**PAULO SÉRGIO DE ANDRADE**

# WATER SORPTION, DIFFUSION, AND PERMEATION BEHAVIOR IN MODIFIED STARCH-POLYVINYL ALCOHOL POLYMER BLENDS FOR FLEXIBLE FOOD PACKAGING

**LAVRAS – MG**
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Trabalho de Conclusão de Curso apresentado à Universidade Federal de Lavras, como parte das exigências do Curso de Engenharia de Alimentos, para a obtenção do título de Bacharel.

Profa. Dra. Marali Vilela Dias
Orientadora

Ma. Bruna Rage Baldone Lara
Coorientadora

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**COMPORTAMENTO DE SORÇÃO, DIFUSÃO E PERMEAÇÃO DE ÁGUA EM BLENDAS POLIMÉRICAS DE AMIDO MODIFICADO-ÁLCOOL POLIVINÍLICO PARA EMBALAGENS FLEXÍVEIS DE ALIMENTOS**

> Trabalho de Conclusão de Curso apresentado à Universidade Federal de Lavras, como parte das exigências do Curso de Engenharia de Alimentos, para a obtenção do título de Bacharel.

APROVADO em 04 de maio de 2021.
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*Aos meus pais, Joaquim (in memoriam) e*
*Teresinha, que sempre acreditaram no poder*
*de realização dos meus sonhos.*

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*"O conhecimento emerge apenas através da invenção e da reinvenção, através da inquietante, impaciente, contínua e esperançosa investigação que os seres humanos buscam no mundo, com o mundo e uns com os outros."*

*(Paulo Freire)*

# RESUMO

Na busca de novos materiais competitivos e mais sustentáveis para embalar alimentos, muitos estudos avaliam o uso de polímeros biodegradáveis de fontes renováveis, através da sua mistura com outros polímeros e com a adição de reticulantes. Esta tendência está relacionada à resistência à degradação de embalagens plásticas comerciais somada ao seu descarte inadequado pós-consumo, o que têm causado danos ao meio ambiente e, principalmente, aos animais aquáticos. De modo a diminuir os impactos negativos dos plásticos convencionais sem perder suas ótimas características, investigou-se a confecção de filmes flexíveis de amido de mandioca e álcool polivinílico (PVOH) bem como suas blendas pelo método *casting*. As concentrações em volume utilizadas na elaboração dos filmes foram de 100S0P, 90S10P, 80S20P, 70S30P e 0S100P (dadas em % de solução filmogênica de amido (S) e % de solução filmogênica de PVOH (P)), com adição de 8 % (em relação à massa dos polímeros) de ácido cítrico como agente reticulante. Após a secagem, os filmes flexíveis foram caracterizados em relação às propriedades mecânicas de tração e punctura e ao comportamento de sorção, difusão e permeação da água. Os resultados mostraram que a inserção de 10, 20 e 30 % de PVOH às blendas as tornaram cerca de 24, 58 e 80 % mais flexíveis e 36, 71 e 83 % mais resistentes à punctura, respectivamente, comparadas ao filme de amido. Entretanto, a inserção de 20 % ou mais de PVOH mais que duplicou o teor de umidade na monocamada ($M_0$) das blendas, em relação ao filme de amido, o qual apresentou $M_0$ de 0,11 g $H_2O$/g filme, conforme mostrou o modelo de isoterma de sorção de umidade GAB, que melhor se ajustou aos dados. Além disso, a inserção de 20 e 30 % de PVOH aumentou significativamente ($p<0,05$) o coeficiente de difusão da água em cerca de 163 e 300 %, respectivamente, em comparação ao filme de amido. Assim, a inserção de 10 % de PVOH foi mais vantajosa, pois reforça as propriedades mecânicas da blenda, com o aumento significativo ($p<0,05$) de 24 % na flexibilidade, 57 % na penetração da sonda e 36 % na resistência à punctura, sem aumentar sua hidrofilicidade ou diminuir suas propriedades de barreira ao vapor de água, em comparação ao filme de amido. Isto resulta em um maior controle da entrada e saída indesejada de vapor de água, evitando reações de degradação e alterações físico-químicas e sensoriais nos alimentos, e promove uma maior resistência da embalagem quando esta está em contato com materiais perfurantes, o que assegura sua integridade.

**Palavras-chave:** Embalagem Biopolimérica para Alimentos. Amido de Mandioca. Álcool Polivinílico. Permeação da Água.

# ABSTRACT

In the search for new competitive and more sustainable materials for food packaging, many studies evaluate the use of biodegradable polymers from renewable sources by blending them with other polymers and adding cross-linkers. This trend is related to the resistance to degradation of commercial plastic packaging added to its inadequate post-consumption disposal, which has caused damage to the environment and, especially, to aquatic animals. To reduce the negative impacts of conventional plastics without losing their optimum characteristics was investigated the production of flexible cassava starch and polyvinyl alcohol (PVOH) films and their blends by the casting method. The volume concentrations used in the films elaboration were 100S0P, 90S10P, 80S20P, 70S30P, and 0S100P (given in % starch film solution (S) and % PVOH film solution (P)), with the addition of 8 % (based on polymers mass) of citric acid as cross-linking agent. After drying, the flexible films were characterized concerning tensile and puncture mechanical properties and water sorption, diffusion, and permeation behavior. The results showed that the insertion of 10, 20, and 30 % of PVOH to the blends made them about 24, 58, and 80 % more flexible and 36, 71, and 83 % more puncture-resistant, respectively, compared to the starch film. However, the insertion of 20 % or more of PVOH more than doubled the monolayer moisture content ($M_0$) of the blends compared to the starch film, which showed $M_0$ of 0.11 g $H_2O$/g film, by the GAB moisture sorption isotherm model, which best fitted the data. Also, the insertion of 20 and 30 % of PVOH significantly ($p<0.05$) increased the water diffusion coefficient by about 163 and 300 %, respectively, compared to the starch film. Thus, the 10 % of PVOH insertion was more advantageous as it strengthens the mechanical properties of the blends, with the significant ($p<0.05$) increase of 24 % in flexibility, 57 % in probe penetration, and 36 % in puncture resistance, without increasing its hydrophilicity or decreasing its water vapor barrier properties, compared to the starch film. That results in greater control of unwanted water vapor ingress and egress, preventing degradation reactions and physicochemical and sensory alterations in the food, and promotes greater package strength when it is in contact with perforating materials, ensuring its integrity.

**Keywords:** Biopolymer Food Packaging. Cassava Starch. Polyvinyl Alcohol. Water Permeation.

# SUMÁRIO

**PRIMEIRA PARTE**

# 1 APRESENTAÇÃO

As embalagens desempenham imprescindíveis funções na indústria alimentícia e atuam desde as etapas de fabricação até a entrega dos alimentos ao consumidor. Dentre as atribuições principais, as embalagens para alimentos e bebidas são responsáveis pela proteção contra choques e compressões durante o transporte. Também promovem a conservação e integridade dos alimentos, podendo agir como barreira à umidade, oxigênio e/ou luz, impedindo a entrada e desenvolvimento de microrganismos e garantindo qualidade e segurança ao produto. As embalagens, através de seu rótulo, agem como meios informativos para os consumidores, dando suporte às informações legais e orientações de consumo, e também para os seus produtores e distribuidores, ajudando na gestão de estoque e rastreabilidade. Por fim, mas não menos importante, as embalagens trazem conveniência por meio da facilidade de manuseio, estocagem, abertura e dosagem e ainda podem ser utilizadas para aquecer, cozinhar e servir os alimentos.

Para assegurar estas funcionalidades, são explorados os mais variados tipos de materiais para compor a embalagem dos produtos alimentícios, uma vez que estes possuem variadas características e finalidades. Alguns materiais mais convencionais cumprem muito bem algumas destas funções, mas deixam a desejar em outras. Como é o caso do vidro, por exemplo, que possui excelentes impermeabilidade e transparência, mas é frágil e pesado, o que exige maior atenção durante o transporte e manuseio. Então, com o avanço da tecnologia e com a busca por embalagens mais versáteis e funcionais, surgiram novos materiais mais promissores e alternativos e, entre eles, destacam-se os plásticos, os quais revolucionaram não só o mundo das embalagens, mas toda a indústria de consumo.

Os plásticos possuem propriedades físico-químicas interessantes que potencializam sua aplicação na área de embalagens para alimentos, como leveza, facilidade de serem moldados em diversos tamanhos e formatos, versatilidade (podem ser flexíveis, rígidos, transparentes, coloridos), são estáveis e podem ser reciclados e/ou reutilizados. Além de atender quase todas as necessidades no mundo das embalagens, outro fator que contribui fortemente para a utilização de plástico é o preço mais competitivo quando comparado a outros materiais mais tradicionais, como o vidro, o metal e a madeira. Contudo, dada a sua resistência à degradação física e química somada ao seu descarte inadequado, as embalagens plásticas têm causado danos ao meio ambiente e, principalmente, aos animais aquáticos.

Uma das soluções de grande potencial, tanto para a gestão, quanto para destinação de resíduos sólidos, incluindo as embalagens plásticas descartadas pós-consumo, é a busca por

materiais mais sustentáveis e biodegradáveis como alternativas às embalagens plásticas comerciais de longa degradação. Nesse sentido, os impactos negativos promovidos pelo descarte incorreto de plásticos convencionais seriam amplamente minimizados. O desafio é manter as ótimas propriedades mecânicas, ótica e de barreiras apresentadas por estes polímeros sintéticos. Para atingir este objetivo, as principais tendências na busca por novos materiais incluem o uso de biopolímeros, materiais e aditivos (como plastificantes e agentes reticulantes) biodegradáveis e atóxicos, subprodutos da indústria, além de recursos renováveis.

Desta forma, aventando estudos e pesquisas de novos materiais sustentáveis, avaliou-se neste trabalho a possibilidade de produção de um novo compósito polimérico, utilizando o amido de mandioca e o álcool polivinílico como matérias-primas principais, reticuladas com o ácido cítrico. Sua viabilidade de uso comercial se deu por meio de testes mecânicos de tração e punctura e análises de sorção, difusão e permeação de água.

A primeira seção do artigo introduz e elucida o cenário das embalagens poliméricas flexíveis para alimentos e as principais tendências e aplicações de materiais biodegradáveis, destacando o papel de todos os componentes da blenda polimérica. Em um segundo momento, o artigo descreve as metodologias e procedimentos realizados, desde a elaboração dos filmes até a análise de resultados dos testes aplicados. Na terceira parte, são discutidos os resultados e as prováveis interações e atuações de cada um dos materiais da blenda produzida. Por fim, na conclusão, é destacada a composição mais promissora dentre as avaliadas, no que se refere às propriedades mecânicas e à barreira à migração de água, para aplicação como embalagem de alimentos.

Espera-se que este trabalho possa alimentar as discussões do uso de biopolímeros nas embalagens para alimentos, assim como aprofundar a avaliação e compreensão do comportamento e interações da água em contato com a embalagem.

