



UNIVERSIDADE ESTADUAL PAULISTA
"JÚLIO DE MESQUITA FILHO"
Campus de São José do Rio Preto

KEILA DE SOUZA SILVA

**EFEITOS DOS AGENTES DE IMPREGNAÇÃO E
COBERTURAS COMESTÍVEIS SOBRE A SECAGEM E
SOBRE A QUALIDADE FÍSICA E NUTRICIONAL DO
ABACAXI**

**SÃO JOSÉ DO RIO PRETO
2013**

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Tese apresentada ao Instituto de Biociências, Letras e Ciências Exatas da Universidade Estadual Paulista “Júlio de Mesquita Filho”, Campus de São José do Rio Preto, para obtenção do título de Doutor em Engenharia e Ciência de Alimentos, área de Engenharia de Alimentos.

Orientadora: Prof^a. Dr^a. Maria Aparecida Mauro
Co-orientadora: Prof^a. Dr^a. Cristina Maria Ribeiro
Rocha Soares Vicente

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**São José do Rio Preto
13 de Setembro de 2013**

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*“A falsa ciência cria os ateus,
a verdadeira, faz o homem prostrar-se
diante de Deus”*

Voltaire

RESUMO

Neste trabalho, propôs-se combinar tecnologias e avaliar sua influência sobre a cinética de secagem e sobre características nutritivas e físico-químicas de abacaxi, com intuito de melhorar a qualidade dessa fruta desidratada. Abacaxis cortados no formato de trapézio foram desidratados osmoticamente em solução ternária de sacarose (40 e 50%), lactato de cálcio (2 e 4%) e água, por diferentes tempos (0, 1, 2, 4 e 6 horas) em temperatura e agitação constante (27°C e 1850 rpm), com o objetivo de avaliar a eficiência do processo, a atividade de água e as alterações na composição, cor e textura do produto, durante o processo, bem como a difusividade dos três componentes, água, sacarose e cálcio, no abacaxi. Observou-se que a impregnação de cálcio foi maior em amostras submetidas a soluções com maiores concentrações de sacarose e lactato de cálcio. A adição de cálcio acentuou a perda de água do produto e reduziu o ganho de sacarose, aumentando a eficiência do processo e diminuindo a atividade de água no produto. As difusividades da sacarose e da água decresceram com a adição de cálcio na solução osmótica. Por outro lado, os coeficientes de difusão de cálcio aumentaram com a elevação de sua concentração na solução. Nem a adição de lactato de cálcio na solução e nem o tempo de processo alteraram a claridade e a cromaticidade das amostras. As mudanças observadas na cor do produto foram devido ao aumento da concentração de sacarose. Apesar da efetiva impregnação de cálcio nas amostras, não foi possível perceber aumento na firmeza em relação às frutas frescas. Todavia, o processo foi eficiente quanto à impregnação de cálcio, cujo conteúdo encontrado em 100 g de abacaxi tratado por 6 horas em soluções de sacarose adicionadas de 4% de lactato de cálcio correspondeu a 10% da ingestão diária recomendada. Investigou-se também a impregnação de cálcio juntamente com vitamina C, no abacaxi, a partir da adição desses componentes em solução aquosa de sacarose. Diferentes composições foram avaliadas quanto à capacidade de enriquecer a fruta processada. Para tanto, foi realizado um planejamento fatorial 2^3 com 4 repetições no ponto central. As variáveis independentes estudadas foram concentração de sacarose (40 e 50%), concentração de lactato de cálcio (2 e 4%) e concentração de ácido ascórbico (1 e 2%). O tempo (2 horas), a temperatura (27°C) e a agitação (165 rpm) foram mantidos constantes. Baseando-se na maior impregnação de cálcio e vitamina C nas amostras, as concentrações de 4% de lactato de cálcio e 2% de vitamina C foram selecionadas para o estudo da cinética de desidratação osmótica. Para tanto, variou-se a concentração de sacarose (40 e 50%) e o tempo de tratamento (0, 1, 2, 4 e 6 horas). As difusividades da água e da sacarose, que diminuíram com a adição de cálcio numa solução de sacarose+água,

aumentaram consideravelmente com a adição de ácido ascórbico na solução ternária (água + sacarose + lactato de cálcio). A difusividade de cálcio também foi afetada positivamente. O processo mostrou-se eficiente, tendo em vista que consideráveis quantidades de cálcio e de vitamina C foram impregnadas no abacaxi, após 1 hora de imersão na solução quaternária. Com o objetivo de testar coberturas comestíveis com boas propriedades de barreira ao oxigênio, que sejam capazes de proteger substâncias bioativas da oxidação, filmes compostos por proteína isolada de soro de leite (WPI) e goma alfarroba (LBG) foram investigados, uma vez que efeitos sinérgicos entre goma e proteína têm sido amplamente descritos em termos de propriedades funcionais. Filmes comestíveis de proteína isolada de soro de leite (5%) com adição de diferentes concentrações de goma alfarroba (LBG) foram fabricados e caracterizados com o objetivo de escolher a melhor formulação e aplicar como cobertura comestível antes da secagem convectiva. Verificou-se que o tempo de tratamento térmico aumentou a sinergia entre os componentes do filme, aumentando as propriedades de barreira ao oxigênio, ao gás carbônico e à luz, aumentando a flexibilidade e diminuindo a solubilidade do filme. Esses resultados sugerem que a adição de LBG à WPI pode ser usado para sintonizar as propriedades de filmes comestíveis à base de WPI para satisfazer as necessidades específicas de embalagem de alimentos. Com base nos resultados que proporcionaram as melhores propriedades de barreira a gases e à luz, foi selecionada uma formulação para ser aplicada como cobertura comestível sobre pedaços de abacaxi impregnados com cálcio e vitamina C por imersão em solução osmótica. O objetivo foi avaliar o efeito de coberturas comestíveis sobre propriedades nutricionais e físico-químicas de abacaxi pré-tratado durante a secagem convectiva. A composição selecionada foi 5% (p/p) proteína isolada de soro de leite + 0,05% (p/p) LBG + 2% (p/p) de glicerol. Cobertura comestível à base de pectina de baixa metoxilação (2%), geleificada em lactato de cálcio (1%), também foi testada. Amostras de abacaxi osmo-impregnadas em solução contendo 50% sacarose + 4% lactato de cálcio + 2% vitamina C por 1 hora foram revestidas ou não (controle) com coberturas comestíveis, deixadas em descanso por 15 hs e então desidratadas em secador à 60 °C/11 horas e 70 °C/7horas. Curvas de secagem, difusividade da água, taxas de secagem, atividade de água, cor do produto e teor de vitamina C foram avaliados. Observou-se que as coberturas comestíveis não aumentaram a resistência à desidratação e à redução da atividade de água durante a secagem convectiva, todavia reduziram a oxidação da vitamina C das amostras durante o processo, se apresentando como eficientes barreiras ao oxigênio. Durante a secagem a 70°C, a cobertura à base de pectina proporcionou retenção de vitamina C superior à cobertura WPI+LBG. A temperatura do processo apresentou maior

influência sobre a degradação da vitamina C que o tempo. Elevados conteúdos de vitamina C foram detectados em abacaxi submetido à osmo-impregnação, com ou sem cobertura, e desidratado com ar aquecido. Entretanto, as coberturas mostraram ser efetivas durante a secagem convectiva, proporcionando grande retenção da vitamina.

Palavras-chave: Secagem. Desidratação osmótica. Cobertura comestível. Abacaxi. Pectina. Proteína isolada de soro de leite.

ABSTRACT

In this work, we proposed to combine technologies and evaluate their influence on the drying kinetics and on nutritional characteristics and physicochemical pineapple, with the aim of improving quality of dried fruit. Pineapples cut in the shape of a trapezoid were osmotically dehydrated in ternary solution of sucrose (40 to 50%), calcium lactate (2 and 4%) and water for different times (0, 1, 2, 4 and 6 hours) at room temperature constant stirring (27°C and 1850 rpm), in order to evaluate the efficiency of the process, the water activity and changes in the composition, color and texture of the product during the process, as well as the diffusivity of the three components, water, sucrose, and calcium, on pineapple. It was observed that calcium impregnation was higher in the samples submitted at solutions with higher concentrations of sucrose and calcium lactate. Calcium addition accentuated the water loss on the product and reduced the sucrose gain, increasing the efficiency of the process and reducing the water activity of the product. Sucrose and water diffusivity decreased with calcium addition in the osmotic solution. Moreover, the diffusion coefficients of calcium increased with increasing its concentration in the solution. Neither calcium lactate addition in the solution and neither the process time changed the brightness and chromaticity of the samples. The observed changes in the color of the product were due to the increasing sucrose concentration. Despite the effective uptake of calcium in the samples, it was not possible to see an increase in firmness compared to fresh fruit. However, the process has been efficient regarding to calcium impregnation, whose content found in 100 g of pineapple treated for 6 hours in solution of sucrose added 4% of calcium lactate corresponding to 10% of the recommended daily intake. It was also investigated the uptake of calcium together with vitamin C in pineapples, from the addition of these components from aqueous solutions of sucrose. Different compositions were evaluated for their ability to enrich the processed fruit. Therefore, it was conducted a 2³ factorial design with 4 repetitions at the center point. The independent variables were sucrose concentrations (40 and 50%), calcium lactate (2 and 4%) and ascorbic acid concentrations (1 and 2%). The time (2 hours), temperature (27 ° C) and agitation (165 rpm) were kept constant. Based on the greater impregnation of calcium and vitamin C in the samples, concentrations of 4% calcium lactate and 2% Vitamin C were selected for the study of kinetic of osmotic dehydration. To this end, was varied sucrose concentration (40 and 50%) and time of treatment (0, 1, 2, 4 and 6 hours). Water and sucrose diffusivity, which decreased with calcium addition in a solution of sucrose + water, increased substantially with the ascorbic acid addition in a ternary solution (water + sucrose + calcium

lactate). Calcium diffusivity was also positively affected. The process was effective, taking into account that considerable amounts of calcium and vitamin C were impregnated in pineapple, after 1 hour of immersion in solution quaternary. With the aim of testing edible coatings with good barrier properties to oxygen, which are able to protect bioactive substances from oxidation, films composed of whey protein isolate (WPI) and locust bean gum (LBG) were investigated, once effects synergistic between starch and protein have been widely described in terms of functional properties. Edible films of whey protein isolate (5%) with addition of different concentrations of locust bean gum (LBG) were manufactured and characterized in order to choose the best formulation and apply as edible coating prior to convective drying. It was found that the thermal treatment time increased the synergy between the components of the film, enhancing the barrier properties to oxygen, carbon dioxide and light, increasing the flexibility and decreasing the solubility of the film. These findings suggest that the addition of LBG to WPI can be used to tune the properties of WPI-based edible films to meet specific food packaging needs. Based on the results which provided the best barrier properties to gases and light, it was selected a formulation to be applied on edible coating on pineapple pieces impregnated with calcium and vitamin C by immersion in an osmotic solution. The objective was to evaluate the effect of edible coatings on nutritional properties and physicochemical pretreated pineapple during convective drying. The composition selected was 5% (p/p) whey protein isolate + 0,05% (p/p) LBG + 2% (p/p) of glycerol. Edible coating based on low-methoxyl pectin (2%), gelled with calcium lactate (1%) was also tested. Samples of pineapple osmo-impregnated in a solution containing 50% sucrose + 4% calcium lactate + 2% vitamin C for 1 hour were coated or not (control) with edible coatings, left at rest for 15 hours and then air-dried at 60°C/11 hours and 70°C/7hours. Drying curves, water diffusivity, drying rates, water activity, color of product and vitamin C content were evaluated. It was observed that the edible coatings have not increased the resistance to dehydration and reduction of water activity during convective drying, however reduced the oxidation of vitamin C of the samples during the process, presenting as effective barriers to oxygen. During drying at 70°C, the coating based on pectin provided vitamin C retention superior to cover WPI+LBG. The process temperature had a greater influence on the degradation of vitamin C than the time. High content of vitamin C have been detected in osmo-pineapple subjected to osmo-impregnation with or without coating, and dried with hot air. However, the coatings have proven to be effective during convective drying, providing great vitamin retention.

Keywords: Drying. Osmotic dehydration. Osmo-impregnation. Edible coating. Pineapple.
Pectin. Whey Protein Isolate

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1. INTRODUÇÃO

A importância das frutas numa dieta benéfica à saúde está relacionada à presença de componentes essenciais como fibras, sais minerais, açúcares e, principalmente, compostos biologicamente ativos com atividade antioxidante, como o ácido ascórbico, o alfa-tocoferol e o beta-caroteno (KAUR; KAPOOR, 2001). O Brasil é um importante produtor de frutas e hortaliças no cenário mundial se destacando como o segundo maior produtor mundial de abacaxi (FAOSTAT, 2011). Em 2011, foram produzidos 1.576.972 milheiros de abacaxis (IBGE, 2011). A alta perecibilidade das frutas decorrentes da abundância de colheita, da sazonalidade da produção, da distância dos mercados consumidores e da ausência de tratamentos e manuseio pós-colheita eficientes, resulta em grandes perdas de pós-colheita (LACERDA et al., 2004). Nesse contexto, a utilização de tecnologias viáveis para pequenas escalas, como a desidratação osmótica, a aplicação de coberturas comestíveis e a secagem convectiva, permitiria a obtenção de novos produtos, com boa qualidade sensorial e nutricional.

Um dos métodos mais importantes de preservação de vegetais é a secagem, pois remove a umidade do alimento, reduzindo a atividade de água e o risco de desenvolvimento de microorganismos e reações de deterioração em geral. Além disso, o vegetal desidratado ocupa menos espaço e não necessita de baixas temperaturas de conservação, reduzindo, dessa forma, o custo com transporte e armazenamento (VEGA-MERCADO et al., 2001; KAVAK AKPINAR et al., 2005; MANDALA et al., 2005). O fenômeno é bastante complexo, envolvendo transferência simultânea de calor e massa em regime transiente, além de transformações bio-físico-químicas (MUJUMDAR, 2010). Todavia, esse método pode apresentar alterações sensoriais e nutricionais indesejáveis, sendo um dos maiores problemas enfrentados na seleção, projeto e operação de secadores e por isso é necessário levar em conta as transformações ocorridas no produto durante a remoção de água (MUJUMDAR, 1997).

O processo de desidratação osmótica (DO) aplicado previamente à secagem convectiva (SC) pode minimizar os impactos negativos devido às alterações físicas, químicas e bioquímicas decorrentes do processo de secagem e melhorar as características do produto desidratado, mostrando-se uma importante ferramenta para o desenvolvimento de novos produtos. Esse processo foi recomendado pela Empresa Brasileira de Pesquisa Agropecuária, Embrapa (CELESTINO, 2009) para agregar valor e estender a vida de prateleira de frutas desidratadas. Germer (2010), por sua vez, demonstrou a viabilidade econômica da aplicação

do processo combinado de pré-secagem osmótica em soluções de sacarose com secagem convectiva, empregando reutilização do xarope.

A desidratação osmótica de tecidos vegetais é uma tecnologia que proporciona grande saída de água do material, mas também alguma impregnação de solutos, em geral em menor quantidade, o que dependerá, dentre muitas variáveis, da integridade da estrutura celular do tecido (MAURO et al., 2002). As vantagens da combinação dos processos de DO com SC, a princípio, estão associadas à difusão do soluto no tecido, o qual proporciona proteção física durante a secagem, minimizando efeitos adversos como escurecimento oxidativo, perdas nutricionais por oxidação de vitaminas, perda de compostos voláteis, encolhimento excessivo, dentre outros (RODRIGUES; MAURO, 2008). Entretanto, o enriquecimento com vitaminas, sais minerais ou outras substâncias benéficas à saúde pode ser realizado através da desidratação osmótica, com o intuito de melhorar a qualidade nutricional, ou mesmo compensar ou minimizar as perdas ocorridas durante o processamento (SOUSA, 2008). O ácido ascórbico tem sido utilizado como agente antioxidante em diferentes alimentos industrializados, podendo também ser encontrado em quantidades recomendáveis em produtos enriquecidos. Por ser um dos nutrientes mais sensíveis à degradação por ação térmica, enzimática e química durante o processamento e armazenamento de alimentos (WAWIRE et al., 2011), é frequente seu uso como indicador da qualidade do processamento de alimentos (SANTOS; SILVA, 2008). Por essa mesma razão, torna-se importante a investigação de métodos que possam minimizar ou suprir as perdas de vitamina C durante essas etapas (SOUSA, 2008). Além das mudanças causadas no perfil nutricional das frutas e hortaliças, a DO pode causar algumas alterações físicas e químicas que provocam mudanças na textura e na aparência do produto, dependendo das condições de processo e das características do material (CHIRALT; TALENS, 2005). Uma opção para preservar a integridade estrutural da parede celular dos alimentos desidratados osmoticamente é a adição de sais de cálcio na solução osmótica, que melhoraram as características de textura do produto final (FITO et al., 2001; MARTÍN-DIANA et al., 2007).

Os revestimentos comestíveis estendem a vida útil de produtos minimamente processados, pois podem proteger contra a ação microbiana, umidade e oxigênio, reduzindo a perda de cor, aroma e nutrientes, além de manter a integridade estrutural do produto durante sua comercialização (OLIVAS; BARBOSA_CÀNOVAS, 2005). Quando esse revestimento é aplicado antes da secagem, pode reduzir a oxidação de nutrientes durante o processo de desidratação (ZHAO e CHANG, 1995; LAGO-VANZELA et al., 2013).

A capacidade de proteção e interação das coberturas comestíveis com os alimentos depende de alguns fatores como: boas propriedades mecânicas, de barreira e boa adesão ao produto (VARGAS et al., 2008). Algumas dessas propriedades não são passíveis de serem medidas na forma de cobertura comestível, sendo necessária, portanto, a fabricação de filmes comestíveis semelhantes às coberturas, para viabilizar tais análises (HAN et al., 2005).

A realização de estudos mais aprofundados sobre coberturas comestíveis é de grande interesse para o desenvolvimento de tecnologias viáveis que possam aumentar a vida de prateleira do produto e a retenção de nutrientes durante o processamento.

A apresentação do trabalho está dividida em introdução, objetivos, revisão bibliográfica geral sobre os temas abordados e quatro capítulos com os resultados da pesquisa, na forma de artigos, contendo introdução, materiais e métodos, resultados e discussões, conclusões e referências bibliográficas. Ao final da Tese são apresentadas as conclusões gerais.

- Capítulo I: Apresenta o efeito da concentração de sacarose e lactato de cálcio sobre a cinética de desidratação osmótica e difusividade de cada componente no abacaxi. A influência de cada soluto acrescentado na solução e o tempo de processo sobre a cor, textura e atividade de água das amostras também foi investigado.

- Capítulo II: aborda o efeito da concentração da sacarose, lactato de cálcio e ácido ascórbico em solução aquosa quaternária sobre a perda de água e incorporação de solutos em amostras durante o processo de desidratação osmótica. A difusividade de cada componente também foi investigada.

- Capítulo III: apresenta a avaliação do efeito da adição de goma alfarroba (LBG) sobre propriedades de barreira, mecânica e ótica, microestrutura, solubilidade e isotermas de sorção de filmes de proteína de soro de leite isolada. Um estudo preliminar reológico foi realizado com a finalidade de avaliar a sinergia entre proteína de soro de leite isolada e LBG

- Capítulo IV: aborda os estudos sobre a influência da desidratação osmótica + aplicação de cobertura (pectina ou proteína de soro de leite isolada + LBG) na cinética de secagem, difusividade de água, atividade de água, cor e conteúdo de vitamina C de fatias de abacaxi.

2. Objetivos

2.1. Objetivos gerais

Os objetivos gerais foram: - obter parâmetros cinéticos de impregnação de cálcio e vitamina C durante a desidratação osmótica de abacaxis em pedaços, visando enriquecer os produtos através da osmo-impregnação; - desenvolver formulação de filme comestível com propriedades específicas tal que, quando aplicado como cobertura comestível, contribua para a preservação de nutrientes durante a secagem; - obter parâmetros cinéticos de secagem de abacaxis osmo-impregnados e revestidos com coberturas comestíveis, visando máxima preservação de nutrientes e de características físicas desejáveis durante o processo.

2.2. Objetivos específicos

- Avaliar a influência da concentração de sacarose, de cálcio e vitamina C sobre a cinética de desidratação osmótica de abacaxi em solução aquosa de sacarose/lactato de cálcio/ácido ascórbico;
- Determinar a difusividade da água, sacarose, ácido ascórbico e cálcio durante a desidratação osmótica em amostras de abacaxi;
- Avaliar o efeito dos solutos de soluções osmóticas binárias (água+sacarose), ternárias (água+sacarose+lactato de cálcio) e quaternárias (água+sacarose+lactato de cálcio+ácido ascórbico) sobre cor, textura, atividade de água e composição dos produtos obtidos;
- Avaliar a capacidade de enriquecimento de pedaços de abacaxi com as substâncias cálcio e vitamina C, através da osmo-impregnação;
- Desenvolver formulações de filmes à base de proteína isolada de soro (WPI) com adição de goma alfarroba (LBG);
- Investigar as propriedades de barreira (permeabilidade ao oxigênio, gás carbônico e à água), as propriedades óticas, a solubilidade, a microestrutura, a reologia e a interação entre os componentes das formulações (WPI+LBG) desenvolvidas, para serem utilizadas como coberturas comestíveis;
- Investigar a cinética de secagem de abacaxis impregnados osmoticamente com cálcio e vitamina C, revestidos ou não com coberturas comestíveis à base de WPI e à base de pectina;
- Avaliar o efeito de coberturas comestíveis à base de WPI e à base de pectina, sobre a retenção de vitamina C, cor e textura de amostras osmo-impregnadas, durante secagem com ar aquecido.

Referências Bibliográficas

- CELESTINO, S. M. C. (2009). **Desidratação osmótica na produção de frutas passa e sulfitação**, EMBRAPA Cerrados, Planaltina, DF. Disponível em: <<http://www.cpac.embrapa.br/noticias/artigosmidia/publicados/152/>> (Acessado em 30 de janeiro de 2010).
- CHIRALT, A.; TALENS, P. (2005) Physical and chemical changes induced by osmotic dehydration in plant tissues. **Journal of Food Engineering**, 22(1-2), 167-177.
- FAOSTAT (2011) - FAO Statistical Databases. Disponível em: <<http://faostat.fao.org/site/339/default.aspx>>.
- FITO, P.; CHIRALT, A.; BETORET, N.; GRAS, M.; CHÁFER, M.; MARTÍNEZ-MONZÓ, J.; ANDRÉS, A.; VIDAL, D. (2001) Vacuum impregnation and osmotic dehydration in matrix engineering. Application in functional fresh food development. **Journal of Food Engineering**. 49,175-183.
- GERMER, S. P. M. **Cultivares, variáveis de processo, reuso do xarope de sacarose e viabilidade econômica da pré-secagem osmótica de pêssegos**. 183 f. Tese (Doutorado em Engenharia e Ciência de Alimentos) – Universidade Estadual de Campinas - Faculdade de Engenharia Agrícola, Campinas, 2010.
- HAN, J.H.; GENNADIOS, A. (2005) **Edible Films and Coatings: a Review**. In: HAN, J.H (Ed.). *Innovations in Food Packaging*. New York: Elsevier Science & Technology Books. p.239-262.
- INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA - IBGE (2011) **Produção agrícola municipal. Culturas temporárias e permanentes**. ISSN 0101-3963, Rio de Janeiro, v. 38, p.1-97. Disponível em: <[ftp://ftp.ibge.gov.br/Producao_Agricola/Producao_Agricola_Municipal_\[anual\]/2011/pam2011.pdf](ftp://ftp.ibge.gov.br/Producao_Agricola/Producao_Agricola_Municipal_[anual]/2011/pam2011.pdf)>
- KAUR, C.; KAPOOR, H. C. (2001) Antioxidants in fruits and vegetables – the millennium's health. **International Journal of Food Science and Technology**, 36, 703-725.
- KAVAK AKPINAR, E.; MIDILLI, A.; BICER, Y. (2005) The first and second law analyses of thermodynamic of pumpkin drying process. **Journal of Food Engineering**, v.72, p. 320-331.
- LACERDA, M. A. D. DE; LACERDA, R. D. DE; ASSIS, P. C, DE OLIVEIRA (2004). A participação da fruticultura no agro negócio brasileiro. **Revista de Biologia e Ciências da Terra**, 4 (1), 1-9. Universidade Estadual da Paraíba. EDUEP, Editora Universitária. Disponível em http://www.uepb.edu.br/eduep/rbct/sumarios/sumario_v4_n1.htm. Acessado em 20 agosto de 2011.
- LAGO-VANZELA, E. S.; NASCIMENTO, P.; FONTES, E. A. F.; MAURO, M. A.; KIMURA, M. (2013) Edible coatings from native and modified starches retain carotenoids in pumpkin during drying. **LWT - Food Science and Technology** 50, 420-425

- MANDALA, I. G.; ANAGNOSTARAS, C. K.; OIKONOMOU, C. K. (2005) Influence of osmotic dehydration conditions on apple air-drying kinetics and their quality characteristics. **Journal of Food Engineering**, 69, 307-316.
- MARTÍN-DIANA, A. B.; RICO, D.; FRÍAS, J. M.; BARAT, J. M.; HENEHAN, G. T. M.; BARRY-RYAN, C. (2007) Calcium for extending the shelf life of fresh whole and minimally processed fruits and vegetable: a review. **Trends in Food Science & Technology**, 18, p.210-218.
- MAURO, M. A.; TAVARES, D. Q.; MENEGALLI, F. C. (2002) Behavior of plant tissue in osmotic solutions. **Journal of Food Engineering**, 56, p. 1-15.
- MUJUMDAR, A. S. (1997). Drying Fundamentals. In C. G. J. Baker (Ed.), **Industrial Drying of Foods**. Baker, (pp 7-30). London: Blackie Academic & Professional.
- MUJUMDAR, A. S; Law, L. C. (2010) Drying Technology: Trends and applications in postharvest processing. **Food Bioprocess Technology**, v.3, p.843-852.
- OLIVAS, G.I.; BARBOSA-CÁNOVAS, G.V. (2005) Edible Coatings for Fresh-Cut Fruits. **Critical Reviews in Food Science and Nutrition**, v.45, n.7-8, p.657-670.
- RODRIGUES, A. E.; MAURO, M. A. (2008) Effective diffusion coefficients behavior in osmotic dehydration of apple slices considering shrinking and local concentration dependence. **Journal of Food Process Engineering**, 31, p. 207–228.
- SANTOS, P.H.S. AND SILVA, M.A. (2008), Retention of Vitamin C in Drying Processes of Fruits and Vegetables - A Review, **Drying Technology**, Vol. 26, pp. 1421–1437.
- SOUSA, S. (2008) **Obtenção de figos secos por desidratação osmótica e secagem convectiva**. Campinas, SP. Tese (doutor em Engenharia de Alimentos), faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas.
- VARGAS, M.; PASTOR, C.; CHIRALT, A.; McCLEMENTS, D. J.; GONZÁLEZ-MARTINÉZ, C. (2008) Recent Advances in Edible Coatings for Fresh and Minimally Processed Fruits. **Critical Reviews in Food Science and Nutrition**. Vol. 48, p.496-511.
- VEGA-MERCADO, H.; GONGORA-NIETO, M.M.; BARBOSA-CANOVAS, G.V. (2001) Advances in dehydration of foods. **Journal of Food Engineering**, vol. 49, p. 271-289.
- ZHAO, Y. P.; CHANG, K. C. (1995) Sulfite and starch affect color and carotenoids of dehydrated carrots (*Daucus carota*) during storage. **Journal of Food Science**, Chicago, v. 60, n. 2, p. 324-347.
- WAWIRE, M., OEY, I., MATHOOKO, F., NJOROGE, C., SHITANDA, D.; HENDRICKX, M. (2011), Thermal Stability of Ascorbic Acid and Ascorbic Acid Oxidase in African Cowpea Leaves (*Vigna unguiculata*) of Different Maturities, **Journal of Agriculture and Food Chemistry**, Vol. 59, pp. 1774–1783.

3. REVISÃO BIBLIOGRÁFICA

3.1. Abacaxi

O abacaxi é um fruto pertencente à família *Bromeliaceae*, que compreende aproximadamente, 46 gêneros e cerca de 1.900 espécies de plantas. Apesar da grande família, destaca-se apenas, devido a sua importância econômica, o gênero *Ananas Mill.* Este gênero é vastamente distribuído por cultura nas regiões tropicais por intermédio da espécie *Ananas comosus (L.) Merril*, a qual abrange todas as cultivares atualmente plantadas (SMITH, 1993). As principais cultivares, da espécie *Ananas comosus (L.) Merril*, de importância comercial são: Smooth Cayenne, Singapore Spanish, Red Sapanish e Selangor Green (MEDINA, 1987).

Segundo dados da FAO (Organização das Nações Unidas para a Agricultura e Alimentação), o Brasil é segundo maior produtor mundial de abacaxi (FAOSTAT, 2011). Em 2011, foram produzidos 1.576.972 milheiros de abacaxis (IBGE, 2011). O rendimento médio alcançou a marca de 25.239 frutos/ha e a área colhida, 62.481 ha (IBGE, 2011). As cultivares mais conhecidas no Brasil são Pérola ou Branco de Pernambuco, Smooth Cayenne, Perolera e Primavera (NASCENTE et al., 2005).

O abacaxi é classificado como fruto não climatérico, isto é, só amadurece enquanto estiver ligado à planta. Após a colheita, os frutos não climatéricos não melhoram suas qualidades sensoriais e nutricionais, embora ocorra pequena mudança na textura (amolecimento) e perda da coloração verde (MEDLICOTT, 1986). Quando o fruto se destina à industrialização ou ao consumo imediato, deve ser colhido maduro, que é quando atinge os níveis ótimos de constituintes físico-químicos que conferem a qualidade ideal ao fruto. No caso do consumo “in natura” em mercados distantes, deve-se fazer a colheita antes que os frutos atinjam a maturação completa, ou seja, no estágio “de vez”, para que cheguem ao consumidor em boas condições (CUNHA et al., 1999).

O sabor e aroma característicos do abacaxi são conferidos pelos açúcares, ácidos e compostos voláteis que se destacam por serem responsáveis pela doçura, acidez e aroma, respectivamente. A acidez do abacaxi é devida, principalmente, aos ácidos cítrico e málico, que contribuem em média, respectivamente, com 87 e 13% da acidez total. O pH do fruto está, geralmente, entre 3,2 e 4,15. No interior do fruto, a acidez aumenta da base para o topo, acompanhando o desenvolvimento da maturação. Numa mesma altura do fruto, a acidez é muito mais acentuada na zona próxima à casca do que na do cilindro central (DULL, 1971).

O abacaxi apresenta vida de prateleira bastante curta, o que eleva as perdas de produção. O consumidor, por sua vez, procura cada vez mais praticidade e qualidade nos produtos que pretende consumir, o que aponta para a necessidade de investigar formas alternativas para o consumo e a extensão da vida de prateleira de produtos de abacaxi.

3.2. Desidratação osmótica

A desidratação osmótica (DO) aplicada previamente à secagem possibilita obtenção de produtos atrativos, por minimizar perda de aroma, escurecimento enzimático, perda da cor natural dos mesmos (PONTING, 1973, QUINTERO-RAMOS et al., 1993, KARATHANOS, et al., 1995), promover efeito protetor sobre a estrutura do alimento, gerando produtos mais flexíveis e macios (LENART, 1996, MANDALA et al., 2005), obter melhor aceitação sensorial (SHIGEMATSU et al., 2005) e maior retenção de nutrientes (SHI et al., 1999).

A desidratação osmótica é um processo de transferência de massa que tem como finalidade remover a umidade do material celular sem mudança de fase da água através da imersão do produto em soluções aquosas hipertônicas (RASTOGI et al., 1997; SERENO et al., 2001). As membranas celulares dos vegetais, que são parcialmente seletivas, propiciam três tipos de transferência de massa com fluxo contra-corrente, um fluxo de água do vegetal para solução, um fluxo de soluto da solução para o vegetal e um fluxo de solutos originais do vegetal para a solução (RAOULT-WACK, 1994). O conteúdo de umidade diminui e simultaneamente há um incremento de sólidos, que provoca uma modificação na composição química do alimento desidratado (LENART, 1996). A transferência de soluto dependerá da permeabilidade da membrana celular (RAOULT-WACK, 1994). Enquanto o tecido mantiver sua integridade, a membrana plasmática, pouco permeável a solutos de alto peso molecular, restringirá a transferência dessas substâncias aos espaços celulares externos à membrana plasmática (BIDWELL, 1979).

O processo de desidratação osmótica varia com o tipo de agente osmótico, a concentração da solução, a temperatura, o sistema de agitação, o tamanho e a espessura do produto a ser desidratado. A escolha do soluto é uma questão fundamental por estar relacionada a alterações de propriedades sensoriais e ao valor nutritivo do produto final, além do custo de processo (LENART, 1996, QI et al., 1998, HAWKES; FLINK, 1978). Características do agente osmótico usado, como seu peso molecular e seu comportamento iônico, afetam fortemente a desidratação, tanto na quantidade de água removida quanto no

ganho de sólidos (TELIS et al., 2004, ERTEKIN; CAKALOZ, 1996). Soluções hipertônicas, geralmente, são constituídas por sacarídeos, cloreto de sódio, sorbitol ou glicerol (LENART, 1996). A sacarose é considerada por muitos autores como um ótimo agente osmótico, uma vez que a redução de escurecimento enzimático e perda de aromas têm sido associadas a esse soluto (LENART, 1996, QI et al., 1998). Saputra (2001) verificou que a sacarose proporcionava maiores perdas de água e menores ganhos de soluto, quando comparada à glicose, em amostras de abacaxi submetidos à desidratação osmótica.

Ao estudar a desidratação osmótica de cubos de batata doce em diferentes temperaturas e concentrações de solução de sacarose, Genina-Souto et al. (2001) verificaram que quanto maior a temperatura e a concentração, maior a perda de água da amostra e maior a absorção de sólidos solúveis. Lazarides et al. (1995) verificaram que altas concentrações de sacarose favoreceram a incorporação de açúcar em maçãs desidratadas osmoticamente em solução aquosa de 45 e 65% p/p de sacarose.

De acordo com Raoult-Wack (1994), a perda de água ocorre, principalmente, durante as duas primeiras horas de tratamento osmótico de frutas ou vegetais submetidos à pressão atmosférica, diminuindo, progressivamente, após esse período. Valente (2007) observou que altas concentrações e temperaturas potencializam a perda de água do abacaxi durante a desidratação osmótica em solução de sacarose por 2 horas, entretanto não recomenda o uso de altas temperaturas no processo, pois a mesma causa danos na estrutura da membrana celular resultando em mudanças significativas na textura do produto, além de perda de nutrientes e alta incorporação de soluto.

A desidratação osmótica não necessita de temperaturas altas para remoção de água, pois a mesma é removida sem mudança de fase, em função apenas de um gradiente de concentração, o que pode reduzir o custo do processo como um todo. Entretanto, quando a temperatura usada no processo for maior que a temperatura ambiente, a transferência de massa será potencializada e o tempo de processo poderá ser reduzido. Apesar desse fato, Torreggiani (1993) afirma que temperaturas acima de 45°C afetam características estruturais da membrana celular, o que pode favorecer o escurecimento enzimático e a deterioração do flavor do produto.

O efeito de diferentes temperaturas (30, 40 e 50°C) na desidratação osmótica de abacaxi em solução aquosa de 60% (w/w) de sacarose foi estudado por Ramallo et al. (2004) que observaram pouca influência da variação da temperatura sobre a perda de água da fruta.

Valente (2007) realizou um planejamento fatorial completo 2^2 com 4 pontos axiais e 3 pontos centrais para avaliar a influencia da temperatura e concentração da solução osmótica na perda de água e ganho de soluto no abacaxi. O tempo de processo foi fixado em 2 horas e a agitação em 100rpm. A temperatura variou de 30 a 50°C e a concentração da solução variou de 40 a 60% de sacarose. Segundo os autores, os valores mais altos para eficiência de desidratação osmótica de abacaxi em solução de sacarose, definida segundo a relação entre perda de água e ganho de sólidos, encontraram-se nos ensaios realizados a temperaturas próximas do ambiente (30 a 35°C). Além disso, o autor constatou escurecimento enzimático e a deterioração do *flavor* das amostras em temperaturas acima de 45°C. Outro fator que favorece a utilização de temperaturas próximas a ambiente para os ensaios de DO é a economia de energia no processo, pois, nesse caso, não há necessidade de gastos energéticos para aquecimento.

O processo de desidratação osmótica é mais eficiente quando conduzido sob agitação. A agitação garante que a solução concentrada seja renovada ao redor da amostra criando uma diferença favorável de concentração à transferência de massa (RAOULT-WACK et al., 1989). A desidratação osmótica (DO) proporciona a perda de alguns sólidos do alimento que pode afetar seu perfil nutricional (RAOULT-WACK, 1994). As perdas de ácido ascórbico podem ocorrer basicamente através de dois fenômenos, pela difusão da vitamina para a solução ou por degradação química, que ocorre principalmente quando se utilizam temperaturas mais altas no processo de desidratação osmótica (VIAL et al., 1991).

Abacaxi (*Ananas comosus variety Cayena lisa*) cortado no formato de meio anel de 0,6 cm de espessura foi submetido à desidratação osmótica em solução de sacarose a 60°Brix e 40°C por 30, 60, 120, 180 e 240 minutos. Após o tratamento, os autores analisaram o conteúdo de ácido ascórbico e verificaram que a perda dessa vitamina foi de aproximadamente 70% após a DO (RAMALLO; MASCHERONI, 2010).

Um dos métodos para compensar a perda do ácido ascórbico na fruta é a adição desse componente na solução desidratante. A desidratação osmótica permite introduzir solutos na estrutura porosa das frutas, que poderão favorecer características sensoriais e nutricionais dos produtos (FITO et al., 2001). Robbers et al. (1997), trabalhando com kiwi, verificaram que a adição de ácido ascórbico e ácido cítrico como antioxidantes na solução osmótica, preveniu o escurecimento e significativas perdas de ácido ascórbico durante a desidratação osmótica. Sousa (2008) observou que a incorporação de vitamina C foi intensa ao longo da desidratação

osmótica de figos em soluções de sacarose e ácido ascórbico e que a impregnação de vitamina C durante a DO compensou as perdas ocorridas durante a secagem.

A adição de ácido ascórbico na solução osmótica também, representa uma alternativa para aumentar a taxa de desidratação do alimento (ARGADOÑA et al., 2002), além de aumentar a impregnação de solutos no tecido devido ao aumento da porosidade da parede celular em soluções ácidas (MAVROUDIS et al., 2012).

Além das mudanças causadas no perfil nutricional das frutas e hortaliças, a DO pode causar algumas alterações físicas e químicas que provocam mudanças na textura e na aparência do produto, dependendo das condições de processo e das características do material (CHIRALT; TALENS, 2005). As principais alterações induzidas pelo tratamento osmótico e que afetam o comportamento mecânico e a estrutura celular dos tecidos vegetais são deformação e/ou ruptura de parede celular, colapso celular e encolhimento dos tecidos, além de mudanças nas frações de volume de ar e líquido na amostra (CHIRALT et al., 2001). De acordo com Chiralt e Talens (2005) e Moraga et al. (2009), as propriedades estruturais e sensoriais dos produtos osmoticamente desidratados dependem das mudanças de composição devido à impregnação de solutos, do impacto do processo na parede celular, assim como do grau de dano dentro da membrana plasmática provocado pelo processo.

Uma opção para preservar a integridade estrutural da parede celular dos alimentos desidratados osmoticamente é a adição de sais de cálcio na solução osmótica, que melhoraram as características de textura do produto final. Algumas formas de cálcio utilizadas na indústria são lactato de cálcio, cloreto de cálcio, fosfato de cálcio, propionato de cálcio e gluconato de cálcio, geralmente utilizados quando o objetivo é a preservação e/ou o reforço da firmeza dos produtos (ALZAMORA et al., 2005; LUNA-GUZMÁN; BARRET, 2000; MANGANARIS et al., 2007). O uso de cloreto de cálcio em concentrações altas para a preservação da textura de frutas apresenta, como desvantagem, o relativo sabor amargo do sal e indesejável sabor residual no produto final (LUNA-GUSMÁN; BARRET, 2000; YANG; LAWSLESS, 2003). O uso de lactato de cálcio, por sua vez, atua como agente firmador da textura com a vantagem de não causar alterações no sabor do produto final (FITO et al., 2001; MARTÍN-DIANA et al., 2007). Muntada et al. (1998) observaram que o lactato de cálcio adicionado no tratamento osmótico de kiwis minimizou alterações na textura da fruta ocasionadas devido ao processo osmótico. Heredia et al. (2007), observaram que o uso de lactato de cálcio se apresentou muito eficiente na preservação da textura de tomates cerejas desidratados osmoticamente em soluções combinadas de açúcar e sal, seguida de secagem em equipamento com fluxo de ar aquecido e microondas até a umidade intermediária.

Concentrações de sal de cálcio acima de 1,5% na solução osmótica, contudo, resulta em plasmólise das células vegetais e aumento da solubilização da pectina, reduzindo a tensão de ruptura e favorecendo o amolecimento do tecido (CASTELLÓ et al, 2009 and FERRARI et al, 2010). Anino et al. (2006) observaram amolecimento do tecido de maçãs depois de 2 horas de desidração em solução contendo glicose + sais de cálcio (5266ppm) + sorbato de potássio + ácido cítrico.

Outro benefício que provém do uso de tratamentos osmóticos com cálcio é a possibilidade de sua impregnação na matriz do tecido vegetal com o intuito de fortificar o produto. Entretanto, há necessidade de muita investigação, uma vez que cada tecido apresenta particularidades que influenciam no transporte de massa (MARTÍN-DIANA, et al., 2007). Anino et al. (2006), explorando a possibilidade de obtenção de um produto fortificado com cálcio, analisaram a capacidade da matriz de maçãs minimamente processadas incorporar cálcio por técnicas de impregnação, usando lactato de cálcio e gluconato de cálcio. A quantidade de cálcio incorporada na matriz das amostras de maçã atingiu níveis entre 23 e 63% (para 200 g de fruta) da ingestão recomendada. De acordo com a FAO/WHO (1974), a quantidade diária de consumo requerida por um adulto é de 800mg.

A consciência dos consumidores sobre os benefícios do cálcio é relativamente alta (MARTÍN-DIANA, et al., 2007). O conteúdo de cálcio das dietas é crítico na maioria dos estágios da vida (GRAS, et al., 2003). O interesse em cálcio tem se intensificado recentemente como resultado de evidências que relacionam osteoporose, hipertensão e câncer com a deficiência de cálcio. Apesar da causa dessas doenças envolver vários fatores e pouco se saber a respeito, alguns estudos mostram que o aumento da ingestão de cálcio pode reduzir o risco de ocorrência dessas doenças (APPEL et al., 1997; CUMMING et al., 1997). Para permitir aos consumidores a oportunidade de aumentar a sua ingestão de cálcio sem recorrer à suplementação, a indústria está recorrendo à fortificação de alimentos e bebidas com cálcio (CERKLEWSKI, 2005). Portanto, o uso do cálcio mostra-se vantajoso tanto na preservação da textura dos vegetais quanto como fortificador do alimento, permitindo ao consumidor complementar uma eventual deficiência do mineral em sua dieta.

3.3. Filmes e coberturas comestíveis

Biofilmes podem ser finas camadas de material comestível que agem como barreira a elementos externos como umidade, gases e microorganismos, prolongando a vida de

prateleira do produto fresco ou minimamente processado. Os biofilmes podem ser de dois tipos: coberturas, quando são aplicadas diretamente nas superfícies dos alimentos, ou filmes, que são películas finas formadas sobre um suporte e utilizadas como embalagem de um produto (DONHOWE; FENNEMA, 1994; HAN; GENNADIOS, 2005; OLIVAS; BARBOSA-CÂNOVAS, 2005).

A extensão da vida de prateleira de frutas e hortaliças tem sido um dos mais importantes usos da cobertura e filmes comestíveis.

Segundo Baldwin et al. (1996), o uso de coberturas comestíveis pode minimizar mudanças indesejáveis devido ao processamento mínimo através da formação de uma barreira parcial ao vapor de água e à troca gasosa e da geração de uma atmosfera modificada em torno do vegetal que será responsável pela redução da taxa de respiração, da produção de etileno e do amadurecimento da fruta.

O emprego de coberturas comestíveis associada com outros tratamentos também tem sido estudado. Alguns trabalhos reportam a aplicação de coberturas comestíveis antes da desidratação osmótica com o objetivo de reduzir o ganho de solutos (BRANDELEIRO et al., 2005; MATUSKA et al., 2006; GARCÍA et al., 2010), outros reportam o uso da cobertura comestível antes da secagem convectiva visando a proteção contra a oxidação dos carotenóides e da vitamina C durante o processo (ZHAO; CHANG, 1995; LAGO-Vanzela, 2013; EIK, 2008; GONÇALVES, 2010).

A capacidade de proteção das coberturas comestíveis depende de alguns fatores como: permeabilidade do revestimento, boa adesão ao produto, propriedades mecânicas e propriedades de barreira (VARGAS et al., 2008). Algumas dessas propriedades não são possíveis de serem obtidas em coberturas comestíveis, sendo necessária a fabricação de filmes comestíveis (HAN et al., 2005).

Os métodos mais usados para aplicação de coberturas comestíveis são: *dipping*, que consiste no mergulho do produto na solução filmogênica e *spraying*, ou aspersão da solução formadora de filme sobre o produto. Para a formação de filmes, as técnicas mais usadas são: *casting* e *knife coating*. A técnica *casting* consiste na aplicação da solução formadora de filme em moldes com posterior etapa de secagem (Figura 1). A técnica *Knife coating* é realizada através de uma máquina automática. A solução formadora de filme é despejada na base e espalhada com auxílio de uma faca que é mantida a uma distância ajustável do suporte (Figura 2). Após espalhamento da solução, o filme é seco e retirado da base.



Figura 1: Filme formado pelo método *Casting*

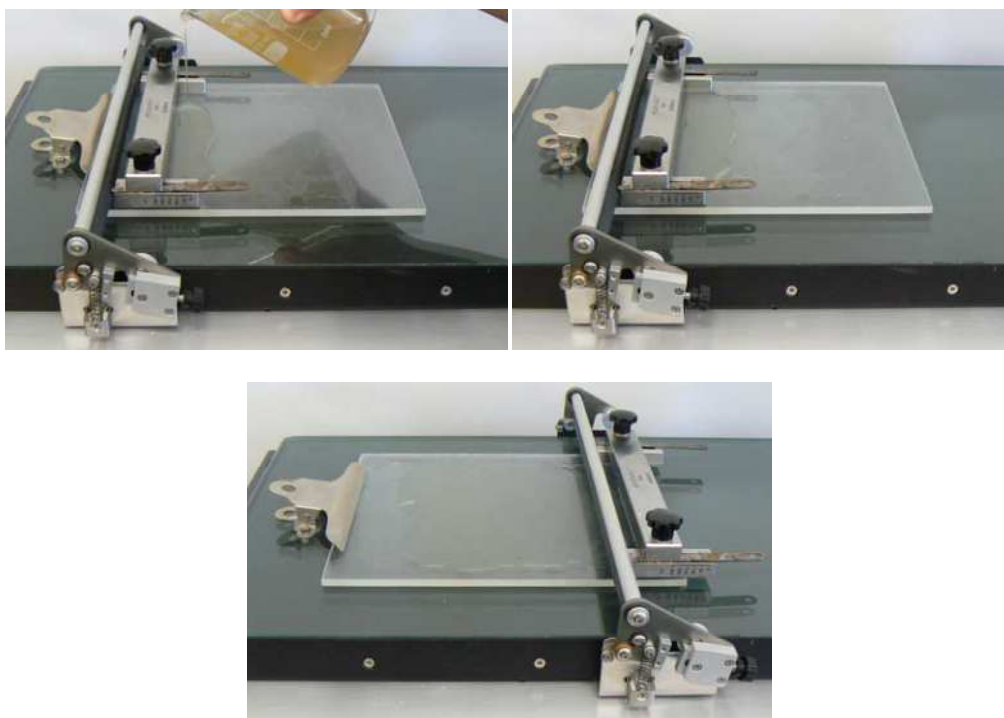


Figura 2: Filme formado pelo método *Knife coating*

A estrutura e composição química dos biopolímeros, a natureza do solvente, a presença de aditivos e as condições de formação do filme e cobertura são fatores que determinam suas propriedades.

Os biopolímeros mais utilizados para a formulação de biofilmes são lipídeos, polissacarídeos, proteínas ou a combinação desses componentes.

As coberturas ou filmes comestíveis compostos de lipídeos (cera de carnaúba e os ácidos graxos esteárico, ácido palmítico, etc.) apresentam boas propriedades de barreira ao vapor de água, mas apresentam sabor residual, são pouco flexíveis e opacas. As coberturas elaboradas a partir de polissacarídeos (ex.: gomas vegetais, amidos, celulose, pectina, alginato, etc) ou proteínas (ex.: proteína do soro de leite, proteína da soja, colágeno, caseína, proteína do glúten, zeína, etc.) possuem excelentes propriedades de barreira, a gases, ópticas, mecânicas e sensoriais, porém são sensíveis à umidade e apresentam alto coeficiente de permeabilidade ao vapor de água (FAKHOURI et al., 2007). Para aperfeiçoar as propriedades dos biofilmes, misturas de polissacarídeos e/ou proteínas estão sendo extensivamente estudadas (GONÇALVES et al., 2004; IBANOGLU, 2005; BENICHOU et al., 2007; BERTRAND et al., 2007; GOUNGA et al., 2007; FERREIRA et al., 2009; PEREZ et al., 2009; OSÉS et al., 2009; LIMA et al., 2010; WANG et al., 2010; YOO; KROCHTA, 2011; PIERRO et al., 2011).

O comprimento da cadeia polimérica e sua polaridade exercem grande influência sobre as propriedades dos biofilmes. Maiores cadeias poliméricas proporcionam biofilmes com maior coesão e menor flexibilidade, porosidade e permeabilidade para vapor de água, gases e soluto (KESTER; FENNEMA, 1986; MAIA et al., 2000).

O método de secagem dos biofilmes pode afetar significativamente sua morfologia, aparência, propriedades de barreira e propriedades mecânicas (PEREZ-GAGO; KROCHTA, 2000). A secagem de filmes e coberturas comestíveis ocorre em dois períodos: período de taxa constante, onde predomina a transferência da água da superfície para o ambiente e período de taxa decrescente, onde a transferência da água do filme para o ambiente é limitada pela difusão da água do interior da película para a superfície (JOOYANDEH, 2001).

3.4. Materiais usado em filmes e coberturas comestíveis

3.4.1. Pectina

Pectina é um polissacarídeo linear, solúvel em água, geralmente obtida da casca e polpa de frutas cítricas, maçãs, sementes de girassol e polpa de beterraba. É encontrada nas paredes celulares em maior quantidade na lamela média das células (THAKUR et al., 1997).

Quimicamente, as pectinas são compostas por ácido galacturônico que é parcialmente esterificado com grupos metoxilas. O grau de metoxilação é definido como a porcentagem de

unidades de ácido galacturônico que são metil esterificados. Dessa forma, o grau de metoxilação de 70% significa que 70% de grupos ácidos galacturônicos na molécula são esterificados com metanol. As pectinas podem ser classificadas em: baixo teor de metoxilas (25-50%) e alto teor de metoxilas (50-80%). Pectinas com baixo teor de metoxilas são mais estáveis à umidade e ao calor (THAKUR et al., 1997).

A geleificação da pectina varia com seu grau de metoxilação. Pectinas com alto teor de metoxilas (HM) formam gel na presença de um soluto, como a sacarose, e em pH abaixo de 3,6. A geleificação das pectinas de baixo teor de metoxilação (PM) pode ser provocada pela ligação iônica entre íons cálcio (Ca^{+2}) e grupos carboxílicos (COO^-). O mecanismo de geleificação da PM ocorre em dois estágios, sendo que o primeiro é caracterizado pela dimerização e o segundo pela agregação no formato de caixa de ovos (egg boxes) (BEAULIEU, 2001; THAKUR et al., 1997). Maiores quantidades de cálcio tendem a aumentar a força do gel, todavia, concentrações acima do nível ótimo podem promover a sinerese, devido a danos na estrutura do gel, tornando-o quebradiço (GROSSO, 1998).

