manufacturing industry**, 2019. Disponível em: <http://cdn.aigroup.com.au/Environment/21_Food_Processing_Confectionery_Manufacturing_Energy_Reduction_Factsheet.pdf>. Acesso em 22 de Julho de 2019.

ANVISA. **Regulamento Técnico para balas, bombons e gomas de mascar** - RDC nº 265, de 22 de setembro de 2005, 2005. Disponível em: <http://portal.anvisa.gov.br/documents/394219/RDC_265_2005.pdf/>. Acesso em 23 de Novembro de 2020.

ALAMAR, P. D.; CARAMÊS, E. T. S.; POPPI, R. J.; PALLONE, J. A. L. Quality evaluation of frozen guava and yellow passion fruit pulps by NIR spectroscopy and chemometrics. **Food Research International**, v. 85, p. 209–214, 2016.

AOAC. **Official Methods of Analysis of AOAC International**. 19th ed. Gaithersburg, MD: Association of Official Analytical Chemists, 2012.

ASAMI, D. K.; HONG, Y. J.; BARRETT, D. M.; MITCHELL, A. E. Comparison of the total phenolic and ascorbic acid contents of freeze-dried and air-dried marionberry, strawberry, and corn grown using conventional, organic, and sustainable agricultural practices. **Journal of Agricultural and Food Chemistry**, v. 51, p. 1237-1241, 2003.

ASCHEMANN-WITZEL, J. Consumer perception and trends about health and sustainability: trade-offs and synergies of two pivotal issues. **Current Opinion in Food Science**, v. 3, p. 6–10, 2015.

AVELAR, M. H. M.; SILVA, L. B.; AZEVEDO, F. B.; EFRAIM, P. A byproduct of uvaia (*Eugenia pyriformis*) processing as a natural source for coloring sugar hard-panning confections. **Journal of Food Process Engineering**, v. 42, n. 7, p. 1-8, 2019.

AVELAR, M. H. M.; EFRAIM, P. Alginate/pectin cold-set gelation as a potential sustainable method for jelly candy production. **LWT–Food Science and Technology**, v. 123, p. 109119, 2020.

AVELAR, M. H. M.; LIMA, L. N.; EFRAIM, P. Maintenance of Fruit Bioactive Compounds in Jelly Candy Manufacturing by Alginate/Pectin Cold-Set Gelation. **Journal of Food Processing Technology**, v. 11, n. 826, 2020.

AVELAR, M. H. M.; QUEIROZ, G. C.; EFRAIM, P. Sustainable performance of cold-set gelation in the confectionery manufacturing and its effects on perception of sensory quality of jelly candies. **Cleaner Engineering and Technology**, v. 1, p. 100005, 2020.

BAUERNFEIND, J. C.; PINKERT, D. M. Food Processing with Added Ascorbic Acid. **Advances in Food Research**, v. 18, p. 219–315, 1970.

BILEK, S. E.; ÖZKAN, G. Encapsulation of zinc-chlorophyll derivatives in whey protein matrix by emulsion/cold-set gelation. **GIDA/ The Journal of Food Research**, v. 43, n. 1, p. 174-183, 2018.

BOLDER, S. G.; HENDRICKX, H.; SAGIS, L.; VAN DER LINDEN, E. Ca2+-induced cold set gelation of whey protein isolate fibrils. **Applied Rheology**, v. 16, p. 258–264, 2006.

BREJNHOLT, S. M. Pectin. In: IMESON, A. (Ed.). **Food Stabilisers, Thickeners and Gelling Agents**. Blackwell Publishing, 2010, p. 237-265.

BRITO-OLIVEIRA, T. C.; BISPO, M.; MORAES, I. C. F.; CAMPANELLA, O. H.; PINHO, S. C. Cold-Set Gelation of Commercial Soy Protein Isolate: Effects of the Incorporation of Locust Bean Gum and Solid Lipid Microparticles on the Properties of Gels. **Food Biophysics**, v. 13, n. 3, p. 226–239, 2018.

BUNCE, M. G. **Anthocyanin and tea extract enriched hard candy to increase visual appeal and total phenolics**. Ohio State University, 2007. Disponível em: <https://etd.ohiolink.edu/!etd.send_file?accession=osu1406642018&disposition=inline>. Acesso em 23 de Novembro de 2020.

BUSINESSWIRE. **Correcting and Replacing Sugar Confectionery Market - Global Forecast and Opportunity Assessment by Technavio**, 2020. Disponível em: <https://www.businesswire.com/news/home/20170614006004/en/CORRECTING-REPLACING-Sugar-Confectionery-Market---Global>. Acesso em 23 de Novembro de 2020.

CARDOSO DE LIMA, G. S.; LOPES, E. C.; MOTTA, J. G.; ASANO, R.; VALVERDE, M.; SUYAMA, R.; LEITE, P. T. Sustainable development enhanced in the decision process of electricity generation expansion planning. **Renewable Energy**, v. 123, p. 563–577, 2018.

CAPPA, C.; LAVELLI, V.; MARIOTTI, M. Fruit candies enriched with grape skin powders: physicochemical properties. **LWT - Food Science and Technology**, v. 62, n. 1, p. 569–575, 2015.

CASTKA, P.; CORBETT, C. J. Management Systems Standards: Diffusion, Impact and Governance of ISO 9000, ISO 14000, and Other Management Standards. **Foundations**

and Trends in Technology, Information and Operations Management, v. 7, n. 3–4, p. 161-379, 2015.

CAVALLIERI, A. L. F. **Gelificação a frio de proteínas do soro do leite: efeito da taxa de acidificação, pH final e adição de polissacarideos**. Campinas: Unicamp, 2007, 218 p.

CHALA, G.; ABD AZIZ, A.; HAGOS, F. Natural Gas Engine Technologies: Challenges and Energy Sustainability Issue. **Energies**, v. 11, n. 11, 2934, 2018.

CHEFTEL, H.; PIGEAUD, M. L. Estimation of Ascorbic Acid (Vitamin C) by Titration. **Nature**, v. 138, n. 3497, p. 799–799, 1936.

CONFECTIONERY NEWS. **Organic candy: The future of confectionery, says new report,** 2019. Disponível em: <https://www.confectionerynews.com/Article/2007/08/08/Organic-candy-the-future-of-confectionery-says-new-report>. Acesso em 22 de Julho de 2019.

CORY, H.; PASSARELLI, S.; SZETO, J.; TAMEZ, M.; MATTEI, J. The Role of Polyphenols in Human Health and Food Systems: A Mini-Review. **Frontiers in Nutrition**, v. 5, n. 87, 2018.

COYLE, S. J. Cooking Equipment for Jelly Candy. **The Manufacturing Confectioner**, v. 99, n. 8, p. 36-42, 2007.

DA SILVA, L. B.; ANNETTA, F. E.; ALVES, A. B.; QUEIROZ, M. B.; FADINI, A. L.; DA SILVA, M. G.; EFRAIM, P. Effect of differently processed açai (*Euterpe oleracea Mart.*) on the retention of phenolics and anthocyanins in chewy candies. **International Journal of Food Science & Technology**, v. 51, n. 12, p. 2603–2612, 2016.