**SEGUNDA PARTE – ARTIGO**

# ARTIGO 1 - WATER SORPTION, DIFFUSION, AND PERMEATION BEHAVIOR IN MODIFIED STARCH-POLYVINYL ALCOHOL POLYMER BLENDS FOR FLEXIBLE FOOD PACKAGING

Adaptado às normas da revista Food Hydrocolloids (*Versão preliminar*)

## ABSTRACT

In the search for sustainable materials for food packaging, many studies evaluate the use of biopolymers by blending them and adding cross-linkers. This trend is related to the resistance to degradation of commercial plastic added to its inadequate disposal, which has caused damage to the environment. To reduce the impact of plastic was investigated the production of cassava starch and polyvinyl alcohol (PVOH) flexible films and their blends by the casting method. The volume concentrations used in the films elaboration were 100S0P, 90S10P, 80S20P, 70S30P, and 0S100P (given in %Starch (S) and %PVOH (P) film solutions), with the addition of 8 % (based on polymers mass) of citric acid. The films were characterized concerning mechanical properties and water sorption, diffusion, and permeation behavior. The PVOH insertion of 10, 20, and 30 % to the blends made them about 24, 58, and 80 % more flexible and 36, 71, and 83 % more puncture-resistant, respectively, compared to the starch film. However, the insertion of 20 and 30 % of PVOH more than doubled the monolayer moisture content of the blends and increased their water diffusion coefficient by about 163 and 300 %, respectively, compared to the starch film. Thus, the 10 % of PVOH insertion was more advantageous as it strengthens the mechanical properties of the blends, without decreasing its water vapor barrier properties, compared to the starch film. That ensures package integrity and controls unwanted water migration, preventing degradation reactions and physicochemical changes in the food.

**Keywords:** Biopolymer food packaging. Cassava starch. Polyvinyl alcohol. Water permeation.

## 1  INTRODUCTION

Plastics, usually derived from petroleum, have been used in various fields of application, mainly for food packaging, and their production is increasing exponentially worldwide (Ritchie & Roser, 2020) due to favorable physicochemical characteristics and economic possibilities that are more advantageous than conventional materials such as wood, glass, and metals (Mills et al., 2020). They can be woven and processed in various ways, resulting in products with distinct properties, and are little susceptible to physical and chemical degradation, which makes them stable for years. Plastics stability allows for their reuse and saves appreciable amounts of natural raw materials, contributing to the ecological footprint reduction. Besides, they can facilitate product transportation because of their high moisture, deformation, and impact resistance. Also, plastics are lightweight, which reduces fuel consumption and greenhouse gas

emissions (Piringer & Baner, 2008). The use of plastic packaging has promoted a significant advance in the preservation and prevention of contamination and has given access to needy populations because of the low costs, which increases the number of consumers and contributes to the generation of jobs and growth of the global economy (Pinto et al., 2012).

However, plastics lightness and stability, coupled with the significant increase in the disposal of these post-consumption materials, become a concern, as they facilitate the dispersion of the packaging in the environment and hinder its degradation (Andrady, 2017). Most plastics, either through improper disposal or poor waste management, are dumped into oceans, rivers, and soils, causing much harm, especially to aquatic animals (Lebreton et al., 2017; Urbanski et al., 2020). Thus, the production from renewable sources of sustainable, biodegradable, and non-toxic plastics appears as a possibility to reduce the environmental impacts attributed to the accumulation of packaging on the planet (Kabir et al., 2020; S. Mathew et al., 2019). Besides reducing the use of non-renewable resources such as petroleum, these bioplastics conform to laws and regulations that prohibit disposable plastic utensils in commercial establishments (Pertussatti, 2020).

Starch is present in several segments, mainly in agriculture and in the food and packaging industries (Aqlil et al., 2017; Guimarães et al., 2015; Mendes et al., 2016; J. Zhang et al., 2019). Starch shows a potential for sustainable food packaging since it is an abundant, cheap, biodegradable, biocompatible, renewable, and edible biopolymer. However, among the starchy crops in Brazil, cassava has the highest yield. Moreover, Brazil is one of the largest producers of this tuberous root (Luchese et al., 2017). Starch films, nevertheless, have limitations due to their low mechanical strength properties and high humidity sensitivity. The latter can even modify their other properties during application (Mittal et al., 2016; Ray & Bousmina, 2005; Shi et al., 2008).

Some strategies are applied to improve biopolymers properties, such as blending them with other polymers and incorporating plasticizers and cross-linking agents into the polymer matrix (Cassagnau et al., 2007; Ning et al., 2007). Among the biodegradable synthetic polymers, polyvinyl alcohol (PVOH) is a non-toxic vinyl polymer, widely used in packaging due to its nature of film formation with oxygen barrier properties, tensile strength, and flexibility (J. Zhang et al., 2019). PVOH can be considered from a renewable source when synthesized by vinyl acetate monomer derived from biomass or natural products, such as sugarcane ethanol (Ben Halima, 2016; Cherubini & Strømman, 2011; Rose & Palkovits, 2011). Due to the excellent compatibility between PVOH and starch, their blends can overcome single-component deficiencies (Bof et al., 2015; Cano et al., 2016; Liu et al., 2017). By blending with

polyvinyl alcohol, thermoplastic starch has increased its mechanical properties and stability of the polymer matrix (Cano et al., 2016; Guimarães et al., 2015; K. Zhang et al., 2020).

Glycerol, produced mainly as a waste product in the biodiesel process, is used very effectively as a plasticizer in polymer blends of starch and PVOH for improved system integrity. This enhancement is due to the solubility parameter of the compounds being close to each other (Rahman et al., 2010). Also, it can influence the properties of these starch and polyvinyl alcohol composites by increasing their flexibility through its plasticizing effect (Srinivasa et al., 2007; Zanela et al., 2015).

Citric acid is a non-toxic cross-linking agent for starch films and its polymer blends. According to Garcia et al. (2011), the multi-carboxylic structure of citric acid, together with possible esterification reactions between starch and other film components, can lead to the formation of cross-links that outperform natural bonds. Thus, citric acid can improve tensile strength and decrease water vapor permeability when used as a cross-linking agent (Reddy & Yang). Many works have already shown the antioxidant and antimicrobial effect of citric acid when added in films and polymer blends, which increases the potential of food preservation (Ibrahim et al., 2021; Ounkaew et al., 2018; Wu et al., 2017).

But it is still necessary to deeply analyze the influence of citric acid addition to starch and PVOH films concerning the material exposure to moisture (regarding adsorption, diffusion, and permeation) and the characterization of some mechanical properties, such as modulus of elasticity and puncture resistance. The study of these properties can help direct the materials to different applications. Through the modulus of elasticity, it is possible to evaluate the flexibility of the packaging. Puncture resistance, on the other hand, measures the force required to film perforation. It is a substantial attribute, as puncture can alter the gas composition and allow undesirable microorganisms to enter the package (Kanatt & Makwana, 2020). Moreover, when dealing with food packaging, analyzing the water-film interaction is of utmost significance. Depending on the capacity of water adsorption and migration in the film, this interaction can influence the film mechanical properties (Cazón et al., 2020) and also allow the unwanted ingress and egress of water in the packaging, causing physicochemical and organoleptic changes in the food, which compromises not only its sensory quality, but also its safety.

Therefore, the present research had the following aims: (1) to elaborate a sustainable, flexible food packaging of starch and up to 30 % of PVOH, using citric acid as a non-toxic cross-linking agent and glycerol as a plasticizer; and (2) to evaluate the influence of adding PVOH to starch films by characterizing the mechanical properties, moisture sorption isotherm model, and water diffusion, permeability, and solubility behavior of films.

## 2 MATERIALS AND METHODS

### 2.1 Materials

In this research, the following materials were used in the polymer films and blends developed: Modified cassava starch (Cassava 406, lot R03_10/09), produced by Cassava, Rio do Sul, Brazil; Highly hydrolyzed polyvinyl alcohol (Exceval® HR-3010, degree of hydrolysis of 99.0-99.4 mol%, lot P6NP11), from Kuraray America, Inc; Glycerol (G9012-1L, ≥ 99.5 %, density 1.25 g/mL, MW 92.09 g/mol, lot # BCBN3647V), produced by Sigma-Aldrich; Granulated anhydrous citric acid (lot 6098), a product of the company Cargill, Campinas, Brazil; and distilled water.

### 2.2 Experimental design

A completely randomized design (CRD) with three repetitions and five treatments was used in the experiments. The analyses in which your standard required more samples than three per treatment have this information added to your methodology. Compositions for each treatment are arranged in Table 1.

Table 1. Composition of the produced polymer blends and films, given in volume/total volume percent of the primary polymer solutions.

| Treatment | Concentration of the primary starch film solution %(v/v) | Concentration of the primary polyvinyl alcohol film solution %(v/v) |
|---|---|---|
| MSTC | 100 | 0 |
| 90S10P | 90 | 10 |
| 80S20P | 80 | 20 |
| 70S30P | 70 | 30 |
| PVOH | 0 | 100 |

The total volume is 60 mL for each treatment. The MSTC and PVOH treatments are the same as 100S0P and 0S100P, i.e., they are the controls for the cassava starch film and the polyvinyl alcohol film, respectively.

### 2.3 Preparation of polymer blends and films conditioning

For films production by casting method, two aqueous polymer primary solutions were prepared, one with modified cassava starch as base polymer and another with polyvinyl alcohol

as base. Pre-tests and research were performed to find the best concentration of the solutions components.

Primary cassava starch film solution was produced with 3 % starch (polymer mass/volume of solution percent) and, as a plasticizer, 12 % glycerol (based on polymer mass) was added. The solution was kept under magnetic stirring (750 rpm) for 20 min at 70 °C. Primary polyvinyl alcohol film solution was developed with 4 % PVOH (mass/volume percent) and 25 % glycerol plasticizer (based on polymer mass), remaining under magnetic stirring (750 rpm) at 90 °C for 20 min.

60 mL of each primary solution (starch and PVOH solutions) were separated to form respective MSTC and PVOH control films. Blends of the two polymers were produced according to ratio of primary solutions volume to total volume, mentioned in Table 1 (from 90S10P to 70S30P), also totaling 60 mL for each polymer blend. In each treatment, including controls, 8 % citric acid was added to polymer solution (based on polymer mass), which was conditioned at 90 °C for 15 min, on a magnetic stirrer (750 rpm).

After cooling to room temperature, the polymer solutions were poured onto acrylic plates (15.4 cm diameter) and allowed to dry for two days for films formation. Finally, films were stored under the conditions of temperature (23 ± 2 °C) and relative humidity (50 ± 10 %) for 48 hours to then proceed to the analyses, according to ASTM D618-13 (ASTM International, 2013a). Before all analyses, samples were prepared according to the cutting standard, ASTM D6287-17 (ASTM International, 2017). Fig. 1 shows the appearance of the produced films.



Fig. 1. Photo of the developed films, already cut for isothermal/diffusion analysis (from left to right): MSTC, 90S10P, 80S20P, 70S30P, and PVOH.

## 2.4 Film characterization and evaluation of the water-film interaction

### 2.4.1 Mechanical properties

For the mechanical properties analysis, both for the tensile and puncture resistance tests, the TA.XT2i Texture Analyzer (Texture Technologies Corp., Hamilton, MA/Stable Micro

Systems, Godalming, Surrey, UK) was used, with a load cell of 1 kN. Exponent Lite software (version 6.1.11.0), linked to the equipment, obtained the results.

In the tensile test, was measured films Young's modulus ($E$), also known as tensile modulus, elastic modulus or modulus of elasticity, according to ASTM D882-18 (ASTM International, 2018). The 15 samples per treatment, of 10 mm of width and 100 mm of length, were submitted to the tensile test (with a deflection height of 50 mm), using a speed of 10 mm/s. Young's modulus was calculated from the tangent of the initial linear function of the stress-strain curve, considered as an elastic behavior.

