



**UNIVERSIDADE ESTADUAL DO OESTE DO PARANÁ
CENTRO DE ENGENHARIAS E CIÊNCIAS EXATAS
PROGRAMA DE PÓS-GRADUAÇÃO EM QUÍMICA**

**EFEITO DA CONCENTRAÇÃO DE PLASTIFICANTE EM
REVESTIMENTOS COMESTÍVEIS À BASE DE BLENDS DE
POLI(ÁLCOOL VINÍLICO) (PVA) E AMIDO CATIÔNICO (CS)**

JAIANE MAIARA PETRY

**Toledo – PR
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Dissertação apresentada ao Programa de Pós-Graduação em Química da Universidade Estadual do Oeste do Paraná, Unioeste/*Campus* de Toledo, como parte dos requisitos para a obtenção do Título de Mestre em Química.

Orientador(a): Douglas Cardoso Dragunski

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JAIANE MAIARA PETRY

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Dissertação apresentada ao Programa de Pós-Graduação em Química em cumprimento parcial aos requisitos para obtenção do título de Mestre em Química, área de concentração Química, linha de pesquisa Obtenção e Aplicação de Materiais (OAMat), APROVADA pela seguinte banca examinadora:

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Efeito da concentração de plastificante em revestimentos comestíveis à base de blendas de poli(álcool vinílico) (PVA) e amido catiônico (CS)

Jaiane Maiara Petry

RESUMO

Filmes à base de poli(álcool vinílico) (PVA) e amido catiônico (CS) foram combinados com diferentes porcentagens de sorbitol (S) para avaliar o efeito do plastificante sobre as propriedades dos filmes. As análises de FTIR e DRX confirmaram a interação entre eles. No entanto, micrografias MEV confirmaram a formação de cristais de sorbitol na superfície dos filmes. Estes cristais tornaram-se mais evidentes com o aumento da quantidade de sorbitol. A mistura entre polímero/sorbitol é estável por um curto período. As misturas apresentaram baixos valores de taxa de transmissão de vapor de água, atingindo $(7,703 \pm 0,00) \text{ g h}^{-1} \text{ m}^{-2}$ e baixos valores de solubilidade para os filmes contendo maiores quantidades de CS. A falta de diferenças estatísticas na maioria dos parâmetros sugere, que o aumento da quantidade de sorbitol, não promove nenhum ganho significativo, em porcentagens superiores a 15% m/m. Como revestimento, a mistura composta por 75% de PVA, 25% de CS e 15% de S diminuiu com sucesso a perda de umidade nas acerolas, e preservou a cor vermelha brilhante dos frutos para períodos mais longos. Além disso, o revestimento levou a uma maturação mais homogênea, e aumentou a vida útil das acerolas em um dia (temperatura de 25°C). Isso confirma a adequação desta mistura para fins de revestimento de alimentos.

Palavras-chave: Sorbitol; filme biodegradável; acerola; preservação de alimentos.

Plasticizer concentration effect on edible coatings based on poly(vinyl alcohol) (PVA) and cationic starch (CS) blends

Jaiane Maiara Petry

ABSTRACT

Films based on poly(vinyl alcohol) (PVA) and cationic starch (CS) were combined with different percentages of sorbitol (S) to evaluate the effect of the plasticizer on the properties of the films. FTIR and DRX analyzes confirmed the interaction between them. However, SEM micrographs confirmed the formation of sorbitol crystals on the surface of the films. These crystals became more evident with increasing amount of sorbitol. The polymer/sorbitol mixture is stable for a short period. The mixtures showed low values of water vapor transmission rate, reaching (7.703 ± 0.00) g h⁻¹ m⁻² and low solubility values for films containing higher amounts of CS. The lack of statistical differences in most parameters suggests that increasing the amount of sorbitol does not promote any significant gain in percentages greater than 15% m/m. As a coating, the mixture composed of 75% PVA, 25% CS and 15% S successfully reduced moisture loss in the acerolas, and preserved the bright red color of the fruits for longer periods. In addition, the coating led to a more homogeneous maturation, and increased the shelf life of the acerolas by one day (temperature of 25°C). This confirms the suitability of this mixture for food coating purposes.

Keywords: Sorbitol; biodegradable film; Barbados Cherry; food preservation.

1 – INTRODUÇÃO

As preocupações relacionadas aos problemas ambientais causados por diferentes atividades humanas, vem aumentando. Dentre elas, pode-se citar a utilização de polímeros sintéticos (plásticos) de forma desenfreada [1]. Visando minimizar tais problemas, inúmeros estudos vêm sendo desenvolvidos promovendo a substituição desses polímeros sintéticos, que tem como matéria prima principal o petróleo [1], por polímeros chamados “plásticos verdes” ou bioplásticos [2]. Tais materiais, provém de polímeros biodegradáveis, sendo o amido um dos principais exemplos [3]. Estes podem dar origem aos biofilmes, que por sua vez, possuem inúmeras aplicações, como por exemplo a utilização em curativos, recobrimento de frutas, entre outros [4].

Quando o assunto é aplicação dos biofilmes, eles podem atuar como uma embalagem primária no revestimento de alimentos. Esse revestimento ainda não elimina a necessidade de embalagens secundárias, mas ainda assim, contribui para a manutenção da textura e valor nutricional dos alimentos [5].

O amido é um dos principais biopolímeros para a produção de biofilmes, uma vez que possuem baixo custo, alta disponibilidade, são transparentes, incolores, inodoros, e possuem baixa permeabilidade ao oxigênio [6].

Os amidos em geral, podem ser tanto naturais, sendo extraídos de tubérculos, sementes e frutos, como também podem ser modificados industrialmente por processos físicos, como o tratamento térmico, ou processos químicos, onde empregam-se reagentes específicos para alterar a estrutura do amido [7]. Nos processos químicos, os amidos catiônicos promovem características importantes ao amido, como por exemplo, alta dispersibilidade e aderência a diversas aplicações [8]. Enquanto isso, os amidos oxidados apresentam propriedades de superfície interessante e despertam o interesse na indústria alimentícia, têxtil e papelreira [9].

Além do amido, o Álcool polivinílico (PVA) também é considerado biodegradável, trata-se de um polímero sintético solúvel em água, que, devido suas propriedades de biocompatibilidade, não toxicidade e por ser um polímero totalmente biodegradável tem se tornado de grande interesse [10]. Este polímero possui uma elevada capacidade de adsorção de água, além de propriedades como semipermeabilidade, e estabilidade de pH que ajudam na formação de um ambiente adequado para o crescimento celular [11].