Maftoonazad e Ramaswamy (2008) estudaram o uso da pectina como cobertura comestível em abacate minimamente processado e relataram a preservação da massa, cor e textura durante o armazenamento por até 40 dias em ambientes a 10, 15 e 20°C (MAFTOONAZAD; RAMASWAMY, 2008). Scalon et al (2012) avaliaram o efeito das coberturas de carboxi metilcelulose (CMC), pectina e pectina + cálcio em guavira armazenadas por 0, 7, 14 e 21 dias em câmara a 5, 10 e 15°C e constataram que amostras cobertas com pectina + cálcio apresentaram a menor perda de massa a 5°C e o maior teor de vitamina C a 5 e 10°C de armazenamento. Outros trabalhos ressaltaram o emprego da pectina antes da desidratação osmótica com a finalidade de aumentar a eficiência do processo (AZEREDO; JARDINE, 2000; LENART; PIOTROWSKI, 2001). Recentemente, alguns pesquisadores têm abordando a atuação de coberturas comestíveis como tratamento prévio à secagem convectiva e reconhecem a eficácia da pectina nesse papel. Eik (2008) observou que fatias de caqui apresentavam maior retenção de carotenóides durante a secagem quando estes eram revestidos de pectina. Garcia (2012) e Canizares (2013) observaram que a cobertura de pectina, não interferiu na secagem, mas protegeu o ácido ascórbico e a cor de fatias de mamões durante a secagem convectiva a 60 e 70°C.

3.4.2. Galactomananos

Galactomananos são polissacarídeos heterogêneos obtido do endosperma das sementes de dicotiledôneas de numerosas plantas. Esse polissacarídeo possui a habilidade de aumentar a viscosidade de soluções com pequenas concentrações da goma, ser pouco afetada pelo pH, calor de processo e força iônica (SITTIKIYOTHIN et al., 2005; DAKIA et al., 2008, CERQUEIRA et al., 2011). As três variedades de galactomananos de importância comercial em alimentos são goma tara (GT - *Caesalpinia spinosa*), goma guar (GG- *Cyamopsis tetragonolobo*) e goma Carob ou alfarroba ou “locust bean gum” (LBG – *Ceratonia siliqua*) (DAKIA et al., 2008).

Recentemente, a goma carob (locust bean gum (LBG)) vem ganhando importância como componente de embalagens biodegradáveis (CERQUEIRA et al., 2011). Obtida do endosperma das sementes da vagem da alfarrobeira (*Ceratonia siliqua* L.), LBG é constituída por uma cadeia principal composta por β -(1-4) D- manose e por uma cadeia lateral de D- galactose ligado via α -(1-6) (DA SILVA; GONÇALVES, 1990).

A compatibilidade da goma Carob com outras gomas e agentes espessantes contribui para aumentar a força e elasticidade dos géis (GOYCOOLEA et al., 1995; DAKIA et al., 2008). Em temperatura ambiente apresenta baixa solubilidade, sendo necessário o aquecimento da goma a 80°C por 20 a 30 minutos para garantir sua total solubilização na água (SRIVASTAVA; KAPOOR, 2005).

Bozdemir e Tutas (2003) prepararam diferentes formulações de filmes a base de LBG e verificaram que o polissacarídeo tinha potencial para ser utilizado na preparação de filmes e coberturas comestíveis.

Mikkonen et al. (2007) observaram que filmes de LBG apresentavam melhor propriedades mecânicas que filmes feitos com goma guar.

3.4.3. Proteína de soro de leite

O soro de leite é um produto da fabricação do queijo com excelentes propriedades funcionais e amplamente usada na formulação de alimentos (TURGEON; BEAULIEU, 2001).

A extração da proteína do soro pode resultar em dois produtos: proteína concentrada do soro (WPC) e proteína isolada do soro (WPI). WPC pode conter de 35 a 80% (p/p) de

proteína em base seca e é obtido através da ultrafiltração do soro de leite. A produção de WPI pode ser realizada através de separação por membranas, seguido por concentração e secagem resultando em um produto com maior teor de proteína (90% p/p em base seca) (KHWALDIA et al., 2004; RAMOS et al., 2013).

As principais proteínas presentes no soro de leite bovino são: β -lactoglobulina, α -lactalbumina, α -albumina bovina sérica e imunoglobulinas. A β -lactoglobulina é a proteína mais abundante, representando 60% das proteínas encontradas no soro de leite. A α -lactalbumina é a segunda proteína em maior proporção no soro (DEWIT; KLARENBECK, 1983; NICOLAI et al., 2011).

Para a formação de filmes e coberturas comestíveis com proteína de soro de leite (WP) é necessário que ocorram interações físicas (eletrostáticas e hidrofóbicas) e químicas (dissulfeto) através do processo de gelatinização (RAMOS et al., 2012). Fatores como tempo de desnaturação, taxas de aquecimento, pH, força iônica, conteúdo mineral, composição e concentração da proteína irão determinar o processo de formação do gel e suas características.

O tempo de desnaturação e a taxa de aquecimento da proteína de soro influenciam diretamente na interação intermolecular, pois o aquecimento modifica a estrutura tridimensional da proteína, abrindo a estrutura globular da β -lactoglobulina e expondo os grupos hidrofóbicos (-SH) que oxidam e formam pontes dissulfeto (S-S) (RAMOS et al., 2012). Essas pontes contribuem para a estrutura de filmes e coberturas a base de proteína de soro, sendo que a falta dessa etapa resultaria em filmes quebradiços após a secagem (KHWALDIA et al., 2004). Stading et al., 1993 mostraram que altas taxas de aquecimento (5-10°C/min) resultaram em géis de β -lactoglobulina com redes mais homogêneas.

O ajuste do pH da emulsão de WP para valor próximo do ponto isoelétrico ($pI=5,0$), bem como a adição de sal na emulsão reduz a repulsão eletrostática entre as moléculas da proteína propiciando a agregação das moléculas e a formação do gel (RAMOS et al., 2012). Quando o pH está distante do PI e a força iônica é baixa, a repulsão eletrostática no sistema aumenta e durante o período de agregação ocorre a formação de um gel de estrutura fina e translúcido. Se o pH do sistema está mais próximo do ponto isoelétrico da proteína e a força iônica é alta, ocorrerá a formação de um gel opaco de coloração branca (STADING; HERMANSSON, 1991; IKEDA; FOEGEDING, 1999; KAVANAGH et al., 2002, PICONE, 2005).

A concentração da proteína aumenta a densidade do gel, reduzindo seu espaço intersticial resultando em filmes com menor permeabilidade ao oxigênio e ao gás carbônico (MILLER; KROCHTA, 1997; ANKER et al., 2000; GOUNGA et al., 2007).

Propriedades de filmes de proteína de soro foram estudadas por diversos autores. McHugh et al., 1994 observaram que a permeabilidade ao oxigênio de filmes de proteína de soro de leite isolada (WPI) aumentavam exponencialmente com a umidade relativa. Gounga et al., 2007 verificou que filmes com maior concentração de WPI foram mais permeáveis ao vapor de água. Ramos et al., 2013 concluíram que filmes de proteína de soro exibiram propriedades de barreira ao oxigênio melhor que outras fontes de proteína como zeína de milho, glúten de trigo, proteína isolada de soja. Ramos et al., 2013 ainda observaram menor solubilidade e permeabilidades ao oxigênio e gás carbônico e maior transparência dos filmes de WPI quando comparados aos filmes de proteína de soro de leite concentrada (WPC).

Por apresentar boas propriedades de barreira ao oxigênio, coberturas de proteína de soro foram estudadas visando redução de reações oxidativas de batata (LE TIEN et al., 2001), maçã (LE TIEN et al., 2001; LEE et al., 2003; PEREZ GAGO et al., 2005 and 2006) e amendoim (MATÉ et al., 1996).

Nenhum estudo sobre a atuação da cobertura de soro de leite como pré-tratamento à secagem foi encontrado na literatura.

3.4.4. Misturas de biopolímeros

A mistura de polissacarídeos e proteínas na solução pode ser associativa (os biopolímeros se atraem) ou segregativa (ocorre a repulsão entre os biopolímeros) dependendo do tipo de interação. Se a mistura for segregativa, podem ocorrer formação de coacervatos ou incompatibilidade termodinâmica entre os biopolímeros. O processo de coacervação ocorre quando biopolímeros se associam excluindo o solvente para a vizinhança e formando duas fases aquosas e imiscíveis, sendo que uma das fases é rica em biopolímeros e a outra é quase isenta desses compostos. Soluções com polieletrólitos de cargas opostas tendem a formar coacervatos. O mecanismo de coacervação é entropicamente e entalpicamente dirigido. O mecanismo de separação devido à incompatibilidade termodinâmica ocorre quando os biopolímeros são segregados em duas fases aquosas, sendo que cada uma delas é carregada com as espécies de biopolímeros. Esse mecanismo é predominantemente entropicamente dirigido (DE KRUIF; TUINIER, 2001).

Misturas de proteínas e polissacarídeos sob específicas condições (pH, força iônica, temperatura, agitação) ou em determinadas quantidades (taxas de polissacarídeo com relação a proteína) podem resultar em soluções conjugadas sem formação de coacervatos

(BENICHOU et al., 2007). Todavia, mesmo em condições ótimas de sinergias, misturas entre proteínas e polissacarídeos tendem a segregar a nível microscópico (DOUBLIER et al., 2000).

Algumas pesquisas relataram sinergias entre polissacarídeos e proteínas (CHEN et al., 2001; TURGEON; BEAULIEU, 2001; BERTRAND; TURGEON, 2007; ROCHA et al., 2009). A mistura desses biopolímeros vem sendo estudada por diversos pesquisadores que visam melhorar as propriedades de filmes e coberturas comestíveis.

Ferreira et al., 2009 verificaram um grande potencial na fabricação de filmes de WPI + quitosana. Osés et al., 2009 estudaram o efeito da adição de diferentes concentrações de goma mesquita no filme de WPI e constataram que a adição do polissacarídeo formou filmes homogêneos com melhores propriedades mecânicas. Pierro et al., 2011 sugeriram coberturas comestíveis feitas de WPI + quitosana para estender a vida de prateleira de produtos lácteos. Wang et al., 2010 concluíram que as propriedades do filmes comestíveis formulados com WPI + gelatina + alginato de sódio melhoraram com a combinação de polissacarídeos e proteína. Gounga et al., 2007 observaram que a adição de pululana ao filme de WPI decresceu a permeabilidade ao vapor de água e ao oxigênio, contudo altas concentrações desse polissacarídeo reduziu as propriedades de barreira. Nenhum estudo sobre filmes ou coberturas de WPI + LBG foram encontrados na literatura.

Rocha et al., 2009 encontrou efeitos de sinergia entre proteína de soro de leite concentrada (WPC) e LBG, o que potencializa o uso dessa mistura em filmes e coberturas comestíveis.

3.4.5. Plastificantes

Os plastificantes são importantes componentes na fabricação de filmes e coberturas comestíveis, pois reduzem as forças intermoleculares, promovem o aumento da mobilidade das cadeias poliméricas resultando no aumento da flexibilidade dos filmes (SOTHORNVIT; KROCHTA, 2005).

Os plastificantes mais comuns utilizados na formulação de biofilmes são monossacarídeos (glucose), oligossacarídeos, polióis (exemplo: glicerol, sorbitol and polyethylene glycol 400), lipídeos e derivados. A seleção de um plastificante é baseado em alguns critérios como: compatibilidade, eficiência e permanência. O plastificante precisa ser compatível com o polímero usado para fabricação do biofilme, precisa proporcionar alta

plastificação com baixas concentrações e ter baixa volatilidade (SOTHORNVIT; KROCHTA, 2005).

Glicerol é um plastificante que tem sido muito utilizado na formulação de biofilmes. Gouna et al., 2007 observaram que a incorporação de glicerol na formulação reduzia a fragilidade dos filmes de WPI. Ramos et al., 2013 observaram que a solubilidade dos filmes de WPI aumentava com o conteúdo de glicerol.

Osés et al., (2009b) estudaram a atuação do glicerol e do sorbitol sobre as propriedades de filme de proteína de soro de leite e concluíram que o glicerol era o plastificante mais eficiente, pois proporcionava filmes mais estáveis, flexíveis e menos frágeis em diferentes umidades relativas.

Apesar de melhorar as propriedades mecânicas dos biofilmes, plastificantes também aumentam a permeabilidade dos mesmos.

Kokoska et al., 2010 elaboraram filmes de WPI com diferentes concentrações de glicerol (30, 40, 50 e 60% (w/w) de WPI) e observaram que propriedades de barreira foram melhores em filmes com 40% (w/w, de WPI) de glicerol.

Bozdemir e Tutas (2003) estudaram a permeabilidade ao vapor de água (WVP) de filmes comestíveis feitos com LBG e diferentes plastificantes (glicerol, propileno glicol e Polietileno glicol 200 e sorbitol) e constataram que filmes contendo glicerol apresentaram os maiores valores de permeabilidade ao vapor de água.

3.5. Propriedades dos filmes comestíveis

3.5.1. Reologia

Ensaio reológico em regime dinâmico podem ser usados para determinar as propriedades viscoelásticas de géis (RAO, 1999). Nesse ensaio, a amostra é submetida a uma deformação ($\gamma(t)$) que varia senoidalmente com o tempo t de acordo com a equação 1

$$y(t) = \gamma_0 \sin(\omega t) \quad (1)$$

onde γ_0 é a amplitude máxima da deformação e ω é a frequência angular (RAO, 1999).

Dentro da faixa de viscoelasticidade linear, faixa onde a razão entre a deformação e a tensão é independente da amplitude da deformação aplicada na gama de frequências utilizada, a tensão produzida poderá ser representada em termos de módulo elástico ou armazenamento (G') e módulo viscoso ou de dissipação (G'') de acordo com a equação 2.

$$\sigma_0 = G' \gamma_0 \sin(\omega t) + G'' \gamma_0 \cos(\omega t) \quad (2)$$

Para um material viscoelástico, a tensão resultante é calculada conforme equação 3.

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad (3)$$

onde δ representa o ângulo de fase.

Combinando a equação 2 e 3 obtém-se as equações 4, 5 e 6 que definem o comportamento viscoelásticos dos géis.

$$G' = \left(\frac{\sigma_0}{\gamma_0} \right) \cos \delta \quad (4)$$

$$G'' = \left(\frac{\sigma_0}{\gamma_0} \right) \sin \delta \quad (5)$$

$$\tan \delta = \frac{G''}{G'} \quad (6)$$

Para um sólido elástico toda a energia é armazenada e G'' é zero, enquanto que para um fluido com propriedades não elásticas, toda energia é dissipada na forma de calor e G' passa a ser zero (MARFIL, 2010).

Os módulos de conservação e dissipação definidos são grandezas utilizadas na interpretação dos processos de gelificação e cura do gel (TORRES, 2005).

Durante o aquecimento de uma suspensão de proteínas, o módulo elástico começa a aumentar até o momento que cruza com o módulo viscoso. O tempo necessário para que o encontro dos módulos ocorra é o tempo de gelificação para soluções de proteína (IKEDA et al., 2001).

No momento da gelificação ocorre o estabelecimento das interações intermoleculares (cura do gel) e aumento da elasticidade do gel aumentando, portanto, valores de G' . À

medida que o módulo de elasticidade aumenta mais interações intermoleculares são formadas e mais forte é o gel (TORRES, 2005).

3.5.2. Propriedades de barreira

As propriedades de barreira de um filme comestível indicam qual a sua capacidade em proteger o alimento contra agentes externos como umidade e oxigênio. Para tanto, a permeabilidade ao vapor de água e a permeabilidade a gases é utilizada para quantificar essa barreira.

Permeabilidade é definida como taxa de transmissão de vapor ou gás através de uma unidade de área e espessura, induzida pela diferença de pressão existente entre duas superfícies do material sob condições específicas de umidade e temperatura (YANG; PAULSON, 2000). O mecanismo que ocorre na transmissão de vapor ou gases através do filme (ausente de rachaduras, furos ou falhas) é o da difusão ativa onde o vapor ou gás se dissolve na matriz do filme ao lado de alta concentração e por diferença de concentração, percorre o filme até o outro lado (menor concentração). A forma, polaridade e tamanho da molécula a ser difundida, bem como a estrutura e característica do filme determinam como serão a dissolução e difusão do componente no biofilme (KESTER; FENNEMA, 1986). A primeira lei de Fick (Equação 1) é aplicada para obtenção do fluxo do gás ou vapor em regime permanente (CUSSLER, 1984).

$$J_1 = -D \frac{dc_1}{dx} \quad (7)$$

onde J_1 é o fluxo de difusão ($g/m^2.s$ ou $mol/m^2.s$), c_1 é a concentração (g/m^3 ou mol/m^3), x é a espessura do filme (m) e D é o coeficiente de difusão (m^2/s).

Combinando a equação 7 com a equação 8 que expressa a lei da solubilidade de Henry

$$c = S.p \quad (8)$$

onde c é a concentração do penetrante (g/m^3 ou mol/m^3), S é o coeficiente de solubilidade da lei de Henry ($mole/m^3 \times atm$) e p é a pressão parcial do penetrante no ar adjacente (Pa), e fazendo um rearranjo obtém-se a equação 9.

$$D.S = -J \frac{dx}{dp} = P \quad (9)$$

onde P é permeabilidade ((ml ou g). $m/m^2.s.Pa$)

A equação 9 é baseada na hipótese de que não há interação significativa entre o filme e o vapor ou gás, sendo assim, D e S são considerados independentes da concentração do penetrante e não há desvios na Lei de Fick. Quando o coeficiente de solubilidade aumenta com a pressão de vapor de água a permeabilidade torna-se uma característica do filme sob dadas condições ambientais e não pode ser usada no senso geral para descrever sua propriedade de barreira (KESTER; FENNEMA, 1986).

Admitindo-se regime permanente e gradiente linear através do filme, o fluxo de difusão pode ser representado pela equação (10)

$$J = \frac{Q}{A.t} \quad (10)$$

onde, Q é a quantidade de vapor ou gás que atravessa o filme em g (no caso do vapor de água) ou ml (no caso do O_2 e CO_2), A é a área (m^2) transversal através da qual a difusão ocorre e t é o tempo em segundos.

Dessa forma a permeabilidade também pode ser obtida através da equação 11:

$$P = \frac{Q.x}{A.t.\Delta p} \quad (11)$$

As propriedades de barreira mais estudadas nos filmes e coberturas comestíveis são permeabilidade ao vapor de água (WVP), permeabilidade ao oxigênio (O_2P) e permeabilidade ao gás carbônico (CO_2P).

3.5.3. Permeabilidade ao vapor de água

A migração de vapor de água é um dos principais fatores de alterações indesejáveis nos alimentos, pois pode favorecer o crescimento microbiano, ação enzimática, reações de oxidação, perda de textura, perda de peso, alterações na cor e sabor dos alimentos.

O método mais comum de determinação da permeabilidade ao vapor de água é o método ASTM E96-92 (ASTM, 1990). Esse método gravimétrico consiste em selar um filme em um recipiente (Figura 3) e colocá-lo em uma câmara à umidade relativa e temperatura controladas. O recipiente poderá conter sal anidro com atividade de água próximo de zero (exemplo: cloreto de cálcio) ou água destilada ($a_w=1$). Um dessecador poderá fazer o papel da câmara, sendo que deverá conter o composto oposto ao adicionado no recipiente. Nesse caso, se o recipiente for preenchido parcialmente com sal anidro, o dessecador deverá conter água destilada para que um gradiente de concentração seja criado entre o lado externo e o interno do filme. Pesagens periódicas deverão ser realizadas.

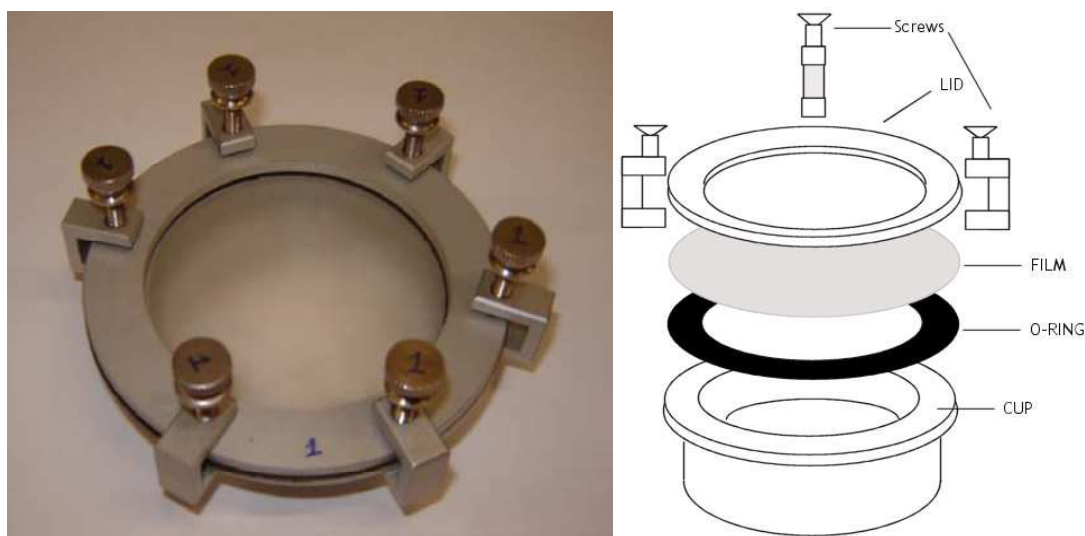


Figura 3: Recipiente utilizado para determinação da permeabilidade ao vapor de água de filmes

As pesagens devem ser realizadas após o transporte de umidade atingir estado estacionário. Uma variação constante de massa em função do tempo será verificada e o declive representará a taxa de transmissão de vapor de água através do filme ao longo do tempo (g/s), conforme equação 12.

$$WVTR = \frac{\Delta m}{\Delta t} \quad (12)$$

Assim, a permeabilidade ao vapor de água (WVP) é obtida através da equação 13

$$WVP = \frac{WVTR \cdot x}{A \cdot \Delta p} \quad (13)$$

3.5.4. Permeabilidade ao oxigênio e ao gás carbônico

O oxigênio é responsável por muitas reações de degradação em alimentos, como alterações na cor, perda de vitamina e reações de oxidação indesejáveis. Devido a isso, embalagens com baixa permeabilidade a gases são desejadas. Todavia, a permeabilidade ao O₂ e ao CO₂ é essencial para a respiração dos tecidos vivos, como frutos e vegetais. Por isso, o conhecimento sobre a permeabilidade de um filme comestível é muito importante (AYRANCI; TUNC, 2003).

O método de determinação da permeabilidade ao O₂ e ao CO₂ é baseado na norma ASTM D3985-02 (ASTM D3985-02, 2002) e envolve o fluxo do oxigênio ou gás carbônico de um dos lados do filme e, do outro lado, fluxo de gás hélio. O filme é fixado na célula de difusão de volume e área conhecidos. No instante inicial a concentração de oxigênio no interior da célula é nula. No decorrer do tempo, o gás hélio conduz o oxigênio ou gás carbônico pela película, sendo que o gás difundido é detectado do outro lado do filme através de cromatógrafo a gás. A taxa de oxigênio (OTR) ou gás carbônico (COTR) através do filme ao longo do tempo pode ser determinada pelo declive da zona linear da curva, volume de O₂ ou CO₂ versus tempo.

$$OTR = \frac{\Delta V}{\Delta t} \quad (14)$$

$$COTR = \frac{\Delta V}{\Delta t} \quad (15)$$

Assim, a permeabilidade ao oxigênio ou gás carbônico (O₂P, CO₂P) é obtida através das equações 16 e 17, respectivamente.

$$O_2P = \frac{OTR.x}{A.\Delta p} \quad (16)$$

$$CO_2P = \frac{COTR.x}{A.\Delta p} \quad (17)$$

3.5.5. Isotermas de sorção

Devido à natureza hidrofílica de biofilmes fabricados com proteína e polisacarídeos, grande quantidade de água pode ser absorvida em condições de umidade relativa alta afetando as propriedades físicas e de barreira dos filmes (CHO; RHEE, 2002). A construção de isotermas de sorção poderia caracterizar a absorção dessa umidade pelos filmes.

Curvas de isotermas de sorção relacionam o equilíbrio entre a atividade de água e o conteúdo de umidade do filme a uma determinada temperatura e pressão constante (RIZVI, 1986).

As isotermas podem ser divididas em três regiões. Na primeira, com umidades mais baixas, a água é fortemente ligada ao produto e inviável para reações, representando a adsorção da primeira camada de água sobre a superfície do material adsorvente. Na segunda, a água não tão fortemente ligada e presente em pequenos capilares, corresponde à adsorção de uma segunda camada de água e cobre uma faixa de a_w em torno de 0,25-0,60. Na terceira região, a água é encontrada em largos capilares e é relativamente livre para reações, agindo como solvente de compostos solúveis presentes (VAN DEN BERG; BRUIN, 1981).

As isotermas de sorção são influenciadas por vários fatores, como a estrutura física, composição química do material e a afinidade com a água, o que confere individualidade das características de sorção de umidade para os alimentos. Dessa forma, é necessário determinar experimentalmente as isotermas de cada produto, quando os dados não estão disponíveis na literatura.

Existem muitos modelos matemáticos utilizados para ajustar as curvas de isotermas. Esses modelos podem ser empíricos, semi-empíricos ou teóricos (VAN DEN BERG; BRUIN, 1981). O modelo de GAB (Guggenheim, Anderson e de Boer) (eq. 18) é o mais usado para representar dados de sorção experimental.

$$X = \frac{X_m \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w)(1 - K \cdot a_w + C \cdot K \cdot a_w)} \quad (18)$$

onde: C e K são constantes; a_w é a atividade de água; X é o conteúdo de umidade em base seca (kg água/kg matéria seca) e X_m é o conteúdo de umidade da mono-camada em base seca (kg água/kg matéria seca), ou seja, o conteúdo de água no momento da saturação de todos os sítios primários de sorção por uma molécula de água.

3.5.6. Solubilidade

A solubilidade em água é uma propriedade importante dos filmes comestíveis, pois algumas aplicações requerem insolubilidade em água para manter a integridade do produto (PEREZ-GAGO; KROCHTA, 2001).

A solubilidade das proteínas é fortemente afetada pelo pH e pela temperatura. O pH igual ao ponto isoelétrico diminui a solubilidade da proteína, pois diminui a força eletrostática das moléculas aumentando a interação proteína-proteína e diminuindo interações com a água. Quando as proteínas são desnaturadas, grupos hidrofóbicos interagem, se agregam e reduzem as interações com a água, diminuindo a solubilidade da proteína (PELEGRINE et al., 2005).

A solubilidade de um biofilme direciona a sua aplicação. A total solubilização de um biofilme pode ser positiva, como nos produtos semi-prontos onde é desejável que o filme dissolva na água durante o cozimento, ou em coberturas comestíveis onde se espera que a película seja dissolvida na boca durante a mastigação.

3.5.7. Propriedades mecânicas

O conhecimento das propriedades mecânicas de filmes e coberturas comestíveis é extremamente importante para garantir a sua integridade durante o processamento, manuseamento e armazenamento.

O teste mais utilizado para determinar as propriedades mecânicas de um filme é o teste de tração (CUQ et al., 1996). Através desse teste é possível obter a tensão máxima de ruptura

(dada em MPa) e a alongação máxima (dada em %). A tensão máxima de ruptura é medida através da força máxima de tração que o filme pode sustentar durante um teste elástico em unidade de área de sua secção transversal. A alongação é obtida através do ponto de quebra do filme durante o teste e representa a habilidade do filme em se distender (MCHUGH; KROCHTA, 1994).

As propriedades mecânicas de filmes e coberturas comestíveis são influenciadas pelo tipo de material utilizado na formação do filme, pela sua coesão estrutural, isto é, a capacidade que o polímero tem em formar fortes e numerosas ligações entre as cadeias poliméricas, pela técnica de fabricação do filme ou cobertura e pela taxa de evaporação e resfriamento (GUILBERT et al., 1996). As propriedades mecânicas podem variar, também, com a espessura do filme e com a velocidade do teste usado (ASTM, 1997).

3.5.8. Propriedades óticas

A cor e transparência de filmes e coberturas comestíveis são propriedades importantes que devem ser avaliadas, pois podem afetar a aceitação sensorial do produto coberto. Dependendo da aplicação, uma maior transparência da cobertura e filmes comestíveis pode ser desejável, contudo uma menor transparência indica maior bloqueio a passagem de luz e, portanto, maior proteção a reações químicas indesejáveis no alimento.

A transparência de um filme pode ser quantificada através do espectrofotômetro e os resultados podem ser expressos através da transmitância (fração da luz incidente com um comprimento de onda específico, que atravessa uma amostra de matéria) ou absorbância (capacidade intrínseca dos materiais em absorver radiações em frequência específica). As equações 19 e 20 definem a transmitância (T) e a absorbância (A_λ):

$$T = \frac{I}{I_0} \quad (19)$$

$$A_\lambda = -\log_{10}(T) \quad (20)$$

onde I = intensidade da luz com um comprimento de onda (λ) específico, I_0 é a intensidade da luz incidente (VOGEL, 2002).

A faixa de comprimento de onda correspondente a luz visível ou ultra violeta (UV) está entre 180 e 800nm. Quanto maior a transparência de um filme na região UV, maior será o valor de transmitância e menor será o valor de absorbância.

A separação de fase devido à incompatibilidade termodinâmica entre polissacarídeos e proteínas pode diminuir a transparência de filmes compostos (YOO; KROCHTA, 2011).

3.6. Secagem

Um dos métodos mais importantes de preservação de vegetais é a secagem, pois remove a umidade do alimento, reduzindo a atividade de água e o risco de desenvolvimento de microorganismos e reações de deterioração em geral. Além disso, o vegetal desidratado ocupa menos espaço e não necessita de baixas temperaturas de conservação, reduzindo, dessa forma, o custo com transporte e armazenamento (VEGA-MERCADO et al., 2001; KAVAK AKPINAR et al., 2005; MANDALA et al., 2005). Entretanto, a secagem causa alterações físicas, químicas e bioquímicas indesejáveis no alimento, sendo de crucial importância conhecer essas transformações para a seleção, projeto e operação de secadores (MUJUMDAR, 1997).

A secagem é uma operação unitária que envolve transferência de calor e transferência de massa. No processo de secagem, a água se movimenta de zonas de alta umidade, encontradas no interior do sólido, para zonas de baixa umidade, presentes na superfície do produto, onde é removida sob a forma de vapor (TREYBAL, 1980).

A secagem pode ser dividida em três períodos de acordo com o mecanismo de transferência de calor e massa:

1. Período de adaptação: aquecimento do material acarretando em aumento da taxa de secagem;
2. Período de taxa constante: evaporação da umidade não ligada que se encontra na superfície do sólido, sendo que a migração interna da água é suficiente para compensar a evaporação superficial e manter a condição de saturação na superfície. Nesse período todo o calor fornecido pelo ar aquecido que é transferido para a superfície do produto corresponde ao calor requerido para a evaporação da água.
3. Período de taxa decrescente: ocorre a redução da taxa de secagem e a elevação da temperatura do produto. Nesse período a velocidade de transferência de massa no interior do sólido é menor que a taxa de evaporação na superfície.

No período de taxa decrescente, partes externas do material já estão secas, o processo consome muita energia, o produto tem sua temperatura elevada e atributos físicos, sensoriais e nutricionais podem ser prejudicados (NIJHUIS et al., 1996). O processo é encerrado quando o produto atinge a umidade de equilíbrio com o ar de secagem (PARK et al., 2001).

Grande parte dos modelos matemáticos que descrevem os processos de secagem no período de taxa decrescente baseia-se na teoria da difusão líquida de água. Essa teoria é representada pela segunda lei de Fick (CUSSLER, 1984) apresentada numa forma modificada pela equação 21.

$$\frac{\partial X}{\partial t} = D_{ef} \nabla^2 X \quad (21)$$

onde X = fração de massa de água em base seca, D_{ef} = coeficiente de difusão efetivo, e t = tempo.

A difusividade efetiva engloba todos os efeitos que podem intervir no fenômeno de migração da água no produto, como a dependência com a temperatura e a concentração, além de encolhimento, porosidade e tortuosidade. As soluções analíticas obtidas através da equação (21) aplicam-se aos sólidos de geometria simples e constante ao longo do processo (CRANK, 1975).

Dentre os métodos existentes de secagem, a convectiva é a mais utilizada na indústria de alimentos (KIRANOUDIS et al., 1997), sendo estimada como responsável por mais de 90% da produção de alimentos desidratados (MUJUMDAR, 1997).

Determinadas condições de operação (como altas temperaturas, tempos longos de secagem) comprometem a qualidade sensorial (aparência, textura, cor e sabor) e nutricional do produto. Ramallo e Mascheroni (2012) observaram que conteúdo de ácido ascórbico e a textura do abacaxi foi fortemente afetado pela secagem. Cortellino et al. (2011) notaram decréscimo na claridade de anéis de abacaxi com a secagem convectiva.

Alterações na qualidade sensorial e nutricional do produto tem motivado a condução de estudos de processos alternativos que visam à manutenção da qualidade da fruta desidratada, em relação à textura, à aparência (como escurecimento ou perda de pigmentos) como também à preservação de nutrientes (SHI et al., 1999; MASKAN, 2001; RAMESH et al., 2001).

A fim de melhorar a qualidade sensorial e nutricional do produto desidratado, muitos autores (PONTING et al., 1966; TORREGGIANI, 1993; RAOULT-WACK, 1994;

LENART,1996) sugerem a desidratação osmótica como um pré-tratamento para a secagem. Entretanto, diversos trabalhos mostram a redução da taxa de remoção de água do alimento pré-tratado ao longo da secagem quando comparado com produtos sem pré-tratamento. Esse comportamento é explicado pela formação de uma camada de sólidos na superfície do material, que pode dificultar a evaporação de água, e pela redução do teor de água livre do alimento devido à incorporação de solutos que se associam mais fortemente à água (TORREGGIANI, 1993; LENART, 1996).

Karathanos et al. (1995) e Rodrigues et al. (2003) notaram que maçãs previamente tratadas por osmose apresentaram redução nas taxas de secagem em comparação com o produto in natura. Dionello et al. (2007) também notaram menores taxas de secagem em abacaxis desidratados osmoticamente por duas horas em solução de 40 e 50% de sacarose, quando comparado ao material fresco. Nicoletti et al. (2001) observaram que a taxa de difusividade da água, durante a secagem de amostras de abacaxi desidratadas osmoticamente foi menor do que daquelas in natura. As taxas de secagem geralmente caem com a incorporação de soluto devido ao pré-tratamento. Porém mesmo que as taxas de secagem de amostras pré-tratadas sejam menores que de não tratadas, os tempos de secagem podem ser menores para as primeiras, que dependerá da umidade desejada no produto final. Gonçalves; Blume (2008) observaram que a atividade de água desejada ($a_w < 0,75$) foi atingida mais rapidamente no produto pré-tratado osmoticamente e o teor de umidade residual foi menor nessas amostras.

Por outro lado, pesquisadores como Park et al. (2002), Garcia et al. (2007) e Shigematsu et al. (2005), verificaram aumento da difusividade da água na secagem com o pré-tratamento osmótico em peras e carambolas, respectivamente, o que foi atribuído à desidrataç o superficial muito r pida das frutas n o tratadas devido   alta umidade, com aparecimento de  reas endurecidas que contribuíram para a diminui o das taxas de secagem em compara o com amostras desidratadas osmoticamente.

Uma das mais importantes mudan as f sicas que ocorre com o alimento durante a secagem   o encolhimento. Al m de ser considerado um indicativo da qualidade do produto desidratado, o estudo do encolhimento   de grande import ncia para um melhor entendimento do processo de secagem (NIJHUIS et al., 1996).

A diminui o das dimens es do produto se deve   altera o na microestrutura do tecido fresco, em que se verifica um aumento de cavidades, c lulas alongadas, dentre outras modifica es (LEWICKI; PAWLAK, 2003), promovidas pelo tratamento t rmico e, principalmente, pela remo o de umidade.

Muitos estudos têm demonstrado que a impregnação do tecido com açúcar reduz o encolhimento indesejável que ocorre durante a secagem. Del Valle et al. (1998) observou que cilindros de maçãs pré-tratadas em diferentes concentrações de sacarose e posteriormente submetidos à secagem apresentaram menor encolhimento quando comparados aos cilindros de maçãs secas sem pré-tratamento.

Outro parâmetro que é afetado pela secagem é a cor. Estudos com batata e abacaxi demonstraram que amostras desidratadas osmoticamente previamente à secagem, apresentaram menor redução da coloração durante a secagem em comparação com amostras não tratadas (TAN et al., 2001).

O tratamento osmótico aplicado previamente à secagem também é capaz de aumentar a retenção de nutrientes durante a secagem convectiva. Alguns pesquisadores observaram que amostras pré-tratadas em solução contendo açúcar ou cálcio reduziu a perda de vitamina C durante a secagem (RIVA et al., 2005; SANJINEZ-ARGANDOÑA et al., 2005; VÉGA-GALVES et al., 2008).

3.7. Cor

A importância da cor como um parâmetro de qualidade de alimentos tem sido demonstrada extensivamente na literatura (MELÉNDEZ-MARTÍNEZ et al., 2007, SÁNCHEZ-MORENO et al., 2006, ANDREU-SEVILLA et al., 2006, ORNELAS-PAZ et al., 2008). Consumidores frequentemente julgam a qualidade de um alimento baseado na aparência global e, principalmente, na cor (ORNELAS-PAZ et al., 2008). Produtos de cor forte e brilhante são os preferidos sendo que a preferência se deve à correlação visual entre frescor e sabor (CHUA et al., 2000). Alimentos expostos a tratamento térmico sofrem degradação de pigmentos, especialmente de carotenóides, reações de escurecimento tal como a reação de Maillard e a oxidação do ácido ascórbico (MASKAN, 2001, BARREIRO et al. 1997).

Para uma padronização mais efetiva, vários pesquisadores vêm avaliando as alterações de cor através de sistemas de cor por determinação instrumental, uma vez que a importância tecnológica da cor reside na possibilidade de utilizá-la como índice de transformações naturais de alimentos frescos ou de mudanças ocorridas durante o processamento industrial (CALVO; DURAN, 1997).

Uma comissão fundada em Viena em 1913 por pesquisadores, chamada CIE (Commission Internationale de l'Eclairage), ou Comissão Internacional de Iluminação, padronizou termos relativos à iluminação com o objetivo de aumentar a uniformidade das cores percebidas pelo sistema visual humano (LEÃO et al., 2007).

O modelo de cor uniforme definido pela CIE usa os valores conhecidos como L^* , a^* , b^* e o sistema é chamado CIE $L^*a^*b^*$ (ou CIELAB). O valor L^* é a dimensão da claridade e representa as variações do branco ($L^*=100$) ao preto ($L^*=0$). O valor a^* representa as variações do verde ($-a^*$) ao vermelho ($+a^*$). O valor b^* representa as variações do amarelo ($+b^*$) ao azul ($-b^*$).

Para duas cores diferentes, variáveis L^* , a^* , b^* podem ser representadas como ΔL^* , Δa^* , Δb^* ou ainda ΔE , definido como a raiz quadrada de $(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2$. ΔE representa a magnitude da diferença em cor, mas não indica a direção da diferença, podendo detectar alguma diferença imperceptível para a visão, mas perceptível em outra parte do espectro. Dois atributos qualitativos de cor, baseados em a^* e b^* , são ângulo *hue* e *chroma*. O primeiro determina a tonalidade da cor, permitindo que qualquer cor seja graduada como avermelhado, esverdeado, etc., para uma mesma claridade, e o segundo, determina a saturação da cor, representando a intensidade ou pureza do tom, para uma mesma claridade (MELÉNDEZ-MARTÍNEZ et al., 2007, PÉREZ-LÓPEZ et al., 2006).

A cor nos alimentos é resultado da presença de pigmentos, tais como carotenos, antocianinas, clorofila, entre outros. Esses pigmentos são indicadores das transformações ocorridas no alimento, pois são susceptíveis às reações químicas e bioquímicas que ocorrem durante o processamento.

No caso de frutas submetidas à desidratação osmótica, o grau de interferência na cor irá depender das condições de processo (solução desidratante, concentração, temperatura, tempo, agitação). Assim, o aumento da temperatura (acima de 50°C) e a duração do processo (tempos maiores que duas horas) são fatores críticos que podem afetar a perda dos pigmentos da fruta (HENG et al., 1990; SHI et al., 1999). No entanto, em condições apropriadas de processamento, é possível reduzir a mudança de cor, mantendo boas taxas de desidratação (CHUA, et al., 2000).

Matuska et al. (2006) relatam que um processo com altas temperaturas (>50°C) resulta em substancial degradação da cor, o que foi observado após a segunda hora de pré-tratamento osmótico de morangos revestidos com alginato de sódio. Silveira et al. (1996) verificaram que

abacaxis desidratados osmoticamente em soluções com temperatura acima de 50°C apresentaram cor mais escura.

A incorporação de solutos durante a desidratação osmótica pode modificar a composição da fruta favorecendo a retenção de nutrientes, melhorando a cor durante a secagem e evitando o escurecimento enzimático (TORREGGIANI; BERTOLO, 2001).

Tan et al. (2001) estudaram a alteração da cor em batata e abacaxi que foram desidratados através de secagem, com um pré-tratamento osmótico e infravermelho. Os autores puderam constatar que, apesar da desidratação osmótica afetar a coloração do alimento, assim como o processo de secagem, as amostras tratadas osmoticamente previamente à secagem, apresentaram uma menor redução da coloração durante a secagem.

Valente (2007) verificou que a secagem intensificou a cor do abacaxi fresco, aumentando os valores de a^* , b^* e C^* e atribuiu o resultado a concentração de pigmentos devido à perda de água. O autor notou, também, que abacaxis secos pré-tratados osmoticamente apresentaram menor alteração de cor que os abacaxis frescos e secos.

Pereira et al. (2006) verificaram que a adição de lactato de cálcio na solução osmótica com sacarose propiciou efeito protetor na claridade e cromaticidade de goiaba e mamão. Mastrantonio et al. (2005) observaram que a DO em soluções de baixa concentração de maltose adicionadas de lactato de cálcio ocasionou diminuição da cromacidade de pedaços de goiaba, porém, para altas concentrações de solução, a cromacidade das amostras aumentou por causa do efeito de concentração.

Rodrigues et al. (2003) avaliaram a cor de paralelepípedos de mamão Formosa desidratados osmoticamente em soluções de sacarose com aditivos (cálcio e sódio), observando intensificação da cor (aumento do croma – C^*) e escurecimento (diminuição de L^*) ao longo do processo de DO.

3.8. Textura

A textura é um importante atributo de qualidade de alimentos desidratados. Alguns pesquisadores têm estudado técnicas mais eficientes de preservação desse atributo.

Os ensaios instrumentais trazem a vantagem de fornecer dados padronizados e uma linguagem única entre pesquisadores (ABBOT, 1999). Instrumentalmente, a textura é quantificada de acordo com as propriedades mecânicas das amostras em ensaios que procuram, muitas vezes, imitar o comportamento humano (PONS; FISZMAN, 1996).

O comportamento mecânico ou reológico de alimentos é dependente de fatores relacionados à estrutura e suas propriedades. A textura em vegetais é fortemente influenciada pelas condições da lamela média da parede celular (BIDWELL, 1979). As forças de ligação entre as células são predominantemente dependentes do material péctico na lamela média, que se encontra na forma de protopectina, insolúvel em água, sustentando as paredes celulares. Com o amadurecimento, o armazenamento ou a ruptura do vegetal devido a choques ou a processamentos, a pectina é enzimaticamente solubilizada tanto pela redução do tamanho da cadeia quanto pela desesterificação parcial do polímero (remoção dos grupos metílicos). Isso causa a perda da rigidez do material estrutural (POMERANZ; MELOAN, 2000; PILNIK; VORAGEN, 1993; EL-BULUK et al., 1995).

Torreggiani (1993) coloca que a textura da fruta desidratada está associada com a plasticidade e o efeito de inchaço produzido pela água sobre a matriz celulósica e péctica do tecido, dependendo, principalmente, dos sólidos insolúveis, da quantidade de água em solução com os sólidos solúveis e da atividade de água.

Valente (2007) observou, através da determinação dos parâmetros reológicos de tensão e deformação na ruptura, que amostras de abacaxi secas, pré-tratadas osmoticamente, apresentaram maior resistência à deformação da estrutura celular quando comparadas às amostras secas sem pré-tratamento.

4. Referências Bibliográficas

- ARGADOÑA, E.J.S., NISHIYAMA, C.; HUBINGER, M.D. (2002) Qualidade final de melão osmoticamente desidratado em soluções de sacarose com adição de ácidos. **Pesquisa Agropecuária Brasileira**, Brasília, 37, 1803-1810.
- ABBOT, J. Quality Measurement of Fruits and Vegetables. **Postharvest Biology and Technology**, v.15, p. 207-225, 1999.
- ALZAMORA, S. M. et al. (2005) Novel functional foods from vegetables matrices impregnated with biological active compounds. **Journal of Food Engineering**, 67(1-2), 205-214.
- ANDREU-SEVILLA, A.; HARTMANN, A.; SAYAS, E.; BURLÓ-CARBONELL, F.; DELGADO-ESTRELLA, P.; VALVERDE, J.M.; CARBONELL-BARRACHINA, Á.A. (2006) Mathematical quantification of total carotenoids in Sioma® oil using color coordinates and multiple linear regression during deep-frying simulations. **European Food Research and Technology**, v. 6, n.226, p. 1283-1291.
- ANINO, S. V.; SALVATORI, D. M.; ALZAMORA, S. M. (2006) Changes in calcium level and mechanical properties of apple tissue due to impregnation with calcium salts. **Food Research Internacional**, 39, 154-164.

- ANKER, M., STADING, M.; HERMANSSON, A.-M. (2000). Relationship between the microstructure and the mechanical and barrier properties of whey protein films. **Journal of Agricultural and Food Chemistry**, 48, 3806-3816.
- APPEL, L. J.; MOORE, T. J.; OBERZANEK, E.; VOLLMER, W. M.; SVETKEY, L. P.; SACKS, F. M. (1997) A clinical trial of the effects of dietary patterns on blood pressure. **New England Journal of Medicine**, 336, 1117-1124.
- ASTM (1997). **Standard Test Method for Tensile Properties of Thin Plastic Sheeting**, D882-97. In: Annual Book of ASTM, pp. 165-173, American Society for Testing and Materials, Philadelphia, PA.
- ASTM D3985-02, 2002. **Standard test method for oxygen gas transmission rate through plastic film and sheeting using a coulometric sensor**. In: Annual book of ASTM. Amer. Soc. for Testing & Materials, Philadelphia, PA.
- ASTM E96-92, 1990. **Standard test methods for water vapor transmission of materials**. In: Annual Book of ASTM standards. Amer. Soc. for Testing & Materials, Philadelphia, PA.
- AYRANCI, E; TUNC, S. (2003) A method for the measurement of the oxygen permeability and the development of edible films to reduce the rate of oxidative reactions in fresh foods. **Food Chemistry**, 80, 423-431.
- AZEREDO, H.M.C.; JARDINE, J.G.. Desidratação osmótica de abacaxi aplicada à tecnologia de métodos combinados. **Ciência e Tecnologia de Alimentos**, v. 20, n. 1, p. 78-82, 2000.
- BALDWIN, E. A.; NISPEROS, M. O.; CHEN, X.; HAGENMAIER, R. D. (1996) Improving storage life of cut apple and potato with edible coating. **Postharvest Biology and Technology**, v. 9, n.2, p.151-163.
- BARREIRO, J.A.; MILANO, M; SANDOVAL, A.J. (1997) Kinetics of color change of double concentrated tomato paste during thermal treatment. **Journal of Food Engineering**, v.33, p. 359-37.
- BRANDELERO, R. P. H.; VIEIRA, A. P.; TELIS, V. R. N.; TELIS-Romero, J.; YAMASHITA, F. (2005) Aplicação de revestimento comestível em abacaxis processados por métodos combinados: isoterma de sorção e cinética de desidratação osmótica. **Ciência e Tecnologia de Alimentos**, 25(2), 285-290.
- BEAULIEU, M., TURGEON, S. L.; DOUBLIER, J. L. (2001). Rheology, texture and microstructure of whey proteins/low methoxyl pectins mixed gels with added calcium. **International Dairy Journal**, 11(11-12), 961-967.
- BENICHOU, A.; ASERIN, A.; LUTZ, R.; GARTI, N. (2007) Formation and characterization of amphiphilic conjugates of whey protein isolate (WPI)/xanthan to improve surface activity. **Food Hydrocolloids**, 21, 379-391.
- BERTRAND, M. E.; TURGEON, S. L. (2007). Improved gelling properties of whey protein isolate by addition of xanthan gum. **Food Hydrocolloids**, 21(2), 159-166.
- BIDWELL, R.G.S. **Plant Physiology**. Second Edition. p.60. New York: Macmillan Publishing Co., Inc. 726p, 1979.
- BOZDEMIR, O. A.; TUTAS, M. (2003). Plasticiser effect on water vapour permeability properties of locust bean gum-based edible films. **Turkish Journal of Chemistry**, 27, 773-782.
- BOTREL, N.; ABREU, C.M.P. (1985) **Implantação de abacaxizal**. Informe Agropecuário, v.11, n.130, p.22-26.

CALVO, C.; DURÁN, L. (1997) **Propiedades Físicas II – Ópticas y Colo.** In: **J. M. AGUILERA, Temas em Tecnologia de Alimentos**, p. 261-288. Mexico: Instituto Politécnico Nacional.

CANIZARES, D. **Efeito da adição de revestimentos comestíveis sobre a qualidade de mamão desidratado após a secagem e durante o armazenamento.** 99f. Dissertação (Mestrado em Engenharia e Ciência de Alimentos) – Universidade Estadual Paulista “Júlio de Mesquita Filho”, São José do Rio Preto, 2013.

CASTELLÓ, M.L.; IGUAL, M.; FITO, P.J., CHIRALT, A. (2009) Influence of osmotic dehydration on texture, respiration and microbial stability of apple slices (var. granny smith). **Journal of Food Engineering**, v.91, n.1, p.1-9.

CELESTINO, S. M. C. (2009). **Desidratação osmótica na produção de frutas passa e sulfitação**, EMBRAPA Cerrados, Planaltina, DF. Disponível em: <<http://www.cpac.embrapa.br/noticias/artigosmidia/publicados/152/>> (Acessado em 30 de janeiro de 2010).

CERKLEWSKI, F. L. (2005) Calcium fortification of food can add unneeded dietary phosphorus. **Journal of Food Composition and Analysis**, 18, 595-598.

CERQUEIRA, M. A.; BOURBON, A. I.; PINHEIRO, A. C.; MARTINS, J. T.; SOUZA, B. W. S.; TEIXEIRA, J. A.; VICENTE, A. A. (2011) Galactomannans use in the development of edible films/coatings for food applications. **Trends in Food Science & Technology**, 22, 662-671

CHEN, Y.; LIAO, M. L.; BOGER, D. V.; DUNSTAN, D. E. (2001) Rheological characterisation of k-carrageenan/locust bean gum mixtures. **Carbohydrate Polymers**, 46, 117-124.

CHIRALT, A.; FITO, P.; BARAT, J. M.; ANDRES, A.; GONZALEZ-MARTNEZ, C.; ESCRICHE, I.; CAMACHO, M. M. (2001) Use of vacuum impregnation in food salting process. **Journal of Food Engineering**, 49(2-3), 141-151.

CHIRALT, A.; TALENS, P. (2005) Physical and chemical changes induced by osmotic dehydration in plant tissues. **Journal of Food Engineering**, 22(1-2), 167-177.

CHO, S.Y., RHEE, C. (2002). Sorption Characteristics of Soy Protein Films and their Relation to Mechanical Properties. **Lebensmittel-Wissenschaft und-Technologie**, 35, 151-157.

CHUA, K. J., MUJUMDAR, A. J., CHOU, S. K.,; HAWLADER, M. N. (2000) Convective Drying of Banana, Guava and Potato Pieces: Effect of Cyclical Variations of Air Temperature on Drying Kinetics and Color Change. **Drying Technology** , v.18, p. 907-936.

CORTELLINO, G.; PANI, P.; TORREGGIANI, D. (2011) Crispy air-dried pineapple rings: optimization of processing parameters. **11th International Congress on Engineering and Food (ICEF11). Procedia Food Science**, 1, p. 1324-1330.