DAVIS, S. J.; PETERS, G. P.; CALDEIRA, K. The supply chain of CO_2 emissions. **Proceedings of the National Academy of Sciences**, v. 108, n. 45, p. 18554–18559, 2011.

DELGADO, P., & BAÑÓN, S. Determining the minimum drying time of gummy confections based on their mechanical properties. **CyTA - Journal of Food**, v. 13, n. 3, p. 329–335. 2014.

DEMARS, L. L.; ZIEGLER, G. R. Texture and structure of gelatin/pectin-based gummy confections. **Food Hydrocolloids**, v. 15, n. 4-6, p. 643–653, 2001.

DE MOURA, S. C. S. R.; BERLING, C. L.; GARCIA, A. O.; QUEIROZ, M. B.; ALVIM, I. D.; HUBINGER, M. D. Release of anthocyanins from the hibiscus extract encapsulated by ionic gelation and application of microparticles in jelly candy. **Food Research International**, v. 121, p. 542-552, 2018.

DE SOUZA, V. R.; PEREIRA, P. A. P.; DA SILVA, T. L. T.; DE OLIVEIRA LIMA, L. C.; PIO, R.; QUEIROZ, F. Determination of the bioactive compounds, antioxidant activity and chemical composition of Brazilian blackberry, red raspberry, strawberry, blueberry and sweet cherry fruits. **Food Chemistry**, v. 156, p. 362–368, 2014.

DIAZ N.; REDELSHEIMER E.; DORNFELD D. Energy Consumption Characterization and Reduction Strategies for Milling Machine Tool Use. In: HESSELBACH J.; HERRMANN C. (Eds). **Glocalized Solutions for Sustainability in Manufacturing**. Berlin, Heidelberg: Springer, 2011, p. 263-267.

DRAGET, K. I.; SKJÅK-BRÆK, G.; STOKKE, B. T. Similarities and differences between alginic acid gels and ionically crosslinked alginate gels. **Food Hydrocolloids**, v. 20, n. 2-3, p. 170–175, 2006.

EDWARDS, W. P. Gomas, productos gelificados y regaliz. In: EDWARDS, W. P. **La ciencia de las golosinas.** Zaragonza: Ed. Acribia, 2008, p. 121-135.

EIRI BOARD. **Hand Book of Confectionery with Formulations**. New Delhi: Engineers India Research Institute, 2012, 253 p.

ELETROBRÁS. **Eficiência Energética no Uso de Vapor**. Rio de Janeiro: Eletrobrás, 2005, 196 p.

ERGUN, R.; LIETHA, R.; HARTEL, R. W. Moisture and Shelf Life in Sugar Confections. **Critical Reviews in Food Science and Nutrition**, v. 50, n. 2, p. 162–192, 2010.

ERTZ, M.; FRANÇOIS, J.; DURIF, F. How Consumers React to Environmental Information: An Experimental Study. **Journal of International Consumer Marketing**, v. 29, n. 3, p. 162–178, 2017.

FADINI, A. L.; FACCHINI, F.; QUEIROZ, M. B.; ANJOS, V. D. A.; YOTSUYANAGI, K. Influência de diferentes ingredientes na textura de balas moles produzidas com e sem goma gelana. **Boletim do Centro de Pesquisa e Processamento de Alimentos**, v. 21, p. 131–140, 2003.

FADINI, A. L.; CRUZ, C. L. V. Controle e Adequação. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 73–115.

FADINI, A. L.; JARDIM, D. C. P.; QUEIROZ, M. B.; BERTIN, A. P.; EFRAIM, P.; MORI, E. E. M. Características sensoriais e de textura de chicles drageados diet produzidos com diferentes tipos de polióis. **Brazilian Journal of Food Technology**, v. 8, p. 113-119, 2005.

FAO. FOOD AND AGRICULTURE ORGANIZATION. **Human Vitamin and Mineral Requirements**, 2001. Disponível em: http://www.fao.org/3/a-y2809e.pdf. Acesso em 03 de Abril de 2020.

FDA. FOOD AND DRUG ADMINISTRATION. **Guidance for Industry: Evidence-Based Review System for the Scientific Evaluation of Health Claims**, 2009. Disponível em: https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-evidence-based-review-system-scientific-evaluation-health-claims. Acesso em 03 de Abril de 2020.

FDA. FOOD AND DRUG ADMINISTRATION. **Guidance for Industry: Food Labeling Guide**, 2013. Disponível em: https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-food-labeling-guide. Acesso em 03 de Abril de 2020.

FDA. FOOD AND DRUG ADMINISTRATION. Food Labeling: **Serving Sizes of Foods That Can Reasonably Be Consumed at One Eating Occasion; Dual-Column Labeling; Updating, Modifying, and Establishing Certain Reference Amounts Customarily Consumed; Serving Size for Breath Mints; and Technical Amendments: Guidance for Industry Small Entity Compliance Guide**, 2018. Disponível em: https://www.fda.gov/media/111144/download. Acesso em 03 de Abril de 2020.

FDA. FOOD AND DRUG ADMINISTRATION. **Frequently Asked Questions for Industry on Nutrition Facts Labeling Requirements**, 2020. Disponível em: https://www.fda.gov/media/99069/download. Acesso em 03 de Abril de 2020.

FOOD & BEVERAGE INSIDER. **Sweet sustainability in the confectionery space**, 2018. Disponível em: https://www.foodbeverageinsider.com/sustainability/sweet-sustainability-confectionery-space-digital-magazine>. Acesso em 01 de Janeiro de 2021.

FOOD INGREDIENTS BRASIL. **Acidulantes**, 2021. Disponível em: <https://revista-fi.com.br/artigos/acidulantes/acidulantes>. Acesso em 23 de Novembro de 2020.

FREIRE, J. M.; ABREU, C. M. P.; ROCHA, D. A.; CORRÊA, A. D.; MARQUES, N. R. Quantificação de compostos fenólicos e ácido ascórbico em frutos e polpas congeladas de acerola, caju, goiaba e morango. **Ciência Rural**, v. 43, n. 12, p. 2291-2296, 2013.

FRIEDMAN, M.; JÜRGENS, H. S. Effect of pH on the Stability of Plant Phenolic Compounds. **Journal of Agricultural and Food Chemistry**, v. 48, n. 6, p. 2101–2110, 2000.

GARCIA, T. Analysis of gelatin-based confections. **The Manufacturing Confectioner**, v. 80, n. 6, p. 93-101, 2000.

GONÇALVES, G. A. S.; RESENDE, N. S.; CARVALHO, E. E. N.; DE RESENDE, J. V.; VILAS BOAS, E. V. DE B. Physicochemical and volatile profile alterations in pasteurized and frozen strawberry pulp during storage**. Journal of Food Processing and Preservation**, v. 42, n. 1, e13317, 2017.

GOREN, A.; ASHLOCK, D.; TETLOW, I. J. Starch formation inside plastids of higher plants. **Protoplasma**, v. 255, n. 6, p. 1855–1876, 2018.

GUO, J.; KALETUNÇ, G. Dissolution kinetics of pH responsive alginate-pectin hydrogel particles. **Food Research International**, v. 88, p. 129–139, 2016.

GÜZEL, M.; TEKTAŞ TAŞAN, N.; AKPINAR, Ö. Alternative pectin production methods and sources. **AGROFOR International Journal**, v. 5, n. 1, p. 38-45, 2020.