Para obtenção dos materiais a partir do PVA e do amido catiônico, pode-se citar a técnica de casting, que é baseada na solubilização da mistura dos biopolímeros em um solvente adequado, podendo ser adicionado um plastificante. Os plastificantes são moléculas pequenas, utilizadas para melhorar as propriedades da blenda dos biopolímeros. Dentre os plastificantes mais utilizados para a obtenção de filmes biodegradáveis, encontram-se os polióis, como o glicerol e o sorbitol [12][13].

Ao adicionar os plastificantes nas soluções, aumenta-se a mobilidade molecular, a flexibilidade, hidrofobicidade e permeabilidade ao vapor de água, visto que, os plastificantes apresentam caráter hidrofílico [12]. Diante disso, novos materiais fundamentados em diferentes concentrações de amidos catiônicos, polímeros biodegradáveis e plastificantes têm sido desenvolvidos e estudados para revestimento alimentício.

2 – OBJETIVOS

2.1 OBJETIVO GERAL

Estudar o efeito da concentração de plastificante em revestimentos comestíveis à base de blendas de poli(álcool vinílico) (PVA) e amido catiônico (CS).

2.2 OBJETIVOS ESPECÍFICOS

- Produzir diferentes blendas PVA/Amido catiônico avaliando diferentes composições dos polímeros e do plastificante;
- Caracterizar os materiais obtidos por meio de técnicas físico-químicas, morfológicas, térmicas, mecânicas e ópticas.
- Aplicar os filmes para recobrimentos da fruta acerola;
- Avaliar os frutos antes e após o recobrimento por meio de análises destrutivas e não destrutivas.

3 REVISÃO BIBLIOGRÁFICA

3.1 EMBALAGENS BIODEGRADÁVEIS

As embalagens biodegradáveis desempenham diversas funções e apresentam grande importância na obtenção de novos materiais considerados sustentáveis. Isto ocorre, principalmente, pelo fato de utilizarem fontes naturais como matéria prima, apresentarem baixo custo e não são tóxicos [14]. Além disso, atualmente, a maioria das embalagens utilizadas são produzidas a partir de materiais não biodegradáveis, ou seja, polímeros provenientes de fontes não renováveis, como o petróleo [14][15]. Esses materiais causam diversos problemas ambientais devido ao fato de permanecerem praticamente intactos ao longo de muitos anos [14][15]. Dessa forma, estão sendo desenvolvidos materiais biodegradáveis para embalagens, na tentativa de reduzir o impacto ambiental provocado pela degradação lenta das embalagens a base de polímeros sintéticos [16].

Os materiais biodegradáveis são considerados não tóxicos, e são aplicados, dentre outros, em filmes biodegradáveis e revestimentos destinados à conservação e proteção de alimentos. Quando aplicados como revestimento, eles agem como uma barreira a elementos externos tais como sujidades, gases e umidade [16]. Além disso, também podem ser adicionados antioxidantes naturais, fazendo com que a vida de prateleira desses alimentos aumente ainda mais [15][16].

3.2 EMBALAGENS ATIVAS

Nos alimentos, as embalagens exercem principalmente a função de marketing e proteção passiva [17]. Entretanto, nos últimos anos, esse conceito teve uma modificação: além das funções citadas anteriormente, essas embalagens passaram a atuar como um fator ativo na conservação, manutenção da qualidade e na segurança dos alimentos [17]. Embalagens com essas características são chamadas de embalagens ativas porque, além de proteger o alimento, elas interagem com o mesmo, trazendo benefícios não proporcionados por embalagens comuns [17].

Essas embalagens ativas têm sido desenvolvidas a partir de matérias primas naturais e renováveis, de forma que tanto a matriz polimérica quanto os aditivos funcionais apresentam características de materiais biodegradáveis. Esses materiais são produzidos a partir de polissacarídeos, lipídios, proteínas e derivados, dissolvidos em solventes apropriados e com um acréscimo de ativos (plastificante ou agentes de liga) [15][18].

3.3 AMIDOS

O amido é um dos biopolímeros mais utilizados para compor os materiais biodegradáveis, isto pelo seu baixo custo e disponibilidade [19]. Entre as principais fontes comerciais para a obtenção dos amidos encontram-se milho, trigo, arroz, batata e mandioca [14][20]. Dentre os tipos de amidos

citados anteriormente, o amido de milho é o mais predominante em todo o mundo, e ocupa 65% do total [21].

O amido é um polímero com massa molecular elevada, formado por duas frações de homopolímeros: amilose e amilopectina [20]. A amilose (FIG. 1) é uma cadeia não ramificada, linear, composta de unidades ligadas de α -D-glucopiranosose unidas por ligações glicosídicas α 1-4 [20].

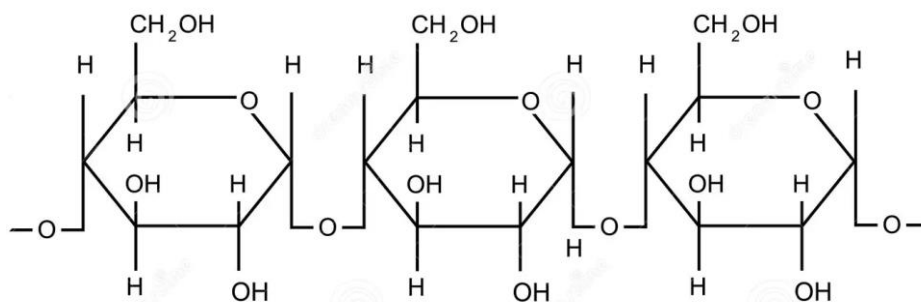


Figura 1: Estrutura química da amilose.

A amilopectina, por outro lado, consiste em uma cadeia principal que carrega o grupo redutor da molécula e ramificações de outras cadeias [20]. Também apresenta em sua cadeia unidades de α -D-glucopiranosose unidas por ligações α 1-4, mas contendo 5 a 6% de ligações cruzadas α 1-6 entre um grupo hidroxila de uma cadeia de glicose e o carbono 6 da glicose de outra cadeia (FIG. 2) [20]. Além disso, a amilopectina apresenta ramificações de aproximadamente, 20 a 30 unidades de glicose [20].