The film performance was also analyzed, in terms of protrusion puncture resistance, according to an adaptation of ASTM D5748-95 (ASTM International, 2019). In this test, were used 12 repetitions for each treatment, in square samples of 9 cm², fixing them, one at a time, in a support with a central hole of 21 mm of diameter. A 5 mm diameter spherical probe (P/5S probe) was moved perpendicularly to the film surface at a speed of 0.8 mm/s until its rupture. The puncture resistance ($PR$), given in N/mm, was calculated by dividing the force at break by the film thickness. Also was determined the membrane deformation (mm), known as penetration distance, which is the depth probe traveled in penetrating film specimen, from initial probe contact with film specimen to penetration at break.

Films thickness was evaluated manually according to ASTM D6988-13 (ASTM International, 2013b). Reading, chosen at random, was taken in 5 different points on samples, using a digital micrometer (Digimess) with a resolution of 0.001 mm. 5 readings average (with a tolerance of 10% deviation) was considered thickness of each sample. All the other analyses, which required membrane thickness in the calculations, used this same method to obtained it.

## 2.4.2 Moisture sorption isotherm

For moisture sorption isotherm analysis, samples were prepared with dimensions 2 x 3 cm. The films were vacuum-dried for 24 h in an oven (at 70 °C and vacuum of 650 mmHg). Thus, the sample weight was noted with an accuracy of 0.001 g (Bourtoom, 2008; Kaymak-Ertekin & Sultanoğlu, 2001).

After the drying step and knowing the initial mass without moisture, the films were conditioned at 15 ± 2 °C with controlled water activities in a range of 0.34 to 0.97, using saturated saline solutions of $MgCl$, $K_2CO_3$, $Mg(NO_3)_2$, $NaCl$, $KCl$ and $K_2SO_4$. The temperature of 15 ºC was chosen as a complement to the other analyses at 25 °C, since some foods are usually stored at this temperature as well (Lemos et al., 2017; Li et al., 2016). Thus, it is

substantial to study the behavior of the film in these conditions. After 8 days, the films reached equilibrium moisture without any change or biological growth, and weight was annotated again to correlate the equilibrium moisture in each water activity.

To evaluate the moisture sorption isotherm behavior, five models, shown in Table 2 as Eq. (1-5), were chosen from similar studies (Lara et al., 2020; Srinivasa et al., 2003) to determine the best model for the films and their parameters.

Table 2. Parameters and equations of the moisture sorption isotherm models used.

| Model | Equation | | Parameters |
|---|---|---|---|
| GAB[a] | $M = \dfrac{M_0 C K a_w}{[(1 - K a_w)(1 + (C - 1)K a_w)]}$ | (1) | $M_0(A)$ is the monolayer moisture content (g $H_2O$/g film, dry basis), $K(B)$ is related to the heat of adsorption in the multilayer, and $C$ is Guggenheim constant, characteristic of the product and related to the heat of adsorption in the monolayer. |
| BET[b] | $M = \dfrac{M_0 C a_w}{1 - a_w}\left[\dfrac{1 - (N + 1)a_w^N + N a_w^{(N+1)}}{1 - (1 - C)a_w - C a_w^{(N+1)}}\right]$ | (2) | $M_0(A)$ is the same as described above, $N(B)$ is the number of water molecular layer and $C$ is the energetic constant, characteristic of the product, and related to the net heat of adsorption. |
| Smith[c] | $M = A - B \ln(1 - a_w)$ | (3) | |
| Oswin[d] | $M = A\left(\dfrac{a_w}{1 - a_w}\right)^B$ | (4) | $A$ and $B$ are model parameters. |
| Halsey[e] | $M = \left(\dfrac{-A}{\ln a_w}\right)^{\left(\frac{1}{B}\right)}$ | (5) | |

$M$ is the equilibrium moisture content (g $H_2O$/g film, dry basis) and $a_w$ is the water activity. GAB and BET models are triparametric, while the others are biparametric. [a](Guggenheim, 1966), [b](Brunauer et al., 1938), [c](Smith, 1947), [d](Oswin, 1946), and [e](Halsey, 1948).

The moisture sorption isotherm can also be used in the estimation of other film parameters, such as the monolayer moisture content ($M_0$), mentioned in Table 2, and specific surface area of sorption ($S_0$), which can be reached from monolayer moisture content result, employing Eq. (6) (Park et al., 2008).

$$S_0 = M_0 \frac{1}{PM_{H_2O}} N_0 A_{H_2O} \approx 3.5 \times 10^3 M_0 \qquad (6)$$

Where: $S_0$ is given in m²/g of film, $PM_{H_2O}$ is the molecular weight of water (18.02 g/mol), $N_0$ is the number of Avogadro ($6 \times 10^{23}$ molecules/mol) and $A_{H_2O}$ is the area of a water molecule ($10.6 \times 10^{-20}$ m²).

### 2.4.3 Water diffusion, permeability, and solubility coefficients

For study of water effective diffusion coefficient was used the Fick's model of diffusion, the Fick's second law, that was simplified in considerations of the diffusion occurring in one direction, reducing in Eq. (7). Applying the conditions of a membrane with a thickness of $2L$, where there is no concentration of water inside, whose surfaces, $x = -L$ and $x = L$, are kept at a known constant water concentration (at 25 °C and 75 % RH), then the diffusion equation has the mathematical solution, Eq. (8) (Crank, 1975). An alternative simplified solution, the short periods solution (Eq. (9)), can be used to adjust the initial experimental points until 2/3 of the solute mass has been absorbed (Crank, 1975).

$$\frac{\partial C}{\partial t} = D_{eff} \left( \frac{\partial^2 C}{\partial x^2} \right) \tag{7}$$

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ \frac{-D_{eff}(2n+1)^2 \pi^2 t}{(2L)^2} \right] \tag{8}$$

$$\frac{M_t}{M_\infty} = 4 \left( \frac{D_{eff}.t}{(2L)^2 \pi} \right)^{\left( \frac{1}{2} \right)} \tag{9}$$

Where: $C$ is the water concentration (g/cm³), $D_{eff}$ is the effective water diffusion coefficient in the membrane (cm²/s), $x$ is the distance along the diffusion direction (cm), $M_t$ (g) denotes the total amount of diffusing substance which has entered the membrane at time $t$ (s), $M_\infty$ (g) is the corresponding quantity after infinite time (until equilibrium moisture), $n$ is the number of terms in the series, and $2L$ is the thickness of film (cm).

The samples were prepared under the same conditions (dimensions and drying) as moisture sorption isotherm analysis and were placed in a hermetic pot with a relative humidity of 75 % (NaCl saturated saline solution) at $25 \pm 2$ °C. The sample weight was noted with an accuracy of 0.001 g from the time it was packed in the pot to equilibrium (approximately 8

days). On the first day, as there were significant changes in mass, it was observed every hour. From the second day onwards, the weight was monitored daily.

With the data from the monitoring of the moisture gain by time to equilibrium and the thickness of each sample, it was possible to estimate the value of $D_{eff}$ through a non-linear regression with Eq. (8), with the number of terms of the series truncated in n = 10. $D_{eff}$ was estimated too through a non-linear regression with the Eq. (9) for solution comparison, using OriginPro 2015 software.

To investigate if the mechanism involved in the diffusion process is Fickian, it was possible to adjust the absorption curve $\left(\frac{M_t}{M_\infty} \text{ versus } t\right)$ according to the model of the Power Law (Eq. (10)) (Crank, 1975; Yui et al., 2004). It is important to note that Power Law is valid to describe the process of transport of water within films for fractions smaller than 2/3 of absorbed water, since for large swellings the thickness of the membrane does not remains constant, so the expression does not fit the reality.

$$\frac{M_t}{M_\infty} = Kt^n \tag{10}$$

Where: $K$, a kinetic constant that incorporates the structural and geometric characteristics of the film, and $n$ (defines the mechanism of sorption) are constants of model.

The permeability coefficient was determined by the procedure of ASTM E96/E96M-16 (ASTM International, 2016), which deals with water vapor transmission. The procedure used was the Desiccant Method at 23 ± 2 °C, where was sealed the specimen to the open mouth (30 cm²) of a test capsule containing silica gel absorbent (relative humidity of 0 % approximately), and the assembly placed in a controlled atmosphere with a relative humidity of 75 % (NaCl saturated saline solution). Daily weighings determined the rate of water vapor movement through the specimen into the silica. The samples of each treatment were tested by the same method for 8 days. For calculation of water vapor transmission ($WVT$, given in g/(h.m²)), water mass permeability or water vapor permeability ($WVP$, given in (g.m)/(m².h.mmHg)), and permeability coefficient ($P_w$, given in Barrer) were used the Eq. (11-13).

$$WVT = \left(\frac{G}{t}\right)\frac{1}{A} \tag{11}$$

$$WVP = \frac{WVT \cdot \delta}{\Delta P} = \frac{WVT \cdot \delta}{S(R_1 - R_2)} \tag{12}$$

Where: $G$ (g) is the weight change, $t$ is time (h), i.e., $\frac{G}{t}$ (g/h) is the slope of linear regression, $A$ (m²) is the test area (cup mouth area), $\delta$ (m) is the film thickness, $\Delta P$ (mmHg) is the vapor pressure difference, $S$ (21.08 mmHg) is the saturation vapor pressure at test temperature (23 °C), $R_1$ (0.75) is the relative humidity at the test chamber expressed as a fraction, and $R_2$ (0.00) is relative humidity at the vapor sink expressed as a fraction.

$$P_w = 10^{10} \times \frac{\widehat{WVP} \times V_m}{M_w} \tag{13}$$

Where: $\widehat{WVP}$ is the water vapor permeability, but now given in (g.cm)/(cm².s.cmHg), $M_w$ (18.02 g/mol) is the molar mass of water, $V_m$ (22,711.06 cm³/mol) is the molar volume at standard temperature and pressure (273.15 K and 1 bar, respectively).

If the diffusion coefficient is constant, and if the intern sorption isotherm is linear, i.e., if there is a linear relationship between the external vapor pressure and the corresponding equilibrium concentration within the membrane, then the partition coefficient or solubility coefficient ($K_S$, given in cm³(STP)/(cm³.cmHg)) may be written as the Eq. (14) (Barrer, 1942).

$$K_S = \frac{\widehat{P_w}}{D_{eff}} \tag{14}$$

Where: $\widehat{P_w}$ is the permeability coefficient, but now given in (cm³(STP).cm)/(cm².s.cmHg).