HABILLA, C.; CHENG, L. H. Quality of jelly candy made of acid-thinned starch added with different non-starch polysaccharides. **Journal of Food Research and Technology**, v. 3, p. 14-22, 2015.

HADLEY, S. W.; SHORT, W. Electricity sector analysis in the clean energy futures study. **Energy Policy**, v. 29, n. 14, p. 1285–1298, 2001.

HARTEL, R. W. Hard Candy: from Hard Crack to the Glass Transition. **The Manufacturing Confectioner**, v. 92, n. 9, p. 70-80, 2012.

HARTEL, R. W.; ERGUN, R.; VOGEL, S. Phase/State Transitions of Confectionery Sweeteners: Thermodynamic and Kinetic Aspects. **Comprehensive Reviews in Food Science and Food Safety**, v. 10, n. 1, p. 17–32, 2010.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018, 542 p.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. Hard Candy. In: HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018a, p. 211-244.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. Aerated confections. In: HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018b, p. 301-328.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. Jellies, Gummies and Licorice. In: HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018c, p. 329-360.

HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. Starches, Proteins, Pectin, and Gums. In: HARTEL, R. W.; ELBE, J H. V.; HOFBERGER, R. **Confectionery Science and Technology**. Berlin: Springer International Publishing, 2018d, p. 125-150.

HARTIKAINEN, H.; ROININEN, T.; KATAJAJUURI, J.-M.; PULKKINEN, H. Finnish consumer perceptions of carbon footprints and carbon labelling of food products. **Journal of Cleaner Production**, v. 73, p. 285–293, 2014.

HELGERUD, T.; GÅSERØD, O.; FJÆREIDE, T.; ANDERSEN, P. O.; LARSEN, C. K. Alginates. In: IMESON, A. (Ed.). **Food Stabilisers, Thickeners and Gelling Agents.** Blackwell Publishing, 2010, p. 50-72.

IMESON, A. **Food Stabilisers, Thickeners and Gelling Agents**. Oxford: Blackwell Publishing Ltd, 2010, 352 p.

ISO 14021. **Environmental labels and declarations Self-declared environmental claims (Type II environmental labelling)**, 2012. Disponível em: http://www.iso.org/iso/catalogue_detail?csnumber=23146. Acesso em 03 de Abril de 2020.

JOU, C.-J. G.; WU, C.-R.; LEE, C.-L. Reduction of energy cost and CO_2 emission for the furnace using energy recovered from waste tail-gas. *Energy*, v. 35, n. 3, p. 1232–1236, 2010.

KAENZIG, J.; WÜSTENHAGEN, R. The Effect of Life Cycle Cost Information on Consumer Investment Decisions Regarding Eco-Innovation. **Journal of Industrial Ecology**, v. 14, n. 1, p. 121–136, 2009.

KARAKASYAN, C.; LEGROS, M.; LACK, S.; BRUNEL, F.; MAINGAULT, P.; DUCOURET, G.; HOURDET, D. Cold Gelation of Alginates Induced by Monovalent Cations. **Biomacromolecules**, v. 11, n. 11, p. 2966–2975, 2010.

KUSUMANINGRUM, A.; PARNANTO, N. H. R.; ATMAKA, W. Study of the effects of carrageenan-konjac variation concentrations as gelling agent on the physical, chemical and sensory characteristics of yellow pumpkins (*Cucurbita maxima*) jelly candy. **Jurnal Teknosains Pangan**, v. 1, p. 1-11, 2016.

LAOS, K.; KIRS, E.; PALL, R.; MARTVERK, K. The Crystallization Behaviour of Estonian Honeys. **Agronomy Research**, v. 9, Edição Especial II, p. 427–432, 2011.

LAVOISIER, A.; AGUILERA, J. M. Starch gelatinization inside a whey protein gel formed by cold gelation. **Journal of Food Engineering**, v. 256, p. 18-27, 2019.

LEACH, A. M.; EMERY, K. A.; GEPHART, J.; DAVIS, K. F.; ERISMAN, J. W.; LEIP, A.; PACE, M. L.; D´ODORICO, P.; CARR, J.; NOLL, L. C.; CASTNER, E.; GALLOWAY, J. N. Environmental impact food labels combining carbon, nitrogen, and water footprints. **Food Policy**, v. 61, p. 213–223, 2016.

LEAHU A.; DAMIAN, C.; OROIAN, M.; ROPCIUC, S. Physico-chemical parameters of fruit juices-evolution during storage. **Lucrări Ştiinţifice-Seria Zootehnie**, v. 59, p. 213-217, 2013.

LEIRE, C., THIDELL, Å. Product-related environmental information to guide consumer purchases – a review and analysis of research on perceptions, understanding and use among Nordic consumers. **Journal of Cleaner Production**, v. 13, n. 10-11, p. 1061–1070, 2005.

LI, J.; HE, J.; HUANG, Y. Role of alginate in antibacterial finishing of textiles. **International Journal of Biological Macromolecules**, v. 94, p. 466–473, 2017.

LÖFGREN, C.; WALKENSTRÖM, P.; HERMANSSON, A. M. (2002). Microstructure and Rheological Behavior of Pure and Mixed Pectin Gels. **Biomacromolecules**, v. 3, n. 6, p. 1144–1153, 2002.

MARFIL, P. H. M.; ANHÊ, A. C. B. M.; TELIS, V. R. N. Texture and Microstructure of Gelatin/Corn Starch-Based Gummy Confections. **Food Biophysics**, v. 7, n. 3, p. 236–243, 2012.

MATTHIENSEN, A. **Uso do Coeficiente Alfa de Cronbach em Avaliações por Questionários**, 2011. Disponível em: <https://www.infoteca.cnptia.embrapa.br/bitstream/doc/936813/1/DOC482011ID112.pdf>. Acesso em 07 de Abril de 2020.

MCTIC. MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E INOVAÇÕES. **Método de Análise de Despacho**, 2018. Disponível em: <https://www.mctic.gov.br/mctic/opencms/ciencia/SEPED/clima/textogeral/emissao_despacho.html>. Acesso em 07 de Abril de 2020.

MCTIC. MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E INOVAÇÕES**. Estimativas Anuais de Emissões de Gases de Efeito Estufa no Brasil**, 2014. Disponível em: <http://sirene.mctic.gov.br/portal/export/sites/sirene/backend/galeria/arquivos/2018/10/11/Estimativas_2ed.pdf>. Acesso em 07 de Abril de 2020.

MIAH, J. **From factory to supply chain: reducing environmental impacts of confectionery manufacturing using heat integration and life cycle assessment.** Guildford: University of Surrey, 2018, 320 p.

MINISTÉRIO DA SAÚDE. **Guia Alimentar para a população brasileira**, 2014. Disponível em: <https://bvsms.saude.gov.br/bvs/publicacoes/guia_alimentar_populacao_brasileira_2ed.pdf>. Acesso em 23 de Novembro de 2020.

MINOLTA, K. **Precise Color Communication: Color Control from Perception to Instrumentation.** Japan: Konica Minolta Inc., 1998, Chapters 1, 4.

MOHAMMADIAN, M.; MADADLOU, A. Cold-set hydrogels made of whey protein nanofibrils with different divalent cations. **International Journal of Biological Macromolecules**, v. 89, p. 499–506, 2016.