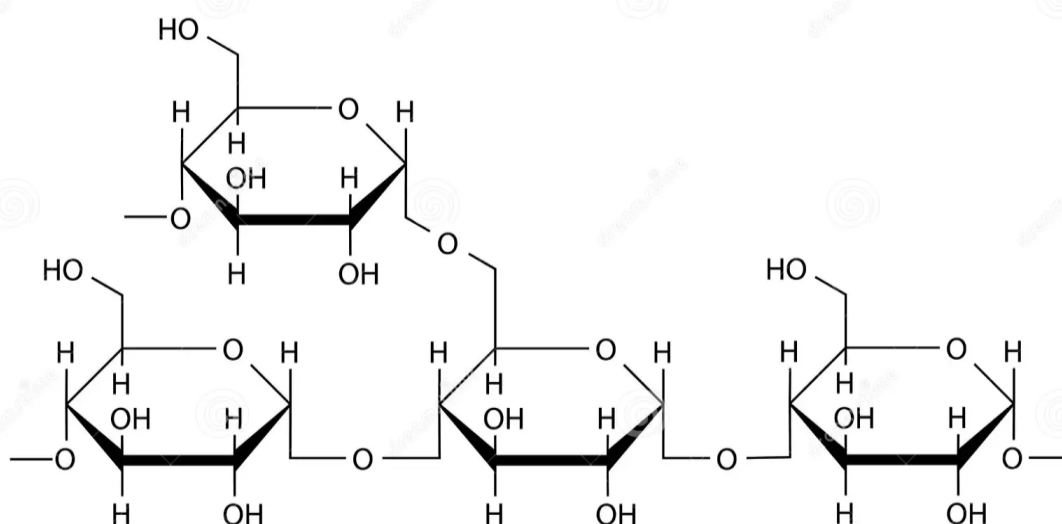


Figura 2: Estrutura química da amilopectina.

Conforme destacam fontes botânicas, os amidos apresentam de 20 a 30% de amilose e 70 a 80% de amilopectina em sua composição [20]. No arranjo da amilose e amilopectina, ocorre a

formação de zonas de deposição mais ou menos densas [20]. A região com amilopectina é caracterizada como mais densa ou cristalina e a região com amilose e as ramificações da amilopectina apresentam características amorfas [20].

3.4 AMIDOS MODIFICADOS

Os amidos, na forma natural, apresentam algumas limitações, como ser insolúvel em água resfriada, com tendência a retrogradar e perder viscosidade [22]. Portanto, para superar essas limitações, o amido pode ser modificado de forma química, física ou genética, melhorando sua performance nas aplicações desejadas [22].

A presença de muitos grupos hidroxila na molécula dos amidos faz com que o amido tenha locais mais reativos para modificações químicas, contudo, só a hidroxila C6 é suscetível a reações de qualquer natureza. As demais hidroxilas são desfavorecidas (1) pelo arranjo equatorial ou (2) pelas interações 1,3-diaxial experimentadas pelas hidroxis na posição axial na unidade glicosídica [23]. As diferentes formas de modificar a estrutura dos amidos nativos fornecem diferentes propriedades a eles, como pode ser visto na (TAB. 1).

Tabela 1 - Propriedades da preparação de amido a partir de diferentes formas de modificação químicas.

FORMAS DE MODIFICAÇÃO	PROPRIEDADES
Reticulação	<ul style="list-style-type: none"> ● Melhor estabilidade de congelamento e descongelamento e estabilidade dos grânulos [22]; ● Baixo poder de dilatação, solubilidade e entalpia de gelatinização [22]; ● Maior calor e estabilidade de cisalhamento [22].
Esterificação	<ul style="list-style-type: none"> ● Maior resistência à umidade e termoplasticidade [22]; ● Melhor compatibilidade [22]; ● Melhor flexibilidade [24]; ● Redução da cristalinidade [24].
Eterificação	<ul style="list-style-type: none"> ● Melhor estabilidade térmica e solubilidade [22][24]; ● Melhor fluidez, permeabilidade e resistência [22].
Oxidação	<ul style="list-style-type: none"> ● Maior solubilidade [22]; ● Maior temperatura de gelatinização [22]; ● Melhor absorção de água [22];

	<ul style="list-style-type: none"> • Elevada transparência [24];
Acidificação	<ul style="list-style-type: none"> • Melhor recuperação e solubilidade [22]; • Viscosidade de colagem mais baixa [22].

Entre os amidos modificados, os amidos catiônicos são os de maior relevância [25]. Amidos catiônicos são amidos que possuem cargas positivas em sua estrutura e, assim, apresentam algumas vantagens, como atrair cargas negativas e aumentar a resistência mecânica [26]. Os amidos catiônicos podem ser preparados por reações de eterificação com 3-cloro-2hidroxipropiltrimetilamônio (CHPTAC) comercializado pelos nomes de QUAT 188 (Dow Chemical Company) e QUAB 188 (Degussa-Huls, Ag), reagente que apresenta características importantes como baixo custo, e leva a altos rendimentos em reações de modificação [25][26].

A reação de cationização do amido com CHPTAC (FIG 3), é uma reação de substituição, que ocorre pelo mecanismo de substituição nucleofílica bimolecular (SN2) [22]. A reação catalisada por uma base é, geralmente, hidróxido de sódio (NaOH).

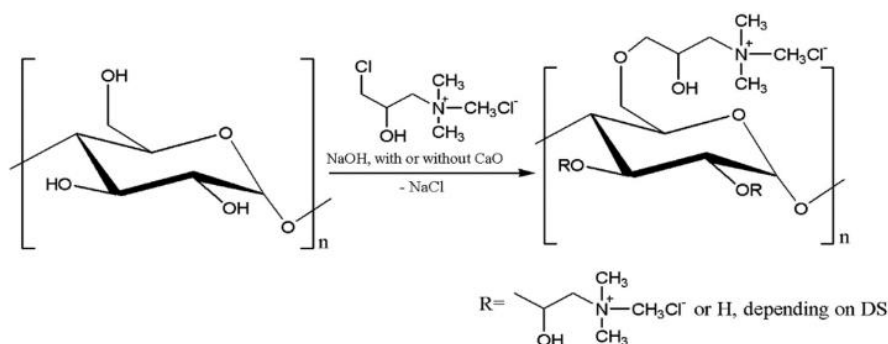


Fig. 1. Synthesis scheme of cationic starches.

Figura 3: Esquema de reação geral da síntese catiônica de amido com CHPTAC na presença de NaOH como catalisador [26].

As propriedades dos amidos catiônicos podem variar significativamente, dependendo da natureza dos substituintes e do grau de substituição (DS) [22]. O grau de substituição indica o número de substituições por unidade de anidroglicose do amido, no qual o valor máximo possível de DS é 3, por conta de existirem três grupos hidroxila disponíveis por anidroglicose [22][27].

Os amidos catiônicos são utilizados principalmente no campo da fabricação de papel [28], aditivos na fabricação de têxteis [29], submetidos a reação de benzilação, formulação de produtos cosméticos e farmacêuticos [30], floculação de colóides [31], remoção de íons metálicos e em óleos brutos para remoção de íons metálicos [32].