Permeability coefficient values at $23 \pm 2$ °C were approximate to 25 °C, since the deviation encompasses this temperature, so that it was possible to determine $K_S$ at ≈25 °C as well. An alternative for the determination of the solubility coefficient was through the GAB model for moisture sorption isotherm (Eq. (1)). According to Larotonda et al. (2005), differentiating GAB model in relation to water activity and dividing the result by water vapor pressure at the experimental system temperature, 15 °C in the case of subsection 2.4.2, then the water mass solubility in the films can be given by Eq. (15), which is valid for the whole isotherm. The solubility coefficient can be given by applying Eq. (16).

$$\beta = \frac{M_0 CK}{p_s}\left[\frac{\frac{1}{[(1-Ka_w)(1+(C-1)Ka_w)]}}{\frac{a_w}{[(1-Ka_w)(1+(C-1)Ka_w)]^2}}[-K(1+(C-1)Ka_w)+(1-Ka_w)(-K+CK)]\right] \quad (15)$$

$$K_S = \frac{\beta \times V_m \times \rho_s}{M_w} \quad (16)$$

Where: $\beta$ is the water mass solubility [g H$_2$O/(g dry solid.cmHg)], $p_s$ is the water vapor pressure at 15 °C (1.2794 cmHg), and $a_w$ is the water activity (chose 0.75 for comparison). For determination of dry matter apparent density ($\rho_s$) were used specimens 5 x 5 cm. The samples were dried at 105 °C for 24 h and weighed. The mass was obtained at a precision of 0.001 g. Thus, dry matter apparent densities were calculated by dividing the mass (g) by sample volume (cm³, area multiplied by thickness measured before drying) (Larotonda et al., 2005; Müller et al., 2009; Scatolino et al., 2017).

## 2.5 Statistical analysis

Statistical analysis of results was performed by comparing repetitions means. Sisvar 5.6 software (Ferreira, 2011) was used to perform analysis of variance (ANOVA) and Tukey's test at the 5 % level of significance. Tukey's test was used at the mean results of Young's modulus ($E$), protrusion puncture resistance ($PR$), penetration distance, diffusion coefficient ($D_{eff}$), Power Law parameters ($K$ and $n$), water vapor transmission ($WVT$), water vapor permeability ($WVP$), and permeability ($P_w$) and solubility ($K_S$) coefficients. In the effective diffusion coefficient results, was evaluated the influence by using Eq. (8-9) in $D_{eff}$ determination. For this purpose, was included a source of variation in the ANOVA, due to the different equations, to be evaluated by the F-test at the 5 % level of significance.

To determine moisture sorption isotherm, diffusion, and Power Law parameters, the models were adjusted to experimental data, using the Levenberg–Marquardt algorithm with OriginPro 2015 software (OriginLab Corporation, Northampton, MA, USA). Adequacy and goodness of the fitted moisture sorption isotherm models were analyzed by error functions, through with an evaluation of Adjusted Coefficient of Determination (Adj. R²), Residual Sum of Squares (RSS), and Residual plots. For the final decision, the Akaike Information Criterion

(AIC) was used as an essential criterion to compare the two models with the best performance in error functions and choose the best one.

# 3  RESULTS AND DISCUSSION

## 3.1 Mechanical properties

For the tensile test, as the ratio of starch/PVOH decreased, i.e., from MSTC to PVOH treatment, the films became more flexible and, consequently, presented lower values for the modulus of elasticity (Fig. 2a). The 70S30P flexibility was not statistically different ($p > 0.05$) from the PVOH treatment, achieving approximately five times the flexibility of the MSTC. The other blends, 90S10P and 80S20P, showed a reduction ($p < 0.05$) of 24 and 58 % in Young's modulus, respectively, compared to the starch film.

The influence on the modulus of elasticity decrease with the presence of PVOH was expected. Guimarães et al. (2015) demonstrated that polyvinyl alcohol promotes greater flexibility to starch/PVOH polymer blends (with a composition of the film solutions very close to those used in this research, except for the absence of citric acid), given the compatibility and stability between the two polymers and the hydrogen bonds between their hydroxyl groups. However, the $E$ values found by them ranged from 119 MPa (PVOH film) to 1697 MPa (cassava starch film), being higher than those found in the present research.

Thus, this may indicate that the addition of the citric acid cross-linking agent also enhanced the flexibility of the PVOH and starch films and their blends. This perception corroborates the results found by Shi et al. (2008) that studied the effect of adding citric acid, acting simultaneously as a plasticizer and cross-linking agent, in starch and PVOH polymer blends and concluded that the acid addition of 5 to 30% provided an increase in film flexibility, when compared to films without this addition. This effect, according to Wu et al. (2017), is mainly due to the physical attraction between the polymer matrix PVOH and a residual citric acid, accompanied by glycerol acting as a plasticizer, and the citric acid carboxylation with the polyvinyl alcohol hydroxyl groups, where the distribution of citric acid generates tremendous interfacial contacts with the polymer matrices, which could lead to effective stress transfer and results in an increased in flexibility. Cross-linking also interconnects the starch molecules in the film, which provides better intermolecular interactions between the polymers, could lead to higher flexibility than non-cross-linked films (Reddy & Yang).
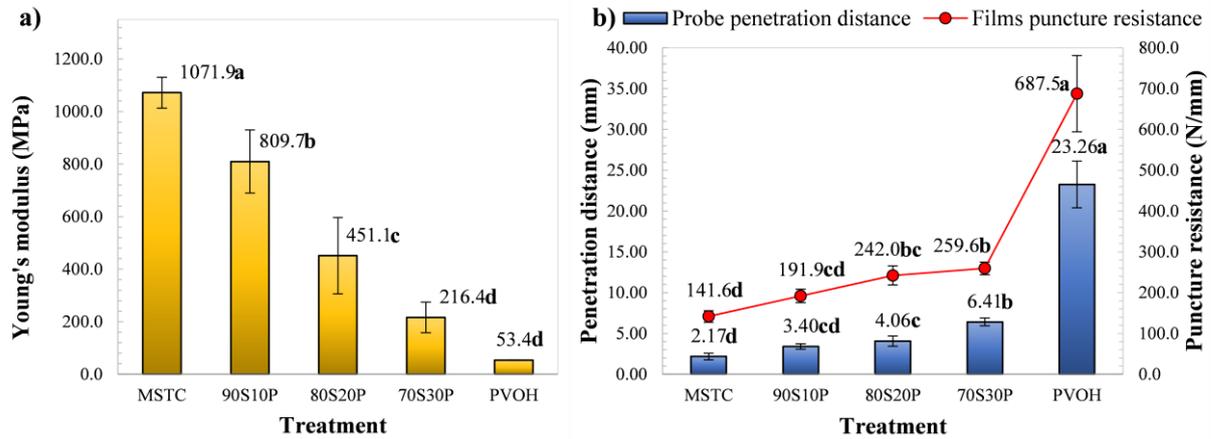
Fig. 2. Mechanical properties results: (a) tensile modulus of elasticity and (b) protrusion puncture resistance. Different letters in Young's modulus, puncture resistance, and penetration distance values indicate statistically significant difference (p<0.05) by the Tukey's test.

Regarding the puncture test, the presence of 10 to 30 % PVOH granted the polymer blends higher puncture resistance (increase of approximately 36 to 83 %) and longer probe penetration distance (increase of 57 to 195 %) when compared to the MSTC film (Fig. 2b). The influence of PVOH can be explained by its higher degree of hydrolysis, which increases the number of hydroxyl groups present in the molecule, allowing the formation of hydrogen interactions between these groups and the starch hydroxyls and with other polar groups of the blend components, such as the glycerol and citric acid groups. Thus, the polyvinyl alcohol strengthens the film structure and increases the puncture resistance and the probe penetration distance. This mechanical behavior is typical of homogeneous and thermodynamically miscible systems (Elizondo et al., 2009; Kanatt & Makwana, 2020; Muppalla et al., 2014). The thickness of the films ranged from 0.080 to 0.137 mm.

## 3.2 Moisture sorption isotherms

The results of moisture sorption isotherm curves fitting at 15 °C are shown in Table 3. As can be noted, the GAB and BET models were adequate to describe the moisture sorption isotherm of starch and PVOH films and their blends. Thus, the AIC test was applied to determine the best model, and the GAB model was considered more satisfactory than BET, in all films, for presenting lower AIC.

The Oswin, Smith, and Halsey models were inadequate to describe the moisture sorption isotherm in any of the treatments, as they showed clear patterns in the analysis of the residual plots. A residual plot with a uniform distribution (uniform scatter around the horizontal value of zero) represents an adequate model. But a residual plot with a clean pattern (systemic

tendency) indicates that the isotherm model has fixed model errors and is not adequate (Aviara, 2020).

Table 3. Estimated parameters and error functions values for isotherm models evaluation.

| Treatment | Model | Parameters values | | | Error functions values | | | Final test |
|---|---|---|---|---|---|---|---|---|
| | | *A* | *B* | *C* | Adj. R² | RSS | Residual plots | AIC |
| MSTC | GAB* | 0.11 | 0.93 | 0.28 | *0.999* | **6.0E-5** | UD | -21.1 |
| | BET | 0.051 | 38.7 | 0.69 | *0.999* | 1.3E-4 | UD | -16.7 |
| | Smith | -0.14 | 0.25 | | **0.963** | *1.3E-2* | CP | |
| | Oswin | 0.066 | 0.70 | DNA | 0.990 | 3.6E-3 | CP | - |
| | Halsey | 0.021 | 1.32 | | 0.984 | 5.7E-3 | CP | |
| 90S10P | GAB* | 0.10 | 0.92 | 0.39 | *0.999* | **7.1E-5** | UD | -20.1 |
| | BET | 0.051 | 36.4 | 0.89 | *0.999* | 1.7E-4 | UD | -14.9 |
| | Smith | -0.12 | 0.24 | | **0.973** | *8.6E-3* | CP | |
| | Oswin | 0.074 | 0.66 | DNA | 0.987 | 4.0E-3 | CP | - |
| | Halsey | 0.020 | 1.40 | | 0.980 | 6.4E-3 | CP | |
| 80S20P | GAB* | 0.25 | 0.88 | 0.12 | *0.999* | **4.8E-5** | UD | -22.4 |
| | BET | 0.056 | 33.2 | 0.53 | *0.999* | 8.4E-5 | UD | -19.0 |
| | Smith | -0.13 | 0.24 | | **0.971** | *9.2E-3* | CP | |
| | Oswin | 0.068 | 0.68 | DNA | 0.985 | 4.9E-3 | CP | - |
| | Halsey | 0.019 | 1.36 | | 0.977 | 7.3E-3 | CP | |
| 70S30P | GAB* | 0.23 | 0.89 | 0.12 | *0.999* | **2.0E-4** | UD | -14.0 |
| | BET | 0.053 | 35.8 | 0.55 | *0.999* | 3.0E-4 | UD | -11.4 |
| | Smith | -0.14 | 0.24 | | **0.968** | *1.1E-2* | CP | |
| | Oswin | 0.064 | 0.70 | DNA | 0.987 | 4.4E-3 | CP | - |
| | Halsey | 0.020 | 1.32 | | 0.980 | 6.6E-3 | CP | |
| PVOH | GAB* | 0.31 | 0.89 | 0.10 | *0.999* | **1.4E-4** | UD | -16.1 |
| | BET | 0.064 | 34.1 | 0.48 | *0.999* | 2.4E-4 | UD | -12.9 |
| | Smith | -0.16 | 0.27 | | **0.969** | *1.3E-2* | CP | |
| | Oswin | 0.073 | 0.70 | DNA | 0.986 | 6.2E-3 | CP | - |
| | Halsey | 0.024 | 1.32 | | 0.979 | 9.2E-3 | CP | |

*Best model. DNA: Does not apply, i.e., the model does not have this parameter. Values in **bold** represent minimum error function value. Values in *italics* represent maximum error function value. CP: Clean pattern of residual plots. UD: Uniform distribution of residual plots.