MONGIA, G. Fruit ingredients in confectionery applications. **The Manufacturing Confectioner**, n. 94, v. 8, p. 73-82, 2014.

MONTENEGRO, F. M.; LUCCAS, V. Os setores bakery & confectionery. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 18–31.

MOORE, C. O. Starch jelly candy. **The Manufacturing Confectioner**, v. 87, n. 10, p. 79-85, 2007.

MORRIS, V. J. & CHILVERS, G. R. Cold Setting Alginate-pectin Mixed Gels. **Journal of the Science of Food and Agriculture**, v. 35, n. 12, p. 1370-1376, 1984.

MOSER, P.; TELIS, V. R. N.; DE ANDRADE NEVES, N.; GARCÍA-ROMERO, E.; GÓMEZ-ALONSO, S.; HERMOSÍN-GUTIÉRREZ, I. Storage stability of phenolic compounds in powdered BRS Violeta grape juice microencapsulated with protein and maltodextrin blends. **Food Chemistry**, v. 214, p. 308–318, 2017.

MUTLU, C., TONTUL, S. A., ERBAS, M. Production of a minimally processed jelly candy for children using honey instead of sugar. **LWT - Food Science and Technology**, v. 93, p. 499–505, 2018.

NAIDU, K. A. Vitamin C in human health and disease is still a mystery? An overview. **Nutrition Journal**, v. 2, n. 7, 2003.

NILSSON, K.; SUND, V.; FLOREN, B. **The environmental impact of the consumption of sweets, crisps and soft drinks.** Copenhagen: Nordic Council of Ministers, 2011, 57 p.

NOCELLA, G.; KENNEDY, O. Food health claims – What consumers understand. **Food Policy**, v. 37, n. 5, p. 571–580, 2012.

ONAT, N.; BAYAR, H. The sustainability indicators of power production systems. **Renewable and Sustainable Energy Reviews**, v. 14, n. 9, p. 3108–3115, 2010.

OTÁLORA, M. C.; DE JESÚS BARBOSA, H.; PERILLA, J. E.; OSORIO, C.; NAZARENO, M. A. Encapsulated betalains (*Opuntia ficus-indica*) as natural colorants. Case study: Gummy candies. **LWT - Food Science and Technology**, v. 103, p. 222-227, 2018.

PATRAS, A.; BRUNTON, N. P.; O'DONNELL, C.; TIWARI, B. K. Effect of thermal processing on anthocyanin stability in foods; mechanisms and kinetics of degradation. **Trends in Food Science & Technology**, v. 21, n. 1, p. 3–11, 2010.

PATTARA, C.; RUSSO, C.; ANTRODICCHIA, V.; CICHELLI, A. Carbon footprint as an instrument for enhancing food quality: overview of the wine, olive oil and cereals sectors. **Journal of the Science of Food and Agriculture**, v. 97, n. 2, p. 396–410, 2016.

PELEGRINE, D. H.; SILVA, F. C.; GASPARETTO, C. A. Rheological Behavior of Pineapple and Mango Pulps. **LWT - Food Science and Technology**, v. 35, n. 8, p. 645–648, 2002.

PÉREZ-JIMÉNEZ, J.; NEVEU, V.; VOS, F.; SCALBERT, A. Identification of the 100 richest dietary sources of polyphenols: an application of the Phenol-Explorer database. **European Journal of Clinical Nutrition**, v. 64, p. S112–S120, 2010.

PETROBRÁS. **Gás Liquefeito de Petróleo**, 2013. Disponível em: <http://sites.petrobras.com.br/minisite/assistenciatecnica/public/downloads/manual-tecnico-gas-liquefeito-petrobras-assistencia-tecnica-petrobras.pdf>. Acesso em 07 de Abril de 2020.

PIVARO, J. **Chocolates e Confeitos – Doces Indulgências**, 2019. Disponível em: <http://www.revistait.com.br/download/edicoes/IT-44-final-site.pdf/>. Acesso em 11 de outubro de 2020.

QUEIROZ, G. C. Sustentabilidade e Transparência. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 232-257.

QUEIROZ, M. B., & NABESHIMA, E. H. Naturalidade e Autenticidade. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 159–195.

QUEIROZ, G. C. et al. As macrotendências dos setores de *bakery & confectionery*. In: QUEIROZ, G. C.; REGO, R. A.; JARDIM, D. C. P. (Eds.). **Brasil Bakery & Confectionery Trends 2020**. Campinas: ITAL, 2014, p. 59-72.

RAN, T.; YUE, C.; RIHN, A. Does Nutrition Information Contribute to Grocery Shoppers' Willingness to Pay? **Journal of Food Products Marketing**, v. 23, n. 5, p. 591–608, 2016.

REIN, M. **Copigmentation reactions and color stability of berry anthocyanins.** Helsinki: University of Helsinki, 2005, p. 10-14.

SAHA, D.; BHATTACHARYA, S. Hydrocolloids as thickening and gelling agents in food: a critical review. **Journal of Food Science and Technology**, v. 47, n. 6, p. 587–597, 2010.

SANDULACHI, E. **Water activity concept and its role in food preservation**, 2012. Disponível em: <http://www.utm.md/meridian/2012/MI_4_2012/8_Art_Sandulachi_E_Water.pdf>. Acesso em 23 de Novembro de 2020.

SHARMA, B. R., NARESH, L., DHULDHOYA, N. C., MERCHANT, S. U., MERCHANT, U. C. An overview on pectins. **Times Food Processing Journal**, v. 23, n. 2, p. 44-51, 2006.

SHELDRAKE, P. Starch In: IMESON, A. (Ed.). **Food Stabilisers, Thickeners and Gelling Agents**. Blackwell Publishing, 2010, p. 293-324.

SIEW, C. K.; WILLIAMS, P. A.; YOUNG, N. W. G. New Insights into the Mechanism of Gelation of Alginate and Pectin: Charge Annihilation and Reversal Mechanism. **Biomacromolecules**, v. 6, n. 2, p. 963–969, 2005.

SILVA, L. B. **Effect of the use of polyols and açai (*Euterpe oleracea Mart.*) on the physicochemical, sensory and technological characteristics of chewy candies.** Campinas: Unicamp, 2017, 181 p.

SILVA, A. R. A.; BIOTO, A. S.; EFRAIM, P.; QUEIROZ, G. C. Impact of sustainability labeling in the perception of sensory quality and purchase intention of chocolate consumers. **Journal of Cleaner Production**, v. 141, p. 11–21, 2017.

SILVA, L. B.; QUEIROZ, M. B.; FADINI, A. L.; FONSECA, R. C. C; GERMER, S. P. M.; et al. Chewy candy as a model system to study the influence of polyols and fruit pulp (Açai) on texture and sensorial properties. **LWT–Food Science and Technology**, v. 65, p. 268–274, 2016.

SINGLETON, V. L.; OTHOFER, R.; LAMUELA-RAVENTOS, R. M. Analysis of total phenols and others oxidation substrates and antioxidants by folin-ciocauteau reagent. **Methods in Enzimology**, v. 299, p. 152-178, 1999.