CRANK, J. (1975) **The Mathematics of Diffusion**. Second edition. London: Clarendon Press – Oxford.

CUMMING, R. G.; CUMMINGS, S. R.; NEVITT, M. C.; SCOTT, J.; ENSRUD, K. E.; VOGT, T. M. (1997) Calcium intake and fracture risk; results from study of osteoporotic fractures. **American Journal of Epidemiology**, 145, 926-934.

- CUNHA, G.A.P.; CABRAL, J.R.S.; SOUZA, L.F.S. (1999) **O abacaxizeiro: cultivo, agroindústria e economia**. EMBRAPA Mandioca e Fruticultura. Brasília: Embrapa Comunicação para Transferência de Tecnologia, 480p.
- CUQ, B.; GONTARD, N.; CUQ, J. L.; GUILBERT, S. (1996) Rheological Model for the Mechanical Properties of Myofibrillar Protein-Based Films. **Journal Agriculture Food Chemical**, 44, 1116-1122.
- CUSSLER, E.L. **Diffusion – Mass transfer in fluid systems**. Cambridge: Cambridge University Press, 1984.
- DA SILVA, J. A. L.; GONÇALVES, M. P. (1990). Studies on a purification method for locust bean gum by precipitation with isopropanol. **Food Hydrocolloids**, 4, 277–287.
- DAKIA, P. A., BLECKER, C., ROBERT, C., WATHELET, B.; PAQUOT, M. (2008). Composition and physicochemical properties of locust bean gum extracted from whole seeds by acid or water dehulling pre-treatment. **Food Hydrocolloids**, 22, 807-818.
- DE KRUIF, C.G.; TUINIER, R. (2001) Polysaccharide protein interactions. **Food Hydrocolloids**, 15, 555-563.
- DE WIT, J. N.; KLARENBEK, G. (1983) Effects of various heat treatments on structure and solubility of whey proteins. **Journal Dairy Science**, 67, 2701-2710.
- DEL VALLE, J. M., CUADROS, T. R. M.; AGUILERA, J. M. (1998) Glass transition and shrinkage during drying and storage of osmosed apple pieces. **Food Research International**, v. 3, n.31, p. 191-204.
- DIONELLO, R. G.; BERBERT, P. A., MOLINA, M. A. B.; PEREIRA, R. C.; VIANA, A. P.; CARLESSO, V. O. (2009) Secagem de fatias de abacaxi in natura e pré-desidratadas por imersão-impregnação: cinética e avaliação de modelos. **Ciência Tecnologia Alimentos**, Campinas, 29(1): 232-240.
- DONHOWE, I. G.; FENNEMA, O. (1994) **Edible films and coatings: characteristics, formation, definitions, and testing methods**. In J. M. Krochta (Ed), *Edible Coatings and Films to Improve Food Quality* (pp 1-24). Lancaster, Pennsylvania: Technomic Publishing Co.
- DOUBLIER, J. L.; GARNIER, C.; RENARD, D.; SANCHEZ, C. (2000) Protein-polysaccharide interactions. **Current opinion in colloid & interface science**, 5 (3-4), 202-214.
- DULL, C.G. (1971) The pineapple general. In: HULME, A.C. **The biochemistry of fruits and their products**. New York: Academic Press, v.11, p.303-324.
- EIK, M.N. **Avaliação de pré-tratamentos e aplicação de coberturas comestíveis na secagem de frutas**. 148p. Dissertação (Mestrado em Engenharia e Ciência de Alimentos) – Universidade Estadual de Campinas - UNICAMP, Campinas, 2008.
- EL-BULUK, R.; BABIKER, E.; EL TINAY, A. (1995) Biochemical and physical changes in fruits of four guava cultivars during growth and development. **Food Chemistry**, v.54, p. 279-282.
- ERTEKIN, F. K.; CAKALOZ, T. (1996) Osmotic dehydration of peas: influence of process variables on mass transfer. **Journal of Food Processing and Preservation**, 20, 87-104.
- FAKHOURI, F. M. et al. (2007) Filmes e coberturas comestíveis compostas à base de amidos nativos e gelatina na conservação e aceitação sensorial de uvas Crimson. **Ciência e Tecnologia de Alimentos**, v. 27, n. 02, p.369-375.

FAO/WHO (1974) - **Handbook on Human Nutritional Requirements**, FAO, Rome.

FAOSTAT (2011) - FAO Statistical Databases. Disponível em: <<http://faostat.fao.org/site/339/default.aspx>>.

FERRARI, C.C.; CARMELLO-GUERREIRO, S.M.; BOLINI, H.M.A.; HUBINGER, M.D. (2010) Structural changes, mechanical properties and sensory preference of osmodehydrated melon pieces with sucrose and calcium lactate solutions. **International Journal of Food Properties**, 13, p.112–130.

FERREIRA, C. O.; NUNES, C. A.; DELGADILLO, I.; LOPES-DA-SILVA, J. A. (2009) Characterization of chitosan-whey protein films at acid pH. **Food Research international**, 42, 807-813.

FITO, P.; CHIRALT, A.; BETORET, N.; GRAS, M.; CHÁFER, M.; MARTÍNEZ-MONZÓ, J.; ANDRÉS, A.; VIDAL, D. (2001) Vacuum impregnation and osmotic dehydration in matrix engineering. Application in functional fresh food development. **Journal of Food Engineering**. 49,175-183.

GARCIA, CC, MAURO, M.A.; KIMURA, M (2007). Kinetics of osmotic dehydration and air-drying of pumpkins (*Cucurbita moschata*). **Journal of Food Engineering**, 82 (3), 284-291.

GARCIA, C.C. **Avaliação da desidratação de mamão utilizando métodos combinados**. 173 f. Tese (Doutorado em Engenharia e Ciência de Alimentos) – Universidade Estadual Paulista “Júlio de Mesquita Filho”, São José do Rio Preto, 2012.

GARCÍA, M.; DÍAZ, R.; MARTÍNEZ, Y.; CASARIEGO, A. (2010) Effects of chitosan coating on mass transfer during osmotic dehydration of papaya. **Food Research International**, 43 1656–1660.

GENINA-SOUTO, P.; BARRERA-CORTES, J.; GUTIERREZ-LOPEZ, G.; NIETO, E. A. (2001) Temperature and concentration effects of osmotic media on profiles of sweet potato cubes. **Drying Technology**, v. 19, n. 3-4, p. 547-558.

GONÇALVES, M.P.; TORRES, D.; ANDRADE, C.T.; AZERO, E.G.; LEFEBVRE, J. (2004). Rheological study of the effect of *Cassia javanica* galactomannans on the heat-set gelation of a whey protein isolate at pH 7. **Food Hydrocolloids** 18, 181–189.

GONÇALVES, A. A.; BLUME, A. R. (2008) Efeito da desidratação osmótica como tratamento preliminar na secagem do abacaxi. **Estudos tecnológicos** - Vol. 4, nº 2:124-134.

GONÇALVES, J. A. **Secagem de carambolas (*Averrhoa carambola* L.): desenvolvimento e aplicação de coberturas comestíveis aditivadas com agentes oxidantes naturais para a conservação de suas propriedades funcionais**. 160f. Dissertação (Mestrado em Engenharia de Alimentos) – Universidade Estadual de Campinas, Campinas, 2010.

GOYCOOLEA, F. M., MORRIS, E. R.,; GIDLEY, M. J. (1995). Viscosity of galactomannans at alkaline and neutral pH: Evidence of ‘hyperentanglement’ in solution. **Carbohydrate Polymers**, 27, 69–71.

GOUNGA, M. E., XU, S. Y.,; WANG, Z. (2007). Whey protein isolate-based edible films as affected by protein concentration, glycerol ratio and pullulan addition in film formation. **Journal of Food Engineering**, 83, 521–530.

GRAS, M. L.; VIDAL, D; BETORET, N.; CHIRALT, A; FITO, P. (2003) Calcium fortification of vegetables by vacuum impregnation interactions with cellular matrix. **Journal of Food Engineering**, 56, 279-284.

- GROSSO, C. R. F.; RAO, M.A. (1998) Dynamic rheology of structure development in low-methoxyl pectin + Ca^{2+} + sugar gels. **Food Hydrocolloids**, 12, 357-363
- GUILBERT, S., GONTARD, N., GORRIS, L. G. M. (1996). Prolongation of the shelflife of perishable food products using biodegradable films and coatings. **Food Science and Technology – Lebensmittel-Wissenschaft & Technologie**, 29, 10-17.
- HAN, J.H.; GENNADIOS, A. (2005) **Edible Films and Coatings: a Review**. In: HAN, J.H (Ed.). *Innovations in Food Packaging*. New York: Elsevier Science & Technology Books. p.239-262.
- HAWKES, J.; FLINK, J. M. (1978). Osmotic concentration of fruit slices prior to freeze dehydration. **Journal of Food Processing and Preservation**, 2, 265-284.
- HENG, H., GUILBERT, S.,; CUQ, J. L. (1990). Osmotic Dehydration of Papaya: Influence of Process Variables on the Product Quality. **Sciences des Aliments**, 10, pp. 831-848.
- HEREDIA, A.; BARRERA, C.; ANDRÉS, A. (2007). Drying of cherry tomato by a combination of different dehydration techniques. Comparison of kinetics and other related properties. **Journal of food Engineering**, 80(1), 111-118.
- IBANOGLU, E. (2005). Effect of hydrocolloids on the thermal denaturation of proteins. **Food Chemistry**, 90, 621–626.
- INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA - IBGE (2011) **Produção agrícola municipal. Culturas temporárias e permanentes**. ISSN 0101-3963, Rio de Janeiro, v. 38, p.1-97. Disponível em: <ftp://ftp.ibge.gov.br/Producao_Agricola/Producao_Agricola_Municipal_[anual]/2011/pam2011.pdf>
- IKEDA, S., FOEGEDING, E. A. (1999). Effects of lecithin on thermally induced whey protein isolate gels. **Food Hydrocolloids**, v 13, p.239-244.
- IKEDA S; FOEGEDING E.; HAGIWARA T (1999) Rheological study on the fractal nature of the protein gel structure. *Langmuir* 15:8584-8589.
- JOOYANDEH, H. (2011). Whey protein films and coatings: a review. **Pakistan Journal of Nutrition**, 10, 296–301.
- KARATHANOS, V. T.; KOSTRAPOULOS, A. E; SARAVACOS, G. K. (1995). Air-drying of osmotically dehydrated fruits, **Drying Technology**, 13, 1503-1521.
- KAUR, C.; KAPOOR, H. C. (2001) Antioxidants in fruits and vegetables – the millennium’s health. **International Journal of Food Science and Technology**, 36, 703-725.
- KAVANAGH, G. M., CLARK, A. H., ROSS-MURPHY, S. B. (2002). Heat-induced gelation of globular proteins: part 3. Molecular studies on low pH β -lactoglobulin gels. **International Journal of Biological Macromolecules**, v 28, p.41-50.
- KAVAK AKPINAR, E.; MIDILLI, A.; BICER, Y. (2005) The first and second law analyses of thermodynamic of pumpkin drying process. **Journal of Food Engineering**, v.72, p. 320-331.
- KESTER, J.J., FENNEMA, O. R. (1986) Edible films and coatings: a review. **Food Technology**, v. 10, n. 12, p. 4759.
- KIRANOUDIS, C.T.; MAROULIS, Z.B., TSAMI, E.; MARINOS-KOURIS, D. (1997) Drying kinetics of some fruits. **Drying technology**, v. 15, n. 5, p. 1399-1418.

- KHWALDIA, K., PEREZ, C., BANON, S., DESOBRY, S.; HARDY, J. (2004). Milk proteins for edible films and coatings. **Critical Reviews in Food Science and Nutrition**, 44, 239–251.
- KOKOSZKA, S., DEBEAUFORT, F., LENART, A.; VOILLEY, A. (2010) Water vapour permeability, thermal and wetting properties of whey protein isolate based edible films **International Dairy Journal**, 20, 53–60
- LACERDA, M. A. D. DE; LACERDA, R. D. DE; ASSIS, P. C, DE OLIVEIRA (2004). A participação da fruticultura no agro negócio brasileiro. **Revista de Biologia e Ciências da Terra**, 4 (1), 1-9. Universidade Estadual da Paraíba. EDUEP, Editora Universitária. Disponível em http://www.uepb.edu.br/eduep/rbct/sumarios/sumario_v4_n1.htm. Acessado em 20 agosto de 2011.
- LAGO-VANZELA, E. S.; NASCIMENTO, P.; FONTES, E. A. F.; MAURO, M. A.; KIMURA, M. (2013) Edible coatings from native and modified starches retain carotenoids in pumpkin during drying. **LWT - Food Science and Technology** 50, 420-425
- LAZARIDES, H. N.; KATSANIDIS, E.; NICKOLAIDIS, A. (1995) Mass transfer during osmotic preconcentration aiming at minimal solid uptake. **Journal of Food Engineering**, v.25, p.151-166.
- LEÃO, A.C.; SOUZA, L.A.C.; ARAÚJO, A.A. (2007) Gerenciamento de cores – Ferramenta fundamental para a documentação digital de bens culturais. **Revista Brasileira de Arqueometria, Restauração e Conservação**, v.1, n. 4, p. 215-220. Olinda, PE: AERPA Editora.
- LEE, J.Y.; PARK, H. J.; LEE, C. Y.; CHOI, W. Y. (2003) Extending shelf-life of minimally processed apples with edible coatings and antibrowning agents. **Lebensm.-Wiss. U.-Technol.** 36, 323–329.
- LENART, A. (1996). Osmo-convective drying of fruits and vegetables: technology and application. **Drying Technology**, 14 (2), 391-413.
- LENART, A.; PIOTROWSKI, D. Drying characteristics of osmotically dehydrated fruits coated with semipermeable edible films. **Drying Technology** , v. 19, n. 5, p. 849-877, 2001.
- LEWICKI, P. P.; VU LE, H.; POMARANSKA-LAZUKA, W. (2002) Effect of Pre-Treatment on Convective Drying of Tomatoes. **Journal of Food Engineering**, v. 54, p. 141-146.
- LE TIEN, C.; VACHON, C.; MATEESCU, M. A.; LACROIX, M. (2001) Milk protein coating prevent oxidative browning of apples and potatoes. **Journal of Food Science**, 66 (4), 512 – 516.
- LIMA, A. M., CERQUEIRA, M. A., SOUZA, B. W. S., SANTOS, E. C. M., TEIXEIRA, J. A., MOREIRA, R. A.. (2010). New edible coatings composed of galactomannans and collagen blends to improve the postharvest quality of fruits e influence on fruits gas transfer rate. **Journal of Food Engineering**, 97, 101-109.
- LUNA-GUZMÁN, I.; BARRET, D. M. (2000) Comparison of calcium chloride and calcium lactate effectiveness in maintaining shelf stability and quality of fresh-cut cantaloupes. **Postharvest Biology and Technology**, 19, 61-72.
- MAFTOONAZAD, N.; RAMASWAMY, H. S. (2008). Effect of pectin-based coating on the kinetics of quality change associated with stored avocados. **Journal of Food Processing and Preservation** 32, 621–643

- MAIA, L. H.; PORTE, A.; SOUZA, V. F.; (2000). Filmes comestíveis: aspectos gerais, propriedades de barreira a umidade e oxigênio. **Boletim CEPPA**, 18, (1), 105-128
- MANDALA, I. G.; ANAGNOSTARAS, C. K.; OIKONOMOU, C. K. (2005) Influence of osmotic dehydration conditions on apple air-drying kinetics and their quality characteristics. **Journal of Food Engineering**, 69, 307-316.
- MANGANARIS, G. A.; VASILAKAKIS, M. ; DIAMANTIDIS, G. ; MIGNANI, I. (2007) The effect of postharvest calcium application on tissue calcium concentration, quality attributes, incidence of flesh browning and cell wall physicochemical aspects of peach fruits. **Food Chemistry**, 100(4), 1385-1392.
- MARFIL, P. H. M. **Estudo reológico de sistemas gelatina/colágeno/amido para obtenção de géis e aplicação em gomas dietéticas de gelatina**. 127f. Dissertação (Mestrado em Engenharia e Ciência de Alimentos) – Universidade Estadual Paulista “Júlio de Mesquita Filho”, São José do Rio Preto, 2010.
- MARTÍN-DIANA, A. B.; RICO, D.; FRÍAS, J. M.; BARAT, J. M.; HENEHAN, G. T. M.; BARRY-RYAN, C. (2007) Calcium for extending the shelf life of fresh whole and minimally processed fruits and vegetable: a review. **Trends in Food Science & Technology**. 18, p.210-218.
- MASKAN, M; (2001) Kinetics of color change of kiwifruits during hot air and microwave drying. **Journal of Food Engineering**, v.48, p. 169–175.
- MASTRANTONIO, S.D.S.; PEREIRA, L.M.; HUBINGER, M.D. (2005) Osmotic dehydration kinetics of guavas in maltose solutions with calcium salt. **Alimentos e Nutrição**, 16 (4), p.309–314.
- MATÉ, J.I., FRANKEL, E.N., AND KROCHTA, J.M. (1996) Whey protein isolate edible coatings: Effect on the rancidity process of dry roasted peanuts. **Journal Agriculture Food Chemistry**, 44:1736–1740.
- MATUSKA, M., LENART, A.,; LAZARIDES, H. (2006). On the use of edible coatings to monitor osmotic dehydration kinetics for minimal solids uptake. **Journal of Food Engineering**, 72, pp. 85-91.
- MAVROUDIS, N. E.; GIDLEY, M. J.; SJÖHOLM, I. (2012) Osmotic processing: Effects of osmotic medium composition on the kinetics and texture of apple tissue. **Food Research International**, 48, 839–847
- MCHUGH, T. H.,; KROCHTA, J. M. (1994). Milk-protein based edible films and coatings. **Food Technology**, 48, 97–103.
- MEDINA, J. C. (1987) Capítulo I: cultura. **Série frutas tropicais: abacaxi**. 2 ed. ITAL – Campinas, p. 1-132.
- MEDLICOTT, A.P. **Fruit Ripening**. Syllabus of the Post-harvest Fruit, Vegetables & Root Crop Technology Course. Tropical Development & Research Institute, London, 7p., 1986.
- MELÉNDEZ-MARTÍNEZ, A.J.; VICARIO, I.M.; HEREDIA, F.J. (2007) Rapid assessment of vitamin A activity through objective color measurements for the quality control of orange juices with diverse carotenoid profiles. **Journal of Agricultural and Food Chemistry**, v.55, n.8, p. 2808-2815.
- MIKKONEN, K.S., RITA, H., HELÉN, H., TALJA, R.A., HYVÖNEN, L., TENKANEN, M.. (2007). Effect of polysaccharide structure on mechanical and thermal properties of galactomannan-based films. **Biomacromolecules**, 8 (10), 3198–3205.

- MILLER, K. S.; KROCHTA, J. M. (1997). Oxygen and aroma barrier properties of edible films: a review. **Trends in Food Science and Technology**, 8, 228–237.
- MORAGA, M. L.; MORAGA, G.; FITO, P. J.; MARTÍNEZ-NAVARRETE, N. (2009) Effect of vacuum impregnation with calcium lactate on the osmotic dehydration kinetics and quality of osmodehydrated grapefruit. **Journal of Food Engineering**. 90, 372-379.
- MUJUMDAR, A. S. (1997). Drying Fundamentals. In C. G. J. Baker (Ed.), **Industrial Drying of Foods**. Baker, (pp 7-30). London: Blackie Academic & Professional.
- MUJUMDAR, A. S; Law, L. C. (2010) Drying Technology: Trends and applications in postharvest processing. **Food Bioprocess Technology**, v.3, p.843-852.
- MUNTADA, V.; GERSCHENSON, L. N.; ALZAMORA, S. M.; CASTRO, M. A. (1998) Solute Infusion Effects on Texture of Minimally Processed Kiwifruit. **Journal of Food Science**, v. 63, p. 61.
- NASCENTE, A.S.; COSTA, R.S.C.; COSTA, J.N.M. (2005). Cultivo do Abacaxi em Rondônia. **Embrapa Rondônia, Sistemas de Produção**, 3. ISSN 1807-1805 Versão Eletrônica.
- NICOLETI, J. F.; TELIS-ROMERO, J.; TELIS, V. R. N. (2001) Air-drying of fresh and osmotically pré-treated pineapple slices: fixed air temperature versus fixed slice temperature drying kinetics. **Drying Technology**, v.19, p.2175-2191.
- NICOLAI, T.; BRITTEN, M.; SCHMITT, C. (2011) β -Lactoglobulin and WPI aggregates: Formation, structure and applications. **Food Hydrocolloids**, 25, 1945 - 1962
- NIJHUIS, H.H.; TORRINGA, E.; LUYTEN,H.; RENE,F.; JONES,P.; FUNEBO, T; OHISSON, T. (1996) Research needs and opportunities in the dry conservation of fruits and vegetables. **Drying Technology**, v. 14, p. 1429-1457.
- OLIVAS, G.I.; BARBOSA-CÁNOVAS, G.V. (2005) Edible Coatings for Fresh-Cut Fruits. **Critical Reviews in Food Science and Nutrition**, v.45, n.7-8, p.657-670.
- ORNELAS-PAZ, J.D.J., YAHIA, E.M., GARDEA, A.A. (2008) Changes in external and internal color during postharvest ripening of 'Manila' and 'Ataulfo' mango fruit and relationship with carotenoid content determined by liquid chromatography-APcI+-time-of-flight mass spectrometry. **Postharvest Biology and Technology**.
- OSÉS, J.; FABREGAT-VÁZQUEZ, M.; PEDROZA-ISLAS, R.; TOMÁS, S. A.; CRUZ-OREA, A.; MATÉ, J. I. (2009). Development and characterization of composite edible film based on whey protein isolate and mesquite gum. **Journal of Food Engineering**, 92, 56-62.
- OSÉS, J., FERNÁNDEZ-PAN, I., MENDOZA, M.,; MATE, J. I. (2009b). Stability of the mechanical properties of edible films based on whey protein isolate during storage at different relative humidity. **Food Hydrocolloids**, 23, 125e131.
- PARK, KIL JIN; YADO, MAURÍCIO KENZE MORENO; BROD,FERNANDO PEDRO REIS (2001). Estudo de secagem de pêra bartlett (pyrus sp.) em fatias. **Ciência e Tecnologia de alimentos**, Campinas, São Paulo, Brasil, v. 21, n. 3 p. 288-292.
- PARK, K.J.; BIN, A.; BROD, F.P.R. (2002) Drying of pear d'Anjou with and without osmotic dehydration. **Journal of Food Engineering**, vol. 56, p. 97-103.
- PELEGRINE, D.H.G.; GASPARETTO, C.A. (2005) Whey proteins solubility as function of temperature and Ph. **Lebensm.-Wiss. u.-Technol.** 38, 77–80

PEREIRA, L.M.; FERRARI, C.C.; MASTRANTONIO, S.D.S.; RODRIGUES, A.C.C. (2006) Kinetic aspects, texture, and color evaluation of some tropical fruits during osmotic dehydration. **Drying Technology**, v.24, p.475-484.

PEREZ, A. A.; CARRARA, C. R.; SÁNCHEZ, C. C.; PATINO, J. M. R.; SANTIAGO, L. G. (2009). Interactions between Milk whey protein and polysaccharide in solution. **Food Chemistry**, 116, 104–113.

PÉREZ-GAGO, M.B., KROCHTA, J.M.. (2000) Drying temperature effect on water vapor permeability and mechanical properties of whey protein–lipid emulsion films. **Journal Agriculture Food Chemistry**. 48, 2687–2692.

PEREZ-GAGO, M. B.; KROCHTA, J. M. (2001). Denaturation time and temperature effects on solubility, tensile properties, and oxygen permeability of whey protein edible films. **Journal of Food Science**, 66(5), 705-710.

PÉREZ-GAGO, M.B.;SERRA, M.; ALONSO, M.; MATEOS, M.; DEL RÍO, M.A. (2005). Effect of whey protein and hydroxypropyl methylcellulosebased edible composite coatings on color change of fresh-cut apples. **Postharvest Biology Technology**, 36, 77–85.

PÉREZ-GAGO, M.B.; SERRA, M.; DEL RÍO, M.A. (2006) Color change of fresh-cut apples coated with whey protein concentrate-based edible coatings. **Postharvest Biology and Technology**, 39, 84–92.

PÉREZ-LÓPEZ, A.J.; BELTRAN, F.; SERRANO MEGÍAS, M.; LÓPEZ, D. S.; CARBONELL-BARRACHINA, A. A. (2006) Changes in orange juice color by addition of mandarin juice. **Journal European Food Research and Technology**, Publisher Springer Berlin / Heidelberg, V. 222, n.5-6, p. 516-520.

PICONE, C.S. F. **Influência da conformação da gelatina sobre a gelificação das proteínas do leite**. 161f. Dissertação (Mestrado em Engenharia e Ciência de Alimentos) – Universidade Estadual de Campinas - UNICAMP, Campinas, 2005.

PIERRO, P.; SORRENTINO, A.; MARINIELLO, L.; VALERIA L. C.; PORTA, R. (2011) Chitosan/whey protein film as active coating to extend Ricotta cheese shelf-life. **LWT - Food Science and Technology**, 44, 2324 - 2327.

PILNIK, W.; VORAGEN, G.J. (1993) Pectic Enzymes in Fruit and Vegetable Juice Manufacture. **In Enzymes in Food Processing**. Edited by T.Nagodawithana and G. Reed. 3 ed. San Diego: Academic Press, Inc..

POMERANZ, Y.; MELOAN C.E. (2000) **Food Analysis: Theory and Practice**. 3ªedição. Gaithersburg, Maryland. p.778.

PONS, M.; FISZMAN, S.M. (1996) Instrumental Texture Profile Analysis with Particular Reference to Gelled Systems. **Journal of Texture Studies** , 27, p. 597-694.

PONTING, J. D. (1973). Osmotic Dehydration of Fruits – Recent Modification and Applications. **Process Biochemistry**, 8, 18-20.

PONTING, J.D.; WATTERS, G.G.; FORREY, R.B.; JACKSON, R.; STANLEY, W.L. (1966) Osmotic Dehydration of Fruits. **Food Technology**, v. 20, n.10, p.1365-1368.

QI, H.; LE MAGUER, M.; SHARMA, S. K. (1998). Design and selection of processing conditions of a pilot scale contactor for continuous osmotic dehydration of carrots. **Journal of Food Processing and Engineering**, 21, 75-88.

- QUINTERO-RAMOS, A.; DE LA VEJA, C., HERNANDEZ, E.; ANZALDÚA-MORALES, A. (1993). Effect of conditions of osmotic treatment on the quality of dried apple dices. **Aiche Symposium Series**, 89, 108-103.
- RAMALLO, L. A.; SCHVEZOV, C.; MASCHERONI, R. H. (2004) Mass transfer during osmotic dehydration of pineapple. **Food Science Technology International**, v.10 (5), p.323-332.
- RAMALLO, L.A.; MASCHERONI, R.H (2010) Dehydrofreezing of pineapple. **Journal of Food Engineering** v.99, p.269–275.
- RAMALLO, L. A.; MASCHERONI, R. H. (2012) Quality evaluation of pineapple fruit during drying process. **Food and bioproducts processing**, 90, 275-283.
- RAMESH, M. N.; WOLF, W.; TEVINI, D.; JUNG, G. (2001). Influence of processing parameters on the drying spice paprika. **Journal of Food Engineering**, 49,p.63-72.
- RAMOS, O. L., FERNANDES, J. C., SILVA, S. I., PINTADO, M. E.,; MALCATA, F. X. (2012). Edible films and coatings from whey proteins: a review on formulation, and on mechanical and bioactive properties. **Critical Reviews in Food Science and Nutrition**, 52, 533-552.
- RAMOS, O. L., REINAS, I., SILVA, S. I., FERNANDES, J. C., CERQUEIRA, M. A., PEREIRA, R. N., VICENTE, A. A., FATIMA POCAS, M., PINTADO, M. E.,; XAVIER MALCATA, F. (2013). Effect of whey protein purity and glycerol content upon physical properties of edible films manufactured therefrom. **Food Hydrocolloids**, 30(1), 110-122.
- RAO, M. A. Measurement of Flow and Viscoelastic Properties. In: **Rheology of fluid and semisolid foods**, ed. Aspen Publication, Gaithersburg, Maryland, p. 105-139, 1999.
- RAOULT-WACK, A. L., LAFONT, F., RIOS, G.; GUILBERT, S. (1989) Osmotic dehydration: study of mass transfer in terms of engineering properties. In: A. S. Mujumdar (ed.), **Drying 89**, Hemisphere Corporation.
- RAOULT-WACK, A. L. (1994). Recent advances in the osmotic dehydration of foods. **Trends in Food Science and Technology**, 5, 255-260.
- RASTOGI, N. K.; RAGHAVARAO, K. S. M. S.; NIRANJAN, K. (1997). Mass transfer during osmotic dehydration of banana: Fickian diffusion in cylindrical configuration. **Journal of Food Engineering**. 31, 423-432.
- RIZVI, S. S. H. (1986) **Thermodynamic properties of food in dehydration. In: Engineering Properties of Foods** (Rao, M. A; Rizvi, S. S. H, eds), p. 133–214.
- RIVA, M.; CAMPOLONGO, S.; LEVA, A.A.; MAESTRELLI, A.; TORREGGIANI, D. (2005) Structure-property relationships in osmo-air-dehydrated apricots cubes. **Food Research International**, 38, 533–542.
- ROBBERS, M.; SINGH, R.P.; CUNHA, L.M. (1997) Osmotic-convective dehydrofreezing process for drying kiwifruit. **Journal of Food Science**. Chicago, 62(5), 1039-1047.
- ROCHA, C.; TEIXEIRA, J.A.; HILLIOU, L.; SAMPAIO, P.; GONÇALVES, M. P. (2009) Rheological and structural characterization of gels from whey protein hydrolysates/locust bean gum mixed systems. **Food Hydrocolloids**, 23, 1734–1745.
- RODRIGUES, A. C. C.; CUNHA, R. L.; HUBINGER, M. D. (2003) Rheological properties and colour evaluation of papaya during osmotic dehydration processing. **Journal of Food Engineering**, Essex, v. 59, p. 129-135.

- SÁNCHEZ-MORENO, C., PLAZA, L., DE ANCOS, B., CANO, M.P. (2006) Impact of high-pressure and traditional thermal processing of tomato purée on carotenoids, vitamin C and antioxidant activity. **Journal of the Science of Food and Agriculture**, v.86, n.2, p. 171-179.
- SANJINEZ-ARGANDOÑA, E.J.; CUNHA, R.L.; MENEGALLI, F.C.; HUBINGER, M.D. (2005) Evaluation of total carotenoids and ascorbic acid in osmotic pretreated guavas during convective drying. **Italian Journal of Food Science**, 17 (3), 305–314.
- SANTOS, P.H.S. AND SILVA, M.A. (2008), Retention of Vitamin C in Drying Processes of Fruits and Vegetables - A Review, **Drying Technology**, Vol. 26, pp. 1421–1437.
- SAPUTRA, (2001) D. Osmotic dehydration of pineapple. **Drying Technology**, v.19, p.415-425.
- SCALON, S. P. Q.; OSHIRO, A. M.; DRESCH, D. M. (2012) Conservação pós-colheita de guavira (*Campomanesia adamantium* Camb.) sob diferentes revestimentos e temperaturas de armazenamento. Revista Brasileira Fruticultura, Jaboticabal - SP, 34, (4), p. 1022-1029
- SERENO, A. M.; MOREIRA, R.; MARTINEZ, E. (2001). Mass transfer coefficients during osmotic dehydration of apple in single and combined aqueous solutions of sugar and salt. **Journal of Food Engineering**, 47, 43-49.
- SHI, J.; LE MAGUER, M.; KAKUDA, Y.; LIPTAY, A.; NIEKAMP, F. (1999). Lycopene degradation and isomerization in tomato dehydration, **Food Research International**, 32, 15-21.
- SHIGEMATSU, E.; EIK, N.; KIMURA, M.; MAURO, M. A. (2005). Influência de pré-tratamentos sobre a desidratação osmótica de carambolas. **Ciência e Tecnologia de Alimentos**, 25 (3), 536-545.
- SILVA, K.S.; CAETANO, L. C.; GARCIA, C. C., TELIS ROMERO, J.; SANTOS, B. A.; MAURO, M. A. (2011) Osmotic dehydration process for low temperature blanched pumpkin (*Cucurbita moschata*) **Journal of Food Engineering** 105, p. 56–64. ACRESCENTAR
- SILVEIRA, E. T. F.; RAHMAN, M. S.; BUCKLE, K. A. (1996) Osmotic dehydration of pineapple: kinetics and product quality. **Food Research International**, v.29, p.227- 233.
- SRIVASTAVA, M.; KAPOOR, V. P. (2005). Seed galactomannans: an overview. **Chemistry & Biodiversity**, 2(3), 295-317.
- SITTIKIYOTHIN, W., SAMPAIO, P.; GONÇALVES, M. P. (2005). Heat-induced gelation of [beta]-lactoglobulin at varying pH: effect of tara gum on the rheological and structural properties of the gels. **Food Hydrocolloids**, 21(7), 1046–1055.
- SOTHORNVIT, R.; KROCHTA, J. M. (2005). Plasticizers in edible films and coatings. In J. H. Han, (Ed.), *Innovations in Food Packaging* (pp. 403–433). London, UK: Academic Press.
- SMITH, L.G. (1993) **Pineapples**. Encyclopaedia of Food Science, Food Technology and Nutrition. Academic Press.
- SOUSA, S. (2008) **Obtenção de figos secos por desidratação osmótica e secagem convectiva**. Campinas, SP. Tese (doutor em Engenharia de Alimentos), faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas.
- STADING, M.; HERMANSSON, A. M. (1991) Large deformation properties of β -lactoglobulin gel structures. **Food Hydrocolloids**, 5 (4), 339-352.

- STADING, M.; LANGTON, M.; HERMANSSON, A. M. (1993) Microstructure and rheological behavior of particulate β -lactoglobulin gels. **Food Hydrocolloids**, 7 (3), 195-212.
- TAN, M.; CHUA, K. J.; MUJUNDAR, A. S.; CHOU, S. K. (2001) Effect of osmotic pre-treatment and infrared radiation on drying rate and color changes during drying of potato and pineapple. **Drying Technology**, v.19(9), p.2193-2207.
- THAKUR, B. R.; SINGH, R. K.; HANDA, A. K. (1997) Chemistry and uses of pectin – a review. **Critical Reviews in Food Science and Nutrition**, 37 (1), p.47-73.
- TELIS, V. R. N.; MURARI, R. C. B. D. L.; YAMASHITA, F. (2004). Diffusion coefficients during osmotic dehydration of tomatoes in ternary solutions. **Journal of Food Engineering**, 61, 253-259.
- TORREGGIANI, D. (1993) Osmotic dehydration in fruits and vegetables. **Process and Food Research International**, v.26, p.59-68.
- TORREGGIANI, D. e BERTOLO, G. (2001) Osmotic pre-treatments in fruit processing: chemical, physical and structure effects. **Journal of Food Engineering**, v.49, p.247-253.
- TORRES, D. P. M. **Gelificação térmica de hidrolizados enzimáticos de proteínas do soro de leite bovino, comportamento de sistemas aquosos mistos péptidos-polissacarídeos**. Dissertação de mestrado, Universidade do Minho, Braga, 2005.
- TREYBAL, R.E. **Mass Transfer Operations**. New York: McGraw Hill, 1980.
- TURGEON, S. L.; BEAULIEU, M. (2001). Improvement and modification of whey protein gel texture using polysaccharides. **Food Hydrocolloids**, 15(4–6), 583–591.
- VALENTE, P. P. S. S. (2007) **Desidratação osmótica e secagem de abacaxi (Ananás comosus (L.) Merrill), variedade Pérola**. Campinas, SP. Dissertação (mestre em Engenharia de Alimentos), Faculdade de Engenharia de Alimentos, Universidade Estadual de Campinas.
- VAN DEN BERG, C.; BRUIN, S. (1981). **Water activity and its estimation in food systems**. In L. B. Rockland & G. F. Stewart (Eds.), *Water activity: influences on food quality* (p. 147–177). New York: Academic Press.
- VARGAS, M.; PASTOR, C.; CHIRALT, A.; McCLEMENTS, D. J.; GONZÁLEZ-MARTINÉZ, C. (2008) Recent Advances in Edible Coatings for Fresh and Minimally Processed Fruits. **Critical Reviews in Food Science and Nutrition**. Vol. 48, p.496-511.
- VEGA-GÁLVEZ, A.; LEMUS-MONDACA, R.; BILBAO-SÁINZ, C.; FITO, P.; ANDRE'S, A. (2008) Effect of air drying temperature on the quality of dehydrated dried red bell pepper (var. Lamuyo). **Journal of Food Engineering**, 85, 42–50.
- VEGA-MERCADO, H.; GONGORA-NIETO, M.M.; BARBOSA-CANOVAS, G.V. (2001) Advances in dehydration of foods. **Journal of Food Engineering**, vol. 49, p. 271-289.
- VIAL, C.; GUILBERT, S.; CUQ, J.L. (1991) Osmotic dehydration of kiwi fruits: influence of process variables on the color and ascorbic acid content. **Sciences des Aliments**, 11(1), 63-84.
- VOGEL, A. I. **Análise Química Quantitativa**, 6ª Ed. Rio de Janeiro: LTC Editora, 2002. Pg 189, 367
- ZHAO, Y. P.; CHANG, K. C. (1995) Sulfite and starch affect color and carotenoids of dehydrated carrots (*Daucus carota*) during storage. **Journal of Food Science**, Chicago, v. 60, n. 2, p. 324-347.

WANG, L.; AUTY, M. A. E.; KERRY, J. P. (2010) Physical assessment of composite biodegradable films manufactured using whey protein isolate, gelatin and sodium alginate. **Journal of Food Engineering**, 96, 199-207.

WAWIRE, M., OEY, I., MATHOOKO, F., NJOROGE, C., SHITANDA, D.; HENDRICKX, M. (2011), Thermal Stability of Ascorbic Acid and Ascorbic Acid Oxidase in African Cowpea Leaves (*Vigna unguiculata*) of Different Maturities, **Journal of Agriculture and Food Chemistry**, Vol. 59, pp. 1774–1783.

YANG, L.,; PAULSON, A. T. (2000). Effects of lipids on mechanical and moisture barrier properties of edible gellan film. **Food Research International**, 33, 571–578.

YANG, H. H.; LAWSLESS, H. T. (2003) Descriptive analysis of divalent salts. **Journal of Sensory Studies**, 20, 97-113.

YOO, S. R.; KROCHTA, J. M. (2011) Whey protein–polysaccharide blended edible film formation and barrier, tensile, thermal and transparency properties. **Journal Science Food Agriculture**, 91, p. 2628-2636.

CAPÍTULO I

Effect of calcium impregnation on mass transfer and quality of pineapple

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Abstract

The aim of this work was to investigate the effects of sucrose and calcium lactate concentration on the osmotic dehydration kinetics of pineapple and the diffusivity of each component. The influence of sugar, calcium salt and time of osmotic dehydration on color, water activity and texture was also evaluated. Results showed that calcium impregnation was greater in samples submitted to solutions with higher sucrose and calcium lactate concentration. The greatest calcium content (90mg/100g) was reached after 6 hours of impregnation in solutions containing 4% calcium lactate. Calcium addition in osmotic solution reduced water content of product and the solute incorporation rate, inhibiting sucrose impregnation and increasing process efficiency. The sucrose and water diffusivity were affected significantly with calcium concentration in osmotic solution. Calcium impregnation did not influence the color of product and did not improve the texture of samples showing a decrease in the value of failure force, as compared with raw pineapple.

Nomenclature M = mass (kg) ΔM = total mass variation in relation to initial mass (dimensionless) R^2 = determination coefficient (dimensionless) ΔG_{SUC} = sugar gain in relation to initial mass (dimensionless) ΔG_{Ca} = calcium gain in relation to initial mass (dimensionless) ΔW = water loss in relation to initial mass (dimensionless) w_w = water content w_{SUC} = sucrose content w_{Ca} = calcium content $\overline{w}_i(t)$ = mean concentration of the component for a time (t) SUC = sucrose concentration (%) LAC = calcium lactate concentration (%) L^*_F = luminosity C^*_F = Chroma**Subscripts and superscript** $calc$ = calculated; exp = experimental;

OD = osmotic dehydration

 s = sucrose Ca = calcium w = water 0 = initial state F = Fresh**1. Introduction**

Osmotic dehydration (OD) is a water removal process that can be employed to obtain minimally processed food with higher shelf-life and nutritional value. As a pretreatment to drying, OD can reduce the moisture content of a plant by approximately 50%, moreover can be used to reduce aroma loss and enzymatic browning, and increase sensory acceptance and nutrients retention (PONTING et al., 1996; SHI et al., 1999; TORREGGIANI; BERTOLO, 2001; PAN et al., 2003; LOMBARDI et al., 2008). This treatment also allows introducing

substances in porous structure of fruits and vegetables promoting the enrichment these foods with minerals, vitamins or others physiologically active components (FITO et al., 2001).

Osmotic dehydration reduces the moisture of fruits and vegetables through the immersing in aqueous concentrated solution containing one or more solutes (SERENO et al., 2001; GARCIA et al., 2007). Hypertonic solution provides high osmotic pressure that promotes diffusion of water from vegetable tissue into the solution and diffusion of solutes from the osmotic solution into the tissue (RASTOGI et al., 2002). This mass transfer depends upon same factors as geometry of product, temperature, concentration and agitation of the solution.

Characteristics of the osmotic agent used, as its molecular weight and its ionic behavior, strongly affect dehydration, in both water loss and solute gain. Moreover, sensory and nutritive properties of the final product can be affected by solute used in osmotic process (RAMALLO et al., 2004; TELIS et al., 2004; FERRARI et al., 2010). Saputra (2001) verified that sucrose provides larger water loss and smaller solute gain, when compared to glucose, in pineapple samples submitted to osmotic dehydration. Cortelino et al., 2011 observed that the osmotic pretreatment in sucrose solution protected the colour of pineapple rings during drying.

Addition of calcium salts in osmotic solutions has been used to reduce the damages caused in structure of the cell wall due to dehydration (MASTRANTONIO et al., 2005; PEREIRA et al., 2006; HEREDIA et al., 2007; FERRARI et al., 2010). However, the use of these salts in osmotic solutions can also increase the rate of water loss, reduce water activity and increase the calcium content of vegetables and fruits, resulting in fortified products (HENG et al., 1990; RODRIGUES et al., 2003; PEREIRA et al., 2006 and HEREDIA et al., 2007; SILVA et al., 2013).

The demand for minimally processed products has increased lately due to changes in style life and to consume standard of food. Osmotic dehydration is a treatment that can be also used to enhance nutritional characteristics of product.

Anino et al. (2006), exploring the possibility to obtain enriched product with calcium, analyzed the tissue impregnation capacity of minimally processed apples in solution containing 10.9 % (w/w) glucose, 5266ppm of calcium salt (a blend of calcium lactate and calcium gluconate), 1500ppm potassium sorbate and citric acid to correction of pH until 3.5, with and without vacuum applying. The process done without vacuum applying was more efficient. The amount of calcium incorporated in apple samples were 1300ppm after 6 hours

and 3100ppm after 22 hours of process without vacuum. In process with vacuum, the impregnation ranged between 1150 – 2050ppm.

Several works on osmotic dehydration with calcium salts have been published lately aiming reduce the damages caused in structure of the cell wall (MASTRANTONIO et al., 2005; PEREIRA et al., 2006; HEREDIA et al., 2007; FERRARI et al., 2010), however few have considered the kinetics and diffusivity of each component of a ternary solution (sucrose + calcium) in fruit.

This study aims to investigate: - the effects of sucrose and calcium lactate concentration on the osmotic dehydration kinetics of pineapple and the diffusivity of each component; - the influence of sugar, calcium salt and time of osmotic dehydration on color, water activity, texture and calcium content of the pineapple.

2. Materials and methods

2.1 Materials

Pineapple (*Ananás comosus* (L.) Merril) of commercial ripeness degree, weighing approximately 1.2Kg, were washed, manually peeled and its ends were discarded to reduce the variability of tissue. The pieces were sliced (1 ± 0.1 cm thick) and the slices were cut in truncated cone format with the aid of a metal mold.

Osmotic solutions were prepared with commercial sucrose (amorphous refined sugar) purchased in a local market; food grade pentahydrate calcium lactate in powder from PURAC[®] Synthesis – Brazil and distilled water.

2.2 Procedures:

Osmotic dehydration kinetics and diffusion coefficients

The pineapple slices were arranged in four nylon mesh baskets, with approximately 350g of samples in each basket. The baskets were immersed in 20 kg of aqueous solution, continuously stirred by using a 1.6 kw mechanical stirrer (Marconi, model MA-261 - Brazil) with a 10 cm diameter propeller and rotation at 1850 rpm. The temperature of the solution was maintained at 27°C and syrup-to-fruit ratio was approximately 1:14 (1.4kg of sample/ 20kg of solution).

The aqueous solution concentrations studied were 40 and 50% sucrose (*SUC*) with and without 2 and 4% calcium lactate (*LAC*), where each process was carried out for 1, 2, 4 and 6 hours. At the end of each process time, one basket was removed from the osmotic bath and the samples immersed in distilled water at room temperature for 10 seconds in order to remove the osmotic solution from the surface. They were then blotted with absorbing paper and weighted. Experiments were run in duplicate. The total solids, total and reducing sugars and calcium content were analyzed before and after each treatment. The influence of the time and the addition of sucrose and calcium lactate in the osmotic solution on mass transfer were compared. The equilibrium concentration of the water, sucrose and calcium was determined by soaking thin fruit slices (3 mm thickness) in flask containing approximately 600 g osmotic solution. The solutions were maintained at 27°C with orbital agitation of 165rpm and syrup-to-fruit ratio was approximately 1:10. Preliminary experiments showed that 48 hours were enough for equilibrium to be achieved. After 48 hours, the flasks were removed, and the pieces drained, dipped in distilled water for 10 seconds and blotted with absorbent material. Samples were prepared for analysis of water, sucrose and calcium content.

2.3 Analytical methods

The water content of fresh and osmotic dehydrated samples were gravimetrically determined in triplicate by the drying of the samples in a vacuum oven at 60°C and 10 kPa until a constant weight was achieved. The total and reducing sugar contents of fresh and osmotically treated samples were determined in triplicate by the oxidation-reduction titration (AOAC, 1970). The calcium concentration of the fresh and dehydrated samples were determined in duplicate using flame atomic absorption spectrometer (SpectrAA 50B of Varian - Mulgrave, Australia), according to adapted methodology of AOAC (1995). Water activity of the samples was measured in triplicate at 25 °C in a hygrometer (AW SPRINT; NOVASINA, Switzerland). The color of fresh and osmotic dehydrated fruits was evaluated (4 replicates) using a Colorflex spectrophotometer (HunterLab, USA) and version 4.10 of the Universal software. The response was expressed in the form of the parameters L* (lightness: 100 for white and 0 for black) and Chroma (C^*):

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

Texture of fresh and osmotic dehydrated samples was determined by evaluating (10 replicates) of stress at rupture, done in Universal texturometer (TA-XT2i Texture Analyser, Stable Micro System, Surrey, UK.). Method used was measure force in compression holding until rupture time. This uniaxial compression test was performed at compression speed of 5 mm/s and 60% sample deformation. Stress at failure was determined from the peak of the stress-strain curve.

2.4 *Experimental design, mathematical models and statistical analysis*

Aiming to evaluate the influence of solution composition on the water loss and solids gain, was determined mass balance for each concentration and time of the osmotic treatment.

Thus the mass variation (ΔM) and water loss (ΔW) were calculated according to eqs 2 and 3 and sucrose gain (ΔG_{SUC}), calcium gain (ΔG_{Ca}) and efficiency (E_f) were calculated according to Eqs. 4, 5 and 6. All variables are defined in nomenclature section.

$$\Delta M = \frac{M - M^0}{M^0} \times 100 \quad (2)$$

$$\Delta W = \frac{(Mw_w) - (M^0w_w^0)}{M^0} \times 100 \quad (3)$$

$$\Delta G_{SUC} = \frac{(Mw_{SUC}) - (M^0w_{SUC}^0)}{M^0} \times 100 \quad (4)$$

$$\Delta G_{Ca} = \frac{(Mw_{Ca}) - (M^0w_{Ca}^0)}{M^0} \times 100 \quad (5)$$

$$E_f = \frac{\Delta W}{\Delta G_{SUC} + \Delta G_{Ca}} \cdot 100 \quad (6)$$

where M is the mass; w_w is the water content; w_{SUC} is the sucrose content; w_{Ca} is the calcium content.

The diffusion coefficients of water, sucrose and calcium of the pineapple slices were determined according to Fick's Second Law as applied to a plane sheet. The analytical

solution, when integrated along the distance, results in the average concentration of the component i , $\overline{w}_i(t)$ in the solid at time t (CRANK, 1975):

$$\frac{\overline{w}_i(t) - w_i^{eq}}{w_i^0 - w_i^{eq}} = \left(\frac{8}{\pi^2} \right) \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left\{ -(2n-1)^2 \frac{t\pi^2 D_{ef}}{l^2} \right\} \quad (7)$$

where i = water, sucrose or calcium; D_{ef_i} = the effective diffusion coefficient of a component i ; $\overline{w}_i(t)$ = average fraction of component i at time t ; w_i^0 = fraction of the component i at initial time ($t=0$); w_i^{eq} = fraction of the component i at equilibrium; n is number of the series; l , is thickness of the slab; t is the time. The Equation 7 was fitted to the experimental data, using "Prescribed" software (Silva; Silva, 2008). "Prescribed" is used to study water diffusion processes with known experimental data. For each setting, the values for Chi-square were calculated:

$$\chi^2 = \sum_{i=1}^{N_p} \left(\overline{y}_i^{\text{exp}} - \overline{y}_i^{\text{calc}} \right)^2 \frac{1}{\sigma_i^2} \quad (8)$$

where $\overline{y}_i^{\text{exp}}$ is the average content (calcium, water, sucrose or vitamin C) measured at the experimental point i ; $\overline{y}_i^{\text{calc}}$ is the correspondent calculated average content; N_p is the number of experimental points; $1/\sigma_i^2$ is the statistical weights referring to the point i .

To evaluate the influence of the concentrations of sugar and calcium salt on color, texture and water activity of pineapples, variability of the raw material used for the different tests were minimized by using a normalized content, defined as the ratio between the experimental measurements obtained from the osmotically treated sample and the corresponding fresh sample (SILVA et al., 2011b). The results were statistically evaluated using the analysis of variance (ANOVA), with the sources of variation being the sample type and number of samples, and the Tukey Test being applied at the 5% level of significance.

3. Results

The experimental data of mass variation (ΔM), water loss (ΔW), sucrose gain (ΔG_{SUC}), calcium gain (ΔG_{Ca}) and processes efficiency (E_f), calculated according to Eq. 2, 3, 4, 5 and 6, obtained during different times of osmotic dehydration of pineapple are shown in Table 1.

Table 1: Mass variation (ΔM), water loss (ΔW), sucrose gain (ΔG_{SUC}), calcium gain (ΔG_{Ca}), all with respect to the initial mass (M^0), and processes efficiency (E_f), during the osmotic dehydration (OD) of pineapple in six different solutions.