3.5 ÁLCOOL POLIVINÍLICO

Apesar dos amidos apresentarem diversas qualidades para a utilização em materiais biodegradáveis, estes apresentam algumas desvantagens quando comparados aos plásticos tradicionais, sendo estes, feitos de materiais não biodegradáveis. Dentre estas desvantagens, inclui-se seu forte caráter hidrofílico e propriedades mecânicas fracas [21].

Diante disso, a incorporação de polímeros sintéticos aos amidos é de grande importância, pois melhora algumas propriedades do amido como, por exemplo, a resistência mecânica [21]. O PVA é um polímero sintético, hidrofílico, biodegradável, não tóxico, biocompatível e que apresenta boa capacidade de formação de filmes [33].

O PVA é obtido a partir da reação de polimerização do acetato de vinila, formando o acetato polivinílico, seguido da hidrólise para álcool polivinílico [34]. É um polímero promissor para produção de embalagens biodegradáveis devido à sua alta compatibilidade com a matriz polimérica do amido, podendo torná-las tão resistentes quanto às embalagens convencionais [33].

3.6 PLASTIFICANTES

Outra forma de melhorar as propriedades mecânicas dos filmes é a partir da adição de um agente plastificante, visto que estes ficam quebradiços devido às extensivas forças intermoleculares [17].

Os plastificantes são moléculas pequenas, de baixa volatilidade e com natureza similar à do polímero usado para a obtenção do filme [17]. Dentre os plastificantes existentes, os mais utilizados são mono, di e oligossacarídeos (geralmente xaropes de glicose ou de glicose-frutose, mel), polióis (glicerol e derivados, polietilenoglicol, sorbitol), lipídeos e derivados (ácidos graxos, monoglicerídeos e seus ésteres, acetoglicéridos, fosfolipídios e outros emulsionantes) [17].

Para obtenção de filmes de amido, os plastificantes mais indicados são os polióis, como o glicerol e o sorbitol, moléculas que interagem com as cadeias de amido por meio de pontes de hidrogênio [17]. O sorbitol possui seis grupos hidroxilas (FIG. 4), o que faz com que este tenha maior capacidade de interação com as moléculas de amido que o glicerol, sendo considerado, ainda, menos hidrofílico que o glicerol [17][35].

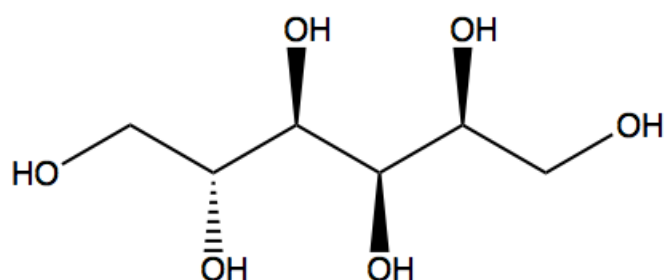


Figura 4: Estrutura química do sorbitol.

3.7 CASTING

O método de casting é muito utilizado para a produção de filmes biodegradáveis. A técnica se baseia na solubilização dos materiais em solventes adequados, seguida da evaporação do solvente [19]. Trata-se de um método rápido, prático e fácil de ser desenvolvido [19]. A técnica pode ser representada conforme indicado na (FIG. 5) [19].

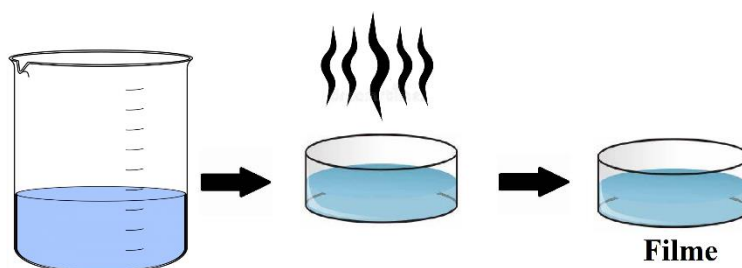


Figura 5: Esquema da técnica de casting

Na técnica de casting, a espessura dos filmes formados é diretamente dependente da viscosidade da solução [36]. Para soluções com alta viscosidade, a solução deve ser espalhada com algum material para controlar a espessura no suporte e no caso de soluções com baixas viscosidades, controla-se a espessura por meio de gramatura do material obtido [36].

3.8 BIOFILMES COMESTÍVEIS EM FRUTAS

Atualmente, o Brasil apresenta uma das maiores taxas de perdas pós colheita de frutas e hortaliças do mundo, onde alcança valores em torno de 35-40%. Em contrapartida, a Europa apresenta valores em média inferiores a 25% e os Estados Unidos aproximadamente 16% de perdas [37].

As perdas de hortifrutícolas no Brasil representam valores superiores a 10 milhões de toneladas/ano de produtos colhidos e não consumidos. Frutas e hortaliças de ambiente tropical, após

serem colhidas apresentam aceleração da maturação e deterioração [38]. Diante disso, os biofilmes comestíveis são utilizados para recobrimento de frutas e assim, fazem com que a durabilidade das frutas após a colheita aumente.

A aplicação de biofilmes comestíveis como recobrimento de frutas, requer conhecimento do material utilizado e do seu modo de degradação, bem como da fisiologia e do metabolismo do produto vegetal [39]. O recobrimento deve reduzir a respiração e a produção de etileno pelo produto, além de carregar aditivos químicos que auxiliem na manutenção da qualidade e que reduzam a deterioração por microorganismos [39].

A aplicação de biofilmes como recobrimento apresentam vantagens como a manutenção dos atributos sensoriais, mantendo a manutenção da aparência dos frutos. Além disso, os filmes de baixa permeabilidade a gases reduzem as taxas de escurecimento enzimático [40]. Frente a isso, utilizando o processo de casting, desenvolveu-se um filme de álcool polivinílico e amido catiônico com diferentes quantidades do plastificante sorbitol para avaliar seu potencial como revestimentos comestíveis.