SØLTOFT-JENSEN, J.; HANSEN, F. New Chemical and Biochemical Hurdles. In: SUN, D. W. (Ed.) **Emerging Technologies for Food Processing**. London: Elsevier, 2005, p. 387-416.

SOKOLOVSKA, I.; KAMBULOVA, J.; OVERCHUK, N. Study of the water binding in the gel systems of pectin and sodium alginate. **Eastern-European Journal of Enterprise Technologies**, v. 2, n. 11, p. 4-11, 2016.

STEVENS, P. Gelatine. In: IMESON, A. (Ed.). **Food Stabilisers, Thickeners and Gelling Agents**. Blackwell Publishing, 2010, p. 116-144.

STONE, H.; SIDEL, J. L. **Sensory Evaluation Practices.** 3rd ed. Amsterdam: Elsevier, 2004, 377 p.

SUFFERLING, K. Gelatin gummies and pectin jellies. **The Manufacturing Confectioner**, v. 87, n. 8, p. 43-50, 2007.

SUBRAMANIAM, P. The Stability and Shelf Life of Confectionery Products. In: SUBRAMANIAM, P. **The Stability and Shelf Life of Food.** Woodhead Publishing, 2016, p. 545–573.

TOFT, K. Gel Formation in Alginate-Pectin Systems Using Slow Acidifier. **European Science Fundation Workshop on Specific Interactions in Polysaccharide Systems.** Uppsala, Sweden, 1983, 26-27.

TOFT, K.; GRASDALEN, H.; SMIDSRØD, O. Synergistic Gelation of Alginates and Pectins. In: FISHMAN, M. L., JE, J. J. **Chemistry and Function of Pectins.** Washington: American Chemical Society, 1986, p. 117-132.

TONUTARE, T.; MOOR, U. L.; SZAJDAK, L. Strawberry anthocyanin determination by pH differential spectroscopic method – how to get true results? **Acta Scientiarum Polonorum Hortorum Cultus**, v. 13, n. 3, p. 35-47, 2014.

TRESSERRA-RIMBAU, A.; MEDINA-REMÓN, A.; PÉREZ-JIMÉNEZ, J.; MARTÍNEZ-GONZÁLEZ, M. A.; COVAS, M. I.; CORELLA, D.; SALAS-SALVADÓ, J.; GÓMEZ-GRACIA, E.; LAPETRA, J.; ARÓS, F.; FIOL, M.; ROS, E.; SERRA-MAJEM, L.; PINTÓ, X.; MUÑOZ, M. A.; SAEZ, G. T.; RUIZ-GUTIÉRREZ, V.; WARNBERG, J.; ESTRUCH, R.; LAMUELA-RAVENTÓS, R. M. Dietary intake and major food sources of polyphenols in a Spanish population at high cardiovascular risk: the PREDIMED study. *Nutrition, Metabolism and Cardiovascular Diseases*, v. 23, n. 10, p. 953-959, 2013.

TSAI, P. J.; HSIEH, Y. Y.; HUANG, T. C. Effect of Sugar on Anthocyanin Degradation and Water Mobility in a Roselle Anthocyanin Model System Using17O NMR. **Journal of Agricultural and Food Chemistry**, v. 52, n. 10, p. 3097–3099, 2004.

TULIPANI, S.; MEZZETTI, B.; CAPOCASA, F.; BOMPADRE, S.; BEEKWILDER, J. et al. Antioxidants, Phenolic Compounds, and Nutritional Quality of Different Strawberry Genotypes. **Journal of Agricultural and Food Chemistry**, v. 56, n. 3, p. 696–704, 2008.

UDDIN, M.; HAWLADER, M. N.; DING, L.; MUJUMDAR, A. Degradation of ascorbic acid in dried guava during storage. **Journal of Food Engineering**, v. 51, n. 1, p. 21–26, 2002.

USDA. **Sugar and sweeteners yearbook tables**, 2020. Disponível em: <https://www.ers.usda.gov/data-products/sugar-and-sweeteners-yearbook-tables/>. Acesso em 20 de Agosto de 2020.

VASLIAUSKAS, R. **Sodium Alginate and applications: a review**, 2020. Disponível em: <https://www.elveflow.com/microfluidic-reviews/droplet-digital-microfluidics/sodium-alginate-and-applications-a-review>. Acesso em 31 de Dezembro de 2020.

VERMEIR, I., VERBEKE, W. Sustainable Food Consumption: Exploring the Consumer "Attitude – Behavioral Intention" Gap. **Journal of Agricultural and Environmental Ethics,** v. 19, n. 2, p. 169–194, 2006.

VOLF, I.; IGNAT, I.; NEAMTU, M.; POPA, V. Thermal stability, antioxidant activity, and photo-oxidation of natural polyphenols. **Chemical Papers**, v. 68, n. 1, p. 1-9, 2014.

WALKENSTRÖM, P.; KIDMAN, S.; HERMANSSON, A. M.; RASMUSSEN, P. B.; HOEGH, L. Microstructure and rheological behaviour of alginate/pectin mixed gels. **Food Hydrocolloids**, v. 17, n. 5, p. 593–603, 2003.

WOJDALSKI, J.; GROCHOWICZ, J.; DRÓŻDŻ, B.; BARTOSZEWSKA, K.; ZDANOWSKA, P.; KUPCZYK, A.; EKIELSKI, A.; FLORCZAK, I.; HASNY, A.; WÓJCIK, G. Energy efficiency of a confectionery plant – Case study. **Journal of Food Engineering**, v. 146, p. 182–191, 2015.

XAVIER, N. M.; RAUTER, A. P.; QUENEAU, Y. Carbohydrate-Based Lactones: Synthesis and Applications. In: RAUTER A.; VOGEL P.; QUENEAU Y. **Carbohydrates in Sustainable Development II. Topics in Current Chemistry vol 295**. Berlin: Springer, 2010, p. 19-62.

ZHOU, S.; JIN, T.; SHEEN, S.; ZHAO, G.; LIU, L.; JUNEJA, V.; YAM, K. Development of sodium chlorite and glucono delta-lactone incorporated PLA film for microbial inactivation on fresh tomato. **Food Research International**, 109067, 2020.