		Osmotic solution composition					
	Time of osmotic dehydration (h)	OD (40% SUC) (1)	OD (40% SUC + 2% LAC) (2)	OD (40% SUC + 4% LAC) (3)	OD (50% SUC) (4)	OD (50% SUC + 2% LAC) (5)	OD (50% SUC + 4% LAC) (6)
ΔM (%)	1	$-8.90 \pm 0.56^{a, AB}$	$-6.49 \pm 0.58^{a, B}$	$-13.18 \pm 1.00^{a, CD}$	$-10.60 \pm 1.36^{a, AC}$	$-10.30 \pm 0.21^{a, AC}$	$-14.81 \pm 1.14^{a, D}$
	2	$-13.09 \pm 0.43^{b, AB}$	$-10.91 \pm 0.77^{a, A}$	$-18.44 \pm 1.10^{b, C}$	$-14.76 \pm 1.06^{a, BC}$	$-12.76 \pm 0.31^{a, AB}$	$-17.34 \pm 0.81^{ab, CE}$
	4	$-15.19 \pm 0.91^{bc, A}$	$-16.64 \pm 1.68^{b, AB}$	$-25.85 \pm 1.35^{c, BC}$	$-22.40 \pm 1.19^{b, CD}$	$-18.50 \pm 1.59^{b, AD}$	$-20.80 \pm 1.07^{b, BD}$
	6	$-17.43 \pm 0.90^{c, A}$	$-19.93 \pm 1.33^{b, AB}$	$-27.56 \pm 1.11^{c, C}$	$-21.70 \pm 1.06^{c, BD}$	$-24.16 \pm 0.87^{c, CD}$	$-29.36 \pm 1.00^{c, C}$
w_w^0 (%)	0	83.27 ± 0.05^A	83.52 ± 0.18^A	86.69 ± 0.08^B	83.27 ± 0.05^A	88.06 ± 0.30^C	85.40 ± 0.06^D
	1	$-14.86 \pm 0.03^{a, A}$	$-11.32 \pm 0.08^{a, B}$	$-20.12 \pm 0.08^{a, C}$	$-16.15 \pm 0.04^{a, D}$	$-18.19 \pm 0.14^{a, E}$	$-21.65 \pm 0.03^{a, F}$
	2	$-19.29 \pm 0.11^{b, A}$	$-16.82 \pm 0.10^{b, B}$	$-26.24 \pm 0.13^{b, C}$	$-23.45 \pm 0.15^{b, D}$	$-21.45 \pm 0.05^{b, E}$	$-25.47 \pm 0.12^{b, F}$
	4	$-21.45 \pm 0.05^{c, A}$	$-23.80 \pm 0.05^{c, B}$	$-33.56 \pm 0.02^{c, C}$	$-30.92 \pm 0.20^{c, D}$	$-30.99 \pm 0.22^{c, D}$	$-31.81 \pm 0.07^{c, E}$
ΔW (%)	6	$-24.43 \pm 0.08^{d, A}$	$-27.62 \pm 0.03^{d, B}$	$-36.03 \pm 0.02^{d, C}$	$-31.31 \pm 0.02^{d, D}$	$-36.33 \pm 0.12^{d, E}$	$-40.04 \pm 0.06^{d, F}$
	48	66.01 ± 0.08^e	64.43 ± 0.13^e	62.46 ± 0.06^e	57.27 ± 0.14^e	55.05 ± 0.19^e	53.02 ± 0.06^e
	48	66.01 ± 0.08^e	64.43 ± 0.13^e	62.46 ± 0.06^e	57.27 ± 0.14^e	55.05 ± 0.19^e	53.02 ± 0.06^e
	48	66.01 ± 0.08^e	64.43 ± 0.13^e	62.46 ± 0.06^e	57.27 ± 0.14^e	55.05 ± 0.19^e	53.02 ± 0.06^e

Table 1: Mass variation (ΔM), water loss (ΔW), sucrose gain (ΔG_{SUC}), calcium gain (ΔG_{Ca}), all with respect to the initial mass (M^0), and processes efficiency (E_f), during the osmotic dehydration (OD) of pineapple in six different solutions. (Continuation)

		Osmotic solution composition					
	Time of osmotic dehydration (h)	OD (40% SUC) (1)	OD (40% SUC + 2% LAC) (2)	OD (40% SUC + 4% LAC) (3)	OD (50% SUC) (4)	OD (50% SUC + 2% LAC) (5)	OD (50% SUC + 4% LAC) (6)
w_{SUC}^0 (%)	0	8.90 ± 0.35 ^A	8.84 ± 0.56 ^A	8.28 ± 0.37 ^A	9.35 ± 0.62 ^A	8.10 ± 0.08 ^A	8.37 ± 0.03 ^A
	1	7.37 ± 0.64 ^{a, AB}	4.23 ± 0.75 ^{a, C}	6.97 ± 0.29 ^{a, A}	9.20 ± 0.56 ^{a, B}	6.73 ± 0.60 ^{a, A}	3.29 ± 0.41 ^{a, C}
ΔG_{SUC} (%)	2	7.93 ± 0.91 ^{a, A}	7.46 ± 0.15 ^{b, A}	6.94 ± 0.19 ^{a, A}	10.17 ± 0.26 ^{b, B}	8.14 ± 0.91 ^{a, A}	7.27 ± 0.09 ^{b, A}
	4	8.10 ± 0.69 ^{a, A}	7.56 ± 0.29 ^{b, A}	6.58 ± 0.22 ^{a, A}	10.78 ± 0.13 ^{b, B}	8.34 ± 1.30 ^{a, A}	10.85 ± 0.22 ^{c, B}
	6	10.06 ± 0.66 ^{a, A}	8.20 ± 0.64 ^{b, B}	8.24 ± 0.05 ^{b, B}	14.50 ± 0.08 ^{c, C}	8.53 ± 0.43 ^{a, AB}	9.44 ± 0.46 ^{d, AB}
w_{SUC}^{eq} (%)	48	28.81 ± 0.91 ^b	30.53 ± 0.88 ^c	30.54 ± 0.13 ^c	42.05 ± 0.67 ^d	41.68 ± 0.41 ^b	38.52 ± 0.45 ^e
w_{Ca}^0 (%)	0	---	0.0015 ± 0.0001 ^A	0.0015 ± 0.00007 ^A	---	0.0015 ± 0.00008 ^A	0.0016 ± 0.00009 ^A
	1	---	0.019 ± 0.001 ^{a, A}	0.037 ± 0.003 ^{a, B}	---	0.032 ± 0.001 ^{a, B}	0.052 ± 0.003 ^{ab, C}
ΔG_{Ca} (%)	2	---	0.031 ± 0.003 ^{b, A}	0.049 ± 0.001 ^{b, B}	---	0.037 ± 0.003 ^{ab, A}	0.056 ± 0.000 ^{a, B}
	4	---	0.034 ± 0.002 ^{b, A}	0.048 ± 0.002 ^{b, B}	---	0.040 ± 0.002 ^{b, A}	0.057 ± 0.001 ^{bc, D}
	6	---	0.037 ± 0.001 ^{b, A}	0.065 ± 0.002 ^{c, B}	---	0.040 ± 0.002 ^{b, A}	0.061 ± 0.001 ^{c, B}
w_{Ca}^{eq} (%)	48	--	0.222 ± 0.0025 ^c	0.216 ± 0.0010 ^d	--	0.191 ± 0.0018 ^c	0.248 ± 0.0023 ^d
E_f	1	2.02 ± 0.17 ^{a, A}	2.72 ± 0.48 ^{a, A}	2.87 ± 0.10 ^{a, A}	1.76 ± 0.11 ^{a, A}	2.69 ±0.22 ^{a, A}	6.52 ± 0.80 ^{a, B}
	2	2.44 ± 0.29 ^{b, A}	2.24 ± 0.05 ^{a, A}	3.77 ± 0.10 ^{b, B}	2.31 ± 0.07 ^{b, A}	2.64 ± 0.28 ^{ab, A}	3.47 ± 0.02 ^{b, B}
	4	2.66 ± 0.23 ^{bc, A}	3.14 ± 0.11 ^{a, AB}	5.06 ± 0.16 ^{c, D}	2.87 ± 0.05 ^{c, AC}	3.76 ± 0.58 ^{bc, BC}	2.92 ± 0.06 ^{b, A}
	6	2.43 ± 0.17 ^{c, A}	3.36 ± 0.26 ^{a, B}	4.16 ± 0.22 ^{b, BC}	2.08 ± 0.10 ^{ab, A}	4.24 ± 0.22 ^{c, C}	4.22 ± 0.20 ^{b, C}

*Results are expressed as Means ± Standard Deviation for triplicates of two experiments;

**Means with the same lower case letter in the same column and in the same concentration did not differ significantly at $p \leq 0.05$ according to the Tukey test

***Means with the same capital letter in the same line did not differ significantly at $p \leq 0.05$ according to the Tukey test

It was observed, in all treatments, mass reduction of the samples with time of process (Table 1), that is explained by rates of water loss that were greater than rates of solute gain. This behavior occurs in preserved tissue, because of the selective permeability of cellular membranes that allows the transport of small molecules like water, but restricts larger molecular weight molecules such as sucrose and hence reduces sucrose diffusion through cell tissue.

Table 1 shows water loss increasing as osmotic dehydration process, reaching reduction from 24 to 40% of the initial mass after 6 hours of dehydration.

When comparing the water loss of the dehydrated samples in solution with and without calcium, at the same sucrose concentration, it was observed that addition of 4% calcium lactate significantly increased water loss of the pineapple in all times of process. However, samples treated with 2% calcium lactate showed a diverse behavior until 2 and 4 hours of dehydration, for 40 and 50% sucrose solutions, respectively.

The increase of sucrose concentration in solution without calcium (from 40 to 50% SUC) and with 2% calcium (from 40% SUC+2% LAC to 50% SUC + 2% LAC) increased significantly the water loss of pineapple (Table 1). However, this behavior was not observed in osmotic solution containing 4% of salt. When samples dehydrated in solutions with 40% SAC+4% LAC were compared to 50% SAC+4% LAC, it was observed that the ΔW differences were slightly lower at 2 and 4 hours of process for the higher sucrose concentration but at 6 hours, water loss increased.

Time of osmotic dehydration and sucrose concentration provide higher sucrose incorporation in pineapple in solutions without calcium addition. The highest sugar gain was verified in samples dehydrated for 6 hours in aqueous solution containing 50% sucrose (Table 1). The calcium presence tends to restrict sucrose gain, being that for 40% sucrose solutions, this restriction was significant only in 1 hour of process in the solution 2 and after 6 hours of dehydration in solution 2 and 3. The 2% salt addition in 50% sucrose solutions reduced significantly the sucrose gain of samples. The 4% calcium lactate addition (Treatment 6) also reduced the sucrose impregnation of the samples when comparing with treatment 4, however provides greater sucrose gains than the 2% salt solution (treatment 5) after 2 hours of process.

This suggests that long process time and the high solute concentration could damage the tissue making easier sucrose impregnation.

The calcium influence on the restriction of sugar gain of the pineapple sample also was observed by Pereira et al. (2006), for guavas osmotically dehydrated in maltose solutions but not for papaya in sucrose solutions, what was attributed by the authors to the specific tissue structure of each fruit. Mavroudis et al. (2012) observed that solute gain in apples decreased with addition of small amount calcium in solution and attributed the result to reduction of cell wall porosity. The limited sucrose transfer into pineapple tissue could be explained from the pectin and enzymes present in this fruit. The hydrolysis of methyl esters on pectins by pectin methylesterases (PME), important enzyme in pineapple (SILVA et al. 2011a; SILVA et al., 2011b), generates carboxyl groups that can interact with calcium (GUILLEMIN et al., 2008) and form calcium pectate. Since cut and damages on the tissue provoke enzymes releasing, calcium pectate could be formed around cut surface areas which in turn would act as a partial barrier to larger molecules diffusion like sucrose into the tissue (BARRERA et al., 2009; SILVA et al., 2013). Moreover, the formation of micro-channels due to osmotic dehydration can also have contributed to the reduction of sucrose transfer. Calcium lactate may have entered these channels obstructing the passage of sugar into cell. Fernandes et al. (2009) observed, in light microscopic, the formation of micro-channels in pineapple tissue due to osmotic dehydration.

Calcium gain increased with the calcium lactate concentration in solution, with sucrose concentration and with time of process. According to FAO/WHO (1974), the reference daily requirements of calcium consume is 800mg. Samples with higher calcium content were obtained, in this study, after 6 hours of process in osmotic solution 3 (40%SUC + 4%LAC) and 6 (50%SUC + 4%LAC) (Figure 1). In this conditions, consume of 100 g of final product will provide an intake of approximately 0.9 g of calcium, which corresponds to 10% of calcium daily requirements. This result is related to the low solubility of the calcium lactate that limited its concentration in osmotic solutions.

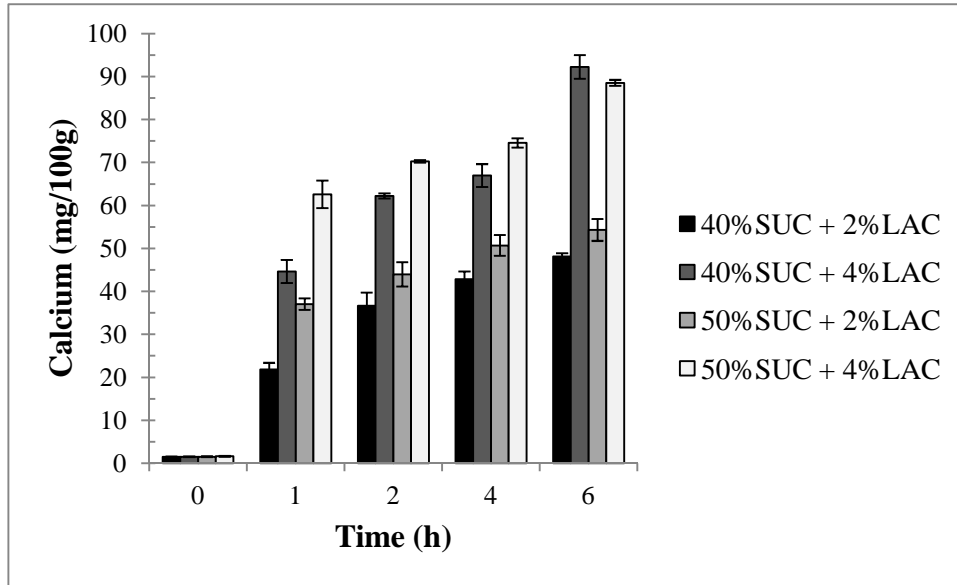


Figure 1: Calcium content (mg/100g) of samples osmotically dehydrated for different times in solution containing sucrose and calcium.

The impregnation of calcium (922.29 ppm) observed in pineapple osmotically dehydrated for 6 hours in an hypertonic solution (solution 3, 40% SUC + 4% LAC) was compared to the atmospheric impregnation of calcium in apple tissue, in an isotonic aqueous solution containing glucose (10.9 %, w/w) containing a blend of calcium lactate and calcium gluconate, potassium sorbate and citric acid (ANINO et al. 2006). Considering 6 hours of the process, impregnation of calcium in pineapple was 29% lower than in apples after 6 hours of process (1300ppm). The porosity of fresh samples is an important factor to be considered. According to Nieto et al. (2004), the fresh apples present porosity around 20%, while the fresh pineapple porosity is approximately 11% (YAN et al., 2008). The high fresh apple porosity can have favored greater impregnation of calcium in the samples observed by Anino et al. (2006). Moreover, the acidification with the citric acid in solution could have promoted damages to the cellular tissue like changes in polysaccharide gels of the cell walls that may increase the porosity (ZEMKE-WHITE et al., 2000) and hence the calcium transfer to tissue in apples. Silva et al. (2013) observed that ascorbic acid addition to solution containing sucrose and calcium lactate increased significantly calcium impregnation in pineapple samples.

Calcium lactate addition in solution enhanced processes efficiency being that the most effective treatments contained 4% of lactate in solution. Addition of 4% of calcium lactate in solution contained 50% sucrose improved 3.8 times the OD efficiency in comparison with

treatment without calcium lactate (treatment 4). The increase of the efficiency can be related to reduction in impregnation of sucrose due to reduction in porosity of cell wall.

The efficiency obtained after 1 hour of process in the solution 2 (40% SUC + 2% LAC) (Table 1) was higher than the efficiency obtained after 2 hours of the osmotic dehydration of melon in solution with 40% sucrose + 2% calcium lactate (FERRARI et al. 2010). In this process conditions, melon samples presented approximated 25% of water loss and 12% of solute gain, expressed in graph format. According to equation 6, the efficiency, in this case, was approximately 2.08. The formation mechanism of micro-channels due to osmotic dehydration can have influenced the efficiency of process. Fernandes et al. (2009) observed that the formation mechanism of microscopic channels in pineapples differed from the mechanism observed in melons (FERNANDES et al., 2008). This difference observed can have influenced in efficiency of osmotic process.

Analyzing results in Table 2, it was observed that majority data showed a good fit to Eq. 7, since values of determination coefficient were high. The data for the samples osmotic dehydrated in solution 1, 3, 4 and 6 were previously determined by the same authors (SILVA et al., 2013).

The effective water and sucrose diffusivities diminished with the addition of 2% calcium lactate, what can be related to calcium pectate forming. Nevertheless, when calcium lactate concentration rose from 2% to 4%, a slight increasing of the effective water diffusion coefficients was verified, while the sucrose ones showed a greater increase, around 40% for 40% SUC + 4% LAC solution and 68% for 50% SUC + 4% LAC solution. These increments suggest damages in pineapple tissue structure due to higher concentration of solution. Monnerat et al. (2010) also observed an increase of the water and sucrose diffusion coefficients in apples osmotically dehydrated in aqueous solution of sucrose + sodium chloride and attributed the result to injuries caused by the salt.

Table 2: Effective diffusion coefficients of water, sucrose and calcium for pineapple osmotically dehydrated.

Treatments	Osmotic solution composition					
	40%SUC (1)	40%SUC +2%LAC (2)	40%SUC +4%LAC (3)	50%SUC (4)	50%SUC +2%LAC (5)	50%SUC+ 4%LAC (6)
$D_{ef_w} \times 10^{10}$	6.16 ±	5.32 ±	5.79 ±	4.99 ±	3.73 ±	4.24 ± 0.22
(m ² /s)	0.28	0.13	0.17	0.02	0.11	
R ²	0.906	0.997	0.958	0.968	0.984	0.992
$\chi^2 \times 10^{-3}$	1.111	0.035	0.991	0.709	0.441	0.278
$D_{ef_{suc}} \times 10^{10}$	5.95 ±	3.34 ±	4.68 ±	3.92 ±	1.89 ±	3.18 ± 0.25
(m ² /s)	0.44	0.17	0.21	0.18	0.45	
R ²	0.938	0.964	0.928	0.966	0.937	0.981
$\chi^2 \times 10^{-3}$	0.970	0.382	1.155	1.053	0.990	0.375
$D_{ef_{Ca}} \times 10^{10}$	--	0.49 ±	1.63 ±	--	0.92 ±	1.40 ± 0.22
(m ² /s)	--	0.09	0.77	--	0.16	
R ²	--	0.956	0.965	--	0.881	0.894
$\chi^2 \times 10^{-7}$	--	0.071	0.181	--	0.282	0.633

*Mean ± SD

**ND – it was not determine

Values obtained for water activity in each time of osmotic dehydration can be verified in Table 3.

Table 3: Water activity (a_w) of the raw pineapple, samples osmotically dehydrated and of the osmotic solution.

Osmotic solution composition						
Time of osmotic dehydration (h)	OD (40% SUC) (1)	OD (40% SUC 2% LAC) (2)	OD (40% SUC 4% LAC) (3)	OD (50% SUC) (4)	OD (50% SUC 2% LAC) (5)	OD (50% SUC 4% LAC) (6)
0	0.990 ± 0.001 ^{a, AB}	0.995 ± 0.001 ^{a, A}	0.988 ± 0.001 ^{a, B}	0.991 ± 0.004 ^{a, AB}	0.990 ± 0.002 ^{a, B}	0.990 ± 0.001 ^{a, AB}
1	0.981 ± 0.001 ^{b, AB}	0.985 ± 0.002 ^{b, B}	0.978 ± 0.002 ^{b, A}	0.975 ± 0.003 ^{b, A}	0.981 ± 0.004 ^{b, AB}	0.975 ± 0.002 ^{b, A}
2	0.979 ± 0.005 ^{b, A}	0.979 ± 0.003 ^{bc, A}	0.976 ± 0.004 ^{b, A}	0.974 ± 0.002 ^{b, A}	0.975 ± 0.006 ^{b, A}	0.973 ± 0.003 ^{b, A}
4	0.979 ± 0.003 ^{b, A}	0.978 ± 0.003 ^{c, A}	0.972 ± 0.003 ^{b, AB}	0.968 ± 0.004 ^{b, B}	0.975 ± 0.004 ^{b, AB}	0.967 ± 0.005 ^{b, B}
6	0.979 ± 0.003 ^{b, A}	0.978 ± 0.003 ^{c, A}	0.971 ± 0.003 ^{b, AB}	0.971 ± 0.006 ^{b, AB}	0.976 ± 0.003 ^{b, AB}	0.965 ± 0.007 ^{b, B}
Solution	0.957 ± 0.003	0.933 ± 0.002	0.921 ± 0.003	0.927 ± 0.002	0.913 ± 0.001	0.909 ± 0.001

*Results are expressed as Means ± Standard Deviation for triplicates of two experiments;

**Means with the same lower case letter in the same column and in the same concentration did not differ significantly at $p \leq 0.05$ according to the Tukey test

***Means with the same capital letter in the same line did not differ significantly at $p \leq 0.05$ according to the Tukey test

At 95% of reliability, osmotic dehydration significantly reduced water activity of pineapple in the six treatments performed in relation to raw pineapple, despite did not present statistically significant differences between times of osmotic dehydration in majority of the treatments (Table 3). Concentration gradient between fresh samples and solution increases with concentration solutes in the solution, favoring faster decay of the water activity of samples.

Addition of calcium in osmotic solution did not change significantly water activity of the pineapple samples although it was possible to observe tendency to reduce a_w when calcium lactate concentration was 4%.

Luminosity (L^*_F) and Chroma (C^*_F) of the fresh samples and normalized values of luminosity (L^*_{DO} / L^*_F) and Chroma (C^*_{OD} / C^*_F) are presented in Table 4.

Table 4: Luminosity and Chroma of the fresh samples and normalized value obtained for each time and treatment of osmotic dehydration.

		Osmotic solution composition						
Color parameters	Time of osmotic dehydration (h)	OD (40% SUC) (1)	OD (40% SUC 2% LAC) (2)	OD (40% SUC 4% LAC) (3)	OD (50% SUC) (4)	OD (50% SUC 2% LAC) (5)	OD (50% SUC 4% LAC) (6)	
L^*_F	----	75.80 ± 0.64 ^A	79.61 ± 0.42 ^B	74.71 ± 1.64 ^A	77.89 ± 0.69 ^C	80.32 ± 0.69 ^B	80.53 ± 0.42 ^B	
	0	1.000 ^{ac}	1.000 ^a	1.000 ^a	1.000 ^a	1.000 ^a	1.000 ^a	
	1	1.043 ± 0.012 ^{b, A}	0.938 ± 0.010 ^{b, B}	0.973 ± 0.005 ^{a, B}	0.946 ± 0.027 ^{b, B}	0.927 ± 0.035 ^{bc, B}	0.943 ± 0.023 ^{ab, B}	
	2	0.959 ± 0.039 ^{cd, A}	0.946 ± 0.005 ^{b, A}	0.962 ± 0.022 ^{a, A}	0.930 ± 0.034 ^{b, A}	0.964 ± 0.024 ^{ab, A}	0.921 ± 0.041 ^{b, A}	
	L^*_{OD} / L^*_F	4	0.979 ± 0.007 ^{ad, A}	0.977 ± 0.009 ^{c, A}	0.956 ± 0.034 ^{a, AB}	0.926 ± 0.024 ^{b, AB}	0.916 ± 0.013 ^{c, B}	0.926 ± 0.045 ^{b, AB}
		6	1.012 ± 0.024 ^{ab, A}	0.933 ± 0.011 ^{b, B}	0.954 ± 0.058 ^{a, AB}	0.932 ± 0.001 ^{b, AB}	0.940 ± 0.008 ^{bc, B}	0.859 ± 0.023 ^{c, C}
	C^*_F	----	25.87 ± 0.91 ^A	24.38 ± 0.34 ^B	30.92 ± 1.77 ^A	22.93 ± 0.18 ^B	23.43 ± 1.40 ^B	22.48 ± 1.14 ^B
0		1.000 ^{ab}	1.000 ^a	1.000 ^a	1.000 ^a	1.000 ^a	1.000 ^a	
1		0.965 ± 0.017 ^{a, A}	1.020 ± 0.016 ^{a, A}	1.011 ± 0.233 ^{a, A}	1.195 ± 0.019 ^{b, A}	1.155 ± 0.003 ^{b, A}	1.194 ± 0.239 ^{a, A}	
2		1.113 ± 0.136 ^{b, A}	1.235 ± 0.006 ^{b, A}	1.085 ± 0.126 ^{a, A}	1.219 ± 0.062 ^{b, A}	1.145 ± 0.072 ^{b, A}	1.141 ± 0.072 ^{a, A}	
C^*_{OD} / C^*_F		4	0.973 ± 0.003 ^{a, AB}	0.892 ± 0.013 ^{c, B}	0.964 ± 0.027 ^{a, B}	1.227 ± 0.042 ^{b, A}	1.185 ± 0.048 ^{b, A}	1.229 ± 0.282 ^{a, A}
		6	0.913 ± 0.007 ^{a, A}	0.952 ± 0.005 ^{d, A, B}	1.003 ± 0.113 ^{a, ABC}	1.189 ± 0.027 ^{b, CD}	1.135 ± 0.057 ^{b, BCD}	1.229 ± 0.158 ^{a, D}

*Results are expressed as Means ± Standard Deviation for triplicates of two experiments;

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***Means with the same capital letter in the same line did not differ significantly at $p \leq 0.05$ according to the Tukey test

In general osmotically dehydrated pineapples presented less luminosity than fresh samples (values below 1.00), although value of L^* has not changed much over time of osmotic dehydration and neither with calcium lactate addition in solution.

There was no significant difference between chroma values in treatments with the same sucrose concentration. However, comparing all treatments, it was observed that values of C^*_{OD}/C^*_F increased with increasing sucrose concentration, despite such variations had been significant only after four hours of process. The rise of sucrose concentration in solution results in greater water loss of samples which may increase the pigments concentration in tissue and, consequently, enhance the chromaticity value in final product. Other authors observed the same result in apricot (FORNI et al., 1997), papaya (RODRIGUES et al., 2003), guava (MASTRANTONIO et al., 2005) and pumpkin (SILVA et al., 2011b).

Results of stress at failure of the fresh samples (σ_{H_F}) and normalized values of stress at failure ($\sigma_{H_{OD}}/\sigma_{H_F}$) for each time of osmotic dehydration are presented in Table 5.

Tabela 5: Stress at failure of the fresh samples and normalized stress at failure for each time of osmotic dehydration.

		Osmotic solution composition					
Stress at failure	Time of osmotic dehydration (h)	OD (40% SUC)	OD (40% SUC 2% LAC)	OD (40% SUC 4% LAC)	OD (50% SUC)	OD (50% SUC 2% LAC)	OD (50% SUC 4% LAC)
		(1)	(2)	(3)	(4)	(5)	(6)
σ_{H_F} (KPa)	----	26.78 ± 7.88	32.02 \pm 3.77	25.45 ± 9.47	30.69 ± 3.71	31.94 ± 14.39	31.57 ± 10.56
	0	1.000 ^a	1.000 ^a	1.000 ^a	1.000 ^a	1.000 ^a	1.000 ^a
	1	1.05 \pm 0.28 ^{a, A}	0.73 $\pm 0.35^{a, A}$	0.92 $\pm 0.22^{a, A}$	0.71 $\pm 0.23^{a, A}$	0.68 $\pm 0.26^{a, A}$	0.67 $\pm 0.12^{a, A}$
	2	0.93 \pm 0.41 ^{a, A}	0.81 $\pm 0.25^{a, A}$	0.93 $\pm 0.36^{a, A}$	0.61 $\pm 0.18^{a, A}$	0.93 $\pm 0.24^{a, A}$	0.84 $\pm 0.24^{a, A}$
	4	1.12 $\pm 0.44^{a, A}$	1.05 $\pm 0.32^{a, A}$	0.87 $\pm 0.18^{a, A}$	0.72 $\pm 0.26^{a, A}$	0.90 $\pm 0.34^{a, A}$	0.80 $\pm 0.24^{a, A}$
	6	1.00 $\pm 0.33^{a, A}$	0.94 $\pm 0.30^{a, A}$	1.04 $\pm 0.35^{a, A}$	0.87 $\pm 0.40^{a, A}$	0.92 $\pm 0.16^{a, A}$	1.05 $\pm 0.25^{b, A}$

* Results are expressed as Means \pm Standard Deviation for triplicates of two experiments;

**Means with the same lower case letter in the same column and in the same concentration did not differ significantly at $p \leq 0.05$ according to the Tukey test

***Means with the same capital letter in the same line did not differ significantly at $p \leq 0.05$ according to the Tukey test

The relatively large standard deviations (Table 5) among the replicates in hardness analysis showed heterogeneity in pineapple and lack of uniformity in its internal structure, since mechanical properties of biological material are determined by structure and constituents of wall cell, affected by maturation degree, harvest time, as well as process conditions. Large standard deviations of hardness due to variability of raw material were observed in guava (PEREIRA et al., 2004), apple (CASTELLÓ et al, 2009), melon (FERRARI et al., 2010), grapefruits (MORAGA et al., 2009) e pumpkin (SILVA et al, 2011b).

It was not observed significant difference ($p < 0,05$) in normalized stress value of samples between treatments and in the majority values obtained along osmotic dehydration, in relation to the fresh samples. However, it was observed reduction in rupture stress (values < 1) of pineapple fresh with osmotic dehydration in majority of solutions.

The rupture stress of samples osmotically dehydrated in solution with 40% sucrose did not trended to increase with calcium addition, despite have been observed slight enhance in the stress with greater calcium concentrations. Addition calcium may have promoted damage in some cells, favoring softening of the tissue and not its stiffness. Generally, impregnation of calcium in tissue favor texture of samples by formation of calcium pectate, however concentrations above 1.5% can also provide cell plasmolysis and increase the solubilization of pectin, reducing the firmness of product (CASTELLÓ et al, 2009 and FERRARI et al, 2010). Anino et al. (2006) observed softening of tissue of apples after 6 hours of impregnation in an isotonic glyucose solution with or without calcium salts. Light microscopy microphotographs of these samples showed the presence of calcium between the cell wall and plasmalema, intercellular spaces and into the cytoplasm of apples evidencing severe internal disruption in the cell and considerable reduction of firmness of tissue.

Similar result was not observed in samples osmotically treated in solution containing 50% sucrose. In this more concentrated solution, the samples tend to become softer than those treated in 40% solution. Calcium addition in 50% solution provided samples with higher rupture stress after two hours of process. However, the calcium did not increase the tissue firmness in comparison to fresh pineapple. On the other hand, the time of exposure to calcium ions seemed to enhance the firmness of the pineapple tissue.

Fernandes et al (2009) observed, in light microscope, the formation of micro-channels in cells of pineapple after 10 minutes of osmotic dehydration in solution of 70°Brix (water + sucrose). These micro-channels were also accompanied by a significant degree of cell rupture and solubilisation of pectin.

Anino et al. (2006) related that the cell membranes of apple were completely disrupted after 22 hours of dehydration osmotic in solution with calcium, despite it was observed slight increase in the matrix resistance to compression in relation 10 hours of process.

4. Conclusions

Calcium addition in solution osmotic reduces sucrose gain in tissue and increases water loss of samples, resulting in higher process efficiency. Water activity of the pineapple also diminished with salt addition.

The osmotic dehydration process with addition calcium in solution increased significantly calcium content of pineapple. Samples dehydrated osmotically for 6 hours in solution containing 4% calcium lactate presented the higher calcium contents being that the consume of 100 g of this product would provide an intake to 10% of calcium daily requirements.

The sucrose and water diffusivity decreased with calcium addition. However, when comparing the effect of concentration of calcium on its diffusivity, it was found increase of this diffusion coefficient with the increase concentration of salt in solution.

There was no significant change in croma of the samples with calcium addition during the osmotic treatment, however the samples presented higher croma values with sucrose concentration in solution.

Calcium addition did not enhanced the rupture stress of fresh pineapple, but improved the firmness of the samples dehydrated in solution with 50% sucrose. More detailed studies about influence of high calcium concentration on the tissue microstructure would be necessary to explain the changes in the firmness of product.

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6. References

- ANINO, S. V.; SALVATORI, D. M.; ALZAMORA, S. M. (2006) Changes in calcium level and mechanical properties of apple tissue due to impregnation with calcium salts. **Food Research Internacional**, 39, 154-164.
- AOAC - ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS (1970) Official Methods of Analysis of the Association of Official Analytical Chemists, 11th ed. Arlington: Association of Official Analytical Chemists AOAC.
- AOAC - ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS (1995) Official Methods of Analysis of the Association of Official Analytical Chemists, 16th ed., v. 1, Arlington: Association of Official Analytical Chemists A.O.A.C., chapter 3. p. 4. (method 985.01).
- BARRERA, C.; BETORET, N.; CORELL, P.; FITO, P. (2009). Effect of osmotic dehydration on the stabilization of calcium-fortified apple slices (var. Granny Smith): Influence of . operating variables on process kinetics and compositional changes. **Journal of Food Engineering**, 92, 416–424.
- CASTELLÓ, M.L.; IGUAL, M.; FITO, P.J., CHIRALT, A. (2009) Influence of osmotic dehydration on texture, respiration and microbial stability of apple slices (var. granny smith). **Journal of Food Engineering**, v.91, n.1, p.1-9.
- CORTELLINO, G.; PANI, P.; TORREGGIANI, D. (2011) Crispy air-dried pineapple rings: optimization of processing parameters. 11th International Congress on Engineering and Food (ICEF11). **Procedia Food Science**, 1, p. 1324-1330.
- CRANK, J. (1975). **The Mathematics of Diffusion**, second ed. Clarendon Press-Oxford, London.
- FAO/WHO (1974) - **Handbook on Human Nutritional Requirements**, FAO, Rome.
- FERNANDES, F.A. N.; GALLÃO, M. I.; RODRIGUES, S. (2008) Effect of osmotic dehydration and ultrasound pre-treatment on cell structure: Melon dehydration. **LWT** 41, 604–610
- FERNANDES, F.A. N.; GALLÃO, M. I.; RODRIGUES, S. (2009) Effect of osmosis and ultrasound on pineapple cell tissue structure during dehydration. **Journal of Food Engineering** 90, 186–190
- FERRARI, C.C.; CARMELLO-GUERREIRO, S.M.; BOLINI, H.M.A.; HUBINGER, M.D. (2010) Structural changes, mechanical properties and sensory preference of osmodehydrated melon pieces with sucrose and calcium lactate solutions. **International Journal of Food Properties**, 13, 112–130.
- FITO, P.; CHIRALT, A.; BETORET, N.; GRAS, M.; CHÁFER, M.; MARTÍNEZ-MONZÓ, J.; ANDRÉS, A.; VIDAL, D. (2001) Vacuum impregnation and osmotic dehydration in matrix engineering. Application in functional fresh food development. **Journal of Food Engineering**. 49,175-183.
- FORNI, E.; SORMANI, A.; SCALISE, S.; TORREGGIANI, D. (1997) The influence of sugar composition on the color stability of osmodehydrofrozen moisture apricots. **Food Research Internacional**, v.30, p.87-94.
- GARCIA, C.C.; MAURO, M.A.; KIMURA, M. (2007) Kinetics of osmotic dehydration and air drying of pumpkins (*Cucurbita moschata*). **Journal of Food Engineering**, 82, 284-291.

- GUILLEMIN, A.; GUILLON, F.; DEGRAEVE, P.; RONDEAU, C. (2008) Firming of fruit tissues by vacuum-infusion of pectin methylesterase: Visualisation of enzyme action. **Food Chemistry** 109, 368–378
- HENG, H., GUILBERT, S.; CUQ, J. L. (1990). Osmotic Dehydration of Papaya: Influence of Process Variables on the Product Quality. **Sciences des Aliments**, 10, pp. 831-848.
- HEREDIA, A.; BARRERA, C.; ANDRES, A. (2007). Drying of cherry tomato by a combination of different dehydration techniques. Comparison of kinetics and other related properties. **Journal of food Engineering**. 80(1), 111-118.
- LOMBARD, G. E.; OLIVEIRA, J. C.; FITO, P; ANDRE'S, A. (2008) Osmotic dehydration of pineapple as a pre-treatment for further drying. **Journal of Food Engineering**, 85, 277–284.
- MASTRANTONIO, S.D.S.; PEREIRA, L.M.; HUBINGER, M.D. (2005) Osmotic dehydration kinetics of guavas in maltose solutions with calcium salt. **Alimentos e Nutrição**, 16 (4), 309–314.
- MAVROUDIS, N. E.; GIDLEY, M. J.; SJÖHOLM, I. (2012) Osmotic processing: Effects of osmotic medium composition on the kinetics and texture of apple tissue. **Food Research International** 48, 839–847.
- MONERAT, S.M.; PIZZI, T.R.M.; MAURO, M.A.; MENEGALLI, F.C. (2010) Osmotic dehydration of apples in sugar/salt solutions: Concentration profile and effective diffusion coefficients. **Journal of Food Engineering**, 100, 604-612.
- MORAGA, M. L.; MORAGA, G.; FITO, P. J.; MARTÍNEZ-NAVARRETE N. (2009) Effect of vacuum impregnation with calcium lactate on the osmotic dehydration kinetics and quality of osmodehydrated grapefruit. **Journal of Food Engineering**. 90, 372-379.
- NIETO, A. B.; SALVATORI, D. M.; CASTRO, M. A.; ALZAMORA, S.M. (2004) Structural changes in apple tissue during glucose and sucrose osmotic dehydration: shrinkage, porosity, density and microscopic features. **Journal of Food Engineering** 61, 269–278
- PAN, Y.K.; ZHAO, L.J.; ZHANG, Y.; CHEN, G.; MUJUMDAR, A.S. Osmotic dehydration pretreatment in drying of fruits and vegetables. **Drying Technology**, v.21, n.6, p.1101-1114, 2003.
- PEREIRA, L.M.; FERRARI, C.C.; MASTRANTONIO, S.D.S.; RODRIGUES, A.C.C. , HUBINGER, M.D. (2006) Kinetic aspects, texture, and color evaluation of some tropical fruits during osmotic dehydration. **Drying Technology**, 24 (4), 475-484.
- PEREIRA, L.M.; RODRIGUES, A.C.C.; SARANTÓPOULOS, C.I.G.L.; JUNQUEIRA, V.C.A.; CUNHA, R.L.; HUBINGER, M.D. (2004) Influence of Modified Atmosphere Packaging and Osmotic Dehydration of Minimally Processed Guavas. **Journal of Food Science**, v.69, n.4, p. 172-177.
- PONTING, J.D.; WATTERS, G.G.; FORREY, R.B.; JACKSON, R.; STANLEY, W.L. (1996) Osmotic Dehydration of Fruits. **Food Technology**, v. 20, n.10, p.1365-1368.
- RAMALLO, L. A.; SCHVEZOV, C.; MASCHERONI, R. H. (2004) Mass transfer during osmotic dehydration of pineapple. **Food Science and Technology International**, 10 (5), p. 323-332.

- RASTOGI, N. K.; RAGHAVARAO, K. S. M. S.; NIRANJAN, K.; KNORR, D. (2002). Recent developments in osmotic dehydration : methods to enhance mass transfer. **Trends in Food Science & Technology** 13, p. 48–59
- RODRIGUES, A. C. C.; CUNHA, R. L.; HUBINGER, M. D. (2003) Rheological properties and colour evaluation of papaya during osmotic dehydration processing. **Journal of Food Engineering**, Essex, v. 59, p. 129-135.
- SAPUTRA, D., (2001) Osmotic dehydration of pineapple. **Drying Technology**, 19, 415-425.
- SERENO, A. M.; MOREIRA, R.; MARTINEZ, E. (2001). Mass transfer coefficients during osmotic dehydration of apple in single and combined aqueous solutions of sugar and salt. **Journal of Food Engineering**, 47, 43-49.
- SHI, J.; LEMAQUER, M.; KAKUDA, Y.; LIPTAY, A.; NIEKAMP, F. (1999) Lycopene degradation and isomerization in tomato dehydration. **Food Research International**, v. 32, p.15-21.
- SILVA, A. C.; SILVA, C. R.; COSTA, L. M. S.; BARROS, N. A. M.; VIANA, A.S.; KOBLITZ, M. G. B.; SOUZA, F. V. D. (2011a). Use of response surface methodology for optimization of the extraction of enzymes from pineapple pulp. **Acta Horticulturae**, 902, 575–584.
- SILVA, K. S.; CAETANO, L. C.; GARCIA, C. C.; ROMERO, J. T.; SANTOS, A. B.; MAURO, M. A. (2011b). Osmotic dehydration process for low temperature blanched pumpkin. **Journal of Food Engineering**, 105, 56 - 64
- SILVA, K. S.; FERNANDES, M. A.; MAURO, M. A. (2013) Osmotic dehydration of pineapple with impregnation of sucrose, calcium and ascorbic acid. **Food Bioprocess Technology**,
- SILVA, W.P. AND SILVA, C.M.D.P.S. Prescribed Adsorption - Desorption V 2.2 (2008), online, available from world wide web: <<http://zeus.df.ufcg.edu.br/labfit/Prescribed.htm>>, date of access: March, 2013
- TELIS, V. R. N.; MURARI, R. C. B. D. L.; YAMASHITA, F. (2004). Diffusion coefficients during osmotic dehydration of tomatoes in ternary solutions. **Journal of Food Engineering**, 61, 253-259.
- TORREGGIANI, D. E BERTOLO, G. (2001) Osmotic pre-treatments in fruit processing: chemical, physical and structure effects. **Journal of Food Engineering**, v.49, p.247-253.
- ZEMKE-WHITE, W. L., CLEMENTS, K. D.,; HARRIS, P. J. (2000). Acid lysis of macroalgae by marine herbivorous fishes: Effects of acid pH on cell wall porosity. **Journal of Experimental Marine Biology and Ecology**, 245, 57–68.
- YAN, Z.; SOUSA-GALLAGHER, M. J.; OLIVEIRA, F. A. R. (2008) Shrinkage and porosity of banana, pineapple and mango slices during air-drying. **Journal of Food Engineering** 84, 430–440.

CAPÍTULO II

1 **Osmotic dehydration of pineapple with impregnation of sucrose, calcium and ascorbic**
2 **acid**

3
4
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11
12 **Abstract**

13 Mass transfer was evaluated during osmotic dehydration of pineapple in solutions with
14 until four components aiming to investigate the solutes concentration influence on
15 impregnation. In the first step, the experimental trials for optimization of solution
16 concentration were based on 2³ factorial design. In the second step, effective diffusion
17 coefficients were determined. Equations representing the influence of the concentration of
18 sucrose, calcium lactate and ascorbic acid in osmotic solutions on water loss and gains of
19 sucrose, calcium and vitamin C, were found. Results showed that both calcium lactate and
20 sucrose concentration affected calcium and sucrose gain. On the other hand, only vitamin C
21 gain was significantly affected by the ascorbic acid concentration in the studied concentration
22 range. However, when comparing diffusivities in pineapple immersed in sucrose solutions,
23 with and without calcium lactate, with and without ascorbic acid, it was possible to verify that
24 diffusivities of water, sugar and calcium increased in presence of ascorbic acid in solution.
25 Calcium in solution diminished the water and sucrose diffusivities. High calcium and vitamin
26 C contents were obtained in 1 hour immersion in the solutions studied.

27

Nomenclature

M = mass (kg)

M^0 = initial mass (kg)

ΔM = total mass variation in relation to initial mass (dimensionless)

R^2 = determination coefficient (dimensionless)

ΔG_{SUC} = sugar gain in relation to initial mass (dimensionless)

ΔG_{Ca} = calcium gain in relation to initial mass (dimensionless)

ΔG_{VitC} = Ascorbic acid gain in relation to initial mass (dimensionless)

ΔW = water loss in relation to initial mass (dimensionless)

$\beta_0, \beta_1, \beta_2, \beta_3, \beta_{12}, \beta_{13}, \beta_{23}, \beta_{123}$ = estimated regression coefficient of the Eq. (1)

w_w = water content

w_{SUC} = sucrose content

w_{Ca} = calcium content

w_{VitC} = ascorbic acid content

$\bar{w}_i(t)$ = mean concentration of the component for a time (t)

$ADM_{(SUC)}$ = dimensionless sucrose content

$ADM_{(Ca)}$ = dimensionless calcium content

$ADM_{(VitC)}$ = dimensionless vitamin C content

$ADM_{(w)}$ = dimensionless water content

SUC = sucrose concentration (%)

LAC = calcium lactate concentration (%)

$VitC$ = Ascorbic acid concentration (%)

Coded variables: $x_{1i}; x_{2i}; x_{3i}; (1=SUC, 2=LAC, 3=VitC)$

Response variables: Y_i . (Y_1 = water loss (ΔW); Y_2 = sucrose gain (ΔG_{SUC}); Y_3 = calcium gain (ΔG_{Ca}); Y_4 = Ascorbic acid gain (ΔG_{VitC}));

Subscripts and superscript

calc = calculated;

exp = experimental;

OD = osmotically dehydrated

s = sucrose

Ca = calcium

VitC = ascorbic acid (vitamin C)

w = water

0 = initial state

1. Introduction

The interest on healthy food provides a fast development in the segment of food industry that aims to contribute for healthy diet (KATZ, 2000). A method that can be applied to enrich fruits and vegetables is the osmotic dehydration (OD). This process reduces the moisture of fruits and vegetables through its immersing in aqueous concentrated solution containing one or more solutes (SERENO et al., 2001; GARCIA et al., 2007). The vegetable cellular membrane, partially selective, allows flow of water and some solids from the food to solution and allows flow of solutes from the solution into the vegetable, inducing a modification in chemical composition of dehydrated food (RAOULT-WACK, 1994; LENART, 1996).

The choice of solute is a fundamental question because is related to alterations of sensory and nutritive properties of the final product, beyond the cost of process. The sucrose is considered by several authors as an optimum osmotic agent, once that the enzymatic browning reduction and aromas loss have been associated at this solute (LENART, 1996, QI et al., 1998). Saputra (2001) verified that sucrose provides larger water loss and smaller solute gain, when compared to glucose in pineapple samples submitted to osmotic dehydration.

Osmotic dehydration allows to introduce solute in tissue of fruits that can favor sensory and nutritional characteristics of these products (FITO et al., 2001). Anino et al. (2006), exploring the possibility to obtain enriched products with calcium, analyzed the ability of apple matrix for incorporation of calcium. For this, it was prepared an isotonic aqueous solution containing glucose and a blend of calcium lactate and calcium gluconate. Potassium sorbate and citric acid also were added to inhibit microbial growth. Microphotographs, recorded by light microscopy (LM) and transmission electron microscopy (TEM), showed the presence of calcium crystals in cell wall, middle lamellae, intercellular space and into cytoplasm of apples treated for 6 hours in osmotic solution. The amount of calcium incorporated in apple samples reached levels between 23 and 62% (to 200g of fruit) of the recommended intake.

Osmotic dehydration provides some solid loss of food that can affect its nutritional profile (RAOULT-WACK, 1994). Pineapples (*Ananas comosus* variety *Cayena lisa*) cut in half-ring form 0.6cm in thickness were subjected to osmotic dehydration in solution of 60°Brix sucrose at 40°C, until 240 minutes. The authors analyzed ascorbic acid content and

1 noticed that vitamin C loss was above 70% after to OD (RAMALLO; MASCHERONI,
2 2010).

3 One method to compensate ascorbic acid loss in fruit is to add this component in the
4 dehydration solution. Robbers et al. (1997), verified that the addition of ascorbic acid and
5 citric acid as antioxidants in osmotic solution, prevented browning and significant ascorbic
6 acid loss during the osmotic dehydration of kiwis.

7 This study aims to investigate the effects of sucrose, calcium lactate and ascorbic acid
8 concentration in quaternary aqueous solutions on the water loss and the solids amount
9 incorporated in pineapples during osmotic dehydration, as well as on the effective diffusion
10 coefficients of water, sucrose, calcium and ascorbic acid, useful to plan and control these
11 processes.

12

13

14 **2. Materials and methods**

15

16 **2.1 Materials**

17

18 Pineapple (*Ananás comosus* (L.) Merrill) of commercial ripeness degree, weighing
19 approximately 1.2Kg, were washed, manually peeled and its ends were discarded to reduce
20 the variability of tissue. The pieces were sliced (1 ± 0.1 cm thick) and the slices were cut in
21 truncated cone format with the aid of a metal mold.

22 Osmotic solutions were prepared with commercial sucrose (refined sugar) purchased
23 in a local market; food grade pentahydrate calcium lactate in powder from PURAC®
24 Synthesis – Brazil; food grade ascorbic acid in powder from Prozyn® – Brazil and distilled
25 water.

26

27 **2.2 Procedures**

28

29 **2.2.1 Osmotic dehydration experiment for optimization of solution concentration and** 30 **process time**

31

32 Approximately 60g of pineapple samples were weighted and immersed in 600g of
33 aqueous solution containing sucrose + calcium lactate + ascorbic acid according to

1 experimental design shown in Table 1. The solutions were maintained at 27°C for 2 hours
 2 with orbital agitation of 165rpm. After this time, the samples were immersed in distilled water
 3 at room temperature for 10 seconds in order to remove the osmotic solution from the surface.
 4 They were then blotted with absorbing paper and weighted. The total solids and the contents
 5 of sucrose, calcium and ascorbic acid (Vitamin C) were analyzed before and after each
 6 treatment.

7 The water content present in each osmotic solution was ranged with the solutes
 8 concentration (sucrose - calcium lactate - ascorbic acid), since the experimental conditions
 9 were based on the specific solids composition (Table 1). Solution of 60% sucrose was tested
 10 but, due to the low solubility of the calcium lactate in this sucrose concentration, its use was
 11 rejected.

12
 13 **Table 1:** Experimental design in coded form of process variables

Coded and (uncoded) Variables			
Trials	x_1 (SUC) (%)	x_2 (LAC) (%)	x_3 (VitC) (%)
1	-1 (40)	-1 (2)	-1 (1)
2	1 (50)	-1 (2)	-1 (1)
3	-1 (40)	1 (4)	-1 (1)
4	1 (50)	1 (4)	-1 (1)
5	-1 (40)	-1 (2)	1 (2)
6	1 (50)	-1 (2)	1 (2)
7	-1 (40)	1 (4)	1 (2)
8	1 (50)	1 (4)	1 (2)
9	0 (45)	0 (3)	0 (1.5)
10	0 (45)	0 (3)	0 (1.5)
11	0 (45)	0 (3)	0 (1.5)
12	0 (45)	0 (3)	0 (1.5)

14

15

16 **2.2.2 Osmotic dehydration kinetics and diffusion coefficients**

17

18 The pineapple slices were arranged in four nylon mesh baskets, with approximately
 19 350g of samples in each basket. The baskets were immersed in 20 kg of aqueous solution in a
 20 jacketed stainless steel vessel (0.30×0.30×0.30 m). The syrup-to-fruit ratio was approximately

1 1:14. The solution temperature was maintained at 27°C with an external circulation of
 2 thermostatically controlled water. A central propeller (10 cm diameter) continuously agitated
 3 the solution by using a 1.6 kw mechanical stirrer (Marconi, model MA-261 – Brazil). A
 4 rotation of 1850 rpm provided constant and vigorous agitation. Thus, a negligible liquid phase
 5 mass transfer resistance was considered and the solution concentration was assumed constant
 6 on the fruit surface during the whole osmotic dehydration.

7 The aqueous solution concentrations studied are presented in Table 2, where each
 8 process was carried out for 1, 2, 4 and 6 hours. The calcium lactate (*LAC*) and ascorbic acid (*VitC*)
 9 concentration were selected from the previous experiment aiming to provide greater
 10 impregnation of this nutrients. At the end of each process time, one basket was removed from
 11 the osmotic bath and the samples immersed in distilled water at room temperature for 10
 12 seconds in order to remove the osmotic solution from the surface. They were then blotted with
 13 absorbing paper and weighted. Experiments were run in duplicate. The total solids, total and
 14 reducing sugars, contents of calcium and ascorbic acid were analyzed before and after each
 15 treatment. The influence of the time and the addition of sucrose, calcium lactate and ascorbic
 16 acid in the osmotic solution were compared. The equilibrium concentration of the water,
 17 sucrose, calcium and vitamin C was determined by soaking thin fruit slices (3 mm thickness)
 18 in flask containing approximately 600 g of osmotic solution. The solutions were maintained at
 19 27°C with orbital agitation of 165rpm and syrup-to-fruit ratio was approximately 1:10. After
 20 48, the flasks were removed, and the pieces drained, dipped in distilled water for 10 seconds
 21 and blotted with absorbent material. Samples were prepared to analyze the content of water,
 22 sucrose, calcium and vitamin C.

23

24 **Table 2:** Experiment conditions chosen for the osmotic dehydration kinetics.