4. ARTIGO

Plasticizer concentration effect on edible coatings based on poly(vinyl alcohol) (PVA) and cationic starch (CS) blends

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Abstract

Films based on poly(vinyl alcohol) (PVA) and cationic starch (CS) were combined with different percentages of sorbitol (S) to assess the effect of plasticizer on the properties of the films. FTIR and XRD analyses confirmed the interaction between them. However, SEM micrographs confirmed the formation of sorbitol crystals on the surface of the films. It became more evident as the amount of sorbitol increased, suggesting the formation of short-term stable polymer/sorbitol interactions. The blends presented low water vapor transmission rate values, reaching (7.703 ± 0.00) $\text{g h}^{-1} \text{m}^{-2}$, and low solubility values for the films containing higher amounts of CS. The lack of statistical differences in most parameters suggests that no significant gain comes from increasing the amount of sorbitol at percentages higher than 15% w/w. As a coating, the blend composed by 75% of PVA, 25% of CS, and 15% of S successfully decreased the loss of moisture content in acerolas, and preserved the bright red color of the fruits for longer periods. Besides, the coating led to a more homogeneous ripening, and increased the shelf-life of acerolas by one day (under room temperature). It confirms the suitability of this blend for food coating purposes.

Keywords: Sorbitol; biodegradable film; Barbados Cherry; food preservation.

5 INTRODUCTION

Currently, issues related to the increase in environmental problems caused by several human activities have gained prominence in scientific researches seeking to reduce or solve these problems. Among the several environmental problems, petroleum-based plastic packaging materials raise a lot of concerns because they are resistant to aging and minimally biologically degraded when disposed [41][42].

The replacement of synthetic polymer-based packaging by the so-called green plastics or bioplastics is an attempt to solve, or at least, minimize this problem. Such materials are considered non-toxic and are used to prepare biodegradable films and food coatings. When applied as food coatings, these green plastics act as protectors against external elements such as gases, dirt, moisture, and aromatic compounds. In addition, these materials often reduce mass loss, food wilting and also create a modified atmosphere inside the products, potentially increasing shelf-life [43][44].

Biodegradable films are basically produced from a film-forming agent, a solvent and a plasticizer [43]. Biodegradable polymers, with starch being one of the most used ones. Starches are appealing for the production of biodegradable films because they are low cost, highly available, and lead to transparent, colorless, odorless films. Besides, it can be combined with different materials, leading to films with unique physical and/or chemical properties [42][45][3][46]. Also, starches have low permeability to oxygen, making post-harvest fruits more durable, especially because oxygen is responsible for accelerating the ripening process. However, starches also have a high concentration of water due to their hydrophilicity, which compromises their mechanical properties [42].

Starches can be classified as natural when they are extracted from tubers, seeds or fruits. They can also be classified as modified starches when they undergo processes that chemically modifies their structure [47][48]. Cationic starches (CS) are some examples of modified starches that can be prepared by several methods (dry, wet, extrusion, etc.). Amine groups bearing positive charges are often added into the polymeric chain in these cases [49], being (3-chloro-2-hydroxypropyl)trimethylammonium chloride (QUAB) a commonly used reactant for this purpose [49].

Cationic starches have some advantages over neutral starches. For example, they can attract negative charges, and the modification reaction usually increases the mechanical strength of materials based on cationic starches [47][48].

Although cationic starches have several qualities for biodegradable materials, they have some disadvantages when compared to traditional plastics. Among these disadvantages are the strong hydrophilic character and poor mechanical properties. Therefore, the formation of mixtures with other polymers and the incorporation of plasticizers have been widely studied as alternatives to improve the performance of starch-based materials [42][10].

Polyvinyl alcohol (PVA) is an example of a polymer blended with starch, because it is a synthetic (yet biodegradable) water-soluble, biocompatible, and non-toxic polymer [10]. This polymer has a high water adsorption capacity in addition to properties such as semi-permeability and pH stability [11].

The casting technique can be used to produce materials from PVA and cationic starch. This technique is based on the solubilization of the polymer mixture in an appropriate solvent, with the

addition of a plasticizer. Plasticizers are small molecules used to improve the blend properties. They increase molecular mobility, flexibility, hydrophobicity, and permeability, especially because plasticizers have a hydrophilic character [12]. Polyols, such as glycerol and sorbitol, are among the plasticizers most used to produce biodegradable films [13].

Considering the pieces of information provided above, the incorporation of polyvinyl alcohol (PVA) and the plasticizer sorbitol into cationic starches is of great importance, as it will improve some of starch properties, allowing the production of new materials with different physical properties [50], increased film flexibility, decreased intermolecular forces [51] and enhanced mechanical strength [52]. Besides, the literature still lacks studies assessing the effect of polymer:plasticizer ratio in blends aimed at food coating. Therefore, this work evaluated how the combination of different ratios of PVA, cationic starch, and sorbitol would affect the physical and chemical properties of biodegradable films. The film with the best performance was also evaluated as a coating to Barbados cherry.

6 MATERIALS AND METHODS

6.1 Materials

Cationic corn starch (CS) (modified with 3-chloro-2-hydroxypropyltrimethylammonium chloride (QUAB), degree of substitution (DS) 0.0290) was kindly donated by a starch factory located in the city of Mercedes-PR. Sorbitol ($C_6H_{14}O_6$; MM 182.17 g mol⁻¹) was acquired from QEEL. Poly(vinyl alcohol) (PVA; 87% hydrolyzed; MM 104,000.00 g mol⁻¹), sodium hydroxide (NaOH), and sulfuric acid (H_2SO_4) were acquired from NEON. Soluble starch and potassium iodate (KIO_3) were acquired from Synth. Potassium iodide (KI) was acquired from Biotec. The Barbados cherries used for the in vivo experiments were harvested on a private farm located in Mercedes, Paraná – Brazil.

6.2 Biodegradable films preparation

The effect of the amount of polymer added to the blend was assessed by varying the amounts of PVA/CS. The chosen percentages were 100/0, 75/25, 50/50, 25/75, 0/100 % w v⁻¹. Regardless of the PVA/CS ratio, the total amount of polymer added into the blend corresponded to 3% w v⁻¹ of the total volume of the filmogenic solution. The percentage of sorbitol was added in relation to the percentage of the two polymers in each mixture also varied (15.0, 22.5, or 30.0% w v⁻¹).

Initially, PVA was dispersed in 50 mL of distilled water at 80 °C. The dispersion was kept in a water bath throughout the entire dissolution process. Starch was also transferred into a beaker containing 50 mL of distilled water. The mixture was manually stirred (using a glass bar) in the water bath ($T = 80\text{ °C}$) until complete gelatinization of starch. Once prepared, the PVA solution and the CS dispersion were cooled to room temperature ($T \approx 25\text{ °C}$).

The filmogenic solution (total volume of 100 mL) was subsequently prepared by mixing the room-temperature PVA solution and CS dispersion in the same beaker. The mixture was manually stirred for homogenization. The respective amount of sorbitol was then added into the mixture, and it was manually stirred for homogenization one more time.

The samples were named PVAxCSySz, where PVA refers to poly(vinyl alcohol), CS refers to cationic starch and S refers to sorbitol. The sub-indexes x and y specify the amount of each polymer in the blend ($x + y = 100\%$) and z refers to the amount of sorbitol.