ANEXO I – REGISTROS FOTOGRÁFICOS DAS BALAS PRODUZIDAS NA TESE

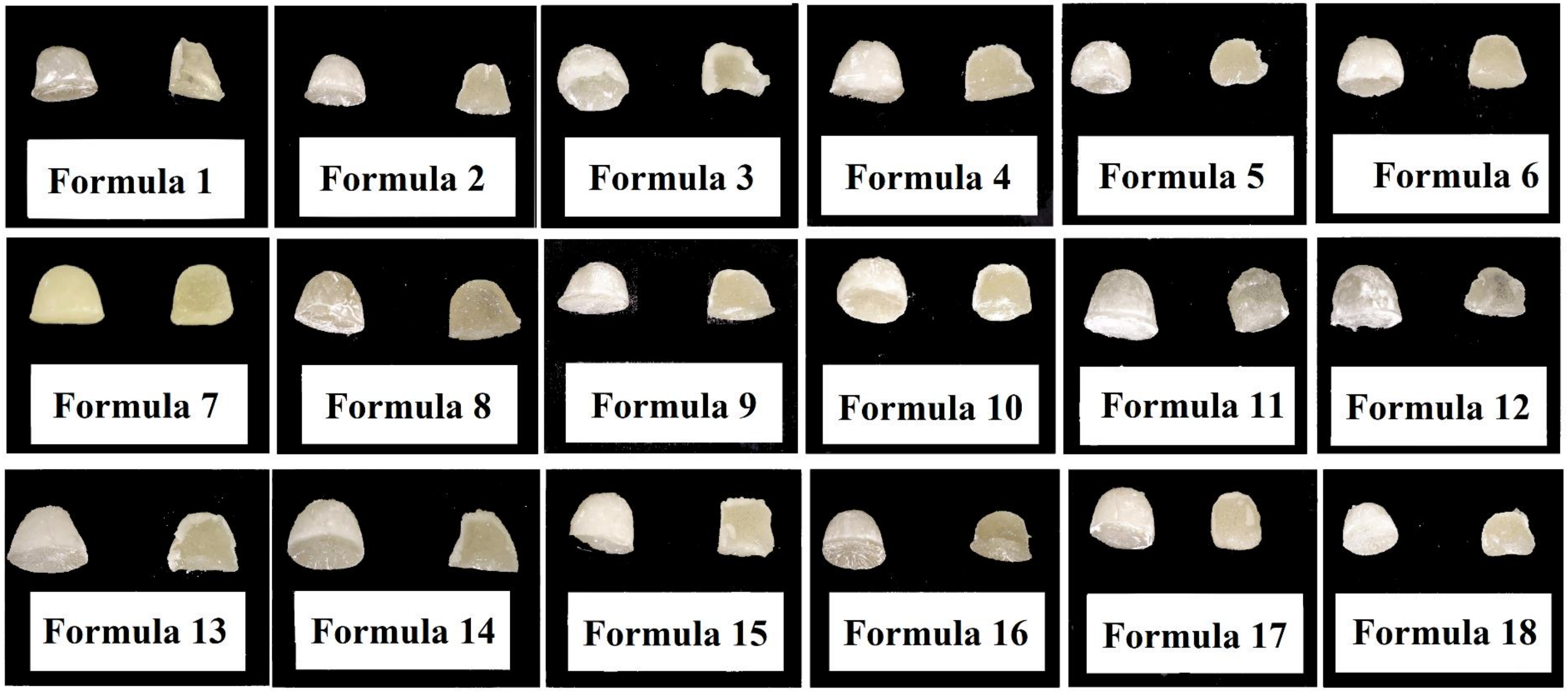

Figura 1. Balas de goma da proposta experimental do Capítulo 2. *Alginate/Pectin cold-set gelation as a potential sustainable method for jelly candy production.*

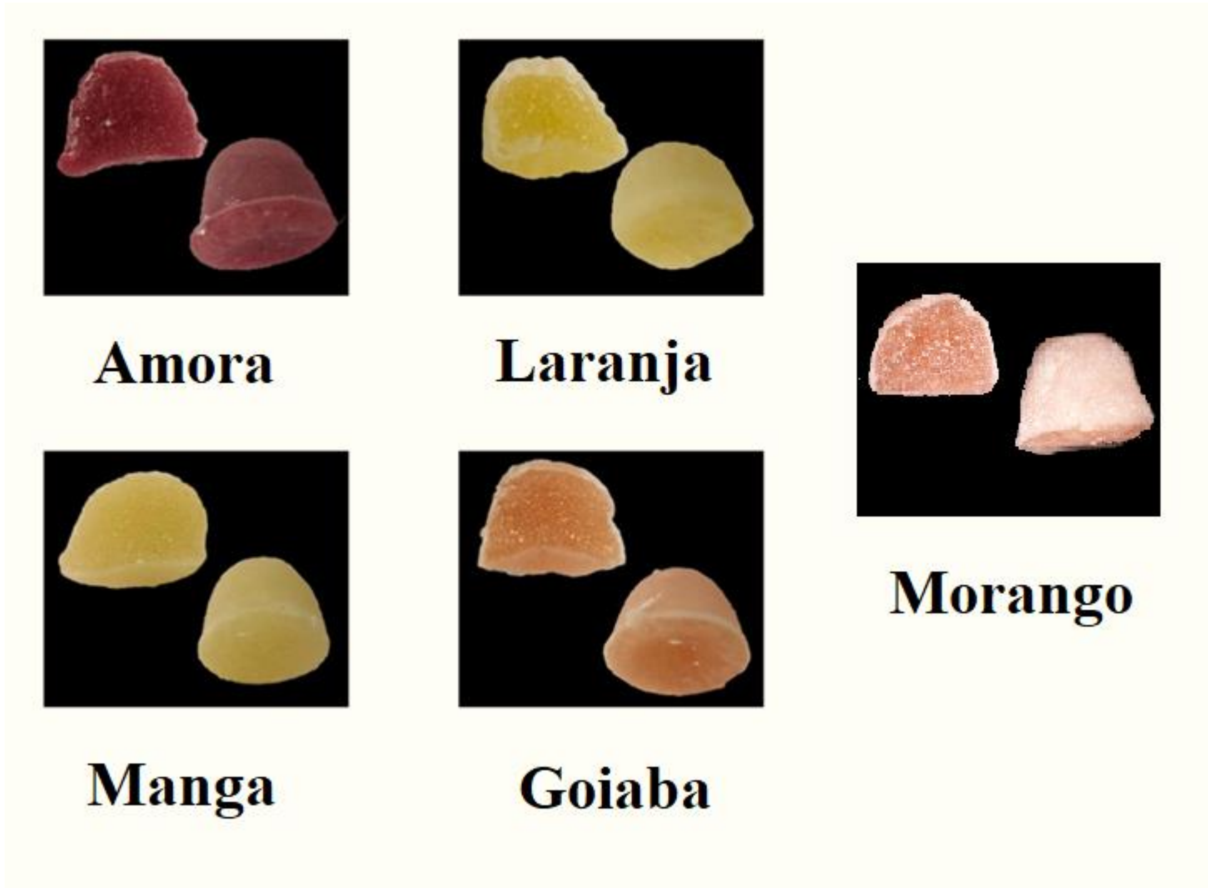

Figura 2. Balas de goma produzidas com polpa de fruta conforme proposta experimental do Capítulo 3. *Maintenance of Fruit Bioactive Compounds in Jelly Candy Manufacturing by Alginate/Pectin Cold-Set Gelation.*

ANEXO II – ESTUDOS COMPLEMENTARES À TESE

Após a conclusão dos capítulos desta tese foram realizados estudos complementares de reformulação das balas de goma produzidas por gelificação a frio de misturas de alginato de sódio com alto teor de ácido gulurônico e pectina com alto teor de metoxilação. Estes estudos tiveram como objetivo promover melhorias na estabilidade e nas características de textura das balas. Os resultados obtidos nesses experimentos foram significativos e bastante promissores, sendo apresentados neste anexo com o intuito de fornecer melhor embasamento científico para a comunidade acadêmica e auxiliar possíveis trabalhos futuros.