The GAB model is mentioned by several authors as the best model to describe moisture adsorption of degradable films (Cassini et al., 2006; Lara et al., 2020; Mali et al., 2005). This model, applied to all treatments, showed that the moisture adsorption has a typical type III isotherm shape (Fig. 3a-e), according to Brunauer's classification (Brunauer et al., 1940). Larotonda et al. (2005) analyzed with the GAB model the behavior of the moisture sorption isotherm of Kraft paper and modified starch, which also had type III isotherm behavior.
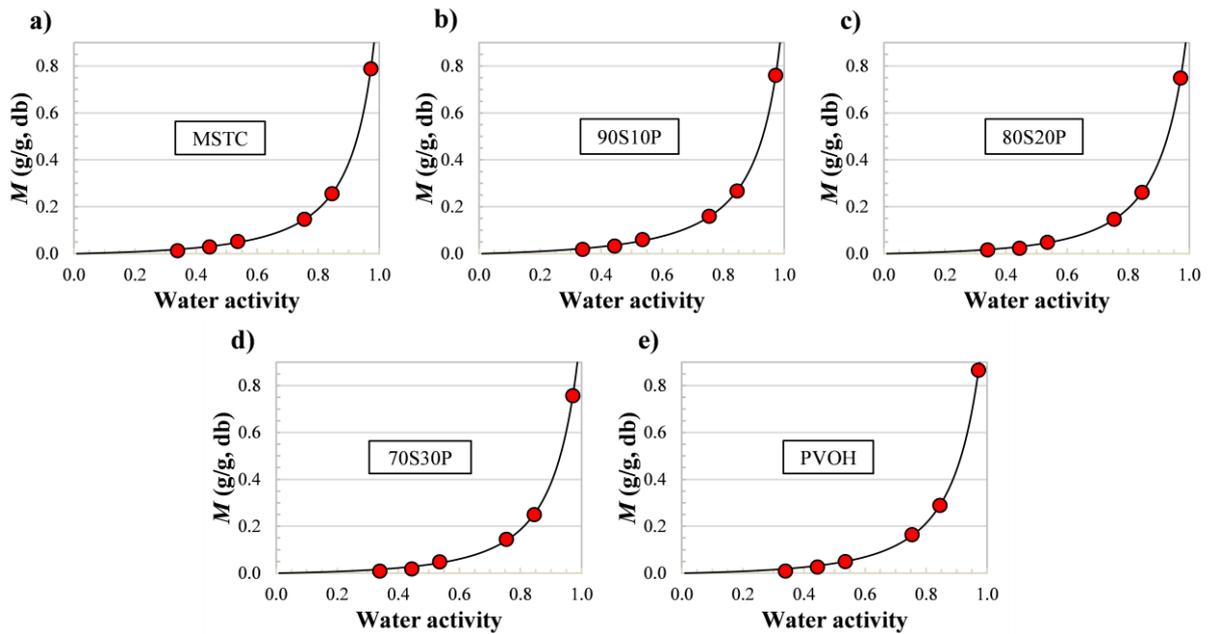
Fig. 3. Water sorption isotherms of (a) starch film, (b) 90S10P, (c) 80S20P, and (d) 70S30P polymer blends, and (e) PVOH film at 15 °C, adjusted through the GAB model. $M$ is the equilibrium moisture content (g of $H_2O$/g of film, dry basis).

In the type III isotherm, the receiving side (film/blend surface) may be filled with a multitude of molecules and a phenomenon of condensation may appears (Khalfaoui et al., 2003). Furthermore, it is mainly characterized by the adsorption heat, which is lower than the adsorbate (water molecules) liquefaction heat. Thus water-water interactions occur, i.e., as the adsorption proceeds, the additional water adsorption is facilitated because its interaction with an adsorbed water layer is greater than its interaction with the film/blend surface (Lowell & Shields, 1984). The development of moisture content is a consequence of the evolution of properties or transitions because water can also act as a plasticizer, but is a volatile one that balances with the environment in mechanisms of sorption/desorption (Avérous, 2004; Hulleman et al., 1998; Shogren, 1993).

Lourdin, Bizot, and Colonna (1997), and Mathew and Dufresne (2002) demonstrated that in starch films, exposed to low relative humidity, the water content decreases in high concentrations of plasticizer, due to the strong interaction between them and the starch, where a hydrogen-bonding network appears, and thus obtained a reinforced film. In this case, plasticizer molecules occupy some sites initially occupied by water. In higher water activities, the film moisture content rise with the tenor of plasticizer, due to the interaction plasticizer-water. In this condition, when the plasticizer content is high, the interactions between plasticizers (including water and residual cross-linking agent) occur with the swelling of the material and with the water plasticizer effect on the polymer. One can associate the low water

adsorption on the film, in lesser water activity, and the higher adsorption, in high water activity, due to the higher concentrations of glycerol and a possible residual citric acid. This behavior results in a type III isotherm.

Through the GAB model (Eq. (1)), it was possible to estimate the monolayer moisture content ($M_0$) of the films, on a dry basis, besides the other equation parameters, $K$ and $C$. The monolayer moisture content indicates the amount of water that is strongly adsorbed to specific sites, considering one layer per gram of film. The parameter $C$ is associated with the differences in chemical potentials between the monolayer and the upper layers. It represents the binding energy of the water molecules in the monolayer with the sorption sites on the surface of the film. The larger $C$, the stronger water is bound in the monolayer, and the higher the difference in enthalpy between the monolayer molecules and multilayer molecules. (Quirijns et al., 2005). The $K$ values involve interactions between the water molecules and the film in the multilayer. There will be fewer interactions between the water molecules and the film for lower $K$ values (Velázquez-Gutiérrez et al., 2015).

Table 3 shows the GAB equation parameters and Table 4 shows the results of specific surface area of sorption. With the presence of 20 % or more PVOH, the monolayer moisture content increased more than twofold in the polymer blends, and about threefold in the PVOH film, in comparison to the MSTC and 90S10P films. The specific surface area of sorption showed similar behavior because it is directly proportional to the monolayer moisture content.

Table 4. Values of specific surface area of sorption ($S_0$) at 15 °C.

| Treatment | $S_0 \left( \frac{\text{m}^2}{\text{g}} \right)$ |
|:---:|:---:|
| MSTC | 385 |
| 90S10P | 350 |
| 80S20P | 875 |
| 70S30P | 805 |
| PVOH | 1085 |

The $C$ values are related to those $M_0$ since the films with a lower concentration of PVOH ($\leq$ 10 %) had lower monolayer moisture content and higher adsorption heat, and those with a higher concentration of PVOH ($\geq$ 20 %) adsorbed more water in the monolayer, obtained lower adsorption heat, and consequently had a weak adsorbent-adsorbate interaction. The $K$ values showed that MSTC and 90S10P films had a little higher interaction with water in the multilayer than the other treatments.

The $S_0$ results indicated that as the PVOH concentration increased ($\geq$ 20 %), the availability of active sites for hydrophilic binding also increased. These increasing trends reveal that the binding energies associated with monolayer moisture sorption on film samples decreased with a PVOH concentration equal to or above 20 %. This behavior may be explained by the high degree of hydrolysis of the polyvinyl alcohol used, in which there is greater availability of hydroxyl groups on the films, increasing the number of sites available for the formation of hydrogen bonds with water. Thus, there was a higher monolayer moisture sorption on films with a higher PVOH concentration ($\geq$ 20 %) (Elizondo et al., 2009; Guimarães et al., 2015).

The values of specific surface area of sorption were higher than the range usually obtained for food products: 100-200 m²/g (Labuza, 1968). A large $S_0$ of biopolymers is due to the existence of an intrinsic microstructure in films. The number and size of pores in the polymer matrix determines the total area of adsorption, and the surface properties of the pores influence the rate and extent of hydration (Rosa et al., 2010; Sing, 2001; Tao et al., 2018).

## 3.3 Water diffusion, permeability, and solubility coefficients

Fig. 4 shows the results for the effective diffusion coefficients through the series solution (Eq. (8)) and the simplified solution (Eq. (9)). For the effective diffusion coefficient determination, both equations were suitable since the $D_{eff}$ values presented the same order of magnitude and obtained a good fit among data. Furthermore, the source of variation due to the use of different equations for the determination of $D_{eff}$ showed no statistically significant difference (p>0.05) in the F-test. It means that up to 2/3 of the moisture sorption occurs in short periods and that the simplified equation of Fick's second law describes the film diffusion process just as well as the serial version.

The PVOH obtained an effective diffusion coefficient almost ten times higher than the starch control. About the blends, adding 10 % of PVOH did not change diffusivity (p>0.05) in comparison to MSTC. But the presence of 20 and 30 % of PVOH caused an increase of 130 to 300 % in the diffusion coefficient (p<0.05), respectively, compared to starch film. This increase in diffusive behavior with increasing polyvinyl alcohol concentration may be related to PVOH acting as a facilitator of water transport through the film due to its chemical structure, in which several hydroxyl groups are present (Guimarães et al., 2015).
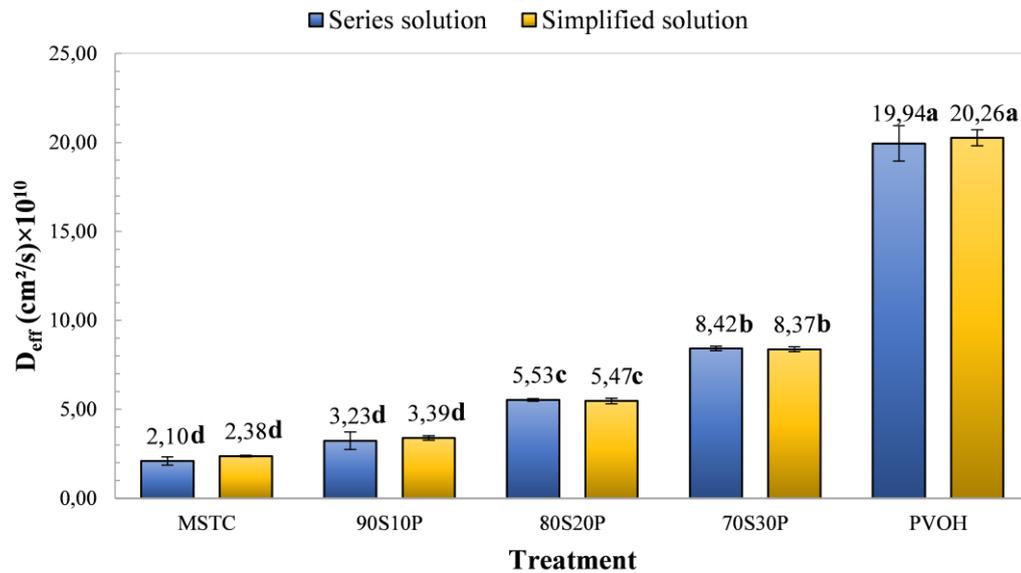
Fig. 4. Diffusion coefficients estimated by the series and simplified equations at $25 \pm 2$ °C. Different letters in effective diffusion coefficient values indicate statistically significant difference ($p<0.05$) by the Tukey's test.

Although PVOH increases the water diffusion in the films, the effective diffusion coefficient in this work were lower than those observed in a similar study with plasticized starch films with glycerol and sorbitol that range from $4.1 \times 10^{-8}$ to $1.8 \times 10^{-7}$ cm²/s (Müller et al., 2008). This difference in results is probably due to the addition of citric acid, which caused a reduction in molecular mobility during cross-linking of the polymer matrix via a cross-linked esterification reaction, resulting in decreased water diffusion in the films (Olsson et al., 2013).