Experiment	Sucrose concentration (%) (<i>SUC</i>)	Calcium lactate concentration (%) (<i>LAC</i>)	Ascorbic acid concentration (%) (<i>VitC</i>)
1	40	0	0
2	40	4	0
3	40	4	2
4	50	0	0
5	50	4	0
6	50	4	2

25

26

2.3 Analytical methods

The water content of fresh and osmotic dehydrated samples were gravimetrically determined in triplicate by the drying of the samples in a vacuum oven at 60°C and 10 kPa until a constant weight was achieved.

The total and reducing sugar contents of fresh and osmotically treated samples were determined in triplicate by the oxidation-reduction titration (AOAC, 1970).

The calcium concentration of the fresh and dehydrated samples were determined in duplicate using flame atomic absorption spectrometer (SpectrAA 50B of Varian - Mulgrave, Australia), according to adapted methodology of AOAC (1995).

Ascorbic acid was analyzed in fresh and osmotically dehydrated samples using the standard method of AOAC (1984), modified by Benassi; Antunes (1988). All analyses were conducted in duplicated. The ascorbic acid content was quantified before and immediately after osmotic dehydration process.

2.4 Experimental design, mathematical models and statistical analysis

Aiming to evaluate the influence of solution composition on the water loss and solids gain, a 2³ factorial design with four replications at the central point was used for optimization of the solution concentration and process time in an osmotic quaternary solution (Table 1), through RSM (Response Surface Methodology). The coded independent variables studied were sucrose concentration (x_1), calcium lactate concentration (x_2) and ascorbic acid concentration (x_3). The dependent variables (responses) evaluated were mass variation, water loss and gains of sucrose, calcium and ascorbic acid. The experiments were processed in a random order.

The results of experiments were fitted to a first-order model:

$$Y_i = \beta_0 + \beta_1 x_{1i} + \beta_2 x_{2i} + \beta_3 x_{3i} + \beta_{12} x_{1i} x_{2i} + \beta_{13} x_{1i} x_{3i} + \beta_{23} x_{2i} x_{3i} + \beta_{123} x_{1i} x_{2i} x_{3i} \quad (1)$$

where Y_i represents the i^{th} response variable (Y_1 = water loss (ΔW); Y_2 = sucrose gain (ΔG_{SUC}); Y_3 = calcium gain (ΔG_{Ca}); Y_4 = vitamin C gain (ΔG_{vitC})); x_{1i} , x_{2i} , x_{3i} are the linear

1 terms; and $x_{1i}x_{2i}$, $x_{1i}x_{3i}$, $x_{2i}x_{3i}$ e $x_{1i}x_{2i}x_{3i}$ mean the cross product terms ; β_0 , β_1 , β_2 , β_3 , β_{12} ,
 2 β_{13} , β_{23} , β_{123} are regression coefficients of the model being x_1 , x_2 , x_3 the coded independent
 3 variables (MEYER, 1971; MONTGOMERY, 1991).

4 The coded values in the above equations can be obtained from the uncoded values
 5 using the following expression:

6

$$7 \quad x_1 = (SUC - 45) / 5 \quad (2)$$

$$8 \quad x_2 = (LAC - 3) / 1 \quad (3)$$

$$9 \quad x_3 = (VitC - 1.5) / 0.5 \quad (4)$$

10

11 where, SUC is the sucrose concentration (%); LAC is the calcium lactate concentration (%)
 12 and $VitC$ is the ascorbic acid concentration (%).

13 The regression coefficients were used to derive a mathematical model. From the
 14 analysis of variance was possible to identify the coded variables that had significant effects on
 15 the responses of interest at the 95% confidence level ($p < 0.05$) and validate the mathematical
 16 models. All statistical analyses were performed using Statistica 7.0 (StatSoft Inc. South
 17 America, Tulsa, OK, USA).

18 The mass balance was determined for each concentration of the osmotic treatment and
 19 the influence of concentrations of sucrose, calcium and ascorbic acid in the quaternary
 20 osmotic solution, on the mass transfer were compared.

21 Thus the mass variation (ΔM) and water loss (ΔW) were calculated according to eqs
 22 5 and 6 and sucrose gain (ΔG_{SUC}), calcium gain (ΔG_{Ca}) and vitamin C gain (ΔG_{VitC}) were
 23 calculated according to Eqs. 7, 8 and 9. All variables are defined in nomenclature section.

24

$$25 \quad \Delta M = \frac{M - M^0}{M^0} \times 100 \quad (5)$$

$$26 \quad \Delta W = \frac{(M^0 \times w_w^0) - (M \times w_w)}{M^0} \times 100 \quad (6)$$

$$27 \quad \Delta G_{SUC} = \frac{(M \times w_{SUC}) - (M^0 \times w_{SUC}^0)}{M^0} \times 100 \quad (7)$$

$$\Delta G_{Ca} = \frac{(M \times w_{Ca}) - (M^0 \times w_{Ca}^0)}{M^0} \times 100 \quad (8)$$

$$\Delta G_{vitC} = \frac{(M \times w_{vitC}) - (M^0 \times w_{vitC}^0)}{M^0} \times 100 \quad (9)$$

where M is the mass; w_w is the water content; w_{SUC} is the sucrose content; w_{Ca} is the calcium content; w_{vitC} is the ascorbic acid content.

To evaluate the influence of the concentrations of sugar, calcium salt and ascorbic acid on osmotic dehydration kinetics of pineapple, the variability of the raw material used for the different tests were minimized by using a normalized content, defined as the ratio between the experimental measurements obtained from the osmotically treated sample and its corresponding fresh sample (SILVA et al., 2011). The results were statistically evaluated using the analysis of variance (ANOVA) for each treatment and for each time process, with the sources of variation being the sample type and number of samples, and the Tukey Test being applied at the 5% level of significance.

The diffusion coefficients of water, sucrose, calcium and vitamin C of the pineapple slices were determined according to Fick's Second Law as applied to a plane sheet. The analytical solution, when integrated along the distance, results in the average concentration of the component i , $\bar{w}_i(t)$, in the solid at time t (CRANK, 1975):

$$ADM = \frac{\bar{w}_i(t) - w_i^{eq}}{w_i^0 - w_i^{eq}} = \left(\frac{8}{\pi^2} \right) \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left\{ -(2n-1)^2 \frac{t \times \pi^2 \times D_{ef}}{l^2} \right\} \quad (10)$$

where i = water, sucrose, calcium or vitamin C; D_{ef_i} = the effective diffusion coefficient of a component i ; $\bar{w}_i(t)$ = average fraction of component i at time t ; w_i^0 = fraction of the component i at initial time ($t=0$); w_i^{eq} = fraction of the component i at equilibrium; n is number of the series; l , is thickness of the slab; t is the time. The Equation 10 was fitted to the experimental data, using "Prescribed" software (SILVA; SILVA, 2008). "Prescribed" is used to study water diffusion processes with known experimental data. For each setting, the values for Chi-square were calculated:

$$\chi^2 = \sum_{i=1}^{N_p} \left(\overline{y_i^{\text{exp}}} - \overline{y_i^{\text{calc}}} \right)^2 \frac{1}{\sigma_i^2} \quad (11)$$

where $\overline{y_i^{\text{exp}}}$ is the average content (calcium, water, sucrose or vitamin C) measured at the experimental point i ; $\overline{y_i^{\text{calc}}}$ is the correspondent calculated average content; N_p is the number of experimental points; $1/\sigma_i^2$ is the statistical weights referring to the point i .

3. Results

The experimental data of water loss (ΔW), sucrose gain (ΔG_{SUC}), calcium gain (ΔG_{Ca}) and vitamin C gain (ΔG_{VitC}) were adjusted to a first order model and the regression coefficients of the significant effects were used to determine a coded model, which described the behavior of the water loss (Eq. (12)), gains of sugar (Eq. (13)), calcium (Eq. (14)) and vitamin C (Eq. (15)). Table 3 shows the experimental and calculated data according to the proposed model (eq 12 to 15) for the optimization of the osmotic dehydration process of the pineapple, in quaternary solution (sucrose-calcium lactate-ascorbic acid).

$$Y_1 = 28.25 + 1.70x_1 \quad (12)$$

$$Y_2 = 7.57 + 0.63x_1 + 0.27x_2 \quad (13)$$

$$Y_3 = 7.62 + 2.37x_2 - 0.78x_1 \cdot x_2 \quad (14)$$

$$Y_4 = 9.40 + 2.70x_3 \quad (15)$$

1 **Table 3:** Values of experimental data for optimization of osmotic dehydration process and values of calculated data from equations 12, 13, 14
 2 and 15.

Trials	Coded and (uncoded) Variables			Response variables (<i>Y</i>)								
	x_1 (<i>SUC</i>) (%)	x_2 (<i>LAC</i>) (%)	x_3 (<i>VitC</i>) (%)	ΔM_{exp} (%)	ΔW_{exp} (%)	ΔW_{calc} (%)	$\Delta G_{SUC(exp)}$ (%)	$\Delta G_{SUC(calc)}$ (%)	$\Delta G_{Ca(exp)}$ (%)	$\Delta G_{Ca(calc)}$ (%)	$\Delta G_{VitC(exp)}$ (%)	$\Delta G_{VitC(calc)}$ (%)
1	-1 (40)	-1 (2)	-1 (1)	-19.24± 1.59	26.20 ± 0.30	26.55	6.31 ± 0.54	6.67	4.58 ± 0.68	4.47	6.37 ± 0.14	6.70
2	1 (50)	-1 (2)	-1 (1)	-18.62 ± 1.34	29.11 ± 0.48	29.95	8.06 ± 0.75	7.93	6.18 ± 0.01	6.03	6.67 ± 0.08	6.70
3	-1 (40)	1 (4)	-1 (1)	-17.61 ± 0.43	26.58 ± 0.32	26.55	7.25 ± 0.35	7.21	9.65 ± 0.18	10.77	7.96 ± 0.20	6.70
4	1 (50)	1 (4)	-1 (1)	-21.87 ± 1.12	29.45 ± 0.03	29.95	7.93 ± 0.23	8.47	9.58 ± 0.82	9.21	5.74 ± 0.23	6.70
5	-1 (40)	-1 (2)	1 (2)	-19.44 ± 1.26	26.25 ± 0.38	26.55	6.82 ± 0.69	6.67	3.59 ± 0.46	4.47	11.09 ± 0.05	12.10
6	1 (50)	-1 (2)	1 (2)	-20.65 ± 0.52	28.54 ± 0.29	29.95	7.99 ± 0.66	7.93	6.02 ± 0.04	6.03	11.28 ± 0.18	12.10
7	-1 (40)	1 (4)	1 (2)	-15.52 ± 1.64	26.07 ± 0.05	26.55	7.36 ± 0.35	7.21	11.10 ± 0.24	10.77	14.10 ± 0.16	12.10
8	1 (50)	1 (4)	1 (2)	-21.08 ± 1.94	31.63 ± 0.13	29.95	8.84 ± 0.38	8.47	9.00 ± 0.88	9.21	11.84 ± 0.24	12.10
9	0 (45)	0 (3)	0 (1.5)	-19.40 ± 1.86	29.35 ± 0.51	28.25	7.56 ± 0.74	7.57	8.34 ± 0.39	7.62	10.39 ± 0.13	9.40
10	0 (45)	0 (3)	0 (1.5)	-21.04 ± 0.94	29.74 ± 0.10	28.25	7.33 ± 0.77	7.57	7.30 ± 0.58	7.62	8.85 ± 0.25	9.40
11	0 (45)	0 (3)	0 (1.5)	-17.38 ± 0.10	28.60 ± 0.11	28.25	7.79 ± 0.86	7.57	8.43 ± 0.47	7.62	9.25 ± 0.20	9.40
12	0 (45)	0 (3)	0 (1.5)	-19.26 ± 0.54	27.45 ± 0.06	28.25	7.65 ± 0.91	7.57	7.64 ± 0.70	7.62	9.34 ± 0.11	9.40

1 The coded model proposed to represent the behavior of the response variables in the
 2 osmotic dehydration showed a reasonable fit for water loss ($R^2=0.816$) and good fit for
 3 sucrose gain ($R^2 = 0.838$), calcium gain ($R^2 = 0.932$) and vitamin C gain ($R^2 = 0.858$) and lack
 4 of fit not significant for all responses (Tables 4 and 5).

5 In a more suitable way for application, the expressions 12, 13, 14 and 15 are showed
 6 in function of uncoded variables:

7

$$8 \quad \Delta W = 12.95 + 0.34SUC \quad (16)$$

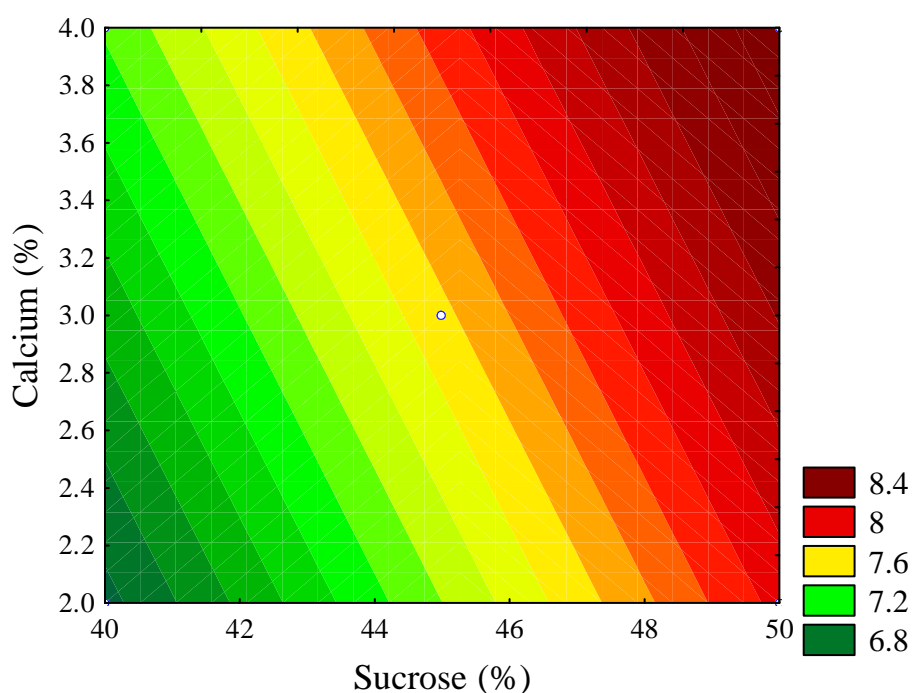
$$9 \quad \Delta G_{SUC} = 1.09 + 0.13SUC + 0.27LAC \quad (17)$$

$$10 \quad \Delta G_{Ca} = -20.55 + 9.39LAC + 0.47SUC - 0.16SUC \cdot LAC \quad (18)$$

$$11 \quad \Delta G_{VitC} = 1.30 + 5.40VitC \quad (19)$$

12

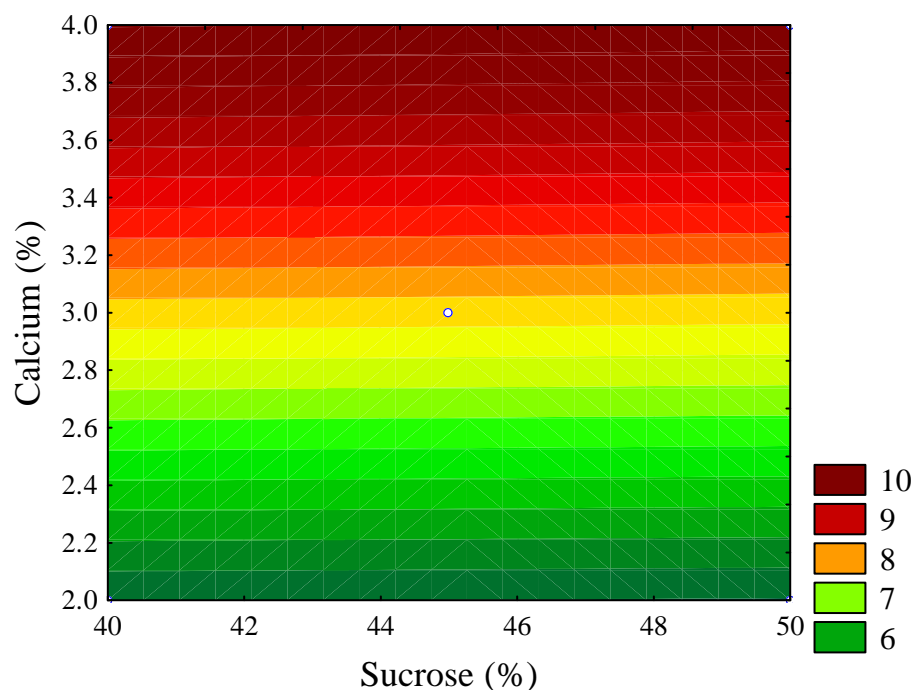
13 Figure 1 and 2 show the response contour graph to sucrose gain and calcium gain,
 14 respectively, in quaternary solution, represented by equations 17 and 18.



15

16

Figure 1: Contour graph for sucrose gain as a function of sucrose and calcium concentration with a constant ascorbic acid concentration of 1.5%.



1 **Figure 2:** Contour graph for calcium gain as a function of sucrose and
 2 calcium concentration with a constant ascorbic acid concentration of
 3 1.5%.

4 Contour graph analysis indicated that greater sucrose and calcium concentration in
 5 solution provide higher impregnation of sucrose in samples (Figure 1). In Figure 2, however,
 6 calcium gain increases as calcium concentration rises and sucrose concentration diminished in
 7 osmotic solution.

8 Mass variation in samples submitted to quaternary solution (sucrose – calcium lactate
 9 – ascorbic acid – water) was evaluated, but none independent variable presented significant
 10 effects ($p < 0.05$) on this response.

11 It was observed by analysis of variance, in Table 4, that only sucrose concentration
 12 significantly ($p < 0.05$) affected the water loss of the samples, being this more intense in
 13 solutions with higher sucrose concentration (Table 3).

1 **Table 4:** Analysis of variance and analysis of perturbation of the investigated variables on the response WL and ΔG_{SUC} .

Source	WL					ΔG_{SUC}				
	SS	d.f.	MS	F	p	SS	d.f.	MS	F	p
x_1	23.2251	1	23.2251	22.8072	0.0174*	3.2248	1	3.2248	87.3278	0.0026*
x_2	1.6559	1	1.6558	1.6260	0.2920	0.6040	1	0.6040	16.3556	0.0272*
x_3	0.1652	1	0.1652	0.1623	0.7141	0.2708	1	0.2708	7.3324	0.0733
x_1x_2	1.2971	1	1.2971	1.2738	0.3412	0.0707	1	0.0707	1.9134	0.2606
x_1x_3	0.5370	1	0.5370	0.5273	0.5203	0.0057	1	0.0057	0.1539	0.7211
x_2x_3	0.6040	1	0.6040	0.5932	0.4973	0.0418	1	0.0418	1.1312	0.3655
$x_1x_2x_3$	1.3702	1	1.3702	1.3455	0.3300	0.2400	1	0.2400	6.4967	0.0840
Lack of Fit	1.7402	1	1.7402	1.7089	0.2823	0.0007	1	0.0007	0.0201	0.8963
Pure Error	3.0550	3	1.0183	-----	-----	0.1108	3	0.0369	-----	-----
Total SS	33.6495	11	-----	-----	-----	4.5691	11	-----	-----	-----
R ²	0.858	-----	-----	-----	-----	0.976	-----	-----	-----	-----
Factor	Effect	Pure error	-95% Cnf. limit	+95% Cnf. limit	p	Effect	Pure error	-95% Cnf. limit	+95% Cnf. limit	p
Mean/Intercept	28.2491	0.2913	27.3220	29.1762	0.0000*	7.5739	0.0555	7.3973	7.7504	0.0000*
x_1	3.4077	0.7136	1.1369	5.6786	0.0174*	1.2698	0.1359	0.8374	1.7022	0.0026*
x_2	0.9099	0.7136	-1.3610	3.1807	0.2920	0.5495	0.1359	0.1171	0.9820	0.0272*
x_3	0.2874	0.7136	-1.9834	2.5583	0.7141	0.3679	0.1359	-0.0645	0.8004	0.0733
x_1x_2	0.8053	0.7136	-1.4655	3.0762	0.3412	-0.1880	0.1359	-0.6204	0.2445	0.2606
x_1x_3	0.5182	0.7136	-1.7527	2.7890	0.5203	0.0533	0.1359	-0.3791	0.4857	0.7211
x_2x_3	0.5496	0.7136	-1.7213	2.8204	0.4973	0.1445	0.1359	-0.2879	0.5770	0.3655
$x_1x_2x_3$	0.8277	0.7136	-1.4432	3.0986	0.3300	0.3463	0.1359	-0.0861	0.7788	0.0840

2 *Significant at 5% level.

1 Table 4 also shows that sucrose concentration (x_1) and calcium lactate concentration (
2 x_2) significantly ($p < 0.05$) affected sucrose gain (Y_2) of the samples. The analysis of
3 perturbation shows that the independent variable x_1 presented higher positive effect on
4 response (Y_2) than the variable x_2 (Table 4).

5 Calcium lactate concentration in quaternary solution was the variable with higher
6 significant effect on calcium incorporation in the pineapple. The interaction between sucrose
7 and calcium concentration in solution also was significant, however presented lower and
8 negative effect on impregnation of this mineral (Table 5).

1 **Table 5:** Analysis of variance and analysis of perturbation of the investigated variables on the response ΔG_{Ca} and ΔG_{VitC} .

Source	ΔG_{Ca}					ΔG_{VitC}				
	SS	d.f.	MS	F	p	SS	d.f.	MS	F	p
x_1	0.4347	1	0.4347	1.4699	0.3121	1.9816	1	1.9819	4.6054	0.1212
x_2	44.9593	1	44.9593	152.0149	0.0011*	2.2400	1	2.2400	5.2053	0.1068
x_3	0.0096	1	0.0096	0.0326	0.8682	58.2538	1	58.2538	135.3686	0.0014*
x_1x_2	4.8103	1	4.8103	16.2646	0.0274*	3.0790	1	3.0790	7.1548	0.0754
x_1x_3	0.1782	1	0.1782	0.6025	0.4942	0.0027	1	0.0027	0.0062	0.9424
x_2x_3	0.5083	1	0.5083	1.7185	0.2812	1.0633	1	1.0633	2.4708	0.2140
$x_1x_2x_3$	1.0294	1	1.0294	3.4807	0.1589	0.0008	1	0.0008	0.0018	0.9687
Lack of Fit	0.5804	1	0.5804	1.9625	0.2557	0.0158	1	0.0158	0.0367	0.8603
Pure Error	0.8873	3	0.2958	-----	-----	1.2910	3	0.4303	-----	-----
Total SS	53.3976	11	-----	-----	-----	67.9281	11	-----	-----	-----
R ²	0.973	-----	-----	-----	-----	0.981	-----	-----	-----	-----
Factor	Effect	Pure error	-95% Cnf. limit	+95% Cnf. Limit	p	Effect	Pure error	-95% Cnf. limit	+95% Cnf. limit	p
Mean/Intercept	7.6164	0.1570	7.1168	8.1160	0.0000*	9.4049	0.1894	8.8022	10.0076	0.0000*
x_1	0.4662	0.3845	-0.7576	1.6900	0.3121	-0.9954	0.4639	-2.4717	0.4808	0.1212
x_2	4.7413	0.3845	3.5175	5.9651	0.0011*	1.0583	0.4639	-0.4179	2.5345	0.1068
x_3	-0.0694	0.3845	-1.2932	1.1544	0.8682	5.3969	0.4639	3.9207	6.8732	0.0014*
x_1x_2	-1.5509	0.3845	-2.7747	-0.3271	0.0274*	-1.2408	0.4639	-2.7170	0.2355	0.0754
x_1x_3	-0.2985	0.3845	-1.5223	0.9253	0.4942	-0.0364	0.4639	-1.5126	1.4398	0.9424
x_2x_3	0.5041	0.3845	-0.7197	1.7279	0.2812	0.7291	0.4639	-0.7471	2.2053	0.2140
$x_1x_2x_3$	-0.7174	0.3845	-1.9412	0.5064	0.1589	0.0198	0.4639	-1.4565	1.4960	0.9687

2 *Significant at 5% level.

Results showed that the impregnation of Vitamin C increased significantly ($p < 0.05$) with the increase of ascorbic acid concentration in the osmotic solution (Table 3). The analysis of variance showed that only ascorbic acid concentration in solution was significant ($p < 0.05$) on vitamin C gain (Table 5).

Further impregnation of calcium in samples would result in more enriched products. However, the insolubility of calcium lactate in concentrations above 4% in the quaternary solution containing 50% sucrose concentration limits this parameter of the process. Higher calcium lactate concentration could be dissolved in quaternary solution with less sucrose concentration, although this procedure would reduce the dehydration process efficiency, once sucrose concentration in solution has greater effect on the water loss of product than calcium lactate concentration. To provide final products with greater vitamin C and calcium contents were selected the higher concentrations of calcium lactate and ascorbic acid (4 and 2% respectively) as process variables to investigate the osmotic dehydration kinetics of pineapple.

The study was extended and the effect of time and addition of each solute (sucrose, calcium lactate and ascorbic acid) on the osmotic dehydration of pineapple was studied. The experiments conditions are given in Table 2. Sucrose concentrations studied were 40 and 50% and the process times varied in 0, 1, 2, 4 and 6 hours. Solutions were composed with and without calcium lactate (4%) as well as with and without ascorbic acid (2%). Table 6 shows water, sucrose, calcium and vitamin C content of fresh and osmotically dehydrated samples in binary, ternary and quaternary solutions as a function of osmotic dehydration time. To minimize the influence of the different raw material on these contents, the results were normalized (Table 7) through the ratio between the experimental measurements from the osmotically treated samples and its corresponding fresh samples.

Table 6: Water, sucrose, calcium and vitamin C content of fresh and osmotically dehydrated samples in binary, ternary and quaternary solutions at different times.

Experiment (Treatment)	a_w of osmotic solution	Time (hours)	w_w (%)	w_{SUC} (%)	w_{Ca} (%)	w_{VitC} (%)
40% SUC (1)	0.957 ± 0.003	0	83.27 ± 0.05 ^a	8.90 ± 0.35 ^a	--	--
		1	75.10 ± 0.04 ^b	17.86 ± 0.70 ^b	--	--
		2	73.62 ± 0.12 ^c	19.36 ± 1.04 ^b	--	--
		4	72.90 ± 0.06 ^d	20.91 ± 0.81 ^{b,c}	--	--
		6	71.28 ± 0.09 ^e	22.96 ± 0.80 ^c	--	--
		Equilibrium	66.01 ± 0.08 ^f	28.81 ± 0.91 ^e	--	--
		40% SUC + 4% LAC (2)	0.921 ± 0.003	0	86.69 ± 0.08 ^a	8.28 ± 0.37 ^a
1	76.67 ± 0.10 ^b			17.57 ± 0.33 ^b	0.045 ± 0.00268 ^b	--
2	74.11 ± 0.16 ^c			18.66 ± 0.24 ^b	0.062 ± 0.00060 ^c	--
4	71.64 ± 0.03 ^d			20.04 ± 0.30 ^c	0.067 ± 0.00267 ^c	--
6	69.93 ± 0.03 ^e			22.93 ± 0.10 ^d	0.092 ± 0.00276 ^d	--
Equilibrium	62.46 ± 0.06 ^f			30.54 ± 0.13 ^e	0.216 ± 0.00104 ^e	--
40% SUC + 4% LAC + 2% VitaC (3)	0.915 ± 0.002			0	88.91 ± 3.50 ^a	6.78 ± 0.50 ^a
		1	76.01 ± 0.19 ^b	18.33 ± 0.18 ^b	0.116 ± 0.00033 ^b	0.70 ± 0.0050 ^b
		2	71.64 ± 0.05 ^c	22.01 ± 0.02 ^c	0.121 ± 0.00055 ^c	0.97 ± 0.0126 ^c
		4	69.17 ± 0.03 ^c	24.44 ± 0.19 ^d	0.094 ± 0.00081 ^d	1.03 ± 0.0008 ^d
		6	67.92 ± 0.06 ^c	27.08 ± 0.78 ^e	0.100 ± 0.00111 ^e	1.06 ± 0.0187 ^d
		Equilibrium	60.20 ± 0.07 ^e	32.30 ± 0.23 ^f	0.244 ± 0.00233 ^f	1.37 ± 0.0145 ^e

Table 6: Water, sucrose, calcium and vitamin C content of fresh and osmotically dehydrated samples in binary, ternary and quaternary solutions at different times. (Continuation)

Experiment (Treatment)	a_w of osmotic solution	Time (hours)	w_w (%)	w_{SUC} (%)	w_{Ca} (%)	w_{VitC} (%)
50% SUC (4)	0.927 ± 0.002	0	83.27 ± 0.05 ^a	9.35 ± 0.62 ^a	--	--
		1	75.09 ± 0.04 ^b	20.75 ± 0.63 ^b	--	--
		2	70.18 ± 0.18 ^c	22.89 ± 0.31 ^b	--	--
		4	67.46 ± 0.26 ^c	25.93 ± 0.16 ^b	--	--
		6	66.30 ± 0.12 ^d	29.35 ± 1.66 ^c	--	--
		Equilibrium	57.27 ± 0.14 ^e	42.05 ± 0.67 ^d	--	--
50% SUC + 4% LAC (5)	0.909 ± 0.001	0	85.40 ± 0.06 ^a	8.37 ± 0.03 ^a	0.0016 ± 0.00009 ^a	--
		1	74.83 ± 0.04 ^b	14.62 ± 0.84 ^b	0.063 ± 0.00322 ^a	--
		2	72.50 ± 0.15 ^c	18.91 ± 0.11 ^c	0.070 ± 0.00031 ^b	--
		4	67.67 ± 0.09 ^d	24.27 ± 0.28 ^d	0.075 ± 0.00108 ^b	--
		6	64.21 ± 0.08 ^e	25.21 ± 0.65 ^d	0.089 ± 0.00069 ^c	--
		Equilibrium	53.02 ± 0.06 ^f	38.51 ± 0.45 ^e	0.248 ± 0.0023 ^d	--
50% SUC + 4% LAC + 2% VitaC (6)	0.897 ± 0.002	0	92.99 ± 0.02 ^a	5.65 ± 0.04 ^a	0.0011 ± 0.00000 ^a	0.03 ± 0.0003 ^a
		1	73.31 ± 0.16 ^b	20.05 ± 0.40 ^b	0.104 ± 0.00156 ^b	0.57 ± 0.0201 ^b
		2	70.54 ± 0.20 ^c	24.87 ± 0.95 ^c	0.127 ± 0.00834 ^c	0.65 ± 0.0103 ^c
		4	64.35 ± 0.00 ^d	28.49 ± 0.23 ^d	0.135 ± 0.00458 ^c	0.84 ± 0.0126 ^d
		6	61.56 ± 0.21 ^e	30.89 ± 0.39 ^e	0.133 ± 0.00254 ^c	0.88 ± 0.0352 ^d
		Equilibrium	50.87 ± 0.15 ^f	42.05 ± 0.45 ^f	0.211 ± 0.00356 ^d	1.38 ± 0.0243 ^e

*Mean ± SD

**Means with the same letter in the same column did not differ significantly at $p \leq 0.05$ according to the Tukey test

Table 7: Ratio between the experimental measurements obtained from the osmotically treated samples at different time and the corresponding fresh sample.

Experiment (Treatment)	Time (hours)	40% SUC (1)	40%SUC + 4%LAC (2)	40%SUC + 4%LAC + 2%VitaC (3)	50%SUC (4)	50%SUC + 4%LAC (5)	50%SUC + 4%LAC + 2%VitaC (6)
w_w / w_w^0	1	0.902 ± 0.0004 ^a	0.884 ± 0.0011 ^b	0.855 ± 0.0021 ^c	0.902 ± 0.0004 ^a	0.876 ± 0.0004 ^d	0.788 ± 0.0017 ^e
	2	0.884 ± 0.0015 ^a	0.855 ± 0.0018 ^b	0.806 ± 0.0006 ^c	0.843 ± 0.0019 ^d	0.849 ± 0.0017 ^e	0.759 ± 0.0022 ^f
	4	0.875 ± 0.0008 ^a	0.826 ± 0.0004 ^b	0.778 ± 0.0003 ^c	0.810 ± 0.0023 ^d	0.792 ± 0.0011 ^e	0.692 ± 0.0000 ^f
	6	0.856 ± 0.0011 ^a	0.807 ± 0.0004 ^b	0.764 ± 0.0007 ^c	0.796 ± 0.0015 ^d	0.752 ± 0.0010 ^e	0.662 ± 0.0022 ^f
w_{SUC} / w_{SUC}^0	1	2.01 ± 0.08 ^a	2.12 ± 0.04 ^a	2.70 ± 0.03 ^b	2.22 ± 0.07 ^a	1.75 ± 0.10 ^a	3.55 ± 0.07 ^c
	2	2.18 ± 0.12 ^a	2.25 ± 0.03 ^a	3.25 ± 0.00 ^b	2.49 ± 0.02 ^a	2.26 ± 0.01 ^a	4.40 ± 0.17 ^c
	4	2.25 ± 0.09 ^a	2.42 ± 0.04 ^a	3.61 ± 0.03 ^c	2.77 ± 0.02 ^d	2.90 ± 0.03 ^d	5.04 ± 0.04 ^e
	6	2.58 ± 0.09 ^a	2.77 ± 0.01 ^{a, c, d}	4.00 ± 0.12 ^b	3.14 ± 0.18 ^c	3.01 ± 0.08 ^c	5.47 ± 0.07 ^d
w_{Ca} / w_{Ca}^0	1	--	30.00 ± 1.76 ^a	105.45 ± 0.31 ^b	--	39.38 ± 1.99 ^c	94.54 ± 1.37 ^d
	2	--	41.33 ± 0.40 ^a	110.00 ± 0.50 ^b	--	43.75 ± 0.19 ^c	115.45 ± 7.31 ^b
	4	--	44.66 ± 1.75 ^a	85.45 ± 0.74 ^b	--	46.88 ± 0.67 ^c	122.73 ± 4.01 ^d
	6	--	61.33 ± 1.81 ^a	90.91 ± 1.02 ^b	--	55.63 ± 0.43 ^c	120.91 ± 2.22 ^d

Table 7: Ratio between the experimental measurements obtained from the osmotically treated samples at different time and the corresponding fresh sample. (Continuation)

Experiment (Treatment)	Time (hours)	40% SUC (1)	40%SUC +			50%SUC (4)	50%SUC +	
			40%SUC + 4%LAC (2)	4%LAC + 2%VitaC (3)	50%SUC + 4%LAC (5)		4%LAC + 2%VitaC (6)	
w_{VitaC} / w_{VitaC}^0	1	--	--	17.50 ± 0.13 ^a	--	--	19.00 ± 0.58 ^b	
	2	--	--	24.25 ± 0.34 ^a	--	--	21.67 ± 0.29 ^b	
	4	--	--	25.75 ± 0.02 ^a	--	--	28.00 ± 0.37 ^b	
	6	--	--	26.50 ± 0.51 ^a	--	--	29.33 ± 1.02 ^a	

*Mean ± SD

**Means with the same letter in the same column did not differ significantly at $p \leq 0.05$ according to the Tukey test

It can be seen in Table 6, for all treatments, that during the first hour of process, the sucrose content increased in the samples sharply to a concentration of approximately two to three times the initial one; after this time, the rate decreased. A similar behavior was observed for calcium and vitamin C contents, since a considerable solute impregnation occurred during the first hour of osmotic dehydration.

Comparison of samples in binary osmotic solution (sucrose + water) shows that the change of the concentration from 40 to 50% reduced the water content in the samples and increased the sugar content (Table 6 and Table 7). The increase of the sucrose concentration in solution increased the osmotic pressure gradient, since water activity of solution (a_w) diminished (Table 6), resulting higher water transfer from product to solution and solute transfer from solution to sample. Similar behavior was observed by GARCIA et al. (2007), SINGH et al. (2007) and AMINZADEH et al. (2010).

The calcium lactate addition in sucrose solutions also reduces the water activity of solution (Table 6) and consequently the water content in the samples, from treatment 1 (40% SUC) to 2 (40% SUC + 4% LAC) and from treatment 4 (50% SUC) to treatment 5 (50% SUC + 4% LAC). However, the sucrose content changes in these samples were not significant, even though from treatment 1 (40% SUC) to treatment 2 (40% SUC + 4% LAC) a slight increase was observed while from treatment 4 (50% SUC) to treatment 5 (50% SUC + 4% LAC) (Table 7) the sucrose content showed a tendency to decrease.

On the other hand, ascorbic acid addition in solution provides the lowest water contents in the samples since reduces a_w of solution (Table 6), mainly when pineapple is dehydrated in solutions with 50% sucrose concentration (Table 6 and Table 7).

After 6 hours of process, the treatment 6 (50%SAC + 4% LAC + 2% VitaC) reduced 33.8% of water content of the samples, while a 24.8 % reduction was obtained by treatment 5 (50%SAC + 4%LAC) and 20.4% by treatment 4 (50%SAC). At the same time, the sucrose content and the calcium content were the highest when the ascorbic acid was present in solution.

The effective diffusion coefficients could be useful to clarify the influence of each compound on the mass transfer. For binary solutions (sucrose + water), effective diffusion coefficients of water were slightly higher than sucrose (Table 8), as expected, since the plant tissue restrict more sucrose than water molecules. Both water and sucrose coefficients for more concentrate solutions were the lowest, as expected for pure binary sucrose-water solutions (HENRION, 1964). However, calcium lactate and ascorbic acid addition in sucrose solution caused unpredictable effects in diffusivities.

Table 8: Diffusion coefficients for water, sucrose, calcium and vitamin C of the samples of pineapple submitted binary, ternary and quaternary solutions, determination coefficient and Chi-square

Treatments	40%SUC (1)	40%SUC	40%SUC +	50%SUC (4)	50%SUC	50%SUC
		+ 4%LAC (2)	4%LAC + 2% VitC (3)		+ 4%LAC (5)	+ 4%LAC + 2%VitC (6)
$D_{ef_w} \times 10^{10}$	6.16 ±	5.79 ±	7.41 ±	4.99 ±	4.24 ±	7.02 ±
(m ² /s)	0.28	0.17	0.53	0.02	0.22	0.11
R ²	0.906	0.958	0.947	0.968	0.992	0.961
$\chi^2 \times 10^{-3}$	1.111	0.991	2.007	0.709	0.278	3.216
$D_{ef_{suc}} \times 10^{10}$	5.95 ±	4.68 ±	7.99 ±	3.92 ±	3.18 ±	5.82 ±
(m ² /s)	0.44	0.21	0.32	0.18	0.25	0.27
R ²	0.938	0.928	0.973	0.966	0.981	0.963
$\chi^2 \times 10^{-3}$	0.970	1.155	0.886	1.053	0.375	1.944
$D_{ef_{ca}} \times 10^{10}$	--	1.63 ±	ND	--	1.40 ±	5.74 ±
(m ² /s)	--	0.77	ND	--	0.22	0.26
R ²	--	0.965	ND	--	0.894	0.841
$\chi^2 \times 10^{-7}$	--	0.181	ND	--	0.633	2.853
$D_{ef_{vitc}} \times 10^{10}$	--	--	9.87 ± 0.77	--	--	4.86 ±
(m ² /s)	--	--	9.87 ± 0.77	--	--	0.54
R ²	--	--	0.932	--	--	0.945
$\chi^2 \times 10^{-6}$	--	--	6.450	--	--	3.384

*ND – it was not determine

It can be seen in Table 8 that sucrose diffusivity was reduced with the calcium lactate presence in solutions without ascorbic acid addition. Probably calcium ions interacted with pectin carboxyl groups generate from pectin of the pineapple tissue, forming calcium pectate that would act as a partial barrier to larger molecules diffusion like sucrose into the tissue (BARRERA et al., 2009). Other authors verified similar inhibition in sugar gain due to the use of calcium salts in osmotic solution (MAVROUDIS et al., 2012; MASTRANTONIO et al.,

2005; PEREIRA et al., 2006; FERRARI et al., 2010). In addition, if calcium reacts and remains immobilized, the cell wall porosity decreases and consequently sucrose diffusion may diminish. The sucrose diffusivities were the lowest coefficients in treatment 2 (40% SUC + 4% LAC) and treatment 5 (50% SUC, 4% LAC) (Table 8).

The increase of the solute concentration in osmotic solution as well as the decreasing molecular weight of solute tend to increase the osmotic pressure gradient between fruit and solution and to affect positively the water transfer from plant tissue to solution. In turn, in liquid phase, diffusivities decrease as the solutes concentration rises. Both driving forces and diffusion coefficients influence the transport phenomena. Moreover, solutes can promote changes in plant tissue which would make diffusion easier. In this study the addition of ascorbic acid in osmotic solution significantly increased the sugar and calcium content in pineapple (Table 6 and 7) as well as the sucrose and calcium diffusion coefficients (Table 8). It was observed that in quaternary osmotic solutions, sucrose gain significantly increased with calcium lactate concentration and sucrose concentration (equation 13 and 17), but not with ascorbic acid. Despite ascorbic acid interference was not observed in the studied concentration ranges during the first experimental trials, kinetics studies with binary and ternary solutions (without ascorbic acid) presented a diverse behavior. Probably both, the lowest water activities (Table 6) and the acidification of solution with ascorbic acid promoted injuries to the cellular tissue. In addition, low pH treatment may cause changes in polysaccharide gels of the cell walls with increased porosity (ZEMKE-WHITE et al., 2000). Consequently, lower resistance to the solutes transport would provide greater sucrose and calcium impregnation in the tissue. This interaction was not observed in analysis of variance of sucrose and calcium gain (Table 5) possibly because acid ascorbic was present in all samples and the changes in tissue occurred in a similar manner. Monnerat et al. (2010), investigating osmotic dehydration of apples immersed in aqueous sugar/salt solution, observed an increase of the effective water and sucrose diffusion coefficients that was attributed to the greater mobility of the sodium chloride and the injuries that may cause in the tissue.

Barrera et al. (2009) attribute to structure modifications of biological tissues, non-diffusional driving forces that also act in mass transfer during osmotic dehydration, since the chemical potential gradient of phases and components depends on the physical cellular structure (CRAPISTE et al., 1988).

Calcium content increased with the time in ternary solutions (sucrose - calcium lactate - water), being that after 1 hour of process the solution 50%SAC + 4% LAC (treatment 5) provided samples with calcium content 40 times higher than the fresh ones ($p < 0.05$) (Table 6).

It was observed that diffusion coefficients of calcium were the smallest and reduced with the increase of sucrose concentration (Table 8). In quaternary solutions, it was verified that diffusion coefficients of calcium of the treatment 3 could not be determined and the calcium diffusivity of the treatment 6 presented the worst fit ($R^2 = 0.841$) compared to the other determination coefficients (Table 8). This irregular behavior suggests that, in the quaternary system, there was influence of the concentration gradients on the fluxes. In the first experimental step, interaction between sucrose and calcium concentration in osmotic solution was found for calcium gain (Equations 14 and 18).

Monnerat et. al. (2010) detected in a ternary system the effect of concentration gradients on the flux of the each component during osmotic dehydration of apples in a sucrose/salt/water solution. The water flux was affected not only by water but by sucrose and salt gradients. Sucrose gradient was the most important driving force on sucrose flux, followed by salt gradient. The sodium chloride diffusion depended on its own gradient.

Figures 3, 4 and 5 show experimental and calculated values of the content (dimensionless) of water, sucrose, calcium and vitamin C obtained during osmotic dehydration kinetics. In this work, thermodynamic equilibrium between the samples and the respective solution was apparently reached in 48 hs (Figures 3, 4 and 5). However, non equilibrium behavior was observed for the calcium component (Figure 5), considering samples submitted to treatment 2 and 5. This fact could be related to the activity of the enzyme pectinmetylerase (PME), important enzyme in the pineapple (SILVA COSTA et al., 2011). This enzyme hydrolyzes the methyl ester linkages in pectin molecules, producing free carboxyl groups. The de-esterified pectin, in turn, can bind calcium ions present in the solution, producing calcium pectates. Probably, equilibrium between calcium of the samples and calcium of the solutions 2 and 5 was not reached due to enzymatic activity of PME. Samples dehydrated in the solution 6, however, showed equilibrium behavior for all analyzed components. Some authors observed that the enzyme pectinmetylerase (PME) have very low activity or even inactivity in pH below 4.0 (ATKINS; ROUSE, 1953; COLLET et al., 2005; WILINSKA et al., 2008). Probably, the ascorbic acid added in solution contributed to

reduce the activity of the PME. Consequently, the absence of pectin hydrolysis would allow to reach thermodynamic equilibrium in short-term.

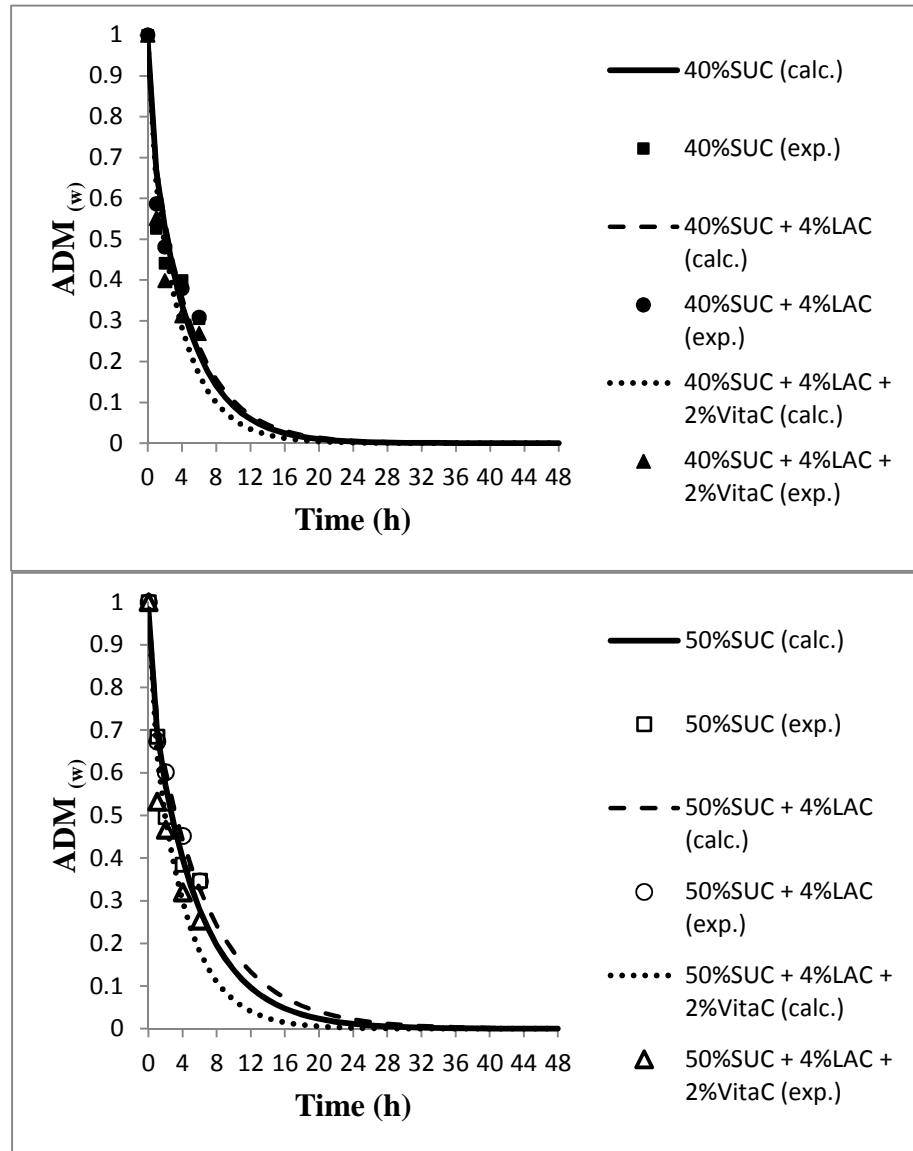


Figure 3: Experimental and calculated values of the content (dimensionless) of water, obtained during osmotic dehydration kinetics.

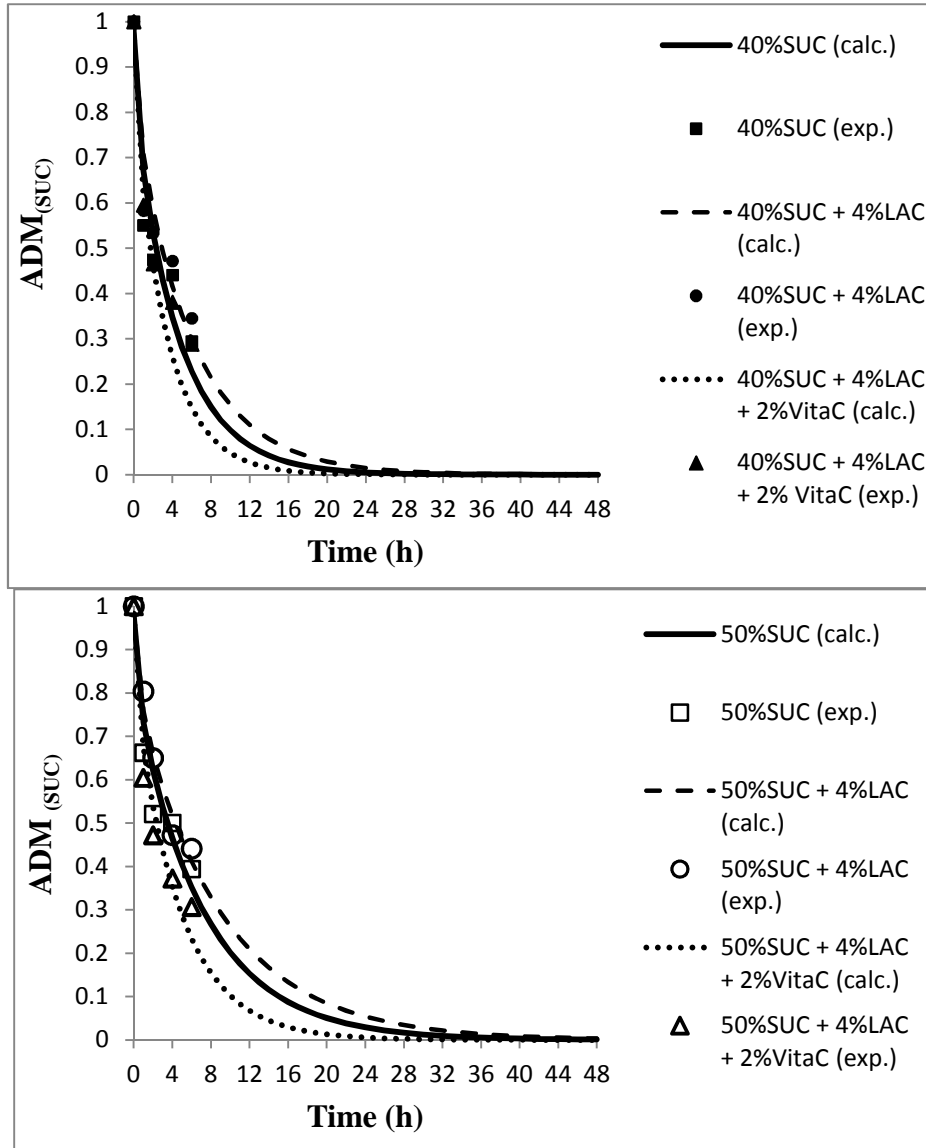


Figure 4: Experimental and calculated values of the content (dimensionless) of sucrose, obtained during osmotic dehydration kinetics.