1. Testes de acidificação

Nesta tese as balas de goma obtidas por gelificação a frio apresentaram médias de pH com elevado desvio padrão, o que sugere que a aplicação direta do GDL em pó na calda pode contribuir para uma acidificação não homogênea, resultando em variabilidade de pH entre as amostras. Diante disso, foi proposta a realização de estudos comparativos de acidificação da calda da bala com o objetivo de avaliar o efeito que diferentes formas de acidificação podem exercer sobre a qualidade dos géis obtidos. Uma calda de bala de goma de alginato e pectina foi produzida e dividida em duas amostras que foram acidificadas com a mesma quantidade de GDL (1%), porém, adicionado em diferentes formas. Na primeira amostra a acidificação foi feita por meio da adição direta de GDL em pó enquanto na segunda a acidificação foi feita pela adição de uma solução aquosa de GDL 50% previamente preparada. Foi verificada a ocorrência de uma acidificação mais homogênea quando promovida a dissolução prévia do GDL, de modo que as amostras de balas apresentaram médias de pH com menor desvio padrão. Os géis obtidos também apresentaram uma textura mais firme e gomosa do que a de géis acidificados com GDL em pó. A promoção da acidificação com a solução de GDL não implicou em alterações significativas na velocidade de gelificação das caldas, conferindo ainda tempo hábil para a formatação das balas.

2. Balanço de sólidos açucarados cristalizantes e anticristalizantes

As formulações de balas desenvolvidas nesta tese foram ajustadas em relação ao teor de sólidos açucarados cristalizantes e anticristalizantes. Balas produzidas com relação de açúcares de 0,45: 0,55 de sacarose: xarope de glicose, em base seca, foram avaliadas durante dois meses de armazenamento em B.O.D. a 25 °C. Neste período os produtos apresentaram melhor estabilidade em relação às balas avaliadas na tese, sem ocorrência de cristalização de sacarose durante o tempo acompanhado.

3. Inclusão de polpas de frutas

Apesar dos resultados promissores obtidos com as cinco polpas de frutas testadas nesta tese, a produção de balas de goma a frio com polpa de framboesa (sugerida nos estudos posteriores à conclusão da tese) não foi bem sucedida. As análises de caracterização físico-química da polpa indicaram que o pH da framboesa se localizou abaixo de 3,3-4,0, faixa indicada para a gelificação mista de alginato de sódio e pectina HM (GUO & KALETUNÇ, 2016). Estes resultados indicam que estudos complementares de gelificação a frio em sistemas com inclusão de polpas de fruta com alevada acidez ainda se fazem necessários. Para estas frutas sugere-se que a adição de sais tampão e/ou o tratamento prévio das caldas por eletrodiálise possam contribuir para a adequação do pH da calda e consumação do processo de formação do gel da bala.

4. Especificações dos hidrocoloides

A literatura descreve que géis de alginato/pectina com máxima firmeza são obtidos quando produzidos com alginatos de sódio com 70% de ácido α-L-gulurônico e pectinas HM com grau de esterificação (DE) de 70% (TOFT et al., 1986). No entanto, em toda a tese foram utilizados alginato de sódio com 60% de ácido α-L-gulurônico (Algin I-3G-150, viscosidade 300 – 400 mPa·s, Kimica, Providencia, Chile) e pectina HM do tipo slow set, com grau de esterificação de 58% (HM 121 Slow, CPKelco, Limeira, Brasil). Devida diferença entre as especificações dos hidrocoloides utilizados na tese e dos indicados pela literatura, foi proposta a realização de testes com diferentes hidrocoloides para averiguar seu efeito sobre as características dos géis obtidos. Uma formulação de bala foi utilizada para a produção de todas as amostras, sendo a única fonte de variação a especificação dos hidrocoloides utilizados. Os resultados obtidos indicaram que o aumento do DE da pectina (de 58% para 70%) e do teor de ácido gulurônico do alginato de sódio (de 60% para 70%) não contribui para a melhoria da textura dos géis das balas. Também foi verificado que o uso de pectinas tamponadas compromete o processo de gelificação a frio de alginato e pectina devida a incompatibilidade entre a ação tamponante dos sais e o mecanismo de acidificação lenta do GDL. Além disso foi identificado que agentes gelificantes de diferentes marcas, porém com as mesmas especificações químicas, podem implicar na obtenção de géis com diferentes características físicas. O uso da pectina HM tipo “slow set”, com grau de esterificação de 58% da empresa Cargill® (ESS 150 C SB, Cargill, Brasil) permitiu a obtenção de balas duas vezes mais firmes, gomosas e mastigáveis em relação às balas produzidas com a pectina da CpKelco® utilizada nesta tese.

5. Tempo de hidratação dos hidrocoloides

Nos testes complementares de reformulação das balas de goma além dos ajustes realizados na etapa de acidificação foram também feitas adequações na etapa de adição dos hidrocolóides. Nos testes realizados foi verificado que após a completa dispersão do alginato de sódio e da pectina HM é recomendado um período de agitação de 5-10 minutos antes de se prosseguir com a etapa de acidificação. Este intervalo sugerido auxilia em uma melhor hidratação dos hidrocoloides e na melhor ativação de sua capacidade gelificante. As caldas de bala após o período sugerido apresentam viscosidade mais acentuada em relação à calda logo após a adição dos agentes gelificadas, comprovando a ocorrência da ativação dos hidrocoloides aqui indicado. No processo de fabricação de balas de goma a frio a aplicação da mistura polimérica é feita após o preparo de uma calda de açúcares com alto teor de sólidos solúveis. O baixo conteúdo de umidade da calda associado à alta afinidade que os hidrocoloides e os açúcares têm pelas moléculas de água faz com que haja uma certa “competitividade” pela água disponível no sistema, o que compromete a correta e total hidratação dos agentes gelificantes. Neste contexto, presume-se que o teor de hidrocoloide empregado para obtenção de balas de gomas sugerido nesta tese possa ser superestimado, no sentido de que caso a mistura polimérica pudesse ser melhor hidratada, uma menor quantidade seria necessária para promover a gelificação. Aumentar o conteúdo de umidade das caldas das balas no entanto reflete em maiores tempos de secagem, iniviabilizando a fabricação de balas pelo processo de gelificação a frio.

ANEXO III - PERMISSÃO PARA INCLUSÃO DO ARTIGO PUBLICADO NA REVISTA LWT – FOOD SCIENCE AND TECHNOLOGY NA TESE

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Food Processing and Technology Journal Office

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ANEXO VI - APROVAÇÃO DO COMITÊ DE ÉTICA EM PESQUISA – UNICAMP

UNICAMP - CAMPUS CAMPINAS

PARECER CONSUBSTANCIADO DO CEP

DADOS DA EMENDA

Título da Pesquisa: Gelificação a frio de alginato e pectina para a produção de balas de goma
Pesquisador: Matheus Henrique Mariz de Avelar
Área Temática:
Versão: 2
CAAE: 86627118.5.0000.5404
Instituição Proponente: Faculdade de Engenharia de Alimentos
Patrocinador Principal: Financiamento Próprio

DADOS DO PARECER

Número do Parecer: 3.845.618

Apresentação do Projeto:
Trata-se de uma emenda que visa solicitar a aplicação de um questionário com perguntas sobre a frequência e o consumo de balas dos participantes voluntários da pesquisa durante o procedimento de análise sensorial e a realização de um teste de aceitação sensorial em que as amostras de balas serão identificadas com informações sobre seu método de produção e sobre a sua composição em relação ao teor de compostos bioativos e atividade antioxidante, a fim de se realizar um estudo de influência de informação na aceitabilidade dos produtos desenvolvidos.