According to the Power Law, there are three classes of distinction of diffusion models. They are categorized according to the relative rates of polymer diffusion and relaxation and identified by the $n$ values (Alfrey et al., 1966). In Case I or Fickian diffusion ($n = 0.5$), the diffusion rate is much lower than the relaxation rate and is controlled by a diffusive process, and the adsorption rate is linear. In Case II ($n = 1.0$), the diffusion rate is much faster than the relaxation. The parameter is the constant velocity of an advancing front which marks the innermost limit of penetration of the diffusant and is the boundary between swollen gel and glassy core. This process can have $n > 1.0$, which defines a complex relaxation process at the interface between swollen and non-swollen regions within the polymeric matrix. And the third class, the non-Fickian or anomalous diffusion ($0.5 < n < 1.0$), occurs when the diffusion and relaxation rates are comparable. It can change sigmoidally from Case I to Case II. Besides, non-Fickian behavior requires two or more parameters to describe the interacting diffusion and relaxation effects inherent in it. Table 5 shows the estimated parameters of the Power Law (Eq. (10)).

Table 5. Power Law parameters and diffusion model class at 25 ± 2 °C.

| Treatment | Power Law parameters | | Model class |
|---|---|---|---|
| | $K$ (s$^{-n}$) | $n$ | |
| MSTC | 0.0048 ± 0.0004a | 0.500 ± 0.001a | Class 1 |
| 90S10P | 0.0061 ± 0.0003a | 0.501 ± 0.001a | Class 1 |
| 80S20P | 0.0061 ± 0.0006a | 0.502 ± 0.002a | Class 1 |
| 70S30P | 0.0060 ± 0.0010a | 0.502 ± 0.003a | Class 1 |
| PVOH | 0.0064 ± 0.0006a | 0.505 ± 0.007a | Class 1 |

Class 1 represents a Case I or a Fickian diffusion. Different letters in columns indicate statistically significant difference (p<0.05) by the Tukey's test.

The water diffusion process in the produced starch/PVOH films and blends had $n$ value close to 0.5, presenting no significant difference between them (p>0.05), which characterizes a Fickian diffusion (Case I). In other words, it indicates that the relaxation rate of the polymer chains is much higher than the water diffusion in the film. This high relaxation rate may be the result of hydrogen bonds of the polymer chains with the water molecules, where the water also acts as a plasticizer (Masaro & Zhu, 1999; Panpinit et al., 2020). As discussed in Subsection 3.2, when films in an environment with high water activity, water can act as a plasticizer (in this case, $a_w = 0.75$).

The permeability results for each film are in Table 6, which contains the values of water vapor transmission ($WVT$), water vapor permeability ($WVP$), and the permeability coefficient ($P_w$).

Table 6. Films water permeability parameters at a RH gradient of 75–0% and 23 ± 2 °C.

| Treatment | $WVT \left( \frac{g}{h \cdot m^2} \right)$ | $WVP \left( \frac{g \cdot m}{h \cdot m^2 \cdot mmHg} \right) \times 10^6$ | $P_w$ (Barrer) $\times 10^{-3}$ |
|---|---|---|---|
| MSTC | 1.34 ± 0.24b | 6.32 ± 0.40b | 2.21 ± 0.14b |
| 90S10P | 1.12 ± 0.23b | 5.91 ± 0.60b | 2.07 ± 0.21b |
| 80S20P | 1.23 ± 0.25b | 7.05 ± 0.69b | 2.47 ± 0.24b |
| 70S30P | 1.56 ± 0.19b | 9.20 ± 0.87b | 3.22 ± 0.30b |
| PVOH | 2.46 ± 0.11a | 26.18 ± 3.59a | 9.17 ± 1.26a |

Different letters in columns indicate statistically significant difference (p<0.05) by the Tukey's test.

Although the PVOH treatment showed higher values (p<0.05) for all water permeability parameters, the presence of 10 to 30% polyvinyl alcohol did not modify the water vapor barrier properties of the starch/PVOH polymer blends. These films obtained values for the permeability parameters statistically equal to those of the starch control (p>0.05).

Mittal et al. (2016) studied properties of starch/PVOH films cross-linked with urea-formaldehyde and found that these polymer blends in the presence of a cross-linking agent can

increase the water vapor barrier when compared to the PVOH film and non-cross-linked polymer blends, due to a decrease in mobility of the polymer chains after cross-linking the matrix. This may indicate that the presence of citric acid may have contributed to the decreased water vapor permeability in the films by acting as a cross-linking agent, as also shown in the study by Reddy & Yang (2010). The starch-citric acid interactions may have been essential for increasing the moisture barrier (formation of cross-links that overcome natural bonds, making the material more resistant to water vapor), introducing a tortuous path for water molecules to pass through (Ghanbarzadeh et al., 2011).

Table 7 shows the results of the solubility coefficient. At 25 °C, the presence of up to 30% polyvinyl alcohol significantly reduced (p<0.05) the solubility coefficient of the starch films. At 15 °C, the results were closer to each other, where the polymer blend 80S20P showed a higher solubility coefficient (p<0.05), while 70S30P obtained a lower $K_S$ value (p<0.05). Although determined by different procedures, the results of the solubility coefficients may indicate that, while for the MSTC, the solubility coefficient hardly changes considering the deviations, for the other treatments, which had polyvinyl alcohol added, the $K_S$ value decreases with increasing temperature (from 15 to 25 °C).

Table 7. Solubility coefficients at different temperatures.

| Treatment | $K_S$ $\left(\frac{cm^3(STP)}{cm^3 \cdot cmHg}\right)$ | |
|---|---|---|
| | **≈25 °C*** | **15 °C**** |
| MSTC | 992 ± 88a | 974 ± 49ab |
| 90S10P | 626 ± 21b | 986 ± 15ab |
| 80S20P | 449 ± 4c | 1023 ± 42a |
| 70S30P | 384 ± 1c | 945 ± 51b |
| PVOH | 456 ± 5c | 970 ± 24ab |

*Solubility coefficient values by Eq. (14).**$K_S$ of 15 °C was determined by Eq. (15-16). Different letters in columns indicate statistically significant difference (p<0.05) by the Tukey's test.

Lara et al. (2020) observed that, in polymer blends of PVOH and whey protein isolate, the solubility coefficient at 25 ℃ was more influenced by the diffusion coefficient than by the permeability coefficient, since the permeability values did not differ statistically (p>0.05) with the increase from 10 to 30 % of PVOH concentration in the films, while the diffusivity increased (p<0.05) with the rise of polyvinyl alcohol concentration. This same effect was observed in Fig. 4 for the $D_{eff}$, which increased (p<0.05) with rising PVOH concentration, and in Table 6

for the $P_w$, which did not change (p>0.05) with increasing up to 30 % PVOH in the starch/PVOH blends.

According to Robertson (2016), diffusion in a polymer is seen as a series of activated jumps from one vaguely defined cavity within the polymer matrix to another. Qualitatively, any agent that increases the number or size of cavities in a polymer or makes chain segments more mobile can also increase the diffusion rate. For the films produced, the presence of a higher amount of PVOH led to larger free volumes and increased chain mobility, allowing water molecules to move at a higher rate (Lara et al., 2020).

As already discussed, the starch film and its blends with polyvinyl alcohol showed the same water permeability coefficient values, but the water diffusion coefficient increased when the PVOH concentration was 20 and 30 %. Thus, there was less flow resistance during the permeation process (adsorption-diffusion-desorption), and, therefore, the water solubility coefficient tended to decrease.

On the other hand, the difference in the results at the two temperatures may is related to the fact that the diffusivity, having a considerable effect on the solubility coefficient in this work, increases with increasing temperature in PVOH films (Monjazeb Marvdashti et al., 2019; Müller-Plathe, 1998), which consequently decreases the solubility coefficient, since they are inversely proportional. Han et al. (2003) already reported a decrease in water solubility with increasing temperature in cross-linked PVOH films. They state that higher temperatures lead to increased polymer chain activity, allowing water molecules to pass easily between the polymer chains, leading to increased water diffusivity and lower solubility.

## 4 CONCLUSIONS

By studying the behavior of cassava starch-polyvinyl alcohol films and their polymer blends, it was possible to observe the effects and properties of starch, PVOH, citric acid, and glycerol in the analyses. PVOH in the concentration of ≥ 10 % made polymer blends more flexible (increasing flexibility by up to 80 %) and more puncture-resistant (up to 83 % increase) than starch film, and decreased the $K_S$ of polymer blends at 25 ºC, compared to the starch film. However, by its higher degree of hydrolysis, the PVOH, when present at 20 and 30 % concentrations, more than doubled the monolayer moisture content and the specific surface area of sorption of polymer blends at 15 °C, in comparison to the MSTC and 90S10P films. The GAB moisture sorption isotherm model determined these parameters, which was the best model to describe the isotherm type III behavior on the PVOH and starch films. The presence of ≥ 20

PVOH also increased (by up to 300 %, compared to the starch film) the water diffusivity at 25 °C. But in terms of *WVT* values, none of the blends were impacted by PVOH. Thus, the PVOH concentration of 10 % in starch films was more interesting because it showed a lower affinity for water adsorption at 15 °C and low diffusion coefficient contrasted to the other two polymer blends at 25 °C, which results in greater control of unwanted water vapor ingress and egress, preventing degradation reactions and physicochemical and sensory changes in the food. Besides, 10 % of PVOH increased the flexibility and puncture resistance of the starch film, promoting greater strength when the film is in contact with perforating materials and ensures package integrity.

## ACKNOWLEDGEMENTS

## REFERENCES

Alfrey, T., Gurnee, E. F., & Lloyd, W. G. (1966). Diffusion in glassy polymers. *Journal of Polymer Science Part C: Polymer Symposia*, *12*(1), 249–261. https://doi.org/10.1002/polc.5070120119

Andrady, A. L. (2017). The plastic in microplastics: A review. *Marine Pollution Bulletin*, *119*(1), 12–22. https://doi.org/10.1016/j.marpolbul.2017.01.082

Aqlil, M., Moussemba Nzenguet, A., Essamlali, Y., Snik, A., Larzek, M., & Zahouily, M. (2017). Graphene Oxide Filled Lignin/Starch Polymer Bionanocomposite: Structural, Physical, and Mechanical Studies. *Journal of Agricultural and Food Chemistry*, *65*(48), 10571–10581. https://doi.org/10.1021/acs.jafc.7b04155

ASTM International. (2013a). *ASTM D618-13, Standard Practice for Conditioning Plastics for Testing.* https://doi.org/10.1520/D0618-13

ASTM International. (2013b). *ASTM D6988-13, Standard Guide for Determination of Thickness of Plastic Film Test Specimen.* https://doi.org/10.1520/D6988-13

ASTM International. (2016). *ASTM E96/E96M-16, Standard Test Methods for Water Vapor Transmission of Materials.* https://doi.org/10.1520/E0096_E0096M-16

ASTM International. (2017). *ASTM D6287-17, Standard Practice for Cutting Film and*

*Sheeting Test Specimens.* https://doi.org/10.1520/D6287-17.