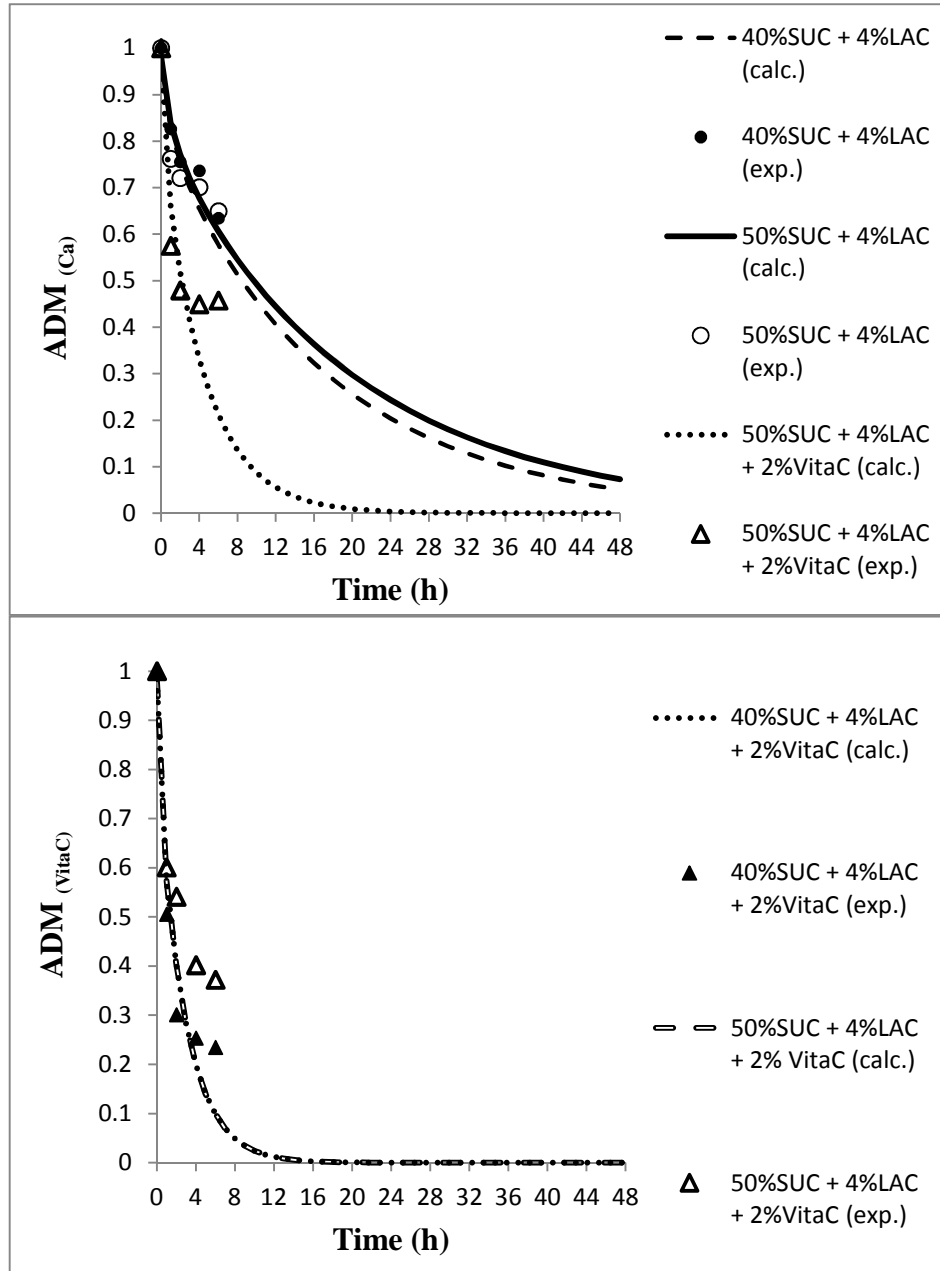


Figure 5: Experimental and calculated values of the content (dimensionless) of calcium and ascorbic acid, obtained during osmotic dehydration kinetics.

Moreover, the acidification of solution can contribute to increase the porosity and impregnation of calcium in tissue (ZEMKE-WHITE et al., 2000; MAVROUDIS et al., 2012).

In the present work, a noticeable impregnation of vitamin C was obtained for the tested experimental conditions. In one hour of process, both treatments 3 and 6 provided samples with respective vitamin C content 17.5 and 19 times higher than vitamin C content of

fresh pineapple. After 6 hours of process, pineapple submitted to treatment 6 presented vitamin C content 29.3 times higher than content of fresh samples (Table 6).

4. Conclusions

Osmotic dehydration was optimized by evaluating the effect of the sucrose, calcium lactate and ascorbic acid concentrations in aqueous quaternary solution on the water loss and gains of sucrose, calcium and vitamin C. Only sucrose concentration significantly reduced water loss of the samples. Sucrose gain and calcium impregnation were significantly affected by sucrose and calcium lactate concentration. It was not observed significant interference of the ascorbic acid in quaternary solution on results, in the studied concentration ranges.

When comparing diffusivity of components in samples osmotically dehydrated in sucrose solutions, with and without calcium lactate, it was found that calcium in solution diminished the water and sucrose diffusivities. In quaternary solutions, it was to verify that the diffusivity of water, sugar and calcium were strongly affected by the ascorbic acid added to the osmotic solution. Ascorbic acid in osmotic solution increases the sucrose and calcium impregnation in pineapple.

A noticeable calcium and vitamin C impregnation was obtained in pineapple after 1 hour of immersion. More detailed studies about influence of ascorbic acid on the tissue microstructure would be necessary to explain the changes in the mass transport found in the present work.

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6. References

AMINZADEH, R.; SARGOLZAEI, J.; ABARZANI, M. (2010) Preserving melons by osmotic dehydration in a ternary system followed by air-drying. **Food and Bioprocess Technology**, 5 (4), 1305-1316

ANINO, S. V.; SALVATORI, D. M.; ALZAMORA, S. M. (2006) Changes in calcium level and mechanical properties of apple tissue due to impregnation with calcium salts. **Food Research Internacional**, Ontário, 39, 154-164.

ATKINS, C.D.; ROUSE, A.H. Time-temperature relationships for heat inactivation of pectinesterase in citrus juices. **Food Technology**, Chicago, v. 7, n. 12, p. 489-491, 1953.

AOAC - ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS (1970) Official Methods of Analysis of the Association of Official Analytical Chemists, 11th ed. Arlington: Association of Official Analytical Chemists AOAC.

AOAC - ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS (1984) Official Methods of Analysis of the Association of Official Analytical Chemists 14th ed. Arlington: Association of Official Analytical Chemists AOAC.

AOAC - ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS (1995) Official Methods of Analysis of the Association of Official Analytical Chemists, 16th ed., v. 1, Arlington: Association of Official Analytical Chemists A.O.A.C., chapter 3. p. 4. (method 985.01).

BARRERA, C.; BETORET, N.; CORELL, P.; FITO, P. (2009). Effect of osmotic dehydration on the stabilization of calcium-fortified apple slices (var. Granny Smith): Influence of . operating variables on process kinetics and compositional changes. **Journal of Food Engineering**, Amsterdam 92, 416-424

BENASSI, M. T.; ANTUNES, A. J. (1988). A comparison of meta-phosphoric and oxalic acids as extractant solutions for the determination of vitamin C in selected vegetables. **Arquivos de Biologia e Tecnologia**, Curitiba, 31(4), 507-513.

COLLET, L.S.F.C.A.; SHIGEOKA, D.S.; BADOLATO, G.G.; TADINI, C.C. (2005) A kinetic study on pectinesterase inactivation during continuous pasteurization of orange juice. **Journal of Food Engineering**, Amsterdam 69, 125-129

CRANK, J. (1975). **The Mathematics of Diffusion**. second ed. Clarendon Press-Oxford, London.

CRAPISTE, G.H.; WHITAKER, S.; ROTSTEIN, E. (1988). Drying a cellular material - I. A mass transfer theory. **Chemical Engineering Science**, 43, (11), 2919-2928.

FERRARI, C.C.; CARMELLO-GUERREIRO, S.M.; BOLINI, H.M.A.; HUBINGER, M.D. (2010) Structural changes, mechanical properties and sensory preference of osmodehydrated melon pieces with sucrose and calcium lactate solutions. **International Journal of Food Properties**, 13, 112-130.

FITO, P.; CHIRALT, A.; BETORET, N.; GRAS, M.; CHÁFER, M.; MARTÍNEZ-MONZÓ, J.; ANDRÉS, A.; VIDAL, D. (2001) Vacuum impregnation and osmotic dehydration in matrix engineering. Application in functional fresh food development. **Journal of Food Engineering**. 49,175-183.

GARCIA, C.C.; MAURO, M.A.; KIMURA, M. (2007) Kinetics of osmotic dehydration and air drying of pumpkins (*Cucurbita moschata*). **Journal of Food Engineering**, 82, 284-291.

HAWKES, J.; FLINK, J. M. (1978) Osmotic concentration of fruit slices prior to freeze dehydration. **Journal of Food Processing and Preservation**, 2, 265-284.

HENRION, P. N. (1964) Diffusion in the sucrose + water system. **Transaction Faraday Soc.**, 60, 72-82.

LENART, A. (1996). Osmo-convective drying of fruits and vegetables: technology and application. **Drying Technology**, 14 (2), 391-413.

KATZ, F. (2000) Research priorities more toward healthy and safe. **Food Technology**, 54 (12), 42-44.

MASTRANTONIO, S.D.S.; PEREIRA, L.M.; HUBINGER, M.D. (2005) Osmotic dehydration kinetics of guavas in maltose solutions with calcium salt. **Alimentos e Nutrição**, 16 (4), 309-314.

MAVROUDIS, N. E.; GIDLEY, M. J.; SJÖHOLM, I. (2012) Osmotic processing: Effects of osmotic medium composition on the kinetics and texture of apple tissue. **Food Research International** 48, 839-847.

MEYER, R.H. (1971) **Response Surface Methodology**.(pp. 126-175), Allen and Bacon, Boston.

MONERAT, S.M.; PIZZI, T.R.M.; MAURO, M.A.; MENEGALLI, F.C. (2010) Osmotic dehydration of apples in sugar/salt solutions: Concentration profile and effective diffusion coefficients. **Journal of Food Engineering**, 100, 604-612.

MONTGOMERY, D.C (1991) **Análisis y Diseño Experimental**. Grupo Editorial Iberoamerica, Mexico.

PEREIRA, L.M.; FERRARI, C.C.; MASTRANTONIO, S.D.S.; RODRIGUES, A.C.C. (2006) Kinetic aspects, texture, and color evaluation of some tropical fruits during osmotic dehydration. **Drying Technology**, 24, 475-484.

QI, H.; LE MAGUER, M.; SHARMA, S. K. (1998). Design and selection of processing conditions of a pilot scale contactor for continuous osmotic dehydration of carrots. **Journal of Food Processing and Engineering**, 21, 75-88.

RAMALLO, L.A.; MASCHERONI, R.H (2010) Dehydrofreezing of pineapple. **Journal of Food Engineering** v.99, 269-275.

RAOULT-WACK, A. L. (1994). Recent advances in the osmotic dehydration of foods. **Trends in Food Science and Technology**, 5, 255-260.

ROBBERS, M.; SINGH, R.P.; CUNHA, L.M. (1997) Osmotic-convective dehydrofreezing process for drying kiwifruit. **Journal of Food Science**. Chicago, 62(5), 1039-1047.

SAPUTRA, D., (2001) Osmotic dehydration of pineapple. **Drying Technology**, 19, 415-425.

SERENO, A. M.; MOREIRA, R.; MARTINEZ, E. (2001). Mass transfer coefficients during osmotic dehydration of apple in single and combined aqueous solutions of sugar and salt. **Journal of Food Engineering**, 47, 43-49.

SILVA, A. C.; SILVA, C. R.; COSTA, L. M. S.; BARROS, N. A. M.; VIANA, A. S.; KOBLITZ, M. G. B.; SOUZA, F. V. D. (2011) Use of response surface methodology for optimization of the extraction of enzymes from pineapple pulp. **Acta Horticulturae**, v. 902, p.575-584.

SILVA, K. S.; CAETANO, L. C.; GARCIA, C. C.; ROMERO, J. T.; SANTOS, A. B.; MAURO, M. A. (2011). Osmotic dehydration process for low temperature blanched pumpkin. **Journal of Food Engineering**, 105, 56 - 64

SILVA, W.P.; SILVA, C.M.D.P.S., Prescribed Adsorption - Desorption V 2.2 (2008), online, available from world wide web: <<http://zeus.df.ufcg.edu.br/labfit/Prescribed.htm>>, date of access: Setembro, 20

SINGH, B; KUMAR, A.; GUPTA, A. K. (2007) Study of mass transfer kinetics and effective diffusivity during osmotic dehydration of carrot cubes. **Journal of Food Engineering** 79, 471–480

ZEMKE-WHITE, W. L.; CLEMENTS, K. D.; HARRIS, P. J. (2000). Acid lysis of macroalgae by marine herbivorous fishes: Effects of acid pH on cell wall porosity. **Journal of Experimental Marine Biology and Ecology**, 245, 57–68.

WILINSKA, A.; RODRIGUES, A. S. F.; BRYJAK, J.; POLAKOVIC, M. (2008) Thermal inactivation of exogenous pectin methylesterase in apple and cloudberry juices. **Journal of Food Engineering**, 85, 459.

CAPÍTULO III

Synergistic interactions of locust bean gum with whey proteins: effect on physicochemical and microstructural properties of whey protein-based films

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Abstract

Locust bean gum synergistic interactions with whey proteins are widely described in terms of functional properties. The aim of this work is to assess how these interactions affect whey protein-based films properties. Blended films were manufactured using whey protein isolate (WPI), three different concentrations levels of locust bean gum (LBG) and two different thermal treatments. A rheological study was performed to assess synergistic effects between WPI and LBG. The influence of glycerol on WPI/LBG synergies was also verified. Barrier, mechanical, and optical properties, as well as microstructure, solubility and moisture sorption behaviour of films were evaluated. The results show that synergistic effects between WPI and LBG and more severe heat treatments provide stronger, more flexible and less soluble films with lower permeability to carbon dioxide, oxygen and light. These findings suggest that the addition of LBG to WPI can be used to tune the properties of WPI-based edible films to meet specific food packaging and edible coating needs.

1. Introduction

Plastics have been increasingly used as packaging materials all over the world. However, due to its non-biodegradability, the interest in packaging from biodegradable

biopolymers has been growing, in the last years. Proteins and polysaccharides are biopolymers widely studied, because they present good adherence to fruits and vegetables surfaces and good barrier properties to gases such as oxygen and carbonic gas (HAN; GENNADIOS, 2005). These biopolymers are presented as possible substitutes of petrochemical-based packaging for specific applications.

Whey protein isolates and concentrates result from the industrial separation of the protein fraction from whey and are by-products of cheese manufacture with excellent functional properties. The functionality and performance of edible films depends on their barrier and mechanical properties (CERQUEIRA et al., 2011). Edible films from whey protein isolates have shown good oxygen and aroma barriers but generally show poor mechanical properties (PÉREZ-GAGO; KROCHTA, 2002; HONG; KROCHTA, 2006). A minimal content of plasticizer like glycerol is needed to reduce brittleness of the protein-based films, increasing extensibility of film (GOUNGA ET AL., 2007; OZDEMIR; FLOROS, 2008). Kokoszka et al. (2010) studied the influence of different glycerol concentrations (30, 40 and 60% (w/w), of WPI) in films from whey protein isolate (WPI) and observed that film barrier properties are better with 40% (w/w, of WPI) of glycerol. The functional properties of whey proteins can also be modified by the addition of other components, such as polysaccharides (ROCHA et al., 2009). Heat treatment also affects the structures and functional properties of proteins, because their structure becomes more mobile, hidden hydrophobic and thiol groups become exposed and can interact with other molecules (NICOLAI et al., 2011).

Galactomannans are heterogeneous polysaccharides commonly used in food industry, mostly obtained from the endosperm of dicotyledonous seeds of numerous plants. Galactomannans present the advantage of forming viscous solutions at relatively low concentration and being little affected by pH, heat and ionic strength (GOYCOOLEA et al., 1995; Sittikijyothin et al., 2005; SITTIKIJYOTHIN et al., 2005; DAKIA et al., 2008; CERQUEIRA et al., 2011). Locust bean gum (LBG) is a kind of galactomannan, found in the endosperm of Leguminosae, compatible with others gums, thickening agents and proteins, usually used to increase the elasticity and strength of the gel (FERNANDES et al., 1991, GONÇALVES et al., 2004; ROCHA et al., 2009). LBG is partially soluble in water at ambient temperature and heat is necessary to achieve best water binding capacity (MAIER et al., 1993; POLLARD & FISHER, 2006).

Edible films from LBG present high water vapor permeability and elongation-at break values range similar to cellophane films, being indicated by some authors like alternatives to synthetic materials (BOZDEMIR; TUTAS, 2003; CERQUEIRA et al., 2012).

Many studies reported positive effects on functional properties of the mixtures of whey protein and anionic polysaccharides (IBANOGLU, 2002; BAEZA et al., 2005; BEAULIEU et al., 2001; IBANOGLU, 2005; NEIRYNCK et al., 2007; SUN et al., 2007). Synergistic effects between whey proteins and galactomanans have also been referred. For instance, Rocha et al. (2009) found synergistic effects between whey protein concentrate (WPC) and locust bean gum (LBG) at pH 7.0 and observed that a small amount of LBG in the presence of salt leads to a big enhancement in the gel strength. To take advantage of these synergies, blends of proteins and polysaccharides as edible film forming agents have been studied for several authors in order to increase the barrier properties or increase mechanical properties (ARVANITOYANNIS et al., 1996, 1997, 1998; LEE et al., 2003; OSÉS et al., 2009). However, though several authors have studied edible films containing whey protein isolate (WPI) with promising results (e.g. SEYDIM; SARIKUS, 2006; PEREIRA et al., 2010; PIERRO et al., 2011; RAMOS et al., 2012), few have reported on polysaccharide/whey protein blended films (e.g. BRINDLE ; KROCHTA, 2008; COUGHLAN et al., 2004; YOO; KROCHTA, 2011) and, to best of our knowledge, no investigation was performed about edible films containing WPI and locust bean gum.

This study aims to evaluate the effect of LBG addition on barrier, optical and mechanical properties, microstructure, solubility and sorption isotherms of whey protein isolate (WPI) films. A preliminary rheological study was performed at pH 7.0 to assess if the WPI/LBG synergies prevail upon the addition of glycerol (the most common plasticizer used in the WPI-based film formulation). Films were prepared without or with two different LBG amounts and two different thermal treatments, at pH 7.0.

2. Materials and Methods

2.1 Materials

Whey Protein Isolate (WPI), LACPRODAN DI-9224, kindly supplied by Arla Foods Ingredients (Viby, Denmark), was used as the protein source. This isolate contains a minimum of 93.5% total protein content (74% α -lactoglobulin, 18% β -lactalbumin and 6%

bovine serum albumin), maximum content of 0.2% lactose and fat, approximately 0.5% sodium, 1% of potassium and 0.1% calcium, as specified by Arla Foods Ingredients.

Locust bean gum (LBG) (>75% galactomannan content) was kindly supplied by Danisco Portugal (Faro, Portugal).

Glycerol was supplied by Merck (Germany) and other chemicals were supplied by Sigma, Co (St. Louis MO, USA).

2.2 WPI/LBG solutions

The stock solution of 1% (w/w) LBG was prepared by stirring the appropriate amount of dry LBG powder dispersed in distilled water for 1 hour, at room temperature. After that, the solution was heated with stirring, for 30 min at 80°C. After cooling, the non-dissolved material was removed by centrifugation at 20,000g for 30 minutes. The final concentration was determined from dry matter content.

WPI mixed solutions were prepared by weighting the appropriate amount of WPI powder, adding the required amounts of LBG stock solution, NaCl solution (20%w/w) to a final salt concentration of approximately 50mM to ensure constant ionic strength, and glycerol and completing to the final volume with distilled water. The mixtures were stirred for 2 hours, at room temperature. The pH was then adjusted to 7.0 with NaOH 1M and the solution was stirred for 2 hours more.

2.3 Rheological measurements

Mixtures of WPI (10%) and LBG (0, 0.05, 0.1%) with addition of glycerol (4%) were prepared for rheological characterization. Measurements were performed with a controlled stress rheometer AR-G2 (TA Instruments, New Castle, USA) fitted with parallel-plate geometry (40mm diameter, gap 800µm). The mixture was poured onto the plate of the rheometer and covered with paraffin oil to prevent water loss. Samples were heated to 80°C, at the rate of 2°C/min, equilibrated for 3 hours at 80°C and cooled from 80°C to 20°C with the same rate of 2°C/min. Mixtures were then equilibrated for 30 minutes at 20°C to obtain non time dependent dynamic shear modules. Frequency of 1Hz was maintained constant and all experiments were performed in the linear viscoelastic region using a target strain of 0.5%.

The experiments were carried out in triplicate with the results reported as the measurements averages.

2.4 Film preparation

Films forming mixed solutions were prepared as described above to achieve a final WPI concentration of 5% (w/w), and 2% (w/w) glycerol (used as plasticizer). Three different LBG concentration (0, 0.025 and 0.05%) were tested. After the four hours stirring period, the mixtures were heated to denature the protein fraction. Two different heat treatments were used: 1) the mixtures were heated until 75°C and immediately cooled back to room temperature; 2) the mixtures were heated until 75°C, kept at 75°C for 10 min and then cooled back to room temperature.

Films were formed by pouring 28g of each film forming solution over disposable polyethylene Petri dishes (8.6 cm in diameter). Films were dried for 12h at 50±1% relative humidity (RH) and 35±2°C in a climate chamber (KBF115, Binder) for 12 hours.

2.5 Characterization of WPI+LBG films

a. Film thickness

The thickness of the films was measured at 10 different points for each film using a digital micrometer (Mitutoyo, Japan).

b. Mechanical Properties

Mechanical properties, tensile strength (TS) and elongation-at-break (E), were measured with a texture analyzer (TA.XT2, Stable Micro Systems, Surrey, UK) equipped with tensile test attachments following the guidelines of ASTM D882-91 (ASTM D882-91, 1991) standard method. The initial grip separation was set at 30 mm and the crosshead speed was set at 5 mm min⁻¹. Tests were replicated eight times for each type of film.

c. Water vapor permeability measurement

The measurement of water vapour permeability (WVP) was performed gravimetrically based on ASTM E96-92 method (ASTM E96-95, 1995). The film was sealed on the top of a permeation cell containing calcium chloride (2% RH), placed in a desiccator at 20 °C containing water (100% RH) and a miniature fan inside (for constant air circulation). The cells was weighed at intervals of 1 h during 9 h using a balance with a resolution of 0.01 mg. The slope of weight gain versus time was obtained by linear regression. Three replicates were performed for each film formulation. The WVP was estimated using regression analysis from Eq. (1) as described in literature (MCHUGH et al., 1993):

$$WVP = \frac{\Delta m \cdot x}{A \cdot \Delta t \cdot \Delta P} \quad (1)$$

Where Δm is the weight gain (g) of the test cell, x is the film thickness (m), A is the permeation area (0.005524 m²), Δt is duration (s), ΔP is the difference of the water vapor partial pressure at 20°C (2337 Pa) across the two sides of the film.

d. Water solubility

Solubility (S) is defined as the content of dry matter solubilized after 24h (CERQUEIRA et al., 2012). The film solubility in water was determined according to the method reported in literature (CUQ et al., 1996). Films were cut in format of disks with 2cm diameter, weighted (W_0) in balance Sartorius BP211D (Sartorius AG, Germany) and immersed in 50mL of water at 23°C, with agitation (60 rpm). After 24 h, disks were taken out and dried in an oven at 105°C until constant weight (W_f). The solubility was determined according to Eq. 2

$$S = \frac{W_0 - W_f}{W_0} \times 100 \quad (2)$$

e. Oxygen and carbon dioxide permeability measurement

Oxygen permeability (O_2P) and carbon dioxide permeability (CO_2P) were determined based on ASTM D3985-02 standard (ASTM D3985-02, 2002). The films were sealed between two chambers and the exposed-film area was 0.0046 m^2 . Oxygen or carbon dioxide was purged into the lower chamber, while nitrogen was purged into the upper chamber. The flow rate was controlled to maintain the pressure constant (1 atm) in both chambers. Nitrogen acted as a carrier for the O_2 (or the CO_2) crossing the film. The values for O_2P and CO_2P were determined by gas chromatography (Chrompack 9001, Middelburg, Netherlands) at 110°C and with a molecular sieve 5 Å 80/100 mesh $1\text{m} \times 1/8'' \times 2 \text{ mm}$ column to separate O_2 , and a Porapak Q 80/100 mesh $2\text{m} \times 1/8'' \times 2 \text{ mm}$ SS column to separate CO_2 , using a thermal conductivity detector at a 110°C . Helium was used as carrier gas. A mixture containing 10% (v/v) CO_2 , 20% (v/v) O_2 , and 70% (v/v) N_2 was used as the standard for calibration. Three replicates were obtained for each formulation. For each replicate three measurements were taken, after the achievement of the stationary state.

f. Moisture sorption isotherms

Sorption isotherms were plotted for pieces of films ($30 \times 30 \text{ mm}$), based on the static gravimetric methods proposed by Jowitt et al. (1987). Eight saturated aqueous salt solutions were prepared corresponding to water activity intervals between 0.11 and 0.90 and placed in small jars. Duplicate samples were weighed for each value of water activity and placed on tripods in the jars, which were then tightly closed and placed in a temperature-controlled chamber. The studied temperature was 25°C . Samples were weighed periodically until they reached constant weight. Samples' dry weight was determined by the gravimetric method, in triplicate, drying to constant weight in a vacuum oven at 60°C . For the mathematical description of sorption isotherms the Guggenheim-Anderson-de-Boer (GAB) model (Eq. 3) (VAN DEN BERG; BRUIN, 1981) was adjusted to the experimental data using the non-linear regression module of Statistica 7.0 software (Statsoft, Tulsa, OK, USA).

$$X = \frac{X_m \cdot C \cdot K \cdot a_w}{(1 - K \cdot a_w)(1 - K \cdot a_w + C \cdot K \cdot a_w)} \quad (3)$$

where, a_w - water activity, dimensionless; X - equilibrium moisture content (% dry basis); X_m - moisture content of monolayer (% dry basis) (water content corresponding to saturation of all primary adsorption sites by one water molecule); C - Guggenheim constant and K - corrective constant (VAN DEN BERG; BRUIN, 1981).

The goodness of fit of the models was evaluated using the regression coefficient (R^2). For each setting, the Residual Root Mean Squares (RRMS) were calculated, defined by:

$$RRMS(\%) = 100 \left\{ \frac{1}{(n-p-1)} \sum_1^n \left[\frac{(x^{\text{exp}} - x^{\text{calc}})}{x^{\text{exp}}} \right]^2 \right\}^{1/2} \quad (4)$$

Where $x^{\text{exp}} - x^{\text{calc}}$ is the residual [the difference between the experimental (x^{exp}) and calculated (x^{calc}) values]; n is the number of observations, or residuals; p is the number of the fitting parameters and $(n-p)$ defines the degrees of freedom (DANIEL; WOOD, 1980).

g. Optical Properties

The visible and ultraviolet (UV) light barrier properties of the dried films were measured using an UV-visible Unicam spectrometer model Helios Alpha. WPI films were cut into pieces (4 x 1cm) and attached to a quartz colorimetric cup. Wavelengths from 190 to 700 nm were selected to measure transmittance and absorbance.

h. Microstructure

Films' microstructure was confirmed by Scanning Electron Microscopy (SEM) at CEMUP, Porto, Portugal. Samples were coated with a sputtered Au-Pd thin film and analyzed in a Type FEI Quanta 400 FEG SEM under high vacuum using an accelerating voltage of 15 kV and working distances (WD) between 9.5 and 10.5 mm.

2.6 Statistical analyses

All statistical analyses on the films' properties were made using the Statistica software version 7.0 (StatSoft, Inc, Tulsa, USA). Analysis of variance (ANOVA) was performed for each property. Statistical significant differences were analysed a posteriori with the Tukey test. The significance level was defined as $p \leq 0.05$, for all tests.

3. Results and discussion

a. Rheological measurements

No reliable results were achieved at 5%WPI due to the low viscosity of the samples and the higher syneresis of the weak gel formed. In addition, films are manufactured by evaporation and concentration of the film forming solutions and the properties of a more concentrated mixture is more likely to reproduce the behavior of the film.

The overall pattern of the viscoelastic moduli in the temperature sweep experiments followed the behaviour reported by several authors for whey proteins gelation (e.g. KAVANAGH et al., 2000; GONÇALVES et al., 2004) and for Whey Protein/LBG mixtures gelation (ROCHA et al., 2009; TAVARES; DA SILVA, 2003). During the first temperature ramp (20-80°C), G' and G'' decreased fastly until the protein molecules started to denature and expose their hydrophobic regions and sulfur groups. A further temperature increase led to the gel threshold near 80°C. At this point, the storage modulus (G') rises sharply and becomes higher than the loss modulus (G'') indicating the formation of a viscoelastic gel. During the first time sweep (at 80°C), the initial protein-based network was reinforced by more and more protein and G' increased continuously until almost stabilization. During the second temperature ramp (80-20°C), the G' rising trend sharpened, as hydrogen bonds reinforced the tridimensional gel. After stabilization of the gels at 20°C, the final relevant rheological parameters (storage modulus (G') and the loss modulus (G'') and loss angle (δ)) were measured; the obtained values are presented in Table 1.

Table 1: Influence of the locust bean gum (LBG) concentration on storage modulus (G') and loss modulus (G'') and phase angle (δ) of whey protein isolate (WPI) aqueous gels containing glycerol.

WPI (%)	LBG (%)	G'	G''	$\tan\delta$
10	0	8106 ± 1165^a	963 ± 147^a	0.12 ± 0.011^a
10	0.05	13696 ± 1941^b	1681 ± 324^b	0.11 ± 0.002^a
10	0.1	12463 ± 700^b	1406 ± 70^b	0.12 ± 0.011^a

*Mean \pm SD

**Means with the same lower case letter, in the same column, did not differ significantly at $p \leq 0.05$ according to the Tukey test

*** Gelation time (t_g) was obtained after temperature ramp

It was observed that the LBG addition modified the gelation behaviour of WPI but this effect did not depend on LBG concentration, in the concentrations range tested (that was chosen to be near the synergistic optimum). Both gel moduli (G' and G'') were higher when LBG was present. The higher values of G' denote an improvement of the gel strength. Rocha et al. (2009) also observed that addition of small amounts of LBG increased G' and G'' of the gels containing 10% of whey protein concentrated (WPC). The authors verified that mixtures with 0.1% (w/w) of LBG presented the higher values for G' and G'' , ascribing that to phase separation that occurs in this kind of system. This phase separation can lead to an increase in the protein concentration in the continuous protein-enriched phase increasing the elastic response of the network. Storage moduli of WPI gels containing glycerol, obtained in the present study (Table 1), were ~40 times higher than storage moduli of WPC gels ($G'=204 \pm 33\text{Pa}$) obtained by Rocha et al. (2009). Both studies were performed in pH 7.0, with addition of NaCl to ensure constant ionic strength. In this way, the high difference observed between these results can be related to the compositions of WPI and WPC. WPI used in this experiment presented protein content above 90% (w/w), while WPC used by Rocha et al (2009) had 82% (w/w) protein content, in dry basis. Besides their distinct protein contents, WPI and WPC differed also in the levels of other constituents such as lactose, minerals and lipids. These differences may influence markedly the intermolecular bonds in the manufactured gels resulting in high differences in their storage moduli.

Viscoelastic character was similar for all gels as no significant changes in $\tan\delta$ were observed with LBG addition. Rocha et al. (2009) also did not find significant changes in $\tan\delta$ of WPC gels with 0.1% (w/w) LBG addition.

Therefore it is possible to conclude that the presence of glycerol did impair LBG/WPI synergies and the overall gelling behavior was similar to the described behavior for mixtures without glycerol.

b. Mechanical Properties

Tensile strength (TS) and elongation-at-break (EB) of WPI films were analyzed for two different LBG contents and severity of thermal treatment. The results are shown in Table 2.

As expected, the time of thermal treatment significantly improved the mechanical properties of WPI films, increasing both of TS and EB. When protein is heated, its structure becomes more mobile, covalent disulphide bonds among polypeptide chains are formed increasing the chain length of the polypeptide and forming a stable network (TOTOSAUS et al., 2002; NICOLAI et al., 2011). Thus, an increase in the TS of ca. 50% was achieved, leading to final TS near 3.5 MPa, in accordance with the 1-14 MPa value reported, depending on the film-making method, glycerol concentration (30% to 50 % of the whey protein) and environmental testing conditions (BRINDLE; KROCHTA, 2008; MCHUGH; KROCHTA, 1994; RAMOS, et al., 2013; USTUNOL; MERT, 2004). In the case of EB, this effect was stronger in the presence of LBG, also leading to ca. 40-50% increases. This improvement has been formerly reported. For instance, Pérez-Gago & Krochta (1999) described that aqueous solutions containing 5% WPI heated at 90°C for 30 minutes in pH 7,0 with addition of glycerol (70:30, WPI:Glycerol) provides films 2.2 times stronger and approximately 6 times more resistant to deformation in comparison with films formed with non-heated WPI.

Phase incompatibility often leads to inferior mechanical properties when no specific interactions are present. However, improved mechanical properties are expected when synergistic effects between the different components are described (BRINDLE; KROCHTA, 2008). Though the presence of low amounts of LBG does not seem to have a significant effect on the films tensile strength ($p < 0.05$), elongation at break is significantly improved for the films with a stronger thermal treatment, providing higher capacity of the film to extend before breaking. Whey protein films are formed through a combination of disulfide bonds, hydrophobic interactions and hydrogen bonds. The nature of these bonds generally leads to

very brittle films (SOTHORNVIT; KROCHTA, 2001). The incorporation of a plasticizer tends to increase polymer chain mobility, thus allowing higher deformations but generally decreasing films' tensile strength. It will position between the biopolymer chains within the polymer network, increasing the mobility by increasing the intermolecular spacing (WIHODO; MORARU, 2013). LBG seems to have a similar effect, since elongation property was enhanced. Nevertheless, tensile strength did not change with LBG addition. A probable phase separation between WPI and LBG would lead to a continuous protein network, similar behavior was observed by Rocha et al. (2009) in gels constituted by WPC+LBG. On the other hand, an enriched phase in LBG would be responsible by the plasticizing effect. Hence, an expected decrease in the tensile strength due to this plasticizer effect may have been compensated by the strengthening of the protein network detected by rheology results.

c. Solubility and water sorption isotherms

The values obtained of solubility for whey protein isolate films with and without addition of LBG are present in Table 2.

Table 2: Values of water solubility, film's thickness, tensile strength (TS) and elongation-at-break (EB) for WPI and WPI/LBG films, with glycerol, submitted to different thermal treatments.

Treatment	Thermal treatment (until 75°C)				Thermal treatment (75°C/10min)			
	Solubility (%)	Thickness (mm)	TS (MPa)	EB (%)	Solubility (%)	Thickness (mm)	TS (MPa)	EB (%)
5% WPI	62.04 ± 0.74 ^{a, A}	0.26 ± 0.062 ^{a, A}	2.34 ± 0.37 ^{a, A}	11.04 ± 1.76 ^{a, A}	59.97 ± 0.18 ^{a, A}	0.29 ± 0.025 ^{a, A}	3.52 ± 0.30 ^{ab, B}	13.89 ± 4.77 ^{a, A}
	5% WP+ 0.025% LBG	73.51 ± 1.64 ^{b, A}	0.28 ± 0.013 ^{a, A}	2.66 ± 0.46 ^{a, A}	10.92 ± 2.33 ^{a, A}	54.52 ± 0.32 ^{b, B}	0.28 ± 0.017 ^{a, A}	3.26 ± 0.46 ^{a, B}
5% WPI + 0.05% LBG	69.70 ± 0.38 ^{c, A}	0.29 ± 0.019 ^{a, A}	2.35 ± 0.28 ^{a, A}	9.68 ± 2.41 ^{a, A}	55.16 ± 1.94 ^{b, B}	0.29 ± 0.019 ^{a, A}	3.65 ± 0.39 ^{b, B}	23.16 ± 1.76 ^{b, B}

*Mean ± SD

**Means with the same capital letter, for the same response variable, in the same line did not differ significantly at p≤0.05 according to the Tukey test

***Means with the same lower case letter, in the same column, did not differ significantly at p≤0.05 according to the Tukey test

Solubility of WPI films decreased with time of thermal treatment indicating that the greater the cross-linking effect in the matrix the less soluble is the film (Table 2). According to Pelegrine & Gasparetto (2005), protein-protein irreversible binding reduce water interaction in solutions reducing the solubility of the films. Heat denaturation enables the formation of intermolecular irreversible disulfide bonds, which are among the strongest intermolecular bonds. For shorter times, this exposure may not be complete and hydrogen bonding and hydrophobic intermolecular interactions may still have a strong contribution to the film formation, leading to more soluble films (FLORIS et al., 2008). This behaviour is also in accordance with the results found by Perez-Gago & Krochta (2001).

LBG addition also decreased solubility in thermally treated films. However in films with thermal treatment until 75°C the solubility increased with polysaccharide addition. This result also confirm that time of heating was not enough to establish enough disulfide bonds and that hydrophobic interactions and hydrogen bonding still play the dominant role. LBG is water soluble and, unless other phenomena are involved, it is likely to increase film water solubility.

The decrease in solubility observed with addition of LBG to thermally treated films is probably related to the increase in the thermal cross-linking effect. Rocha et al. (2009) analyzed the microstructure of whey protein concentrate (WPC) + LBG gels and observed phase-separation with LBG promoting protein aggregation. The protein concentration in the protein-enriched phase was probably higher, leading to a stronger network with more disulfide bonds. A similar mechanism seems to occur also in WPI films with the LBG addition resulting in reduced film solubility. Though these films are still partially soluble, their solubility can be further decreased by chemical modification of the residual accessible thiol groups (by blocking or copper-catalysed oxidation (FLORIS, et al., 2008)).

The sorption isotherms of films WPI films with or without LBG, obtained experimentally, are presented in Figure 1.

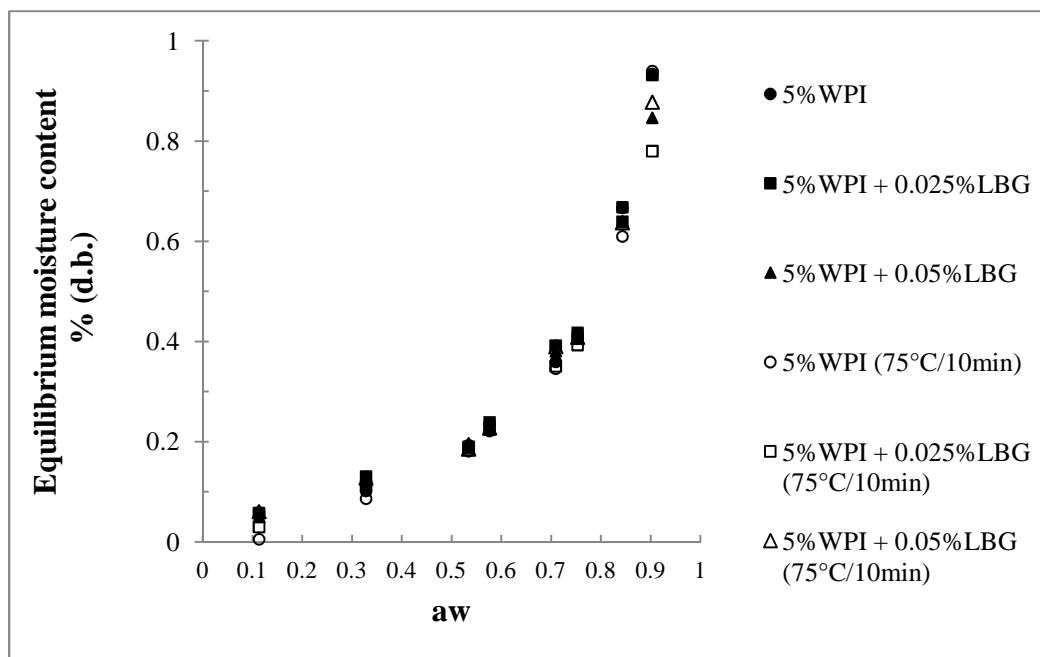


Figure 1: Experimental values of equilibrium moisture content (dry basis), as a function of water activity for different films formulations.

The treatment time and the addition of LBG to WPI films barely changed the amount of moisture adsorbed per mass of dry solids. All curves showed that the films undergo considerable changes with the relative humidity of the environment since the curves presented mixed behavior between types II (sigmoidal) and III (slightly sigmoidal), which adsorb large amounts of water at high relative humidity and small amounts at low relative humidity (Figure 1). However, and though differences are very subtle, films with a stronger heat treatment tend to adsorb less water, indicating a more hydrophobic nature. Also, in terms of water sorption, films with LBG seem to be slightly less sensitive to water activity (a_w) than films without LBG, as at the lower water activity values they adsorb slightly more water and, at the higher a_w values, they adsorb slightly less water.

The results of nonlinear regression analysis of experimental data are presented in Table 3. The results of nonlinear regression analysis of experimental data with the GAB model are presented in Table 3. Though the sigmoidal shape of the fitting curves is not evident, the obtained C (>2) and k ($0 < k < 1$) values and the high correlation coefficients ($R^2 > 0.99$) suggest that the model adequately fits the experimental data.

When the parameters are kept within the following regions: $0.24 < K \leq 1$ and $5.67 \leq C \leq \infty$, GAB model describes sigmoidal type isotherms (type II). Outside these regions the isotherm is either no longer sigmoidal or the monolayer capacity is estimated with an error

greater than $\pm 15.5\%$ (LEWICKI, 1997). Table 3 shows that all films complied with the requirement for parameter K, however only two WPI films complied with parameter C, indicating mixed behavior between types II and III (slightly sigmoidal) for the majority of formulations.

Table 3: Parameters of GAB model fit to experimental data of sorption isotherms of WPI films, with glycerol and with or without thermal treatment time and LBG addition.

	X_0	C	K	R ²	RQMR
5% WPI	0.117	4.284	0.858	0.996	0.843
5% WPI + 0.025% LBG	0.125	5.966	0.856	0.996	0.893
5% WPI + 0.05% LBG	0.133	3.701	0.819	0.996	0.789
5% WPI (75°C/10min)	0.177	1.365	0.791	0.997	0.804
5% WPI + 0.025% LBG (75°C/10min)	0.146	1.949	0.764	0.992	1.152
5% WPI + 0.05% LBG (75°C/10min)	0.116	5.789	0.850	0.993	1.077

d. Oxygen, carbon dioxide and water vapour permeabilities

Oxygen permeability (O₂P), carbon dioxide permeability (CO₂P) and water vapour permeability (WVP) of WPI films with or without LBG are shown in Table 4.

The addition of LBG to WPI films reduced oxygen permeability. However this difference was significant only to films thermal treated for 10 minutes. The thermal treatment does not seem to influence significantly the O₂P values. The carbon dioxide permeability did not change significantly with thermal treatment and LBG addition. However, it is observed a tendency of decrease for the values of CO₂P both with polysaccharide addition and thermal treatment.

The water vapor permeability (WVP) values of WPI films did not show statistically significant differences with addition of LBG (Table 4). However statistical differences were achieved between heat treatments for 0.05% LBG. Also, for all samples, WVP's were always

higher for the stronger heat treatment. Furthermore, for the stronger heat treatment, when the disulfide bonds are fully established, WVP seems to be consistently higher for films with LBG.

Table 4: Values of water vapor permeability (WVP), oxygen permeability (O₂P) and carbon dioxide permeability (CO₂P), absorbance (600nm) in relation of thickness (Abs/thickness) for WPI (Protein Isolate Whey) films, with glycerol, varying LBG (Locust Bean Gum) concentration and time of thermals treatment.

Treatment	Thermal treatment (until 75°C)				Thermal treatment (75°C/10min)			
	WVP × 10 ⁻⁸ (g m ⁻¹ s ⁻¹ Pa ⁻¹)	O ₂ P × 10 ⁻¹³ (g m(Pa s m ²) ⁻¹)	CO ₂ P × 10 ⁻¹² (g m(Pa s m ²) ⁻¹)	Abs _{(600 nm)/thi ckness}	WVP × 10 ⁻⁸ (g m ⁻¹ s ⁻¹ Pa ⁻¹)	O ₂ P ×10 ⁻¹³ (g m(Pa s m ²) ⁻¹)	CO ₂ P × 10 ⁻¹² (g m(Pa s m ²) ⁻¹)	Abs _{(600 nm)/thi ckness}
5% WPI	2.99 ± 0.30 ^{a, A}	0.59 ± 0.09 ^{a, A}	2.72 ± 0.44 ^{a, A}	0.32 ± 0.00 ^{a, A}	3.39 ± 0.24 ^{a, A}	0.61 ± 0.04 ^{a, A}	2.02 ± 0.23 ^{a, A}	0.30 ± 0.04 ^{a, A}
5% WPI + 0.025% LBG	3.50 ± 0.11 ^{a, A}	0.44 ± 0.10 ^{a, A}	2.52 ± 0.36 ^{a, A}	0.41 ± 0.09 ^{a, A}	4.02 ± 0.43 ^{a, A}	0.45 ± 0.00 ^{b, A}	1.65 ± 0.56 ^{a, A}	1.25 ± 0.47 ^{a, A}
5% WPI + 0.05% LBG	2.67 ± 0.30 ^{a, A}	0.51 ± 0.07 ^{a, A}	2.33 ± 0.29 ^{a, A}	0.51 ± 0.13 ^{a, A}	3.95 ± 0.16 ^{a, B}	0.47 ± 0.07 ^{b, A}	1.71 ± 0.43 ^{a, A}	1.10 ± 0.02 ^{a, B}

*Mean ± SD

**Means with the same capital letter, for the same response variable, in the same line did not differ significantly at p≤0.05 according to the Tukey test

***Means with the same lower case letter, in the same column, did not differ significantly at p≤0.05 according to the Tukey test.

Polysaccharide addition increased the intermolecular attractions between polymeric chains, increasing, also structural cohesion of film and the difficulty in the penetration of gas molecules. On the other hand, the presence of the polysaccharide seems to decrease the overall film hydrophobicity, allowing higher affinity towards water and, thus, higher water vapour permeabilities. Contrariwise, carbon dioxide and oxygen permeabilities decrease reinforcing this less apolar character. Oxygen is a non-polar molecule with a very low affinity

towards water. It is expected to absorb to a greater extent in less polar polymers and have an inverse behaviour when compared to water. CO₂ has usually a behaviour similar to O₂, though slightly less marked (O₂ is more apolar). Thus, for highly hydrophilic films such as polysaccharide- or protein-based films, WVP is usually quite high while O₂P and CO₂P are usually remarkably low (e.g. WIHODO et al., 2013) being the former lower than the last.

These results are consistent with the results found by other authors for different heat treatments or degrees of cross-linking of whey proteins. In fact, Perez Gago & Krochta (2001) also found a tendency for decrease of O₂P with the heat treatment. Ustunol et al., (2004) and Yoo & Krochta (2011) found an increase in the WVP and decrease in O₂P when a crosslinking agent was added to the WPI.

Cerqueira et al (2009) observed that the oxygen permeability in galactomannan from seeds of *A. pavonina* and *C. pulcherrima* films reduced as the galactomannan concentration increased and that the carbon dioxide permeability increased as polysaccharide concentration increased. This result indicates that synergistic effect between different components can present higher influence on O₂P and on CO₂P than only the concentration increase of a component of the film.

This higher oxygen and carbon dioxide barrier promoted by gum addition can help in improving food quality and extending food shelf life.

e. Optical properties

Transmittance and absorbance of WPI films with and without LBG at different wavelengths are presented in Figures 2 and 3.

Transmittance of WPI films thermal treated for 10 minutes decreased in the visible range region (350-800 nm) with LBG addition, thereby reducing the transparency of the films. Films thermal treated until 75°C presented reduction in transparency only with 0.05% LBG addition (Figure 2). Phase separation due to thermodynamic incompatibility between polysaccharide and protein can provide a slight enhance of the turbidity of the system that can diminished the transparency of WPI films. Yoo & Krochta (2011) also observed reduction in transparency of WPI films with the addition of polysaccharides that show incompatibility with whey proteins. WPI-based films are usually transparent and colorless (e.g. BRINDLE; KROCHTA, 2008). In two phase systems with a continuous matrix and dispersed domains

with different viscosities, light refracts from these domains causing a translucent appearance (BRINDLE; KROCHTA, 2008) and decreasing transparency.

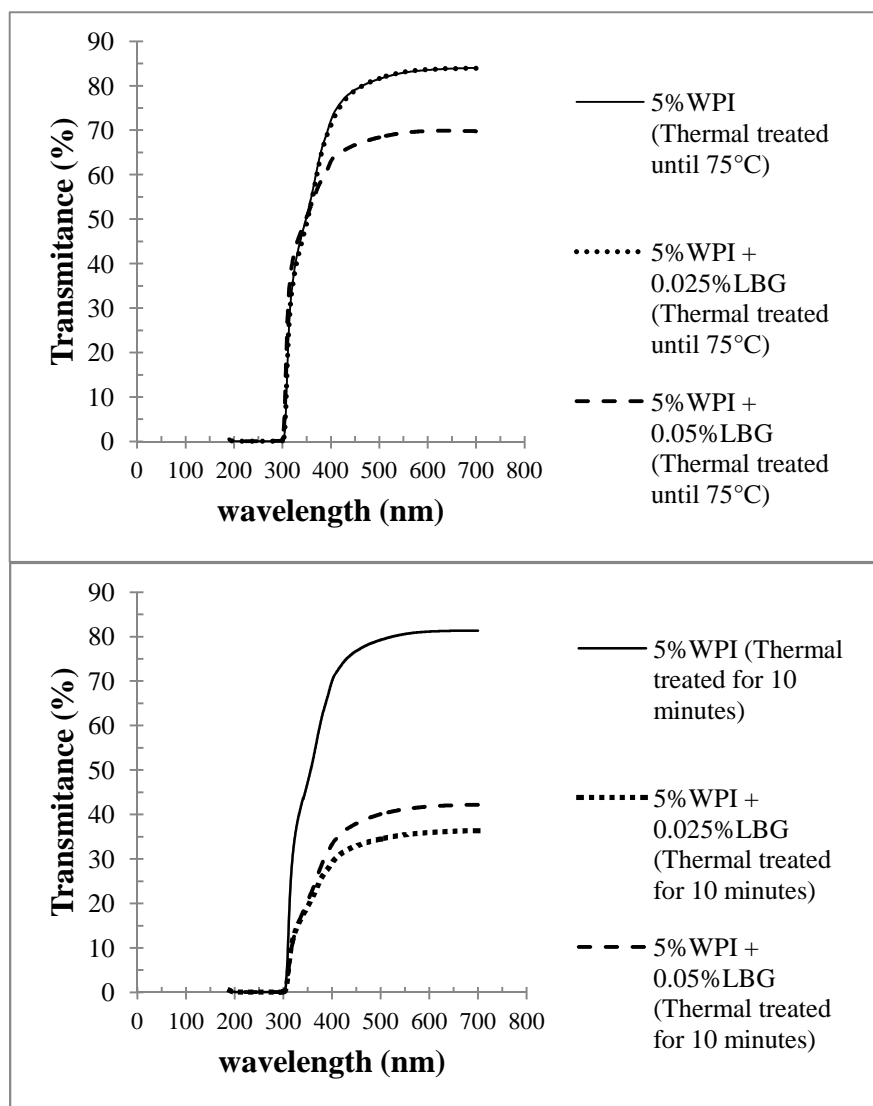


Figure 2: Transmittance of WPI films with and without thermal treatment time and LBG addition at different wavelengths.