Objetivo da Pesquisa:
Mantidos em relação ao projeto original.

Avaliação dos Riscos e Benefícios:
Mantidos em relação ao projeto original.

Comentários e Considerações sobre a Pesquisa:
De acordo com as informações do pesquisador responsável contempladas no documento anexado "PB_INFORMAÇÕES_BÁSICAS_1495709_E1.pdf 05/02/2020 11:27:52":"A Emenda solicitada se refere à dois pontos principais acrescidos no projeto anteriormente aprovado: 1) A proposta de aplicação de um questionário com perguntas sobre a frequência e o consumo de balas dos participantes voluntários da pesquisa durante o procedimento de análise sensorial (item 4.4 - Análise Sensorial); 2) A proposta de realização de um teste de aceitação sensorial em que as amostras de balas serão identificadas com informações sobre seu método de produção e sobre a

sua composição em relação ao teor de compostos bioativos e atividade antioxidante, a fim de se realizar um estudo de influência de informação na aceitabilidade dos produtos desenvolvidos (item 4.6.3 - Estudo do efeito de influência de informações dos processos produtivos na aceitabilidade sensorial das balas); A solicitação da emenda se justifica pela necessidade de coleta de mais informações sobre o comportamento do consumidor de balas, por meio do preenchimento do questionário proposto, assim como pela possibilidade de aquisição de mais dados referentes às possíveis influências de aspectos não sensoriais sobre a aceitabilidade das balas. As metodologias propostas na emenda podem, desse modo, contribuir para a obtenção de dados que permitem uma melhor avaliação dos processos desenvolvidos no projeto de pesquisa. "

Considerações sobre os Termos de apresentação obrigatória:

Na avaliação desta emenda foram analisados os seguintes documentos anexados:

1-PB_INFORMAÇÕES_BÁSICAS_1495709_E1.pdf 05/02/2020 11:27:52;

2-TCLE.pdf 05/02/2020 11:24:14;

3-Projeto.pdf 05/02/2020 11:23:55

Conclusões ou Pendências e Lista de Inadequações:

Emenda aprovada.

Considerações Finais a critério do CEP:

- O participante da pesquisa deve receber uma via do Termo de Consentimento Livre e Esclarecido, na íntegra, por ele assinado (quando aplicável).

- O participante da pesquisa tem a liberdade de recusar-se a participar ou de retirar seu consentimento em qualquer fase da pesquisa, sem penalização alguma e sem prejuízo ao seu cuidado (quando aplicável).

- O pesquisador deve desenvolver a pesquisa conforme delineada no protocolo aprovado. Se o pesquisador considerar a descontinuação do estudo, esta deve ser justificada e somente ser realizada após análise das razões da descontinuidade pelo CEP que o aprovou. O pesquisador deve aguardar o parecer do CEP quanto à descontinuação, exceto quando perceber risco ou dano não previsto ao participante ou quando constatar a superioridade de uma estratégia diagnóstica ou terapêutica oferecida a um dos grupos da pesquisa, isto é, somente em caso de necessidade de ação imediata com intuito de proteger os participantes.

- O CEP deve ser informado de todos os efeitos adversos ou fatos relevantes que alterem o curso normal do estudo. É papel do pesquisador assegurar medidas imediatas adequadas frente a evento adverso grave ocorrido (mesmo que tenha sido em outro centro) e enviar notificação ao CEP e à Agência Nacional de Vigilância Sanitária – ANVISA – junto com seu posicionamento.

- Eventuais modificações ou emendas ao protocolo devem ser apresentadas ao CEP de forma clara e sucinta, identificando a parte do protocolo a ser modificada e suas justificativas e aguardando a aprovação do CEP para continuidade da pesquisa. Em caso de projetos do Grupo I ou II apresentados anteriormente à ANVISA, o pesquisador ou patrocinador deve enviá-las também à mesma, junto com o parecer aprovatório do CEP, para serem juntadas ao protocolo inicial.

- Relatórios parciais e final devem ser apresentados ao CEP, inicialmente seis meses após a data deste parecer de aprovação e ao término do estudo.

-Lembramos que segundo a Resolução 466/2012 , item XI.2 letra e, “cabe ao pesquisador apresentar dados solicitados pelo CEP ou pela CONEP a qualquer momento”.

-O pesquisador deve manter os dados da pesquisa em arquivo, físico ou digital, sob sua guarda e responsabilidade, por um período de 5 anos após o término da pesquisa.

Este parecer foi elaborado baseado nos documentos abaixo relacionados:

Tipo Documento	Arquivo	Postagem	Autor	Situação
Informações Básicas do Projeto	PB_INFORMAÇÕES_BÁSICAS_1495709_E1.pdf	05/02/2020 11:27:52		Aceito
TCLE / Termos de Assentimento / Justificativa de Ausência	TCLE.pdf	05/02/2020 11:24:14	Matheus Henrique Mariz de Avelar	Aceito
Projeto Detalhado / Brochura Investigador	Projeto.pdf	05/02/2020 11:23:55	Matheus Henrique Mariz de Avelar	Aceito
Outros	AtestadoMatricula.pdf	21/03/2018 22:04:36	Matheus Henrique Mariz de Avelar	Aceito

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Folha de Rosto	Folha_de_Rosto.pdf	22/02/2018 18:08:37	Matheus Henrique Mariz de Avelar	Aceito

Situação do Parecer:
Aprovado

Necessita Apreciação da CONEP:
Não

CAMPINAS, 18 de Fevereiro de 2020

Assinado por:
Renata Maria dos Santos Celeghini
(Coordenador(a))

Endereço: Rua Tessália Vieira de Camargo, 126
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ANEXO VII – FOLHA DE ROSTO DA PATENTE DE PRIVILÉGIO DE INOVAÇÃO

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(21) BR 102018076817-4 A2

(22) Data do Depósito: 20/12/2018

(43) Data da Publicação Nacional: 07/07/2020

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(54) Título: PROCESSO DE OBTENÇÃO DE BALAS DE GOMA

(51) Int. Cl.: A23G 4/10.

(52) CPC: A23G 4/10.

(71) Depositante(es): UNIVERSIDADE ESTADUAL DE CAMPINAS - UNICAMP.

(72) Inventor(es): PRISCILLA EFRAIM; MATHEUS HENRIQUE MARIZ DE AVELAR.

(57) Resumo: PROCESSO DE OBTENÇÃO DE BALAS DE GOMA. A presente invenção se insere no campo da engenharia alimentícia, mais precisamente na área de produção de balas de goma, e descreve um processo para a produção de balas de goma em que se elimina a etapa de cozimento de calda de açúcares base por meio da utilização da técnica de gelificação a frio com alginato e pectina. Dita técnica apresenta a vantagem de ter menos gasto energético, uma vez que implica na substituição da etapa de cozimento por uma etapa rápida de mistura de ingredientes que pode ser industrialmente realizada em um tanque agitador simples movido a eletricidade. Além disso, ela preserva melhor os componentes no produto final, pois esta ocorre em temperatura ambiente, indicando a possibilidade se obter balas com um perfil nutricional e funcional melhorado para o consumidor, como a incorporação de frutas no produto final.