6.3 Characterizations of the films

The filmogenic solution was characterized using films rather than a solution. The casting method was employed to produce the films. Therefore, for the characterization techniques described below, 30 g of filmogenic solution was transferred into a Teflon plate and dried in an oven at 40 °C for 48 h. The dry films were stored in a desiccator ($T \approx 25\text{ °C}$).

6.3.1 Fourier Transform Infrared Spectroscopy (FTIR)- Attenuated Total Reflection (ATR)

The FTIR technique was used to identify functional groups characteristic to the polymers used in the films, and to assess potential chemical changes caused by blending the polymers.

The analysis was performed in a Perkin Elmer equipment (model Frontier), using the ATR mode. The spectra were acquired from 4000 to 600 cm^{-1} , at a resolution of 2 cm^{-1} .

6.3.2 X-Ray Diffraction (XRD)

The diffraction pattern of the precursors and the crystallinity of the produced films were determined using XRD analysis. The analysis was performed in a Shimadzu 6000 diffractometer using a $\text{CuK}\alpha$ radiation source ($\lambda = 1.5406\text{ \AA}$), varying Bragg's angle (2θ) from 5 to 80° with an increment of 1° min^{-1} . The equipment operated at a voltage of 40 kV and a current intensity of 30 mA.

The obtained data was processed (baseline subtraction, data normalization, and peak deconvolution) using a data processing software.

6.3.3 Thickness

The thickness of the films was determined using a micrometer (Mitutoyo-2046S). A total of 5 measures were performed in random parts of the films. The results are expressed by mean \pm standard deviation (SD; mean \pm SD), in millimeters (mm).

6.3.4 Solubility

The solubility of the films was determined using the method suggested by Gontard et al (1994). [54]. The films were cut into pieces of areas equal to 2 cm² and dried (first drying step) in an oven (T = 80 °C) for 24 h to determine the initial percentage of dry weight of each sample. After the first weighing, the samples were immersed in a beaker containing 25 mL of distilled (dissolution step) water for 24 h. No stirring was employed in this step. At the end of the dissolution step, the samples were removed from the beaker and dried one more time (80 °C; 24 h; second drying step) to determine the remaining sample weight.

The percentage of solubility was determined using **Eq. (1)**, in which W_{d0} and W_{d24} refer to the weight of the samples after the first and second drying steps, respectively.

$$\text{Solubility (\%)} = \frac{W_{d0} - W_{d24}}{W_{d0}} \times 100 \text{ (Eq. 1)}$$

6.3.5 Water Vapor Transmission Rate (WVTR)

The WVTR was determined according the method ASTM E96-80 (with modifications), as described by Gabas e Cavalcanti (2003) [55]. The films were cut into pieces of 2 cm² of diameter and applied on permeation cells containing 10 mL of distilled water. The cells were placed in a desiccator containing silica gel (T \approx 25 °C), and the WVTR was monitored by weighing the system (film + cell + water) every 24 h for 5 days.

The WVTR was determined using **Eq (2)**, where $\frac{\Delta w}{\Delta t}$ refers to the amount of water absorbed by the silica gel inside the desiccator (obtained by linear regression), and A is the area of the films (in m²). The Δw value was calculated in relation to the values at $t = 0$ h. It is: $\Delta w = (w_0 - w_t)$.

$$\text{WVTR (g h}^{-1} \text{ m}^{-2}\text{)} = \frac{\Delta w}{\Delta t \times A} \text{ (Eq. 2)}$$

6.3.6 Scanning Electron Microscopy (SEM)

The uniformity of the films was assessed using Scanning Electron Microscopy (SEM). The samples were placed in a carbon tape (attached to a stub), gold-metallized (BAL-TEC model SCD 050; $t = 120$ s), and analyzed in a Quanta 250 equipment. The analysis was performed using current intensity of 30 mA, an acceleration voltage of 25 kV, and a spot of 5.0.

6.3.7 Thermogravimetric Analysis

Thermogravimetric analysis was employed to determine the thermal stability of the films. The analysis was performed in a Perkin Elmer STA 6000 thermal analyzer, using a porcelain crucible. The samples ($m = (18.0 \pm 6.0)$ mg) were heated from 25 to 700 °C at a heating rate of 10 °C min⁻¹ under a dynamic nitrogen atmosphere (flow rate of 50 mL min⁻¹).

6.3.8 Mechanical Assay

The mechanical properties of the films were assessed by stretching analyses, producing stress-strain curves. The analyses were performed in a TA HD Plus (Stable Micro Systems) texturometer (equipped with a cell load of 10 kg), according to the ASTM-D882-12 methodology for thin films. The samples were stretched at a traction rate of 1 mm s⁻¹ until the complete rupture of the films [56]. The stress of the linear portion of the curve (up to 5%) was used to calculate Young's modulus (E; MPa). The E value (slope of the curve) was obtained by linearization.

6.3.9 Opacity

The opacity was determined using a Shimadzu spectrophotometer. The absorbance was assessed from 400 to 700 nm, and the opacity was calculated using **Eq. (3)**, in which $A\lambda$ is the chosen wavenumber ($A\lambda = 450$ nm), and x is the thickness of the film [42].

$$Opacity = \frac{A\lambda}{x} \text{ (Eq. 3)}$$

6.4 Coating Conditions

Acerola, also known as Barbados cherry, was chosen for the coating assay. The fruit were immersed in a 0.01% sodium hypochlorite solution for 30 minutes to remove pathogens, and subsequently air-dried. Once dry, the fruit were immersed (for one minute) in a beaker containing the filmogenic solution, and subsequently hang to dry.

Some fruits were analyzed (analyses described below) immediately after the initial washing step and the obtained values were used for comparison. The results are expressed by mean

± standard deviation (SD; mean ± SD), and, unless specified, they refer to the mean value of three replicates (n = 3).

The fruit as whole was used for the non-destructive analysis while its juice (without water addition) was used for the destructive ones. A domestic blender was used to extract the juice.

6.4.1 Mass Loss (ML)

The percentage of mass loss (ML) throughout the storage period was assessed using 8 fruit per treatment (coated or non-coated; n = 8). Each fruit was weighed every 24 h, and the ML was determined using **Eq. (4)**, in which M_i and M_f refer to the initial and final mass.

$$ML = \left(\frac{M_i - M_f}{M_i} \right) * 100\% \text{ (Eq. 4)}$$

6.4.2 Colorimetry

The color variation was qualitatively assessed using the Red, Green, and Blue (RGB) levels, using the software ImageJ [57]. The measures were performed by selecting a rectangle in the center of each fruit. The analysis was performed in triplicate for each treatment, and the results are expressed by (mean ± SD).