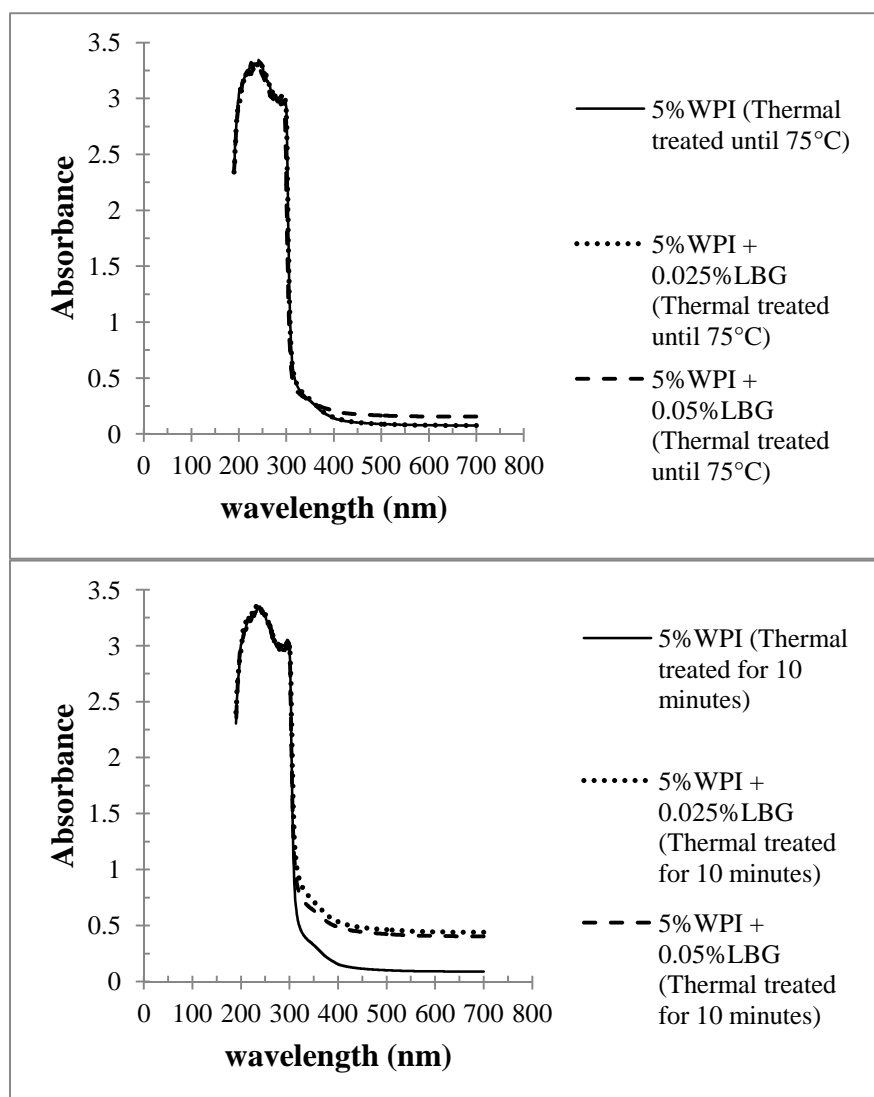


Figure 3: Absorbance of WPI films with and without thermal treatment time and LBG addition at different wavelengths.

Depending on the application, a higher transparency may be desirable from the consumers' point of view, but an increased barrier may be beneficial for the preservation of the food. WPI films presented higher barrier property to light, in the visible range, with time of thermal treatment and with LBG addition, as shown in absorbance spectra (Figure 3). Differences between films' thickness did not influence this result, as observed in Table 4, being that the increased structural cohesion of films due to a higher cross-linking effect with thermal treatment and LBG addition was the determinant factor to increase barrier properties of WPI films.

In the UV range, WPI films generally hold excellent barrier properties due to the high content of aromatic amino-acids, being able to impair UV light induced lipid oxidation (RAMOS et al., 2013). This property was not affected by the presence of a small amount of LBG (Figure 3). The increase in barrier properties to light and the reduction in oxygen permeability make WPI-based films with LBG a good alternative to protect food against oxidative reaction.

f. Integrated evaluation of WPI/LBG film properties based on the microstructure analysis

Figure 4 shows structure of the WPI films with 4% glycerol (w/w) and different LBG concentrations. Differences were not clearly visible between the two heat treatments. Therefore, SEM pictures are presented only for the more severe heat treatment.

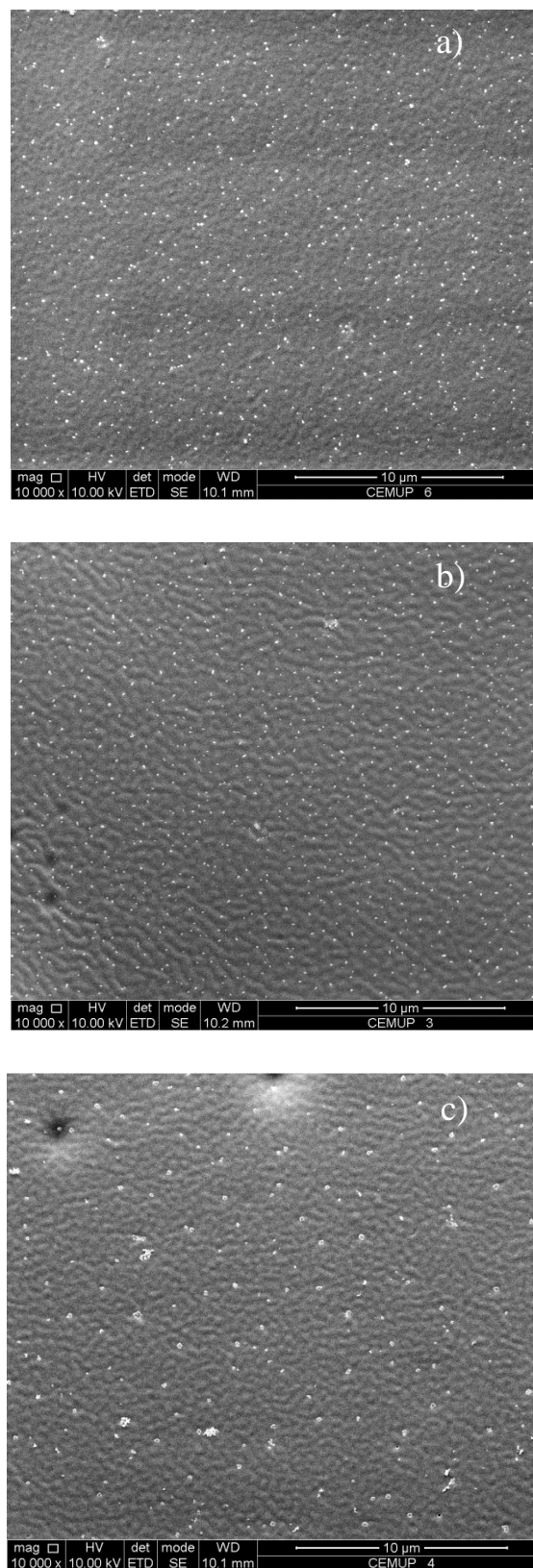


Figure 4: Structure of the WPI/LBG films with 2% glycerol (w/w): a) 5% WPI, 0% LBG; b) 5% WPI, 0.025% LBG; c) 5% WPI, 0.05%.

A “ridge and valley” structure seems to be present in all films, as described for other plasticized protein films (Figure 4). This “ridges and valleys” structure has been described to be related to more ductile materials (WIHODO et al., 2013). Smoother microstructures are usually related to more glassy and brittle materials. In the case of whey protein-based films with glycerol, this kind of microstructure has been associated with phase separation between protein and glycerol. A protein network is formed around the glycerol enriched-domains, leading to a sponge-like structure where the wholes contain the glycerol molecules, allowing more elongation of the film but usually reducing its tensile strength (BODNÁR et al., 2007). A similar porous protein network structure has also been described by Anker et al. (2000).

In Figure 4b and 4c, it is possible to observe that the biphasic character is reinforced in the presence of a small amount of LBG. This is consistent with the fact that the majority of polysaccharide/protein mixed systems presents thermodynamic incompatibility with segregative phase separation, being that each phase is enriched in one of the biopolymers (e.g. GRINBERG; TOLSTOGUZOV, 1997). A thicker continuous protein network seems to be formed and the intervals probably correspond to LBG/glycerol enriched-domains, acting as fillers. Protein is apparently more aggregated and pores (LBG-enriched domains) are larger than for films without LBG. For whey protein gels, this segregative phase-separation has been described to locally increase the protein concentration. For very low amounts of LBG (ca. 0.1%), the LBG enriched domains act as fillers to reinforce the gel structure without affecting the connectivity, leading to an increase in the elastic response (ROCHA et al., 2009). Apparently, the same happens in the LBG/WPI films. This reinforces what has been written above for the mechanical properties.

These larger pores may be responsible for the WVP increase, as it is likely that water vapour moves along the films through these highly hydrophilic domains. On the contrary, O₂ and CO₂ affinity for these domains is reduced and it should be easier for them to move along the protein network (ANKER et al., 2000). Therefore, as the protein network is reinforced in the presence of LBG, O₂ and CO₂ permeabilities are reduced, as it is more difficult to pass through a more compact structure.

As already referred, whey protein films are usually very brittle and need a significant amount of a plasticizer to reduce their brittleness. In order to reduce this need, partial hydrolysis of whey proteins has been suggested (SOTHORNVIT; KROCHTA, 2000). The addition of a very small amount of LBG seems to be as effective and much easier to perform.

4. Conclusions

The inclusion of LBG resulted in more flexible WPI-based films, with greater permeability to water and with improved O₂, CO₂ and light barrier properties making them a good alternative to protect food against oxidative reaction. The severity of the thermal treatment was important to form a stable network with higher cross-linking effect in the matrix, higher molecular interactions and, consequently, stronger and less soluble films with improved barrier properties to carbon dioxide, oxygen and light.

Synergistic effects between WPI and LBG strongly influence film properties and it is thus possible to tune the properties of edible films from WPI adding different amounts of LBG and/or using different thermal treatments.

5. Acknowledgment

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6. References

- ANKER, M.; STADING, M.; HERMANSSON, A.-M. (2000). Relationship between the microstructure and the mechanical and barrier properties of whey protein films. **Journal of Agricultural and Food Chemistry**, 48, 3806_3816.
- ASTM D882-91, 1991. **Standard test methods for tensile properties of thin plastic**. In: **Annual Book of ASTM Standards**. Amer. Soc. for Testing & Materials, Philadelphia, PA.
- ASTM D3985-02, 2002. **Standard test method for oxygen gas transmission rate through plastic film and sheeting using a coulometric sensor**. In: Annual book of ASTM. Amer. Soc. for Testing & Materials, Philadelphia, PA.
- ASTM E96-92, 1990. **Standard test methods for water vapor transmission of materials**. In: Annual Book of ASTM standards. Amer. Soc. for Testing & Materials, Philadelphia, PA.
- ARVANITOYANNIS, I.; PSOMIADOU, E.; NAKAYAMA, A. (1996) Edible films made from sodium caseinate, starches, sugars or glycerol. Part 1. **Carbohydrate Polymers**, 31, 179-192.
- ARVANITOYANNIS, I.; PSOMIADOU, E.; NAKAYAMA, A.; AIBA, S.; YAMAMOTO, N. (1997). Edible films made from gelatin, soluble starch and polyols, Part 3. **Food Chemistry**, 60, 593-604.

ARVANITTOYANNIS, I.; BILIADERIS, C.G. 1998. Physical properties of polyol-plasticized edible films made from sodium caseinate and soluble starch blends. **Food Chemistry** 62 (3), 333–342.

BAEZA, R.; SANCHEZ, C. C.; PILOSO, A. M. R.; PATINO, J. M. R. (2005). Interactions of polysaccharides with β -lactoglobulin adsorbed films at the air-water interface. **Food Hydrocolloids**, 19, p.239-248.

BEAULIEU, M.; TURGEON, S. L.; DOUBLIER, J. L. (2001). Rheology, texture and microstructure of whey proteins/low methoxyl pectins mixed gels with added calcium. **International Dairy Journal**, 11(11–12), 961–967.

BODNÁR, I.; ALTING, A. C.; VERSCHUEREN, M. (2007). Structural effects on the permeability of whey protein films in an aqueous environment. **Food Hydrocolloids**, 21(5–6), 889-895.

BOZDEMIR, O. A.; TUTAS, M. (2003). Plasticiser effect on water vapour permeability properties of locust bean gum-based edible films. **Turkish Journal of Chemistry**, 27, 773-782.

BRINDLE, L. P.; KROCHTA, J. M. (2008). Physical Properties of Whey Protein-Hydroxypropylmethylcellulose Blend Edible Films. **Journal of Food Science**, 73(9), 446-454.

CERQUEIRA, M.A.; BOURBON, A. I.; PINHEIRO, A.C.; MARTINS, J. T.; SOUZA, B. W. S.; TEIXEIRA, J. A.; VICENTE, A.A. (2011) Galactomannans use in the development of edible films/coatings for food applications. **Trends in Food Science & Technology**, 22, 662-671

CERQUEIRA, M. A.; SOUZA, B. W. S.; TEIXEIRA, J. A.; VICENTE, A. A. (2012) Effect of glycerol and corn oil on physicochemical properties of polysaccharide films – A comparative study. **Food Hydrocolloids**, 27, 175-184.

COUGHLAN, K.; SHAW, N.B.; KERRY, J. F.; KERRY, J.P. (2004). Combined effects of proteins and polysaccharides on physical properties of whey protein concentrate-based edible films. **Journal of Food Science**, 69 (6), p. E271-E275.

CUQ, B.; GONTARD, N.; CUQ, J.-L.; GUILBERT, S. (1996) Functional properties of myofibrillar protein-based biopackaging as affected by film thickness. **Journal of Food Science**, 61 (3), 580–584.

DANIEL, C; WOOD, F (1980). **Fitting Equations to Data**, Revised Edition, John Wiley & Sons, New York, USA.

DAKIA, P. A.; BLECKER, C.; ROBERT, C.; WATHELET, B.; PAQUOT, M. (2008). Composition and physicochemical properties of locust bean gum extracted from whole seeds by acid or water dehulling pre-treatment. **Food Hydrocolloids**, 22, 807-818.

FERNANDES, P. B., GONÇALVES, M. P., & DOUBLIER, J. L. (1991). A rheological characterization of kappa-carrageenan/galactomannan mixed gels : a comparison of locust bean gum samples. **Carbohydrate Polymers**, 16, 253-274

FLORIS, R., BODNAR, I., WEINBRECK, F., & ALTING, A. C. (2008). Dynamic rearrangement of disulfide bridges influences solubility of whey protein coatings. **International Dairy Journal**, 18(5), 566-573.

GONÇALVES, M.P.; SITTIKIYOTHIN, W.; SILVA M. V.; LEFEBVRE, J. (2004). A study of the effect of locust bean gum on the rheological behaviour and microstructure of a β -lactoglobulin gel at pH 7. **Rheologica Acta**, 43, 472-481.

GONÇALVES, M.P.; TORRES, D.; ANDRADE, C.T.; AZERO, E.G.; LEFEBVRE, J. (2004). Rheological study of the effect of Cassia javanica galactomannans on the heat-set gelation of a whey protein isolate at pH 7. **Food Hydrocolloids** 18, 181–189.

GOUNGA, M. E.; XU, S. Y.; WANG, Z. (2007). Whey protein isolate-based edible films as affected by protein concentration, glycerol ratio and pullulan addition in film formation. **Journal of Food Engineering**, 83, 521–530.

GOYCOOLEA, F.M.; MORRIS, E.R.; GIDLEY, M.J. (1995) Viscosity of galactomannans at alkaline and neutral pH: evidence of 'hyperentanglement' in solution. **Carbohydrate Polymers**, 27, 69-71.

GRINBERG, V. YA.; TOLSTOGUZOV, V. B. (1997). Thermodynamic incompatibility of proteins and polysaccharides in solutions. **Food Hydrocolloids**, 11, 145–158

HAN, J. H.; GENNADIOS, A. (2005) Edible films and coatings: a review. **Innovations in Food Packaging**, 239-262.

HONG, S.-I.; KROCHTA, J. M. (2006). Oxygen barrier performance of whey-protein-coated plastic films as affected by temperature, relative humidity, base film and protein type. **Journal of Food Engineering**, 77, 739-745.

IBANOGLU E. (2002) Rheological behaviour of whey protein stabilized emulsions in the presence of gum Arabic. **Journal of Food Engineering**, 52, 273–277

IBANOGLU, E. (2005). Effect of hydrocolloids on the thermal denaturation of proteins. **Food Chemistry**, 90, 621–626.

JOWITT, R.; ESCHER, F.; HALLSTOM, B.; MEFFERT, H.F.T.; SPIESS, W.E.L.; VOS, G. (1987) **Physical Properties of Foods**. London and New York : Applied Science Publishers.

KAVANAGH, G.M.; CLARK, A.H.; GOSAL, W.S.; ROSS-MURPHY, S.B. (2000) Heat-induced gelation of β -lactoglobulin/ α -lactalbumin blends at pH 3 and pH 7. **Macromolecules**, 33(19), 7029-7037.

KOKOSZKA, S., DEBEAUFORT, F., LENART, A.; VOILLEY, A. (2010) Water vapour permeability, thermal and wetting properties of whey protein isolate based edible films **International Dairy Journal**, 20, 53–60

LEE, J.Y.; PARK, H. J.; LEE, C. Y.; CHOI, W. Y. (2003) Extending shelf-life of minimally processed apples with edible coatings and antibrowning agents. **Lebensm.-Wiss. U.-Technol.** 36, 323–329.

LEWICKI, P. P. The applicability of the GAB model to food water sorption isotherms. **International Journal of Food Science and Technology**, v. 32, n. 6, p. 553-557, 1997.

MAIER, H.; ANDERSON, M.; KARL, C.; MAGNUSON, K.; WHISTLER, R. L. (1993). **Guar, locust bean, tara and fenugreek gums**. In R. L. Whistler, & J. N. BeMiller (Eds.), *Industrial gums, polysaccharides and their derivatives* (pp. 205–215). San Diego: Academic Press.

MCHUGH, T. H., AVENA-BUSTILLOS, R. J., M., K. J. (1993). Hydrophilic edible film: modified procedure for water vapor permeability and explanation of thickness effects. *Journal of Food Science*, 58, 899-903.

MCHUGH, T. H.; KROCHTA, J. M. (1994). Sorbitol-vs glycerol-plasticized whey protein edible films: Integrated oxygen permeability and tensile property evaluation. *Journal of Agricultural and Food Chemistry*, 42(4), 841-845.

NEIRYNCK, N.; VAN DER MEEREN, P.; LUKASZEWICZ-LAUSECKER, M.; COCQUYT, J.; VERBEKEN, D.; DEWETTINCK, K. (2007) Influence of pH and biopolymer ratio on whey protein–pectin interactions in aqueous solutions and in O/W emulsions. **Colloids and Surfaces A: Physicochem. Eng. Aspects**, 298, 99–107.

NICOLAI, T.; BRITTEN, M.; SCHMITT, C. (2011) β -Lactoglobulin and WPI aggregates: Formation, structure and applications. **Food Hydrocolloids**, 25, 1945 - 1962

OZDEMIR, M.; FLOROS, J. D. (2008). Optimization of edible whey proteins. Films containing preservatives for water vapour permeability, water solubility and sensory characteristics. **Journal of Food Engineering**, 86, 215–224.

OSÉS, J.; FABREGAT-VÁZQUEZ, M.; PEDROZA-ISLAS, R.; TOMÁS, S. A.; CRUZ-OREA, A.; MATÉ, J. I. (2009). Development and characterization of composite edible film based on whey protein isolate and mesquite gum. **Journal of Food Engineering**, 92, 56-62.

PELEGRINE, D.H.G.; GASPARETTO, C.A. (2005) Whey proteins solubility as function of temperature and Ph. **Lebensm.-Wiss. u.-Technol.** 38, 77–80

PEREIRA, R. N.; B. W. S; CERQUEIRA, M. A., TEIXEIRA, J. A.; VICENTE, A. A. (2010) Effects of Electric Fields on Protein Unfolding and Aggregation: Influence on Edible Films Formation. **Biomacromolecules**, 11, 2912–2918.

PEREZ-GAGO, M. B.; KROCHTA, J. M. (1999) Water Vapor Permeability of Whey Protein Emulsion Films as Affected by Ph. **Journal of Food Science**, 64, 4, 695-698

PEREZ-GAGO, M. B.; KROCHTA, J. M. (2001). Denaturation time and temperature effects on solubility, tensile properties, and oxygen permeability of whey protein edible films. **Journal of Food Science**, 66(5), 705-710.

PEREZ-GAGO, M. B.; KROCHTA, J. M. (2002). **Formation and properties of whey protein films and coatings**. In A. Gennadios (Ed.), *Protein-based films and coatings* (pp. 159-180). Boca Raton FL, USA: CRC Press.

PIERRO, P.; SORRENTINO, A.; MARINIELLO, L.; VALERIA L. C.; PORTA, R. (2011) Chitosan/whey protein film as active coating to extend Ricotta cheese shelf-life. **LWT - Food Science and Technology**, 44, 2324 - 2327.

POLLARD, M. A.; FISCHER, P. (2006) Partial aqueous solubility of low-galactose-content galactomannans—What is the quantitative basis? **Current Opinion in Colloid & Interface Science**, 11, 184–190

RAMOS, O. L.; FERNANDES, J. C.; SILVA, S. I.; PINTADO, M. E.; MALCATA, F. X. (2012). Edible films and coatings from whey proteins: a review on formulation, and on mechanical and bioactive properties. **Critical Reviews in Food Science and Nutrition**, 52, 533-552.

RAMOS, O. L.; REINAS, I.; SILVA, S. I.; FERNANDES, J. C.; CERQUEIRA, M. A.; PEREIRA, R. N.; VICENTE, A. A.; FATIMA POCAS, M.; PINTADO, M. E.; XAVIER MALCATA, F. (2013). Effect of whey protein purity and glycerol content upon physical properties of edible films manufactured therefrom. **Food Hydrocolloids**, 30(1), 110-122.

ROCHA, C.; TEIXEIRA, J.A.; HILLIOU, L.; SAMPAIO, P.; GONÇALVES, M. P. (2009) Rheological and structural characterization of gels from whey protein hydrolysates/locust bean gum mixed systems. **Food Hydrocolloids** 23, 1734–1745.

SEYDIM, A. C.; SARIKUS, G. (2006). Antimicrobial activity of whey protein based edible films incorporated with oregano, rosemary and garlic essential oils. **Food Research International**, 39, 639-644

SITTIKIYOTHIN, W.; TORRES, D.; GONÇALVES, M. P. (2005). Modelling the rheological behaviour of galactomannan aqueous solutions. **Carbohydrate Polymers** 59, 339-350.

SOTHORNVIT, R.; KROCHTA, J. M. (2000). Water vapor permeability and solubility of films from hydrolyzed whey protein. **Journal of Food Science**, 65(4), 700-703.

SOTHORNVIT, R.; KROCHTA, J. M. (2001). Plasticizer effect on mechanical properties of beta-lactoglobulin films. **Journal of Food Engineering**, 50(3), 149-155.

SUN, C.; GUNASEKARAN, S; RICHARDS, M. P. (2007) Effect of xanthan gum on physicochemical properties of whey protein isolate stabilized oil-in-water emulsions. **Food Hydrocolloids**, 21, 555–564.

TAVARES, C.; DA SILVA, J. A. L. (2003). Rheology of galactomannan–whey protein mixed systems. **International Dairy Journal**, 13(8), 699–706.

TOTOSAUS, A.; MONTEJANO, J. G.; SALAZAR, J. A.; GUERRERO, I. (2002). A review of physical and chemical protein-gel induction. **International Journal of Food Science and Technology**, 37(6), 589–601.

USTUNOL, Z.; MERT, B. (2004). Water solubility, mechanical, barrier, and thermal properties of cross-linked whey protein isolate-based films. **Journal of Food Science**, 69(3), 129-133.

VAN DEN BERG, C.; BRUIN, S. (1981). **Water activity and its estimation in food systems**. In L. B. Rockland & G. F. Stewart (Eds.), *Water activity: influences on food quality* (p. 147–177). New York: Academic Press.

WIHODO, M.; MORARU, C. I. (2013). Physical and chemical methods used to enhance the structure and mechanical properties of protein films: A review. **Journal of Food Engineering**, 114(3), 292-302.

YOO, S. R.; KROCHTA, J. M. (2011) Whey protein–polysaccharide blended edible film formation and barrier, tensile, thermal and transparency properties. **Journal Science Food Agriculture**, 91, p. 2628-2636.

CAPÍTULO IV

Edible coatings improve the quality of pineapple during convective drying

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Abstract

The effect of osmotic dehydration and edible coating applying on air-drying kinetics and quality of pineapple was evaluated. Samples were osmotically dehydrated in aqueous solution containing 50% sucrose, 4% calcium lactate and 2% ascorbic acid for 1 hour, then were covered or not by pectin or whey protein isolate (WPI) + locust bean gum (LBG) + glycerol, kept at room temperature for 15h and after dried at 60°C/11h and 70°C/7h. Moisture, vitamin C content, water activity and color were evaluated. A simplified model based on the Fick's Law was used to estimate effective diffusion coefficients during air-drying. Edible coating of pectin and WPI-LBG did not affected the efficiency of drying and did not influence the reduction of water activity of samples, considering overall drying time, but increased vitamin C retention during hot-air-drying. However, water diffusion coefficients were significantly affected by edible coatings. Convective drying reduced lightness of samples, but provided more intense colors products. Coatings acted differently on lightness of samples during air dehydration, where pectin coating showed the slightest change in lightness. Even though impregnation had yielded high vitamin C levels in dried pineapples, coating applying contributed to enhance retention of this vitamin during hot-air-drying.

1. Introduction

Drying is an important method of preservation of fruits and vegetables, because it removes moisture of food and reduces water activity, preventing the growth of spoilage

microorganisms, slows down the action of enzymes and minimizes water-mediated deteriorative reactions during storage (VEGA-MERCADO et al., 2001; KAVAK AKPINAR et al., 2005; MANDALA et al., 2005). Although, this method can provide vitamin loss, browning and undesirable texture changes in product (RAMALLO; MASCHERONI, 2004; CHUTINTRASRI; NOOMHORM, 2007; VEGA-GÁLVEZ et al., 2009; KAYA et al., 2010; CORTELLINO et al 2011; RAMALLO; MASCHERONI, 2012). The ascorbic acid is one of most sensitive nutrients to heat, light and oxygen, being easily degraded during convective drying (WAWIRE et al., 2011), and as consequence, this substance is frequently used as an indicator of the quality of food processes (SANTOS; SILVA, 2008; UDIN et al., 2001). The enhancing vitamin C retention during drying would represent improvement of the nutritional food quality. The use of treatments that can prevent oxidation during hot-air-drying can represent an alternative to reduce nutritional loss and to improve the quality of the dried products.

Osmotic dehydration (OD) applied prior to drying can minimize negative impacts due to physical, sensorial and nutritional changes resulting from the drying process (RIVA et al., 2005; SANJINEZ-ARGANDOÑA et al., 2005; VÉGA-GALVES et al., 2008). Moreover, the enrichment of vitamins and mineral salts can be performed in osmotic dehydration (FITO et al., 2001; ANINO et al., 2006; CASTELLÓ et al., 2010; SILVA et al., 2013), favoring the preservation of nutritional quality and compensating or minimizing losses during drying process.

Other potential option of pretreatment is the applying of edible coatings in food before air-drying. Edible coatings are defined as thin layers of edible material applied to the surface of the food to create a selective barrier to the gases transport (VARGAS et al., 2008). Edible coatings have been widely studied aiming to increase shelf life of minimally processed products (OMS-OLIU et al., 2008; ANSORENA et al., 2011; DUAN et al., 2011; LIMA et al., 2010; SONG et al., 2011; BENITEZ et al., 2013; VALERO et al., 2013) and reduce the uptake solids during osmotic dehydration (BRANDELERO et a., 2005; MATUSKA et al. 2006; GARCÍA et al. 2010). Few researchers have investigated the use of edible coatings as pretreatment to convective drying (ZHAO; CHANG, 1995; LAGO-VANZELA et al., 2013; GARCIA, 2012) being that all of them observed that coatings represent a potential pretreatment for drying, which performance depends on the permeability properties of the coat materials.

Polysaccharide and protein edible coatings present good gas barrier properties, such as oxygen (FAKHOURI et al., 2007), and could be used to minimize oxidative reactions in food. This property points out a potential use of edible coats as pretreatment to convective drying, because would reduce undesirable changes due to large exposure time of food to oxygen. Lago-Vanzela et al. (2013) verified that pumpkin coated with starch solution presented higher *trans- α -carotene* and *trans- β -carotene* contents and better color during convective drying than uncoated samples. Garcia (2012) verified that pectin coating reduced vitamin C losses during convective drying of papaya slices, when compared to the uncoated samples.

Edible films from whey protein isolates have shown to be good oxygen barriers (HONG; KROCHTA, 2006; RAMOS et al., 2013). The functional properties of whey proteins can also be modified by the addition of polysaccharides (ROCHA et al., 2009). Silva et al. (2013) observed that locust bean gum addition reduce oxygen permeability of whey protein isolate films.

This work aimed to determine convective drying kinetics and effective moisture diffusivities of coated and uncoated osmotically dehydrated pineapple; and to investigate the influence of two different edible coats on water activity, color changes and vitamin C retention during hot-air-drying of osmotic dehydrated pineapple.

2. Materials

Pineapple (*Ananás comosus* (L.) Merrill) were purchased at Supplying Center (CEAGESP; São José do Rio Preto, São Paulo, Brazil) to be used in the experiments.

Whey Protein Isolate (WPI), LACTOPRODAN DI-9224, kindly supplied by Arla Foods Ingredients (Viby, Denmark), was used as the protein source. This isolate contains a minimum of 93.5% total protein content (74% β -lactoglobulin, 18% α -lactalbumin and 6% bovine serum albumin), maximum content of 0.2% lactose and fat, approximately 0.5% sodium, 1% of potassium and 0.1% calcium, as specified by Arla Foods Ingredients.

Locust bean gum (LBG) (> 75% galactomannan content) was kindly supplied by Danisco Portugal (Faro, Portugal).

Glycerol was supplied by Merck (Germany).

Low methoxylated amidated pectin GRINDSTED[®] LA 210 with degree of methoxylation of 0.34 and degree of amidation of 0.17 was supplied by Danisco (Brazil).

Food grade calcium lactate pentahydrate in power was supplied by PURAC Synthesis (Brazil) and food grade ascorbic acid in powder from Prozyn® (Brazil).

3. Methodologies

3.1 Sample preparation

Pineapples of commercial ripeness degree, weighing approximately 1.2 kg, were washed, manually peeled, and its ends were discarded to reduce the variability of tissue. The pieces were sliced (1 ± 0.1 cm thick) using a manual cutter and the each slice was cut in truncated cone format with the aid of a metal mold. The samples were kept and mixed in a plastic bag until the slices were randomly removed to be used in the experiments. Approximately one hundred slices were used in each experiment.

Samples were osmotically dehydrated in aqueous solution containing 50% sucrose, 4% calcium lactate and 2% ascorbic acid for 1 hour. After that, part of them was coated by pectin or whey protein isolate + locust bean gum + glycerol and part was not coated (control). After coating, all samples were left at room temperature (27 °C) for a holding time of 15 h, aiming to minimize concentration profiles as well as to promote partial drying of the coating surface, before hot-air-drying. The convective drying was carried out at 60 °C by 11 hours and at 70 °C by 7 hours. Water and ascorbic acid contents were analyzed in fresh samples, osmotic dehydrated samples and in samples coated and uncoated, immediately before and after drying. Color and water activity measurements were carried out before and after drying.

3.2 Osmo-impregnation

Osmotic solutions were prepared with commercial sucrose (refined sugar) purchased in a local market; food grade pentahydrate calcium lactate in powder; food grade ascorbic acid in powder and distilled water.

Pineapple slices were dehydrated in 50% (w/w) sucrose aqueous solutions added with 4% (w/w) of calcium lactate and 2% (w/w) of vitamin C for 1 h (SILVA et al., 2013). The fruit slices were arranged in four nylon mesh baskets, with approximately 350 g of samples in

each basket. The baskets were immersed into 20 kg of osmotic solution in a jacketed stainless steel vessel (0.30×0.30×0.30 m). The syrup-to-fruit ratio was approximately 1:14. The solution temperature was maintained at 27 °C with an external circulation of thermostatically controlled water. A central propeller (10 cm diameter) continuously agitated the solution by using a 1.6 kW mechanical stirrer (Marconi, model MA-261—Brazil). A rotation of 1,850 rpm provided constant and vigorous agitation. Thus, a negligible liquid phase mass transfer resistance was considered and the solution concentration was assumed constant on the fruit surface during the whole osmotic dehydration.

After one hour of the process, the baskets were removed from the osmotic bath and the samples immersed in distilled water at room temperature for 10 s in order to remove the osmotic solution from the surface. They were then blotted with absorbing paper and weighted.

3.3 Edible coating application

Solutions of low methoxylated amidated pectin and LGB + WPI were used to coat the osmotically dehydrated pineapple slices. Non-coated samples were used as the control.

Pectin aqueous solution (2%, w/w) was prepared at 70 °C with constant stirring and applied to the surface of the samples at 40 °C by immersion for 1 min. Gelling was activated with subsequent placement of the samples in a 1.0% (w/w) aqueous solution of food grade calcium lactate pentahydrate, prepared at room temperature, for 30 s (SHIGEMATSU et al., 2005).

Stock solution of 1% (w/w) LBG were prepared by stirring dry LBG powder in distilled water for 1 hour. After that, the solution was heated for 30 minutes at 80 °C and cooled. The coats were prepared mixing 5% (w/w) WPI with aqueous solution at 0.05% concentration of LBG stock solution and 2% (w/w) of glycerol as plasticizer. NaCl solution (20% w/w) was added to a final salt concentration of approximately 50 mM to ensure constant ionic strength. The solution was stirred for 2 hours at room temperature. The pH was adjusted to 7.0 and the solution was stirred for 2 hours more and, then, heated at 75 °C for 10 minutes to denaturalize protein fraction and cooled. Osmotically dehydrated pineapple slices were immersed into 5%WPI + 0.05% LGB for 1 minute.

After coated, the samples were kept at room temperature for 15 h before drying.

3.4 Convective drying

After osmotic dehydration, coat addition and holding time at room temperature, samples were placed into driers and dried in convective driers at 60 and 70 °C with an air velocity of 1.0 m·s⁻¹ for 11 h and 7 h, respectively. Each drying was done in duplicate. The average moisture inside the driers was registered at approximately 10% (wet basis) during the drying of the samples. To determine equilibrium water content, samples were kept into the driers for 20 h, until a constant weight was achieved. The air flowed parallel to the bed, which consisted of three wire nets. Samples were weighted every 20 min during the firsts 90 min of drying, every 30 min during the next hour and every 60 min during the remaining time. At the weighting time, the trails inside the driers were rotated to standardize the moisture inside the driers.

3.5 Analytical methodologies

The solid contents of fresh, osmotically dehydrated, dried at room temperature (coated or uncoated) and dried at 60 and 70°C (osmotically dehydrated fruits coated or not with pectin and WPI-LGB) pineapple slices, were gravimetrically determined in triplicate by drying the samples in a vacuum oven at 60 °C and 10 kPa until a constant weight was achieved.

Water activity of the samples (coated or not) before and after drying was measured in triplicate at 25 °C in a hygrometer (AW SPRINT; NOVASINA, Switzerland).

The color of the samples (coated or not) before and after drying was evaluated in 8 replicates using a Colorflex spectrophotometer (HunterLab, Hunter Associates Laboratory, Inc., model MiniScan XE Plus, VA, USA) and version 4.10 of the Universal software with the following settings: illuminant D65, observer at 10° and reading of the absolute values of L* (lightness or darkness), a* (redness or greenness) and b* (yellowness or blueness). In addition chroma (Equation 2) which indicates the purity or saturation of the color and hue angle (Equation 3) which expresses the color change (an angle of 0 or 360° represents red hue, while angles of 90, 180, and 270° indicate yellow, green and blue hue, respectively) were calculated as follows :

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

$$Hue = \arctan\left(\frac{b^*}{a^*}\right) \quad (2)$$

The vitamin C content of the samples fresh, osmotically dehydrated, dried at room temperature (coated or not) and dried at 60 and 70°C (coated or not) was determined in duplicate using the modified method described by Benassi & Antunes (1988). Immediately after processing, samples (25 g) were homogenized in 50 mL of extractor solution (oxalic acid at 2%; w/w) using a Turratec equipment (TECNAL, TE-102 model) for 1 min. An aliquot (20 g) was volumetrically diluted with the extractor solution to 50 mL. Ten milliliters of the diluted solution was titrated with 2,6-dichlorophenolindophenol.

Approximately 4 g of dried pineapple slices were rehydrated with approximately 20 g of distilled water for 20 min before homogenization in 50 mL of extractor solution, to make easy crumbling of dried samples.

3.6. Calculations

3.6.1. Vitamin C

The amount of vitamin C was determined in mg of ascorbic acid in 100 grams of fresh product. The retentions of vitamin C were determined according to Murphy et al. (1975), as described by Equation 3:

$$Ret(\%) = \left(\frac{C_f}{C_i} \frac{M_f}{M_i}\right) \cdot 100 \quad (3)$$

where *Ret* is the retention of vitamin C after a process time; C_f is the amount of vitamin C in the samples at the end (after drying) and C_i is the amount of vitamin C in the samples (coated and uncoated) before convective drying at 60 and 70°C, in mg of ascorbic acid/100 g of sample; M_f is the mass of samples at the end (after convective drying) and M_i is mass of samples at the beginning (before convective drying), in grams.

3.6.2. Effective diffusion coefficients

The effective diffusion coefficients of moisture (D_m) were determined according to Fick's Law applied to an infinite slab. The diffusion model has been applied to the drying of biological materials by changing the fractional contents to express the moisture on a dry basis (db) (GARCIA et al., 2007). The analytical solution of the following diffusion equation (Equation 4) has been previously described by Crank (1975):

$$X = \left(\frac{\bar{X}(t) - X^{eq}}{X^0 - X^{eq}} \right) = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left[-(2n-1)^2 \frac{\pi^2 D_m t}{z^2} \right] \quad (4)$$

where eq indicates equilibrium; 0 indicates initial water content (at $t = 0$); X is the fractional or residual moisture content, dry basis (dimensionless); \bar{X} represents water content (db); \bar{X} is the average moisture (db) at time t (s); X^{eq} is the fraction of the moisture at equilibrium; D_m is the effective diffusion coefficient of moisture ($m^2 \cdot s^{-1}$); z is the thickness of the fresh samples (m) and n is the number of terms of the series. The thickness z in equation (4) was assumed to be 1 cm for all dryings. Since OD and edible coatings did not change considerable the samples size, the initial value was considered.

It was used twelve terms in the calculations of moisture diffusivity, ie $n = 12$ in Equation 4.

3.7. Statistical analysis and fitting

The data were statistically analyzed by an analysis of variance (ANOVA) and Tukey's test at a 5% significance level using Excel 2007 (Microsoft, USA).

Effective diffusion coefficients were calculated from the experimental data according to Equation 4 using Statistica 7.0 software. The fitting efficiency was evaluated by the determination coefficient (R^2) and the mean relative error root square ($RRMS$). $RRMS$ was calculated with Equation 6 (Daniel; Wood, 1980) as follows:

$$RRMS (\%) = 100 \left\{ \frac{1}{N} \sum_{n=1}^N \left[\frac{(x^{calc} - x^{exp})}{x^{calc}} \right]^2 \right\}^{1/2} \quad (5)$$

where x^{calc} represents water content on a dry basis and was calculated according to Equation 4; x^{exp} is the experimental value and N represents the number of observations or residuals.

4. Results and discussion

Table 1 presents the quantity of edible coating addition, moisture content (wet basis) and water activity of fresh, osmotically dehydrated and coated fruits before and after convective drying at 60 and 70 °C.

Figures 1 and 2 show experimental and calculated values of the moisture content (dimensionless) versus drying time.

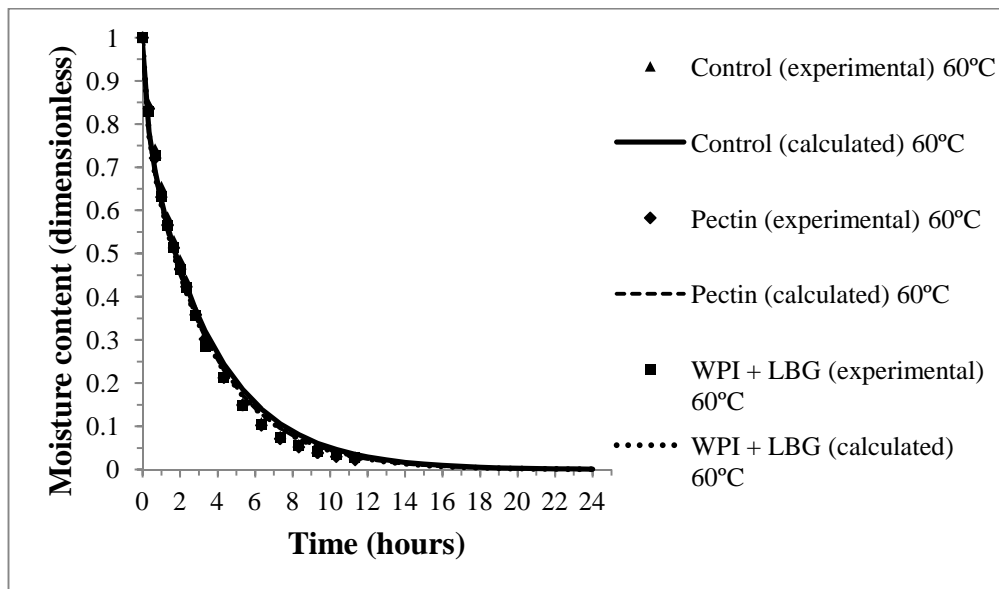


Figure 1: Experimental and calculated variation of the moisture content during drying at 60°C of control and coated pineapple slices.

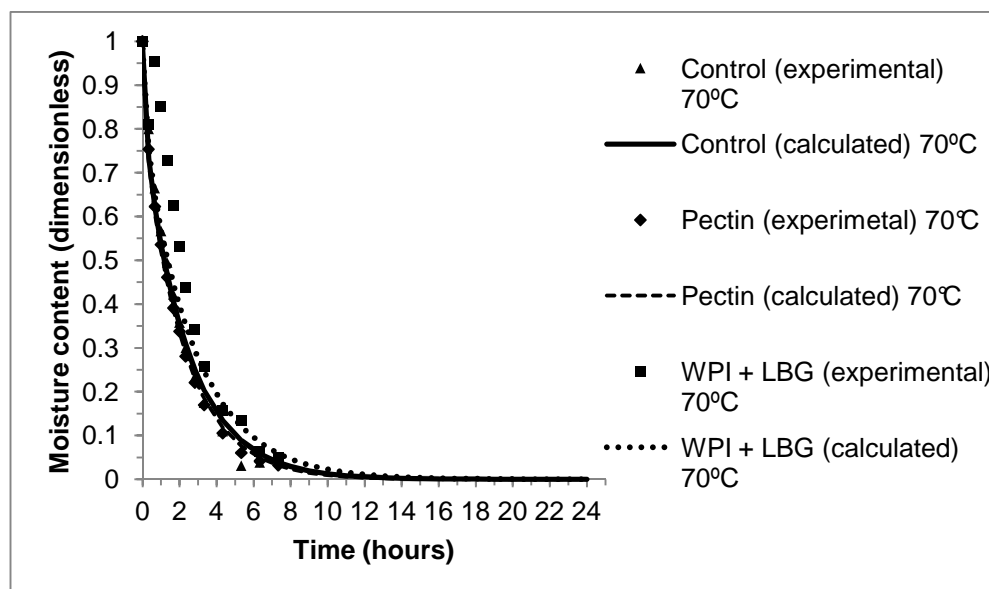


Figure 2: Experimental and calculated variation of the moisture content during drying at 70°C of control and coated pineapple slices.

It was observed that pectin coating applied on samples presented higher mass added in comparison with WPI-LBG coating. This result was related to composition of coating and to viscosity of solution at the moment of its applying. A coating thicker can represent a higher protection to oxidative action during air drying, however, the structural arrangement of the macromolecules also has an important role in the formation of the protective layer of the fruit.

Water content of fresh pineapple was reduced during the osmotic treatment because of the potential chemical gradient existing between the product and the osmotic solution. In one hour of osmotic dehydration the initial moisture of pineapple slices decreased approximately 15%.

After 15 hours of drying at room temperature at 27 °C, it was verified that control samples (uncoated) presented reduction in water content, but coated samples presented water content a little higher than after OD. Moisture of osmodehydrated pineapple increases after coating applying, since the water content of pectin solutions was approximately 98% and of WPI-LBG solutions, around 93%. aqueous solution and even after 15 hours of drying at room temperature the major part of the incorporated water did not evaporate.

The studied pectin and WPI coatings did not increase the resistance to mass transfer during drying since water content. On the contrary, of coated and uncoated samples did not present statistically significant difference after drying at 60 and 70 °C (Table 1). Furthermore, the drying curves of coated and uncoated pineapple slices (Figures 1 and 2) were overlapped.

Edible coatings did not influence the final water activity of samples after drying at 60 and 70 °C (Table 1). However the drying times employed in this work decreased the water activity of the samples to security levels against microorganism growth. According to Yan et al. (2008) water activity of approximately 0.6 reduce or inactive the growth of microorganisms.

Table 1: Percentual of edible coating addition at the samples surface, moisture and water activity of the samples before and after drying at 60 and 70 °C.

		Before drying	After drying	After DO	After drying
	% edible coating addition	Water content (kg·100kg ⁻¹)		Water activity	
Fresh (60°C/11h)	-	84.61 ± 0.05 ^A	-	-	-
After OD (60°C/11h)	-	72.27 ± 0.03 ^B	-	0.965 ± 0.012 ^{a, A}	-
Control (60°C/11h)	-	68.49 ± 0.60 ^{a, C}	12.21 ± 0.62 ^{b, A}		0.545 ± 0.032 ^{b, A}
Pectin Coated (60°C/11h)	16.67	74.19 ± 0.11 ^{a, D}	12.14 ± 0.08 ^{b, A}		0.549 ± 0.027 ^{b, A}
WPI + LBG coated (60°C/11h)	12.83	73.04 ± 0.18 ^{a, E}	12.57 ± 0.21 ^{b, A}		0.557 ± 0.038 ^{b, A}
Fresh (70°C/7h)	-	84.96 ± 0.10 ^A	-	-	-
After OD (70°C/7h)	-	71.11 ± 0.27 ^B	-	0.972 ± 0.002 ^{a, A}	-
Control (70°C/7h)	-	66.58 ± 0.29 ^{a, C}	11.28 ± 0.39 ^{b, A}		0.488 ± 0.015 ^{b, A}
Pectin coated (70°C/7h)	14.72	72.40 ± 0.14 ^{a, D}	11.83 ± 0.34 ^{b, A}		0.540 ± 0.061 ^{b, A}
WPI + LBG coated (70°C/7h)	13.19	69.28 ± 0.12 ^{a, E}	11.08 ± 0.54 ^{b, A}		0.530 ± 0.016 ^{b, A}

*Mean ± SD

**Means with the same lower case letter, for the same response variable, in the same line, did not differ significantly at p≤0.05 according to the Tukey test

***Means with the same capital letter, for the same drying temperature, in the same column, did not differ significantly at $p \leq 0.05$ according to the Tukey test

Table 2 shows the effective diffusion coefficients of water calculated according to Equation 4. The data showed a good fit to Equation 5, the R^2 values being above 0.976 and the values for $RRMS$ below 5%.

Table 2: Effective diffusion coefficients of moisture ($D_m \times 10^{10}$, in $\text{m}^2 \cdot \text{s}^{-1}$), calculated according to Equation 4, considering z as the initial thickness and equilibrium moisture (X^{eq}) of osmotically dehydrated uncoated and coated pineapple slices after convective drying at 60 and 70 °C.

Parameters	Control	Pectin coated	WPI + LBG coated
D_m ($\text{m}^2 \cdot \text{s}^{-1}$) (60°C/11h)	7.12 ± 0.30 ^{a, A}	7.76 ± 0.00 ^{a, A}	7.44 ± 0.51 ^{a, B}
X^{eq}	0.082 ± 0.008	0.078 ± 0.005	0.080 ± 0.005
R^2	0.980 ± 0.006	0.985 ± 0.007	0.989 ± 0.000
$RRMS$	2.93 ± 0.01	2.54 ± 0.01	2.02 ± 0.00
D_m ($\text{m}^2 \cdot \text{s}^{-1}$) (70°C/7h)	11.61 ± 0.51 ^{b, A}	12.36 ± 1.87 ^{b, B}	12.03 ± 0.00 ^{b, B}
X^{eq}	0.051 ± 0.002	0.094 ± 0.061	0.051 ± 0.002
R^2	0.973 ± 0.009	0.996 ± 0.001	0.991 ± 0.001
$RRMS$	3.37 ± 0.01	1.22 ± 0.00	1.75 ± 0.00

*Mean \pm SD

**Means with the same lower case letter, in the same column, did not differ significantly at $p \leq 0.05$ according to the Tukey test

***Means of diffusion coefficients with the same capital letter, in the same line, did not differ significantly at $p \leq 0.05$ according to the Tukey test

The water diffusivities of pineapple slices were significantly higher at the 70 °C drying temperature (Table 2). This is in agreement with the results presented in Figures 1 and 2 which show that drying time decreased greatly when drying temperature increased. Similar results were reported by Nicoletti et al. (2001) for drying of osmotic dehydrated pineapple.

Comparing Figures 1 and 2, it can be seen that drying curves at 70°C fall below the curves at 60 °C. Therefore the results showed that the air temperature had a significant effect on the water content of the pineapple slices (Figures 1 and 2 and Table 2).

In general, water diffusion coefficient was higher for coated samples than for those without coating, due to strong hydrophilic nature of coatings (MCHUGH; KROCHTA, 1994).

Figures 3 and 4 show the changes in the drying rates as a function of moisture at 60 and 70 ° drying temperatures. Moisture decreased continuously with drying time and a constant rate period was not detected. Therefore the drying process of the pre-treated pineapple slices occurs in the range of the falling rate period, where diffusion is the dominant physical mechanism governing moisture movement in the samples. Since plant materials usually contain mostly bound water, a constant rate period in general is not detected. Similar results were found by other authors that studied the drying of osmotic dehydrated pineapples (NICOLETI et al., 2001), apples (DOYMAZ, 2010) and papaya (EL-AOUAR et al., 2003).

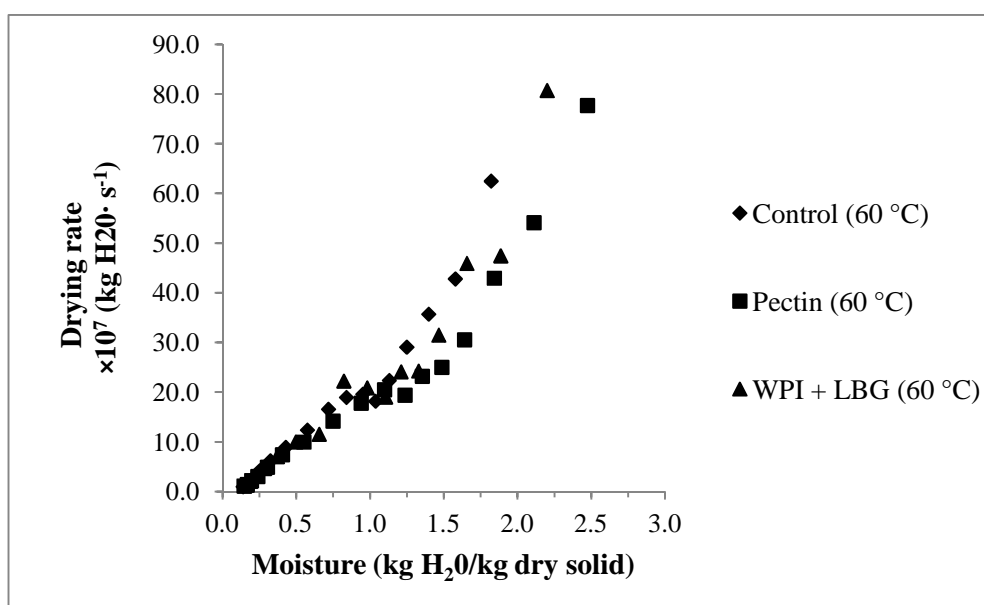


Figure 3: Drying rate as a function of moisture of control and coated samples during drying at 60°C

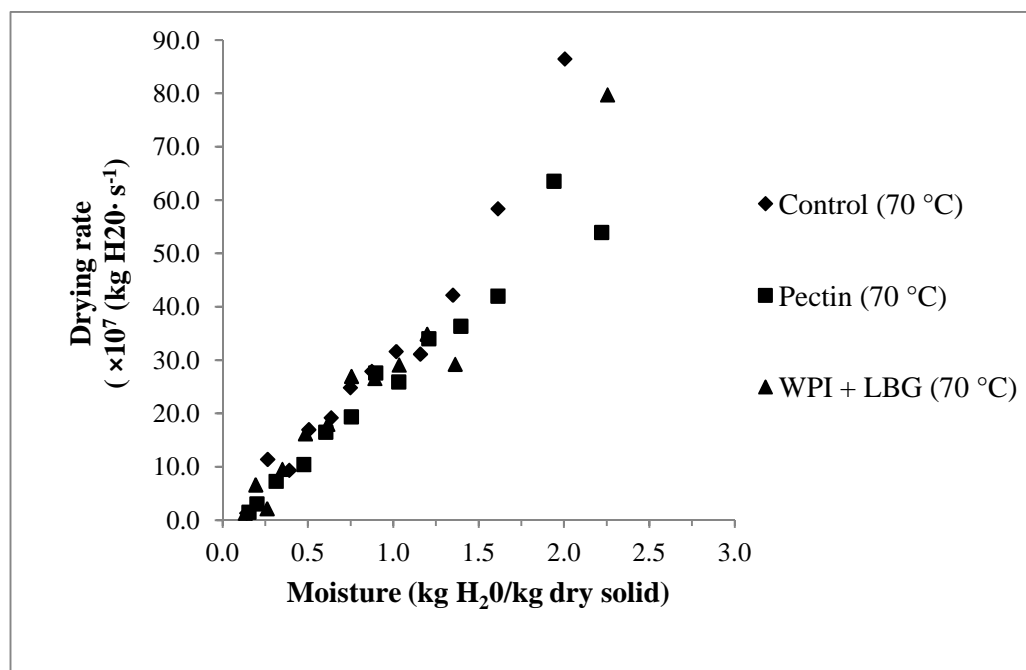


Figure 4: Drying rate as a function of moisture of control and coated samples during drying at 70°C

The effects of the osmotic treatment, coating and the drying temperatures on the vitamin C content of the samples are shown in Table 3.