ASTM International. (2018). *ASTM D882 − 18, Standard Test Method for Tensile Properties of Thin Plastic Sheeting.* https://doi.org/10.1520/D0882-18

ASTM International. (2019). *ASTM D5748-95, Standard Test Method for Protrusion Puncture Resistance of Stretch Wrap Film.* https://doi.org/10.1520/D5748-95R19.2

Avérous, L. (2004). Biodegradable Multiphase Systems Based on Plasticized Starch: A Review. *Journal of Macromolecular Science, Part C*, *44*(3), 231–274. https://doi.org/10.1081/MC-200029326

Aviara, N. A. (2020). Sorption in 2020s. In G. Kyzas & N. Lazaridis (Eds.), *Sorption in 2020s*. IntechOpen. https://doi.org/10.5772/intechopen.77842

Barrer., R. M. (1942). Diffusion in and through Solids. In *The University Press*. Cambridge series of physical chemistry. https://doi.org/10.1021/j150418a018

Ben Halima, N. (2016). Poly(vinyl alcohol): review of its promising applications and insights into biodegradation. *RSC Advances*, *6*(46), 39823–39832. https://doi.org/10.1039/C6RA05742J

Bof, M. J., Bordagaray, V. C., Locaso, D. E., & García, M. A. (2015). Chitosan molecular weight effect on starch-composite film properties. *Food Hydrocolloids*, *51*, 281–294. https://doi.org/10.1016/j.foodhyd.2015.05.018

Bourtoom, T. (2008). Plasticizer effect on the properties of biodegradable blend from rice starch-chitosan. *Songklanakarin Journal of Science and Technology*, *30*(SUPPL. 1), 149–155.

Brunauer, S., Deming, L. S., Deming, W. E., & Teller, E. (1940). On a Theory of the van der Waals Adsorption of Gases. *Journal of the American Chemical Society*, *62*(7), 1723–1732. https://doi.org/10.1021/ja01864a025

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, *60*(2), 309–319. https://doi.org/10.1021/ja01269a023

Cano, A., Cháfer, M., Chiralt, A., & González-Martínez, C. (2016). Development and characterization of active films based on starch-PVA, containing silver nanoparticles. *Food Packaging and Shelf Life*, *10*, 16–24. https://doi.org/10.1016/j.fpsl.2016.07.002

Cassagnau, P., Bounor-Legaré, V., & Fenouillot, F. (2007). Reactive Processing of Thermoplastic Polymers: A Review of the Fundamental Aspects. *International Polymer Processing*, *22*(3), 218–258. https://doi.org/10.3139/217.2032

Cassini, A. S., Marczak, L. D. F., & Noreña, C. P. Z. (2006). Water adsorption isotherms of texturized soy protein. *Journal of Food Engineering*, *77*(1), 194–199. https://doi.org/10.1016/j.jfoodeng.2005.05.059

Cazón, P., Velázquez, G., & Vázquez, M. (2020). Regenerated cellulose films combined with glycerol and polyvinyl alcohol: Effect of moisture content on the physical properties. *Food Hydrocolloids*, *103*, 105657. https://doi.org/10.1016/j.foodhyd.2020.105657

Cherubini, F., & Strømman, A. H. (2011). Chemicals from lignocellulosic biomass: opportunities, perspectives, and potential of biorefinery systems. *Biofuels, Bioproducts and Biorefining*, *5*(5), 548–561. https://doi.org/10.1002/bbb.297

Crank, J. (1975). *The Mathematics of Diffusion* (2nd ed.). Clarendon Press.

Elizondo, N. J., Sobral, P. J. A., & Menegalli, F. C. (2009). Development of films based on blends of Amaranthus cruentus flour and poly(vinyl alcohol). *Carbohydrate Polymers*, *75*(4), 592–598. https://doi.org/10.1016/j.carbpol.2008.08.020

Ferreira, D. F. (2011). Sisvar: Um sistema computacional de análise estatística. *Ciencia e Agrotecnologia*, *35*(6), 1039–1042. https://doi.org/10.1590/S1413-70542011000600001

Garcia, P. S., Grossmann, M. V. E., Yamashita, F., Mali, S., Dall'Antonia, L. H., & Barreto, W. J. (2011). Citric acid as multifunctional agent in blowing films of starch/PBAT. *Química Nova*, *34*(9), 1507–1510. https://doi.org/10.1590/S0100-40422011000900005

Ghanbarzadeh, B., Almasi, H., & Entezami, A. A. (2011). Improving the barrier and mechanical properties of corn starch-based edible films: Effect of citric acid and carboxymethyl cellulose. *Industrial Crops and Products*, *33*(1), 229–235. https://doi.org/10.1016/j.indcrop.2010.10.016

Guggenheim, E. A. (1966). *Applications of Statistical Mechanics*. Clarendon Press. https://books.google.com.br/books?id=5-8yAAAAMAAJ

Guimarães, M., Botaro, V. R., Novack, K. M., Teixeira, F. G., & Tonoli, G. H. D. (2015). High moisture strength of cassava starch/polyvinyl alcohol-compatible blends for the packaging and agricultural sectors. *Journal of Polymer Research*, *22*(10), 192. https://doi.org/10.1007/s10965-015-0834-z

Halsey, G. (1948). Physical Adsorption on Non-Uniform Surfaces. *The Journal of Chemical Physics*, *16*(10), 931–937. https://doi.org/10.1063/1.1746689

Han, B., Li, J., Chen, C., Xu, C., & Wickramasinghe, S. R. (2003). Effects of Degree of Formaldehyde Acetal Treatment and Maleic Acid Crosslinking on Solubility and Diffusivity of Water in PVA Membranes. *Chemical Engineering Research and Design*, *81*(10), 1385–1392. https://doi.org/10.1205/026387603771339609

Hulleman, S. H. D., Janssen, F. H. P., & Feil, H. (1998). The role of water during plasticization of native starches. *Polymer*, *39*(10), 2043–2048. https://doi.org/10.1016/S0032-3861(97)00301-7

Ibrahim, S., Elsayed, H., & Hasanin, M. (2021). Biodegradable, Antimicrobial and Antioxidant Biofilm for Active Packaging Based on Extracted Gelatin and Lignocelluloses Biowastes. *Journal of Polymers and the Environment*, *29*(2), 472–482. https://doi.org/10.1007/s10924-020-01893-7

Kabir, E., Kaur, R., Lee, J., Kim, K.-H., & Kwon, E. E. (2020). Prospects of biopolymer technology as an alternative option for non-degradable plastics and sustainable management of plastic wastes. *Journal of Cleaner Production*, *258*, 120536. https://doi.org/10.1016/j.jclepro.2020.120536

Kanatt, S. R., & Makwana, S. H. (2020). Development of active, water-resistant carboxymethyl cellulose-poly vinyl alcohol-Aloe vera packaging film. *Carbohydrate Polymers*, *227*,

115303. https://doi.org/10.1016/j.carbpol.2019.115303

Kaymak-Ertekin, F., & Sultanoğlu, M. (2001). Moisture sorption isotherm characteristics of peppers. *Journal of Food Engineering*, *47*(3), 225–231. https://doi.org/10.1016/S0260-8774(00)00120-5

Khalfaoui, M., Knani, S., Hachicha, M. A., & Lamine, A. B. (2003). New theoretical expressions for the five adsorption type isotherms classified by BET based on statistical physics treatment. *Journal of Colloid and Interface Science*, *263*(2), 350–356. https://doi.org/10.1016/S0021-9797(03)00139-5

Labuza, T. P. (1968). Sorption phenomena in foods. *Food Technol.*, *22*, 15–19.

Lara, B. R. B., Dias, M. V., Guimarães Júnior, M., de Andrade, P. S., de Souza Nascimento, B., Ferreira, L. F., & Yoshida, M. I. (2020). Water sorption thermodynamic behavior of whey protein isolate/ polyvinyl alcohol blends for food packaging. *Food Hydrocolloids*, *103*(January). https://doi.org/10.1016/j.foodhyd.2020.105710

Larotonda, F. D. S., Matsui, K. N., Sobral, P. J. A., & Laurindo, J. B. (2005). Hygroscopicity and water vapor permeability of Kraft paper impregnated with starch acetate. *Journal of Food Engineering*, *71*(4), 394–402. https://doi.org/10.1016/j.jfoodeng.2004.11.002

Lebreton, L. C. M., van der Zwet, J., Damsteeg, J.-W., Slat, B., Andrady, A., & Reisser, J. (2017). River plastic emissions to the world's oceans. *Nature Communications*, *8*(1), 15611. https://doi.org/10.1038/ncomms15611

Lemos, Á. T., Ribeiro, A. C., Fidalgo, L. G., Delgadillo, I., & Saraiva, J. A. (2017). Extension of raw watermelon juice shelf-life up to 58 days by hyperbaric storage. *Food Chemistry*, *231*, 61–69. https://doi.org/10.1016/j.foodchem.2017.03.110

Li, Y., Liu, K., & Chen, F. (2016). Effect of selenium enrichment on the quality of germinated brown rice during storage. *Food Chemistry*, *207*, 20–26. https://doi.org/10.1016/j.foodchem.2016.03.080

Liu, B., Xu, H., Zhao, H., Liu, W., Zhao, L., & Li, Y. (2017). Preparation and characterization of intelligent starch/PVA films for simultaneous colorimetric indication and antimicrobial activity for food packaging applications. *Carbohydrate Polymers*, *157*, 842–849. https://doi.org/10.1016/j.carbpol.2016.10.067

Lourdin, D., Bizot, H., & Colonna, P. (1997). Correlation between static mechanical properties of starch-glycerol materials and low-temperature relaxation. *Macromolecular Symposia*, *114*(1), 179–185.

Lowell, S., & Shields, J. E. (1984). Adsorption isotherms. In *Powder Surface Area and Porosity* (pp. 11–13). Springer Netherlands. https://doi.org/10.1007/978-94-009-5562-2_3

Luchese, C. L., Spada, J. C., & Tessaro, I. C. (2017). Starch content affects physicochemical properties of corn and cassava starch-based films. *Industrial Crops and Products*, *109*, 619–626. https://doi.org/10.1016/j.indcrop.2017.09.020

Mali, S., Sakanaka, L. S., Yamashita, F., & Grossmann, M. V. E. (2005). Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydrate Polymers*, *60*(3), 283–289. https://doi.org/10.1016/j.carbpol.2005.01.003

Masaro, L., & Zhu, X. . (1999). Physical models of diffusion for polymer solutions, gels and solids. *Progress in Polymer Science*, *24*(5), 731–775. https://doi.org/10.1016/S0079-6700(99)00016-7

Mathew, A. P., & Dufresne, A. (2002). Plasticized waxy maize starch: effect of polyols and relative humidity on material properties. *Biomacromolecules*, *3*(5), 1101–1108.

Mathew, S., Jayakumar, A., Kumar, V. P., Mathew, J., & Radhakrishnan, E. K. (2019). One-step synthesis of eco-friendly boiled rice starch blended polyvinyl alcohol bionanocomposite films decorated with in situ generated silver nanoparticles for food packaging purpose. *International Journal of Biological Macromolecules*, *139*, 475–485. https://doi.org/10.1016/j.ijbiomac.2019.07.187

Mendes, J. F., Paschoalin, R. ., Carmona, V. B., Sena Neto, A. R., Marques, A. C. P., Marconcini, J. M., Mattoso, L. H. C., Medeiros, E. S., & Oliveira, J. E. (2016). Biodegradable polymer blends based on corn starch and thermoplastic chitosan processed by extrusion. *Carbohydrate Polymers*, *137*, 452–458. https://doi.org/10.1016/j.carbpol.2015.10.093

Mills, N., Jenkins, M., & Kukureka, S. (2020). *Plastics: microstructure and engineering applications*. Butterworth-Heinemann.