6.4.3 Soluble solids (SS)

The soluble solids (SS) were determined by placing 0.05 mL of juice in the prisms of an Abbe's refractometer. The results are expressed as degrees of Brix (°Brix).

6.4.4 Titratable acidity (TA)

The titratable acidity (TA) was determined by titration. For the analysis, 1 mL of acerola juice was dissolved in 3 mL of distilled water and titrated using 0.01 M NaOH solution. Phenolphthalein was used as the indicator.

TA was calculated using **Eq. (5)**, in which V refers to the volume (in mL) of NaOH used in the titration; c is the concentration of the NaOH solution ($c = 0.01 \text{ mol L}^{-1}$); P is the volume of acerola juice ($V = 3 \text{ mL}$); MM is the molar weight of citric acid ($MM = 192 \text{ g mol}^{-1}$), and n is the number of label hydrogens in citric acid ($n = 3$).

$$TA = \frac{V.c.MM}{10.P.n} \text{ (Eq. 5)}$$

6.4.5 Vitamin C

The variation in the ascorbic acid (vitamin C) concentration was evaluated by diluting 5 mL of acerola juice in 50 mL of distilled water containing 10 mL of 10% H_2SO_4 , 1 mL of 10% KI, and 1 mL of 1% soluble starch solution, and titrated with 0.002 M KIO_3 until the color changed from redish to blue. This analysis was performed in duplicate (n = 2).

The vitamin C concentration was determined using **Eq. (6)**, in which V represents the volume of KIO₃ consumed in the titration, F is the correction factor (F = 0.8806 for 0.002 M KIO₃), and P is the volume of sample (P = 5 mL).

$$\text{Vitamin C} = \left(\frac{V.F}{P}\right) \cdot 100\% \text{ (Eq. 6)}$$

7. RESULTS AND DISCUSSION

7.1 Physical-chemical characterization

7.1.1 FTIR

FTIR analyzes were performed to confirm the formation of physical interactions between CS, PVA, and sorbitol. Characteristic stretches for the three components of the films were observed in **Figure 6(a)**, where the broad band between 3500 and 3200 cm⁻¹ occurs due to the OH functional group from PVA, starch, and sorbitol [58]. The stretching of the C-H sp³ bonds occurs at 2900 cm⁻¹ [58].

In addition to the already mentioned OH and CH bands, cationic starch still presents C-O bands at ~1000 cm⁻¹ [59]. The bands at 1340 (C-N stretching) and 860 cm⁻¹ (C-Cl stretching) confirm the graftization of QUAB into starch [32]. The spectrum also has a band at 1638 cm⁻¹. This band indicates the stretching of C-N bonds. Since QUAB does not insert amide groups into starch, this particular band could not refer to the amide I stretching. Bands in this region could also indicate the presence of imines or oximes [59]. Both would be possible if QUAB underwent further rearrangement and eventual hydrolysis reactions. Although the FTIR indicates the presence of this band and that it has been previously reported in the literature [32], it is not possible to precisely determine the type of C-N bond responsible for this band.

For polyvinyl alcohol, a band at 1717 cm⁻¹ is observed due to the carbonyl group (C=O) of the residual acetate groups of PVA [60]. The band at 1425 cm⁻¹ refers to the C-H binding of CH₃. The one at 1085 cm⁻¹ refers to the C-O-C characteristic groups and the vibration at 836 cm⁻¹ is attributed to the bending of –CH₂– groups [61][62].

In the sorbitol spectrum (**Figure 6(a)**), the bands at 878 and 1417 cm⁻¹ appear due to O-H in-the-plane and out-of-plane vibrations, respectively [63]. The bands located at 1050 cm⁻¹ and 1311 cm⁻¹ match the C–OH stretching vibrations [63].