The vitamin C content of the dehydrated fruits was expressed as mg/100 g of sample. High contents of vitamin C were verified in the samples osmotically dehydrated as a consequence of the impregnation. However, it was detected vitamin losses during the 15 hours of holding time. The losses were observed as control as in coated samples and related with the high moisture of the edible coatings and very high values in the dehydrated samples due to the concentration effect. In addition, the retention of vitamin C was also calculated according to equation 3.

Significant differences between ascorbic acid content of fresh pineapple can be attributed to heterogeneity amongst the fruits. Factors as climate, fertilizer practice or high intensity of sunlight can result large variations in ascorbic acid content of pineapple (HAMNER; NIGHTINGALE, 1945; SINGLETON; GORTNER, 1965).

Just as found in previous work (SILVA et al., 2013), one hour of osmotic dehydration in quaternary solution (sucrose + calcium lactate + ascorbic acid + water) resulted in noticeable vitamin C impregnation in the samples (more than 19 times of the initial value).

The additional mass applied on the fruit piece was between 12.83 and 16.67% of the initial mass (Table 1), which changed vitamin C concentration, as shown in the column “OD

or OD+coating” of the Table 3. However, after 15 hours at room temperature, it was verified loss of the vitamin C in all samples. Indeed significant difference between the vitamin C content of uncoated and coated pineapple slices was verified in the column “Before drying” (Table 3). It was possible to estimate water and vitamin C losses based on the added mass and composition of the edible coatings. The higher water and vitamin C losses, during the holding time, were observed in control (OD) and WPI coated (OD + WPI) samples. The water loss were $12.8\pm 1.1\%$ (OD control), $7.3\pm 0.7\%$ (OD + pectin) and $10.1\pm 5.9\%$ (OD + WPI-LBG) while the vitamin C retention was $79.4\pm 1.8\%$ (control), $79.2\pm 1.7\%$ (pectin) and $83.3\pm 1.4\%$ (OD +WPI-LBG).

According to Bonilla et al. (2011), wet systems increase oxygen permeability because the network structure is not packed as in dry condition. Gontard et al. (1996) presented increasing oxygen and carbon dioxide permeability, due to the increase of relative humidity of several films based on polysaccharides and proteins. Hong & Krochta (2006) observed great influence of relative humidity on oxygen permeability of WPI coating. Other important parameter to be considered is the high water activity of the samples after OD (Table 1), since high water content in samples reduces the aqueous phase viscosity increasing diffusion and facilitating reaction of oxidation (LEE; LABUZA, 1975; SANTOS; SILVA, 2008).

High vitamin C levels were found in dried samples (Table 3), due to decreasing of moisture that concentrates the vitamin C in the pieces of fruit, but also because of the low losses of ascorbic acid obtained during the hot-air-drying. Control samples had the lowest vitamin C retention during drying (Table 3), even though good retention levels have been found. The protective role of osmotic dehydration on volatiles and sensitive compounds to hot-air-drying is already known (SHI et al., 1999; MASKAN, 2001; RAMESH et al., 2001). The high retention of ascorbic acid verified can be attributed to the protective effect provided by osmotic dehydration. Riva et al (2005) observed that apricot cubes pretreated for 30 and 60 minutes in solution containing 60% (w/w) sucrose presented higher vitamin C retention during air-dehydration than non-treated samples. Guavas pretreated for two hours in sucrose solution (60°Brix) at 40°C presented ascorbic acid retention around 30-35% after 120 minutes of air-dehydration at 60°C. No vitamin C was detected in dried guava without osmotic treatment (Sanjinez-Argandoña et al., 2005). Véga-Galves et al., 2008 studied the effect of calcium salts on quality of red pepper during drying and verified that samples pretreated for 10 minutes at 25°C in aqueous solution of 20% (w/w) NaCl + 1% (w/w) CaCl₂ + 0.3% (w/w) Na₂S₂O₅ showed vitamin C retention higher during air-dehydration at 70°C than non-treated

samples and dried at 50, 60 and 70°C. The authors related the result to protective effect of CaCl_2 on ascorbic acid oxidation. In the present work, it is possible that effect of both, sucrose and calcium, contributed to the good protection against the vitamin C oxidation.

Control samples lost more vitamin C in drying at 70 °C/7h than drying at 60 °C/11h, indicating that temperature had higher effect on vitamin degradation than drying time (Table 3). This behavior is in agreement with the results found by other authors (MCMINN; MAGEE, 1997; ZANONI et al., 1999; ORIKASA et al., 2008; KAYA et al., 2010; RAMALLO; MASCHERONI, 2012).

The highest retention values obtained for coated samples show that pectin and WPI-LBG coatings were efficient barriers to oxygen. At 60 °C drying temperature, vitamin C retention was similar in the samples coated with pectin and WPI-LBG, however at 70 °C drying temperature, pectin was more efficient in avoiding vitamin C oxidation than WPI-LBG coating. Losses were not observed in samples dried at 60 °C that was attributed to fast drying of the coatings on surface, reducing the coating permeability to gases. In addition, experimental errors are not discarded, since values around 100% were obtained. It is possible that the error sources are due to accumulated residuals, since several steps are involved, ie, osmotic dehydration, coating applying, holding time and hot-air-drying. According to Silva et al. (2012), films of WPI- LBG are formed by a network strongly crosslinked via non-covalent and covalent bonds that provide a compact matrix that difficult the gas molecules diffusion. This property of WPI-LBG can have contributed to higher vitamin C retention of the samples during drying at 60 °C. However, the drying temperature of 70°C could have modified oxygen permeability of WPI-LBG coating, resulting in lower retention of vitamin C than the pectin coat samples dried at the same temperature.

Table 3. Vitamin C contents, in mg/100 g of sample, of fresh, osmo-dehydrated, control and coated pineapple before and after drying at 60 and 70 °C and retention (%) of vitamin C after drying (related to the osmotically treated samples before convective drying).

	60 °C/11h					70 °C/7h				
	Vitamin C (mg/100 g sample)					Vitamin C (mg/100 g sample)				
	After OD	Before drying	After drying	Retention during drying (%)		After OD	Before drying	After drying	Retention during drying (%)	
Fresh	27.09 ± 0.12 ^a	522.29 ± 13.94 ^a	-	-	-	18.74 ± 0.11 ^b	513.72 ± 1.82 ^a	-	-	-
Control	-	-	463.43 ± 15.67 ^{a, A}	1016.03 ± 10.27 ^{b, A}	78.70	-	-	479.20 ± 12.82 ^{a, A}	1101.18 ± 27.57 ^{b, A}	70.56
Pectin coated	-	-	386.5 ± 13.86 ^{a, B}	1319.06 ± 49.96 ^{b, B}	100.25	-	-	378.94 ± 6.34 ^{a, B}	1208.36 ± 0.31 ^{b, B}	99.82
WPI + LBG coated	-	-	414.73 ± 8.79 ^{a, A, B}	1376.71 ± 88.92 ^{b, B}	102.37	-	-	435.62 ± 7.35 ^{a, C}	1111.51 ± 5.99 ^{b, A}	88.15

*Mean ± SD

**Means with the same lower case letter, in the same line, did not differ significantly at $p \leq 0.05$ according to the Tukey test

***Means with the same capital letter, in the same column, did not differ significantly at $p \leq 0.05$ according to the Tukey test

The color parameters of the pineapple samples with and without coating, before and after drying are presented in Table 4.

Lightness (L^* value) of samples reduced approximately 15 – 19% during drying, being the higher reduction it was verified at 70 °C. This result can be related to oxidative reactions that occur during air dehydration which is potentiated by drying temperature. Thus this behavior is in agreement with the results found by other authors in pineapple juice (RATTANATHANALERK et al., 2005), pineapple puree (CHUTINTRASRI; NOOMHORM, 2007) and pineapple rings (CORTELLINO et al., 2011).

Coatings acted differently on lightness of samples during air dehydration. Pineapple covered with pectin presented the slightest change in L^* value during drying while OD samples and WPI-LBG coated samples were darker. The use of pectin coating must have minimized the contact between the surface of the pineapple and oxygen, decreasing oxidative browning of pineapple during drying. Wet WPI coating has been used on fresh-cut fruits and vegetables to prevent browning by action of oxygen (LE TIEN et al., 2001; PEREZ GAGO et al., 2005 and 2006). However, during drying, it is probable that temperature provides non enzymatic reactions in coating due to reactions between reducing sugars (such as fructose and glucose present in fruit) and WPI (whey protein isolate).

Before drying, all the samples presented a yellow predominant color (Hue value around 90°). Convective drying reduced significantly the hue angle value, decreasing the predominance of yellow color (represented by angle of 90°) and increasing the presence of red color (represented by angle of 0°) on the samples. Chroma values showed significant increase after drying, indicating that pineapple color became more intense with drying. However, significant differences between dried samples were not observed.

Table 4: L* (lightness), C* (Chroma value) and H* (hue angle value) of osmotically dehydrated samples after drying at room temperature, with or without coating, before and after drying at 60 and 70 °C.

Treatment	Before drying	After drying	Before drying	After drying	Before drying	After drying
	L*		C*		H*	
Control (60°C/11h)	69.53 ± 0.82 ^{a, A}	59.13 ± 2.71 ^{b, A}	25.72 ± 1.26 ^{a, A}	31.65 ± 1.36 ^{b, A}	92.75 ± 0.38 ^{a, A}	76.51 ± 0.90 ^{b, A}
Pectin coated(60°C/11h)	64.79 ± 3.31 ^{a, B}	65.67 ± 2.56 ^{a, B}	24.97 ± 1.81 ^{a, A}	30.50 ± 1.15 ^{b, A}	91.23 ± 1.99 ^{a, B}	78.01 ± 0.71 ^{b, A}
WPI + LBG coated (60°C/11h)	70.57 ± 3.02 ^{a, A}	57.70 ± 4.85 ^{b, A}	21.73 ± 1.05 ^{a, B}	30.96 ± 1.13 ^{b, A}	93.87 ± 0.35 ^{a, A, B}	77.02 ± 2.08 ^{b, A}
Control (70°C/7h)	63.50 ± 1.95 ^{a, A}	52.92 ± 4.65 ^{b, A, B}	28.20 ± 0.74 ^{a, A, B}	32.34 ± 1.97 ^{b, A}	91.94 ± 0.67 ^{a, A}	74.90 ± 0.89 ^{b, A}
Pectin coated (70°C/7h)	62.79 ± 2.24 ^{a, A}	56.68 ± 1.84 ^{b, A}	25.67 ± 2.98 ^{a, A}	30.11 ± 1.47 ^{b, A}	90.34 ± 0.74 ^{a, B}	77.50 ± 0.68 ^{b, B}
WPI + LBG coated (70°C/7h)	63.08 ± 2.52 ^{a, A}	51.27 ± 1.71 ^{b, B}	29.64 ± 1.95 ^{a, B}	35.75 ± 1.98 ^{b, B}	91.21 ± 0.80 ^{a, A}	73.96 ± 0.49 ^{b, A}

*Mean ± SD

**Means with the same lower case letter, for the same parameter, in the same line did not differ significantly at $p \leq 0.05$ according to the Tukey test

***Means with the same capital, for the same temperature drying, letter in the same column did not differ significantly at $p \leq 0.05$ according to the Tukey test

5. Conclusion

Edible coating of pectin and WPI+LBG did not affect the efficiency of drying and did not influence the reduction of water activity of samples during drying. The majority of coated pineapple presented the highest water diffusion coefficients during convective drying.

Convective drying reduced lightness of the pineapple, changed hue from yellowness to slightly orange and provided more intense color products. However, treatments acted differently on lightness of samples during air dehydration being that pectin coating provided the slightest change in lightness.

Impregnation of ascorbic acid during osmotic dehydration yield dried pineapple with high vitamin C content. Drying temperature had greater effect on vitamin C degradation than time of process.

However, even though good retention of ascorbic acid had been found in osmotic dehydrated samples during convective drying, coatings improved this retention.

Pectin and WPI-LBG coatings were effective barriers to oxygen during convective drying at 60 °C. However, samples coated with pectin presented higher vitamin C retention than with WPI-LBG, during drying at 70°C. Coating efficiency was attributed to permeability properties to oxygen.

These results highlight the potential of using edible coatings as an interesting alternative to improve the protection of nutrients during hot-air-drying.

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7. References

- ANINO, S. V.; SALVATORI, D. M.; ALZAMORA, S. M. (2006) Changes in calcium level and mechanical properties of apple tissue due to impregnation with calcium salts. **Food Research Internacional**, 39, 154-164.
- ANSORENA, M. R.; MARCOVICH, N. E.; ROURA, S. I.(2011) Impact of edible coatings and mild heat shocks on quality of minimally processed broccoli (*Brassica oleracea* L.) during refrigerated storage. **Postharvest Biology and Technology**, 59, 53–63.
- BENASSI, MT ; ANTUNES, A.J. (1988). A comparison of meta-phosphoric and oxalic acids as extractant solutions for the determination of vitamin C in selected vegetables. **Arquivos de Biologia e Tecnologia**, 31 (4), 507-513.
- BENÍTEZ, S.; ACHAERANDIO, I.; SEPULCRE, F.; PUJOLÀ, M. (2013) Aloe vera based edible coatings improve the quality of minimally processed 'Hayward' kiwifruit. **Postharvest Biology and Technology**, 81, 29-36.
- BONILLA, J.; ATARÉS, L.; VARGAS, M.; CHIRALT, A. (2012) Edible films and coatings to prevent the detrimental effect of oxygen on food quality: Possibilities and limitations. **Journal of Food Engineering**, 110, 208-213.
- BRANDELERO, R. P. H. ; VIEIRA, A. P. ; TELIS, V. R. N. ; TELIS-ROMERO, J.; YAMASHITA, F. (2005) Aplicação de revestimento comestível em abacaxis processados por

métodos combinados: isoterma de sorção e cinética de desidratação osmótica. **Ciência e Tecnologia de Alimentos**, 25(2), 285-290.

CASTELLÓ, M.L.; IGUAL, M.; FITO, P.J., CHIRALT, A. (2009) Influence of osmotic dehydration on texture, respiration and microbial stability of apple slices (var. granny smith). **Journal of Food Engineering**, v.91, n.1, p.1-9.

CHUTINTRASRI, B., NOOMHORM, A., 2007. Color degradation kinetics of pineapple puree during thermal processing. **Lebensmittel-Wissenschaft und-Technologie** 40, 300–306.

CORTELLINO, G.; PANI, P.; TORREGGIANI, D. (2011) Crispy air-dried pineapple rings: optimization of processing parameters. 11th International Congress on Engineering and Food (ICEF11). **Procedia Food Science**, 1, p. 1324-1330.

CRANK, J. (1975). **The Mathematics of Diffusion**, second ed. Clarendon Press-Oxford, London.

DANIEL, C ; WOOD, F (1980). **Fitting Equations to Data**, Revised Edition, John Wiley & Sons, New York, USA.

DOYMAZ, I (2010). Effect of citric acid and blanching pre-treatmentson drying and rehydration of Amasya red apples. **Food and Bioproducts Processing**, 88, 124-132.

DUAN, J.; WU, R.; STRIK, B. C.; ZHAO, Y.(2011) Effect of edible coatings on the quality of fresh blueberries (Duke and Elliott)under commercial storage conditions. **Postharvest Biology and Technology**, 59, 71–79

EL-AOUAR, AA, AZOUBEL, PM ; MURR, FEX (2003). Drying kinetics of fresh and osmotically pre-treated papaya (Carica papaya L.). **Journal of Food Engineering**, 59, 85-91.

FITO, P.; CHIRALT, A.; BETORET, N.; GRAS, M.; CHÁFER, M.; MARTÍNEZ-MONZÓ, J.; ANDRÉS, A.; VIDAL, D. (2001) Vacuum impregnation and osmotic dehydration in matrix engineering. Application in functional fresh food development. **Journal of Food Engineering**. 49,175-183.

GARCIA, CC, MAURO, MA ; KIMURA, M (2007). Kinetics of osmotic dehydration and air-drying of pumpkins (Cucurbita moschata). **Journal of Food Engineering**, 82 (3), 284-291.

GARCIA, C.C. **Avaliação da desidratação de mamão utilizando métodos combinados**. 173 f. Tese (Doutorado em Engenharia e Ciência de Alimentos) – Universidade Estadual Paulista “Júlio de Mesquita Filho”, São José do Rio Preto, 2012.

GARCÍA, M.; DÍAZ, R.; MARTÍNEZ, Y.; CASARIEGO, A. (2010) Effects of chitosan coating on mass transfer during osmotic dehydration of papaya. **Food Research International**, 43, 1656–1660.

GONTARD, N.; THIBAUT, R.; CUQ,B.; GUILBERT, S. (1996) Influence of Relative Humidity and Film Composition on Oxygen and Carbon Dioxide Permeabilities of Edible Films. **Journal Agriculture Food Chemistry**, 44, 1064 – 1069.

HAMNER, K. C.; NIGHTINGALE, G. T. (1945) Ascorbic acid content of pineapples as correlated with environmental factors and plant composition. **Journal of Food Science**, 11 (6), 535 – 541.

- HONG, S.-I., ; KROCHTA, J. M. (2006). Oxygen barrier performance of whey-protein-coated plastic films as affected by temperature, relative humidity, base film and protein type. **Journal of Food Engineering**, 77, 739-745.
- KAVAK AKPINAR, E.; MIDILLI, A.; BICER, Y. (2005) The first and second law analyses of thermodynamic of pumpkin drying process. **Journal of Food Engineering**, v.72, 320-331.
- KAYA, A.; AYADIN, O.; KOLAYLI, S. (2010) Effect of different drying conditions on the vitamin C (ascorbic acid) content of Hayward kiwifruits (*Actinidia deliciosa* Planch). **Food and Bioproducts Processing**, 88 (2-3), 165-173.
- LAGO-VANZELA, E. S.; NASCIMENTO, P.; FONTES, E. A. F.; MAURO, M. A.; KIMURA, M. (2013) Edible coatings from native and modified starches retain carotenoids in pumpkin during drying. **LWT - Food Science and Technology**, 50, 420-425
- LEE, S.H.; LABUZA, T.P. (1975) Destruction of ascorbic acid as a function of water activity. **Journal of Food Science**, 40, p. 370–373.
- LE TIEN, C.; VACHON, C.; MATEESCU, M. A.; LACROIX, M. (2001) Milk protein coating prevent oxidative browning of apples and potatoes. **Journal of food science**, 66 (4), 512 – 516.
- LIMA, A. M.; CERQUEIRA, M. A.; SOUZA, B. W. S.; SANTOS, E. C. M.; TEIXEIRA, J. A.; MOREIRA, R. A.; VICENTE, A. A. (2010) New edible coatings composed of galactomannans and collagen blends to improve the postharvest quality of fruits – influence on fruits gas transfer rate. **Journal of Food Engineering**, 97, 101-109.
- MANDALA, I.G.; ANAGNOSTARAS, E.F.; OIKONOMOU, C.K. (2005) Influence of osmotic dehydration conditions on apple air-drying kinetics and their quality characteristics. **Journal of Food Engineering**, v. 69, 307-316.
- MASKAN, M; (2001) Kinetics of color change of kiwifruits during hot air and microwave drying. **Journal of Food Engineering**, v.48, p. 169–175.
- MATUSKA, M.; LENART, A.; LAZARIDES, H.N. (2006) On the use of edible coatings to monitor osmotic dehydration kinetics for minimal solids uptake. **Journal of Food Engineering**, 72, 85-91.
- MCHUGH, T.H.; KROCHTA, J.M. In: Edible coatings and films to improve food quality. **Permeability properties of edible films**. Edited by: J.M. Krochta. Lancaster: USA, 1994, p. 139-187.
- MCMINN, W.A., MAGEE, T.R.A., 1997. Physical characteristics of dehydrated potatoes—Part I. **Journal of Food Engineering** 33, 37–48.
- MURPHY, EW, CRINER, PE, ; GRAY, BC (1975). Comparisons of methods for calculating retentions of nutrients in cooked foods. **Journal of Agricultural and Food Chemistry**, 23, 1153-1157.
- NICOLETI, J. F.; TELIS-ROMERO, J.; TELIS, V. R. N. (2001) Air-drying of fresh and osmotically pre-treated pineapple slices: fixed air temperature versus fixed slice temperature drying kinetics. **Drying technology**, 19 (9), 2175-2191.
- OMS-OLIU, G.; SOLIVA-FORTUNY, R.; MARTÍN-BELLOSO, O. (2008) Using polysaccharide-based edible coatings to enhance quality and antioxidant properties of fresh-cut melon. **LWT – Food Science and Technology**, 41, 1862-1870.

- ORIKASA, T.; WU, L.; SHIINA, T.; TAGAWA, A. (2008) Drying characteristics of kiwifruit during hot air drying. **Journal of Food Engineering**, 85, 303–308
- PÉREZ-GAGO, M.B.; SERRA, M.; ALONSO, M.; MATEOS, M.; DEL RÍO, M.A. (2005). Effect of whey protein and hydroxypropyl methylcellulose based edible composite coatings on color change of fresh-cut apples. **Postharvest Biology Technology** 36, 77–85.
- PÉREZ-GAGO, M.B.; SERRA, M.; DEL RÍO, M.A. (2006) Color change of fresh-cut apples coated with whey protein concentrate-based edible coatings. **Postharvest Biology and Technology**, 39, 84–92.
- RAMALLO, L. A.; MASCHERONI, R. H. (2004) Prediction and determination of ascorbic acid content during pineapple drying. **Drying - Proceedings of the 14th International Drying Symposium (IDS 2004)**, C, 1984-1991.
- RAMALLO, L. A.; MASCHERONI, R. H. (2012) Quality evaluation of pineapple fruit during drying process. **Food and bioproducts processing**, 90, 275-283.
- RAMESH, M. N.; WOLF, W.; TEVINI, D.; JUNG, G. (2001). Influence of processing parameters on the drying spice paprika. **Journal of Food Engineering**, 49, p.63-72.
- RAMOS, O. L., REINAS, I., SILVA, S. I., FERNANDES, J. C., CERQUEIRA, M. A., PEREIRA, R. N., VICENTE, A. A., FATIMA POCAS, M., PINTADO, M. E., ; XAVIER MALCATA, F. (2013). Effect of whey protein purity and glycerol content upon physical properties of edible films manufactured therefrom. **Food Hydrocolloids**, 30(1), 110-122.
- RATTANATHANALERK, M.; CHIEWCHAN, N.; SRICHUMPOUNG, W. (2005) Effect of thermal processing on the quality loss of pineapple juice. **Journal of Food Engineering**, 66, 259–265
- ROCHA, C.; TEIXEIRA, J.A.; HILLIOU, L.; SAMPAIO, P.; GONÇALVES, M. P. (2009) Rheological and structural characterization of gels from whey protein hydrolysates/locust bean gum mixed systems. **Food Hydrocolloids**, 23, 1734–1745.
- RIVA, M.; CAMPOLONGO, S.; LEVA, A.A.; MAESTRELLI, A.; TORREGGIANI, D. (2005) Structure-property relationships in osmo-air-dehydrated apricots cubes. **Food Research International**, 38, 533–542.
- SANJINEZ-ARGANDOÑA, E.J.; CUNHA, R.L.; MENEGALLI, F.C.; HUBINGER, M.D. (2005) Evaluation of total carotenoids and ascorbic acid in osmotic pretreated guavas during convective drying. **Italian Journal of Food Science**, 17 (3), 305–314.
- SANTOS, P. H. S.; SILVA, M. A. (2008) Retention of vitamin C in drying processes fo fruits and vegetables – A review. **Drying Technology**, 26 (12), 1421- 1437.
- SHI, J.; LE MAGUER, M.; KAKUDA, Y.; LIPTAY, A.; NIEKAMP, F. (1999). Lycopene degradation and isomerization in tomato dehydration, **Food Research International**, 32, 15-21.
- SHIGEMATSU, E, EIK, NM, KIMURA, M ; MAURO, MA (2005). Influência de pré-tratamentos sobre a desidratação osmótica de carambolas. **Ciência e Tecnologia de Alimentos**, 25 (3), 536-545.
- SILVA, K. S.; FERNANDES, M. A.; MAURO, M. A. (2013) Osmotic dehydration of pineapple with impregnation of sucrose, calcium and ascorbic acid. **Food Bioprocess Technology**, (Preprint online), 2013. <http://dx.doi.org/10.1007/s11947-013-1049-0>

- SILVA, K. S.; MAURO, M. A.; COSTA, M. J.; GONÇALVES, M. P.; ROCHA, C. M. R. Caracterização de filmes de misturas de proteína do soro de queijo com goma de alfarroba. In.: 11° ENCONTRO DE QUÍMICA DOS ALIMENTOS, Bragança, Portugal, 2012, p.40.
- SINGLETON, V. L.; GORTNER, W. A. (1965) Chemical and physical development of the pineapple fruit II. Carbohydrate and acid constituents. **Journal of Food Science**, 30 (1), 19 – 23.
- SONG, Y.; LIU, L.; SHEN, H.; YOU, J.; LUO, Y. (2011) Effect of sodium alginate-based edible coating containing different anti-oxidants on quality and shelf life of refrigerated bream (*Megalobrama amblycephala*). **Food Control**, 22, 608-615.
- TALENS, P.; PÉREZ-MASÍA, R; FABRA, M. J.; VARGAS, M. CHIRALT, A. (2012) Application of edible coatings to partially dehydrated pineapple for use in fruit-cereal products. **Journal of Food Engineering**, 112, 86-93.
- UDDIN, M.S.; HAWLADER, M.N.A.; ZHOU, L. (2001) Kinetics of ascorbic acid degradation in dried kiwifruits during storage. **Drying Technology**, 19, 437–446.
- VALERO, D.; DÍAZ-MULA, H. M.; ZAPATA, P. J.; GUILLÉN, F.; MARTÍNEZ-ROMERO, D.; CASTILLO, S.; SERRANO, M. (2013) Effects of alginate edible coating on preserving fruit quality in four plum cultivars during postharvest storage. **Postharvest Biology and Technology**, 77, 1–6.
- VARGAS, M., PASTOR, C., CHIRALT, A., MCCLEMENTS, D.J.; GONZÁLEZ MARTÍNEZ, C. (2008) Recent advances in edible coatings for fresh and minimally processed fruits. **Critical Reviews in Food Science and Nutrition**, 48, 496-511.
- VEGA-GÁLVEZ, A.; LEMUS-MONDACA, R.; BILBAO-SÁINZ, C.; FITO, P.; ANDRE'S, A. (2008) Effect of air drying temperature on the quality of dehydrated dried red bell pepper (var. Lamuyo). **Journal of Food Engineering**, 85, 42–50.
- VEGA-MERCADO, H.; GONGORA-NIETO, M.M.; BARBOSA-CANOVAS, G.V. (2001) Advances in dehydration of foods. **Journal of Food Engineering**, vol. 49, p. 271-289.
- YAN, Z.; SOUSA-GALLAGHER, M.J.; OLIVEIRA, F.A.R. (2008) Sorption isotherms and moisture sorption hysteresis of intermediate moisture content banana. **Journal of Food Engineering**, 86, 342–348.
- WAWIRE, M., OEY, I., MATHOOKO, F., NJOROGE, C., SHITANDA, D.; HENDRICKX, M. (2011), Thermal Stability of Ascorbic Acid and Ascorbic Acid Oxidase in African Cowpea Leaves (*Vigna unguiculata*) of Different Maturities, **Journal of Agriculture and Food Chemistry**, Vol. 59, pp. 1774–1783.
- ZANONI, B.; PERI, C.; NANI, R.; LAVELLI, V. (1999) Oxidative heat damage of tomato halves as affected by drying. **Food Research International**, 31 (5), 395–401.
- ZHAO, Y.P.; CHANG, K.C. (1995) Sulfite and starch affect color and carotenoids of dehydrated carrots (*Daucus carota*) during storage. **Journal of Food Science**, Chicago, 60, 324-347.

CONCLUSÕES GERAIS

A adição de lactato de cálcio na solução osmótica inibiu a incorporação de sacarose, aumentou a eficiência do processo, mas não alterou a claridade e a cromaticidade das amostras. A impregnação de cálcio no tecido do abacaxi não melhorou a textura das amostras quando comparadas às amostras *in natura*, mas melhorou a firmeza das amostras desidratadas em soluções ternárias contendo 50% de sacarose.

A adição de ácido ascórbico na solução ternária acentuou a perda de água das amostras e aumentou a taxa de incorporação de sacarose, cálcio e vitamina C no abacaxi durante o processo.

As difusividades da água e da sacarose diminuíram com a presença de cálcio em soluções ternárias, contudo o aumento da concentração de lactato de cálcio nessas soluções aumentou a difusividade dos componentes. A adição de ácido ascórbico nas soluções ternárias aumentou significativamente a difusividade de todos os componentes presentes na solução desidratante.

Foi observado que o efeito sinérgico entre WPI e LBG foi reforçado com o tempo de tratamento térmico empregado na fabricação do filme comestível. A sinergia entre os componentes aumentou a permeabilidade ao vapor de água, aumentou a flexibilidade do filme, reduziu a solubilidade e a permeabilidade ao oxigênio, ao gás carbônico e à luz.

Coberturas de pectina ou WPI+LBG aplicadas em amostras de abacaxi desidratadas osmoticamente não aumentaram a resistência à desidratação durante a secagem convectiva, todavia reduziram a oxidação da vitamina C das amostras durante o processo de secagem com ar aquecido. A aplicação da pectina proporcionou menores alterações na claridade do produto, enquanto que amostras sem cobertura e com cobertura de WPI+LBG resultaram mais escuras.

PROPOSTAS PARA ESTUDOS FUTUROS

Estudos de microscopia poderiam contribuir para um melhor entendimento quanto à influência do ácido ascórbico e do lactato de cálcio sobre a integridade da membrana celular durante os tratamentos osmóticos.

Estudos de armazenamento visando avaliação do conteúdo nutricional das frutas secas ao longo do tempo, assim como sua segurança microbiológica, também seriam importantes para a implementação desses processos. O papel desempenhado pela cobertura comestível sobre as propriedades do abacaxi seco também deve ser estudado durante o armazenamento. O aproveitamento das soluções osmóticas também tem papel decisivo na implementação dos processos e, portanto, deve ser estudado. A avaliação sensorial do produto final também será uma análise importante para detectar o comportamento do consumidor em relação a produtos cobertos com pectina ou WPI+LBG e desidratados.

APÊNDICE I:

MATERIAIS E METODOLOGIAS

1. Matéria prima, amostragem e corte

A matéria prima utilizada foi abacaxi *Ananás comosus* (L.) Merrill da cultivar Pérola, adquirido no CEASA de São José do Rio Preto. Os abacaxis utilizados apresentavam casca de cor verde, levemente amarelada, massa aproximada de 1,2 kg, sólidos solúveis variando entre 10° e 15° Brix, altura e diâmetro aproximados de 24,0 e 10,5 cm, respectivamente. Em cada ensaio de DO foram utilizados entre 9 e 10 abacaxis, escolhidos aleatoriamente de um total de 50 frutos selecionados.

Para a higienização dos frutos, cada abacaxi foi lavado com água e detergente tendo sua superfície esfregada com o auxílio de uma escova de nylon. Em seguida, os abacaxis foram sanitizados em solução de hipoclorito de sódio (100 mL de hipoclorito de sódio para 10 L de água) por 5 minutos, lavados em água corrente e secos à temperatura ambiente. Após a higienização e sanitização, os abacaxis foram descascados manualmente e suas pontas foram descartadas. As peças foram fatiadas (1 cm de espessura) com o auxílio de um fatiador elétrico, marca Eco (Figura 1) e cortadas com auxílio de um molde (Figura 2) afiado, construído em metal. As amostras (Figura 3) foram colocadas em saco plástico, homogeneizadas e selecionadas, aleatoriamente, para os ensaios.



Figura 1: Obtenção das fatias de abacaxi através do fatiador elétrico

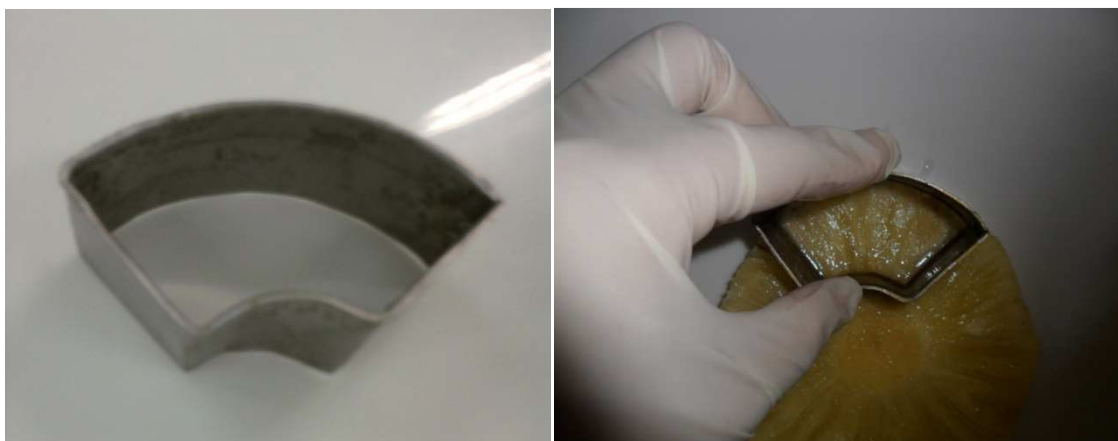


Figura 2: Molde metálico e obtenção da amostra no formato do molde metálico



Figura 3: Formato da amostra obtida

2. Desidratação Osmótica

2.1 Seleção dos tratamentos osmóticos

Ensaio preliminares foram realizados com o objetivo de verificar a influência da adição de lactato de cálcio e do tempo de tratamento sobre a impregnação de cálcio nas amostras de abacaxi. Para tanto, aproximadamente 60g de amostras de abacaxi, pesadas em balança semi-analítica, foram imersas em 600g de solução de lactato de cálcio (2 e 4%), em recipientes de vidro de 800 ml (Figura 4). Em seguida, o conjunto foi colocado em incubadora refrigerada (Marconi, modelo MA 830/A) (Figura 4) com plataforma de agitação orbital (32 rpm) à temperatura controlada de 27°C por 2, 4 e 6 horas. O procedimento foi realizado em duplicata. Ao final desse período, as fatias eram lavadas por 10 segundos em água destilada,

secas com papel absorvente e trituradas para determinar o teor de água e o teor de cálcio nas amostras.



Figura 4: Recipiente de vidro de 800ml e incubadora refrigerada

2.2 *Ensaio de Desidratação Osmótica*

As amostras, previamente pesadas, foram dispostas em quatro cestos construídos em tela de nylon, com dois compartimentos divididos pela mesma tela. Cada cesto continha 26 amostras, perfazendo aproximadamente 350g (Figura 5). Os quatro cestos foram totalmente mergulhados em 20 kg de solução em uma cuba de aço inoxidável de dimensões 30x30x35 cm, com camisa externa (Figura 6 e 7). A relação entre fruta e solução foi de 1:14 (1,4kg de amostra/ 20kg de solução). As soluções foram mantidas sob agitação constante de 1850 rpm, conduzida por um agitador mecânico com potência de 1,6KW (Marconi, modelo MA-261) e hélice naval (10 cm de diâmetro). A temperatura da solução osmótica foi mantida a 27°C através de água circulando na camisa externa, bombeada a partir de um banho ultratermostatizado (Marconi, modelo MA-184) que dispõe de refrigeração. Após o tempo de processamento, as fatias foram retiradas das soluções, lavadas em água destilada por 10 segundos e secas em papel absorvente. A temperatura utilizada nos ensaios de DO foi aproximadamente a ambiente (27°C).



Figura 5: Amostras distribuídas nos cestos de nylon utilizados no processo de desidratação osmótica



Figura 6: Equipamento utilizado na desidratação osmótica:
cuba + banho termostático

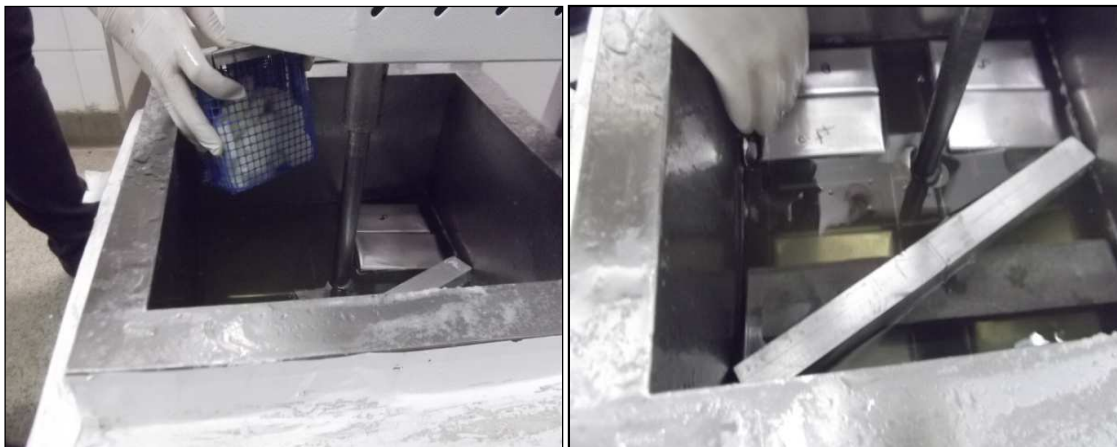


Figura 7: Amostras sendo colocadas na cuba utilizada para o processo de desidratação osmótica

2.3 Desidratação osmótica com impregnação de cálcio

Os ensaios de desidratação osmótica foram realizados por 1, 2, 4 e 6 horas em soluções aquosas de sacarose (controle) e sacarose-lactato de cálcio, variando a concentração dos componentes. As concentrações estudadas foram 40 e 50 % de sacarose, com ou sem lactato de cálcio (2 e 4%). A solução de 60% de sacarose foi testada, porém, devido à baixa solubilidade do lactato de cálcio nessa concentração de sacarose, seu uso foi inviabilizado. Análise de sólidos totais, cor, textura, atividade de água, cálcio, açúcares totais e redutores das amostras foram realizados antes e após cada tratamento.

A escolha dos melhores parâmetros do processo osmótico foi baseada na otimização da impregnação de cálcio na amostra e na eficiência de desidratação osmótica (perda de água / ganho de solutos).

2.4 Desidratação osmótica com impregnação de ácido ascórbico

A desidratação osmótica com impregnação de ácido ascórbico foi realizada após a definição da melhor concentração de lactato de cálcio para a impregnação de cálcio e a eficiência do processo.

Estudou-se a cinética da impregnação de vitamina C e sua influência sobre as propriedades físico-químicas do abacaxi desidratado osmoticamente. Com este estudo foi possível definir e fixar a concentração deste composto para os ensaios finais de desidratação

osmótica. Nestes, fixou-se as concentrações de lactato de cálcio e de ácido ascórbico em, respectivamente, 2% e 4% e avaliou-se a impregnação dos mesmos nas duas concentrações de sacarose utilizadas no projeto (40% e 50% sacarose). Para cada um destes ensaios, foram realizadas análises de sólidos totais, cálcio, ácido ascórbico e açúcares totais e redutores das amostras antes e após cada tempo de desidratação osmótica.

3. Preparo da Cobertura Comestível e aplicação

3.1 Preparo da cobertura de pectina e aplicação

Utilizou-se pectina amidada (grau de amidação: 0,17) de baixa metoxilação (grau de metoxilação: 0,34) GRINDSTED[®] LA 210 (Danisco - Brasil) a 2% p/p para recobrir as fatias de abacaxi desidratado osmoticamente. A solução foi preparada a 70 °C. As frutas foram dispostas em cestos e imersas na solução de pectina mantida a 40 °C em um banho termostaticado. Solução a 1% p/p de lactato de cálcio penta-hidratado grau alimentício em pó da PURAC Sínteses – Brasil foi usada como agente gelificante por imersão (30 s) das fatias cobertas. Em seguida, as amostras foram lavadas em água destilada por 30 s para remover o excesso de cobertura e dispostas sobre tela de nylon até sua utilização nos experimentos.

3.2 Preparo da cobertura de WPI + LBG e aplicação

A cobertura de WPI + LBG foi preparada com 5% p/p de proteína isolada do soro de leite (WPI); 2% p/p glicerol; 0,05% p/p goma de alfarroba (LBG) preparada previamente; NaCl 20% p/v para correção da força iônica para 50 mM e água destilada. Primeiramente adicionou-se o WPI, o glicerol, a goma, o NaCl e uma parcela da água destilada e deixou-se a mistura sob agitação por 3 horas, em seguida corrigiu-se o pH para 7, acrescentou-se o restante da água destilada e deixou-se a solução em agitação por mais 1 hora. Posteriormente realizou-se o tratamento térmico, que consiste em aplicação de temperatura de 75°C durante 10 minutos, sendo resfriada logo em seguida, até temperatura de 40°C, para aplicação nas amostras.

As frutas foram dispostas em cestos e imersas na solução de WPI+LBG por 1 minuto e em seguida, as amostras foram lavadas em água destilada por 30s para remover o excesso de cobertura e dispostas sobre tela de nylon até sua utilização nos experimentos.

4. Secagem convectiva

Os experimentos de secagem foram conduzidos em dois secadores de leito fixo com convecção forçada de ar aquecido, equipado com ventilador centrífugo (motor de 1.5 CV), velocidade do ar controlada por um inversor de frequência (WEG, CWF10 - Brasil) conectado ao motor do ventilador. O ar é aquecido com resistências elétricas. Um controlador digital micro-processado (Novus, model N440 - Brasil) com um termopar tipo J é utilizado para controlar a temperatura do ar. A câmara de secagem tem área seccional de $13,86 \times 10^{-2} \text{ m}^2$ e o fluxo de ar incide paralelamente às amostras, dispostas sobre bandejas de metal construídas em tela. Um anemômetro de fio quente é utilizado para determinar a velocidade média do ar dentro da câmara de secagem. Quatro sensores tipo PT100 e um sensor de umidade (ImPac[®], DO9861T-R1 - Itália) estão conectados a um sistema de aquisição de dados (ImPac[®]) para transmissão dos dados a um computador, onde temperatura e umidade relativa são registrados ao longo do tempo num programa compatível com planilhas eletrônicas Excel da Microsoft.

5. Métodos analíticos

5.1. Determinação dos Sólidos Totais

Os sólidos totais foram determinados em triplicata a 60 °C em estufa a vácuo, 10 kPa, até atingir peso constante.

5.2. Determinação dos Açúcares

Os açúcares totais e redutores foram determinados em triplicata por titulação de oxidação-redução (WILLIAM, 1970) em equipamento Redutec (TECNAL – Brasil).

5.3. Determinação da Atividade de Água

A atividade de água das amostras foi determinada em triplicata a 25 °C em aparelho modelo Aw Sprint da Novasina (Axair Ltd. – Switzerland) (Figura 8).



Figura 8: Equipamento da Novasina para análise da atividade de água

5.4. Determinação da Cor

A cor das amostras de abacaxi foi determinada através do espectrofotômetro modelo ColorFlex45/0 (HunterLab, Estados Unidos) (Figura 9). Quatro amostras foram acomodadas em um copo de vidro em duas camadas, de maneira a não sobrar espaços não cobertos, em seguida o copo de vidro foi tampado e colocou-se um copo plástico preto para a leitura da cor. O software Universal versão 4.10 foi o utilizado nas análises do ColorFlex, com as configurações: iluminante D65, observador a 10° e leitura dos valores absolutos de L* (lightness-claridade), a* (redness-avermelhado) e b* (yellowness-amarelado). As análises da cor foram realizadas em duplicada, sendo que para cada análise foram realizadas 4 medidas, girando o copo de medição de 90° em 90°.



Figura 9: ColorFlex. Do lado esquerdo com o copo de vidro e do lado direito com o copo plástico preto cobrindo o de vidro

5.5. Determinação da textura

A textura foi determinada em 10 réplicas de amostras através da avaliação da tensão na ruptura, realizada em um texturômetro Universal (TA-XT2i Texture Analyser, Stable Micro System, Surrey, UK.) (Figura 10). O método utilizado foi o de medir a força de compressão, mantida até o momento de ruptura da amostra (Measure Force in Compression – Hold Until Time). As amostras frescas e desidratadas osmoticamente foram comprimidas individualmente até 60% de deformação por 10s a uma taxa de 5 mm.s^{-1} , através de um *probe* acrílico de 35 mm de diâmetro.

Os dados da força e altura fornecidos pelo equipamento foram convertidos à tensão de Hencky, de acordo com as equações:

$$\sigma_H = \frac{F(t)}{A(t)} \quad (1)$$

$$A(t) = \frac{A_0 H_0}{H(t)} \quad (2)$$

sendo: σ_H = tensão de Hencky (Pa); $F(t)$ = força (N) em função do tempo t (s); $A(t)$ = área (m^2) em função do tempo (s); A_0 = área do *probe* (supondo-se que a superfície do *probe* recobre toda a amostra) (m^2); H_0 = altura inicial da amostra (m) e $H(t)$ = altura da amostra (m) em função do tempo(s).



Figura 10: Texturômetro

5.6. Determinação da Vitamina C

A vitamina C das fatias frescas e processadas de abacaxi foi determinada em duplicata por titulação conforme metodologia proposta pela AOAC modificada por Benassi e Antunes (1988). 25 g de amostras foram homogeneizadas em 50 mL de solução extratora (ácido oxálico a 2% p/p) em equipamento Turratec (TECNAL, modelo TE-102) por 1 min. Uma alíquota de 20 g foi volumetricamente diluída com solução extratora a 50 mL e 10 mL da solução diluída foi titulada com 2,6-diclorofenolindofenol.

5.7. Determinação do cálcio

A determinação de cálcio foi realizada em espectrômetro de absorção atômica com chama modelo SpectrAA 50B da Varian (Mulgrave, Austrália), segundo metodologia adaptada de AOAC (1995).

A preparação das amostras para a análise se fez primeiramente pela digestão das mesmas por via seca. Cerca de 40g de amostras frescas e 10g de processadas, previamente trituradas, foram pesadas em duplicata em cápsulas de porcelana e levadas à estufa a 105°C até secarem completamente. Depois as amostras foram queimadas em bico de Bunsen com tela de amianto até cessar o desprendimento de fumaça. Então as cápsulas foram colocadas em mufla e seguiu-se um aquecimento gradativo até 550°C por no máximo 4 horas. Após este período as cápsulas foram deixadas em dessecadores para esfriarem. Em cada cápsula, as cinzas foram dissolvidas com 20 mL de ácido clorídrico 0,1M. Transferiu-se, então, 5 mL

desta solução para um balão volumétrico de 10 mL e completou-se o volume com ácido clorídrico 0,1M. As soluções-padrão foram preparadas com cloreto de cálcio P.A. com concentrações conhecidas (20, 100, 200, 400, 800mg/L) para construção da curva padrão de análise de cálcio.

No equipamento, primeiramente registrou-se a curva padrão através das medidas de absorvância das soluções-padrão. Programou-se o equipamento para fornecer leitura das amostras diretamente em concentração. A leitura das amostras necessariamente deveria estar contida na faixa linear de trabalho do equipamento.

APÊNDICE II:**CÁLCULOS DO CONTEÚDO E DA RETENÇÃO DA VITAMINA C**

1. *Cálculo do conteúdo de vitamina C das frutas frescas, desidratadas osmoticamente e cobertas.*

Para calcular o conteúdo de vitamina C nas *frutas frescas, desidratadas osmoticamente e cobertas* utilizou-se a Equação 1:

$$\frac{Vit\ C\ (g)}{100\ g\ amostra} = \left[\frac{V_{DCFI\ amostra}\ (mL)}{V_{DCFI\ padrão}\ (mL)} \frac{100\ (g)}{m_{amostra}\ (g)} \frac{(m_{solvente} + m_{amostra})\ (g)}{m_{extrato}\ (g)} \frac{50\ (mL)}{V_{aliquota}\ (mL)} \right] \quad (1)$$

em que: *Vit C* representa o conteúdo de vitamina C, em g/100 g de amostra; $V_{DCFI\ amostra}$ é o volume de 2,6-diclorofenolindofenol 0,01 % gasto na titulação da amostra; $V_{DCFI\ padrão}$ é o volume de 2,6-diclorofenolindofenol 0,01 % gasto na titulação do padrão de vitamina C (125 mg de ácido ascórbico P.A. diluídos em 50 mL de ácido oxálico 2% p/V); $m_{amostra}$ corresponde à massa da amostra, em g; $m_{solvente}$ corresponde à massa, em g, de 50 mL do solvente (aproximadamente 50 g); $m_{extrato}$ corresponde à massa de amostra, em g, tomada após a diluição em 50 mL de solvente (aproximadamente 20 g) e $V_{aliquota}$ é o volume de amostra nas titulações (5 mL).

2. *Cálculo de retenção da vitamina C após a secagem convectiva*

A retenção da vitamina C foi determinada em relação à amostra pré-tratada osmoticamente e coberta. O conteúdo médio de vitamina C das amostras foi calculado segundo a Equação 1. Os resultados foram expressos em base seca e o valor obtido para as frutas após a secagem foi dividido pelo das amostras antes da secagem (pré-tratadas osmoticamente e cobertas ou não).

APÊNDICE III:

RESULTADOS PRELIMINARES

Seleção dos tratamentos osmóticos com adição de lactato de cálcio

O teor de cálcio, bem como o de umidade das amostras impregnadas com cálcio em solução de lactato de cálcio por diferentes tempos estão presentes na Tabela 1.

Tabela 1: Resultados do teor de cálcio e de umidade para cada amostra na determinação do tempo de impregnação de cálcio

Amostras	Umidade	Teor de Cálcio
	(g água/g produto fresco)	(g Ca/100g produto)
Fresca	0,8485 ± 0,0005	0,0031 ± 0,0002
2% Lactato de Cálcio (2h)	0,8948 ± 0,0013	0,0444 ± 0,0090
2% Lactato de Cálcio (4h)	0,9017 ± 0,0014	0,0559 ± 0,0055
2% Lactato de Cálcio (6h)	0,9037 ± 0,0032	0,0696 ± 0,0031
4% Lactato de Cálcio (2h)	0,8864 ± 0,0005	0,0535 ± 0,0073
4% Lactato de Cálcio (4h)	0,8870 ± 0,0026	0,0727 ± 0,0108
4% Lactato de Cálcio (6h)	0,8912 ± 0,0003	0,0898 ± 0,0008

Os valores mais elevados de impregnação de cálcio foram verificados em ensaios com duração de 6 horas, em ambas as concentrações. A maior impregnação de cálcio foi obtida com 4% de lactato de cálcio (0,0898g ± 0,0008g). Portanto, como se espera obter um produto com alto teor de cálcio, o tempo de 6 horas será utilizado como tempo máximo no estudo da cinética de desidratação osmótica. Tempos de desidratação osmótica superiores a 6 horas poderiam impregnar maiores quantidades de cálcio nas amostras, porém as taxas de transferência de água na desidratação osmótica geralmente são muito baixas após uma ou duas horas de processo, tornando o processo pouco eficiente.