Mittal, A., Garg, S., Kohli, D., Maiti, M., Jana, A. K., & Bajpai, S. (2016). Effect of cross linking of PVA/starch and reinforcement of modified barley husk on the properties of composite films. *Carbohydrate Polymers*, *151*, 926–938. https://doi.org/10.1016/j.carbpol.2016.06.037

Monjazeb Marvdashti, L., Yavarmanesh, M., & Koocheki, A. (2019). In vitro release study of nisin from active polyvinyl alcohol-Alyssum homolocarpum seed gum films at different temperatures. *Polymer Testing*, *79*, 106032. https://doi.org/10.1016/j.polymertesting.2019.106032

Müller-Plathe, F. (1998). Diffusion of water in swollen poly(vinyl alcohol) membranes studied by molecular dynamics simulation. *Journal of Membrane Science*, *141*(2), 147–154. https://doi.org/10.1016/S0376-7388(97)00289-5

Müller, C. M. O., Laurindo, J. B., & Yamashita, F. (2009). Effect of cellulose fibers addition on the mechanical properties and water vapor barrier of starch-based films. *Food Hydrocolloids*, *23*(5), 1328–1333. https://doi.org/10.1016/j.foodhyd.2008.09.002

Müller, C. M. O., Yamashita, F., & Laurindo, J. B. (2008). Evaluation of the effects of glycerol and sorbitol concentration and water activity on the water barrier properties of cassava starch films through a solubility approach. *Carbohydrate Polymers*, *72*(1), 82–87. https://doi.org/10.1016/j.carbpol.2007.07.026

Muppalla, S. R., Kanatt, S. R., Chawla, S. P., & Sharma, A. (2014). Carboxymethyl cellulose–polyvinyl alcohol films with clove oil for active packaging of ground chicken meat. *Food Packaging and Shelf Life*, *2*(2), 51–58. https://doi.org/10.1016/j.fpsl.2014.07.002

Ning, W., Jiugao, Y., Xiaofei, M., & Ying, W. (2007). The influence of citric acid on the properties of thermoplastic starch/linear low-density polyethylene blends. *Carbohydrate Polymers*, *67*(3), 446–453. https://doi.org/10.1016/j.carbpol.2006.06.014

Olsson, E., Hedenqvist, M. S., Johansson, C., & Järnström, L. (2013). Influence of citric acid

and curing on moisture sorption, diffusion and permeability of starch films. *Carbohydrate Polymers*, *94*(2), 765–772. https://doi.org/10.1016/j.carbpol.2013.02.006

Oswin, C. R. (1946). The kinetics of package life. III. The isotherm. *Journal of the Society of Chemical Industry*, *65*(12), 419–421. https://doi.org/10.1002/jctb.5000651216

Ounkaew, A., Kasemsiri, P., Kamwilaisak, K., Saengprachatanarug, K., Mongkolthanaruk, W., Souvanh, M., Pongsa, U., & Chindaprasirt, P. (2018). Polyvinyl Alcohol (PVA)/Starch Bioactive Packaging Film Enriched with Antioxidants from Spent Coffee Ground and Citric Acid. *Journal of Polymers and the Environment*, *26*(9), 3762–3772. https://doi.org/10.1007/s10924-018-1254-z

Panpinit, S., Pongsomboon, S., Keawin, T., & Saengsuwan, S. (2020). Development of multicomponent interpenetrating polymer network (IPN) hydrogel films based on 2-hydroxyethyl methacrylate (HEMA), acrylamide (AM), polyvinyl alcohol (PVA) and chitosan (CS) with enhanced mechanical strengths, water swelling and antibacteria. *Reactive and Functional Polymers*, *156*, 104739. https://doi.org/10.1016/j.reactfunctpolym.2020.104739

Park, K. J. B., Park, K. J., Cornejo, F. E. P., & Fabbro, I. M. D. (2008). Considerações termodinâmicas das isotermas. *Revista Brasileira de Produtos Agroindustriais*, *10*(1), 83–94.

Pertussatti, C. A. (2020). *GESTÃO AMBIENTAL DE RESÍDUOS PLÁSTICOS NO BRASIL:Subsídios Para Uma Diretriz Nacional*.

Pinto, José Carlos; Magrini, Alessandra; Melo, Caio Kawaoka; Castor Jr., Carlos Alberto; Gaioto, CArolina Cazelato; Santos, Dirceu Pereira; Borges, Grazielle; Rosa, Isaías da Silva; Delgado, Jorge Juan Soto; Souza, Márcio Nele; Oliveira, Maria Clara B. R., S. M. R. (2012). *Impactos ambientais causados pelos plásticos. Uma discussão abrangente sobre os mitos e os dados científicos*. Editora E-papers.

Piringer, O. G., & Baner, A. L. (2008). *Plastic packaging materials for food: barrier function, mass transport, quality assurance, and legislation*. John Wiley & Sons.

Quirijns, E. J., van Boxtel, A. J., van Loon, W. K., & van Straten, G. (2005). Sorption isotherms, GAB parameters and isosteric heat of sorption. *Journal of the Science of Food and Agriculture*, *85*(11), 1805–1814. https://doi.org/10.1002/jsfa.2140

Rahman, W. A. W. A., Sin, L. T., Rahmat, A. R., & Samad, A. A. (2010). Thermal behaviour and interactions of cassava starch filled with glycerol plasticized polyvinyl alcohol blends. *Carbohydrate Polymers*, *81*(4), 805–810. https://doi.org/10.1016/j.carbpol.2010.03.052

Ray, S., & Bousmina, M. (2005). Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world. *Progress in Materials Science*, *50*(8), 962–1079. https://doi.org/10.1016/j.pmatsci.2005.05.002

Reddy, N., & Yang, Y. Citric acid cross-linking of starch films. *Food Chemistry*, *118*(3), 702–711. https://doi.org/10.1016/j.foodchem.2009.05.050

Ritchie, H., & Roser, M. (2020). Plastic Pollution. *Our World in Data*, 115–147. https://doi.org/10.1142/9781786347435_0005

Robertson, G. L. (2016). *Food Packaging*. CRC Press. https://doi.org/10.1201/b21347

Rosa, G. S., Moraes, M. A., & Pinto, L. A. A. (2010). Moisture sorption properties of chitosan. *LWT - Food Science and Technology*, *43*(3), 415–420. https://doi.org/10.1016/j.lwt.2009.09.003

Rose, M., & Palkovits, R. (2011). Cellulose-Based Sustainable Polymers: State of the Art and Future Trends. *Macromolecular Rapid Communications*, *32*(17), 1299–1311. https://doi.org/10.1002/marc.201100230

Scatolino, M. V., Bufalino, L., Mendes, L. M., Guimarães Júnior, M., & Tonoli, G. H. D. (2017). Impact of nanofibrillation degree of eucalyptus and Amazonian hardwood sawdust on physical properties of cellulose nanofibril films. *Wood Science and Technology*, *51*(5), 1095–1115. https://doi.org/10.1007/s00226-017-0927-4

Shi, R., Bi, J., Zhang, Z., Zhu, A., Chen, D., Zhou, X., Zhang, L., & Tian, W. (2008). The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature. *Carbohydrate Polymers*, *74*(4), 763–770. https://doi.org/10.1016/j.carbpol.2008.04.045

Shogren, R. L. (1993). *Effects of moisture and various plasticizers on the mechanical properties of extruded starch*. Ching Ch., Kaplan DL, Thomas EL:"Biodegradable polymers and packaging ….

Sing, K. (2001). The use of nitrogen adsorption for the characterisation of porous materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *187–188*, 3–9. https://doi.org/10.1016/S0927-7757(01)00612-4

Smith, S. E. (1947). The Sorption of Water Vapor by High Polymers. *Journal of the American Chemical Society*, *69*(3), 646–651. https://doi.org/10.1021/ja01195a053

Srinivasa, P. C., Ramesh, M. N., Kumar, K. R., & Tharanathan, R. N. (2003). Properties and sorption studies of chitosan–polyvinyl alcohol blend films. *Carbohydrate Polymers*, *53*(4), 431–438. https://doi.org/10.1016/S0144-8617(03)00105-X

Srinivasa, P. C., Ramesh, M. N., & Tharanathan, R. N. (2007). Effect of plasticizers and fatty acids on mechanical and permeability characteristics of chitosan films. *Food Hydrocolloids*, *21*(7), 1113–1122. https://doi.org/10.1016/j.foodhyd.2006.08.005

Tao, Y., Wu, Y., Yang, J., Jiang, N., Wang, Q., Chu, D.-T., Han, Y., & Zhou, J. (2018). Thermodynamic sorption properties, water plasticizing effect and particle characteristics of blueberry powders produced from juices, fruits and pomaces. *Powder Technology*, *323*, 208–218. https://doi.org/10.1016/j.powtec.2017.09.033

Urbanski, B. Q., Denadai, A. C., Azevedo-Santos, V. M., & Nogueira, M. G. (2020). First record of plastic ingestion by an important commercial native fish (Prochilodus lineatus) in the middle Tietê River basin, Southeast Brazil. *Biota Neotropica*, *20*(3). https://doi.org/10.1590/1676-0611-bn-2020-1005

Velázquez-Gutiérrez, S. K., Figueira, A. C., Rodríguez-Huezo, M. E., Román-Guerrero, A., Carrillo-Navas, H., & Pérez-Alonso, C. (2015). Sorption isotherms, thermodynamic properties and glass transition temperature of mucilage extracted from chia seeds ( Salvia hispanica L.). *Carbohydrate Polymers*, *121*, 411–419. https://doi.org/10.1016/j.carbpol.2014.11.068

Wu, Z., Wu, J., Peng, T., Li, Y., Lin, D., Xing, B., Li, C., Yang, Y., Yang, L., Zhang, L., Ma,

R., Wu, W., Lv, X., Dai, J., & Han, G. (2017). Preparation and Application of Starch/Polyvinyl Alcohol/Citric Acid Ternary Blend Antimicrobial Functional Food Packaging Films. *Polymers*, *9*(12), 102. https://doi.org/10.3390/polym9030102

Yui, N., Mrsny, R. J., & Park, K. (2004). *Reflexive polymers and hydrogels: understanding and designing fast responsive polymeric systems*. CRC press. https://doi.org/doi.org/10.1021/ja040974h

Zanela, J., Olivato, J. B., Dias, A. P., Grossmann, M. V. E., & Yamashita, F. (2015). Mixture design applied for the development of films based on starch, polyvinyl alcohol, and glycerol. *Journal of Applied Polymer Science*, *132*(43), n/a-n/a. https://doi.org/10.1002/app.42697

Zhang, J., Zou, X., Zhai, X., Huang, X., Jiang, C., & Holmes, M. (2019). Preparation of an intelligent pH film based on biodegradable polymers and roselle anthocyanins for monitoring pork freshness. *Food Chemistry*, *272*, 306–312. https://doi.org/10.1016/j.foodchem.2018.08.041

Zhang, K., Huang, T.-S., Yan, H., Hu, X., & Ren, T. (2020). Novel pH-sensitive films based on starch/polyvinyl alcohol and food anthocyanins as a visual indicator of shrimp deterioration. *International Journal of Biological Macromolecules*, *145*, 768–776. https://doi.org/10.1016/j.ijbiomac.2019.12.159