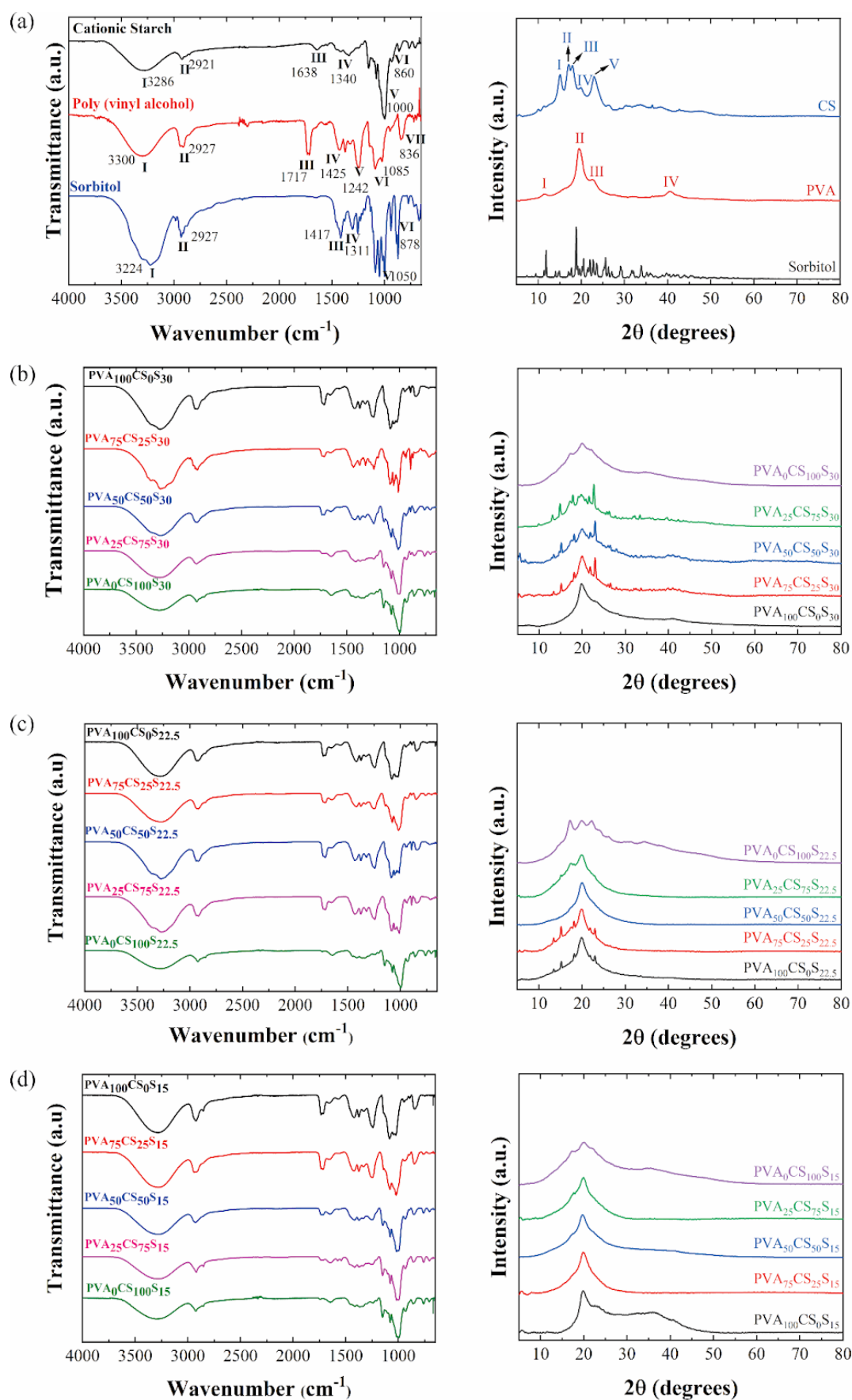


Figure 6: FTIR spectra (right side; from 4000 to 600 cm^{-1}) and diffraction pattern (XRD; left side) of (a) cationic starch (CS), poly(vinyl alcohol) (PVA), and sorbitol (S), and the blends (b) PVA_xCS_yS₃₀, (c) PVA_xCS_yS_{22.5}, and (d)

PVA_xCS_yS₁₅. In the blend, the sub-indexes *x*, *y*, and *z* specify, respectively, the amount of PVA, CS, and sorbitol (*z* = 30, 22.5, or 15%).

Regardless of the amount of sorbitol, all blends portrayed very similar FTIR spectra. However, the higher the amount of a particular polymer in the blend, the more the spectra resembled the respective precursor. Since blends involve the combination of two or more polymers, the chemical interactions formed between them change the position in which their bands appear in FTIR spectra.

In this work, the FTIR spectra of the films showed the occurrence of strong hydrogen bonding interactions between PVA and starch components. Both polymers have a large number of –OH and C–O groups, which can form hydrogen bond networks, improving compatibility between them, and resulting in better composite properties [60]. These interactions changed the center of the bands from the original position. **Figure 7** provides a schematic representation of these hydrogen interactions formed among the polymers and sorbitol.

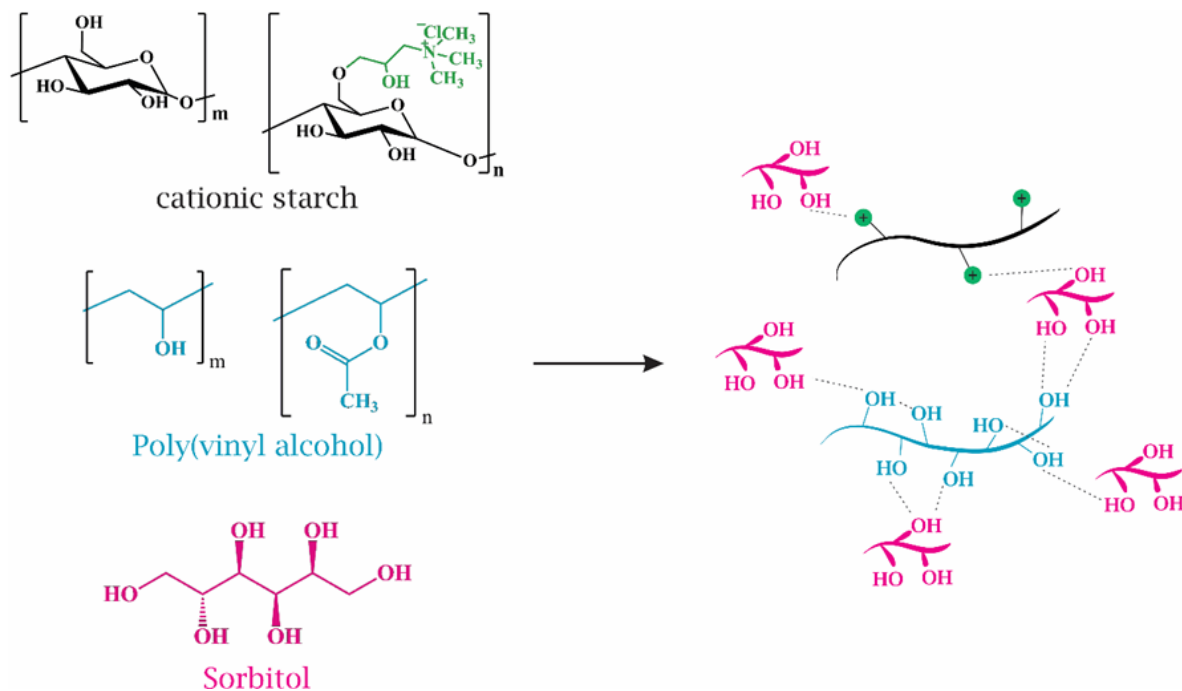


Figure 7. Schematic representation of the hydrogen interaction formed between PVA, CS, and S.

In what concerns the percentage of sorbitol, no drastic changes in the characteristic bands of cationic starch/PVA were observed. However, the presence of higher amounts of sorbitol favored the formation of hydrogen interactions, also helping shift the bands from their original wavenumbers.

7.1.2 XRD

The XRD analysis provide information regarding the crystallinity of a material, being sharp peaks characteristic of crystalline portions while broad peaks are observed in amorphous

regions. **Figure 6** presents the obtained results. The cationic starch (CS) presented four peaks in the diffractogram (**Figure 6(a)**). These peaks at 15.0, 17.1, 18.0, 20.0, and 23.0° are characteristic of native starch [64][65], matching the A-type semi-crystalline starch [66][67].

Since the modification was performed at a low temperature ($T = 40\text{ }^{\circ}\text{C}$), starch did not gelatinize and, therefore, did not lose its crystalline structure. However, the XRD results suggest that, although chemical modification usually changes the crystallinity of starch in drastic ways [32], it was not the case herein. The modification did happen, as confirmed by NMR analysis [32]. Nevertheless, the degree of substitution was very low ($DS = 0.0290$). Hence, the experimental conditions might have preserved the structural integrity of starch.

The second polymer used in the experiments, PVA, also presented characteristic peaks in the diffractograms (**Figure 6(a)**). As a semi-crystalline polymer [68], PVA has regions of higher crystallinity, justifying the relatively sharp peak (compared to the other peaks in the diffractograms) at 19.4°. The peaks at 11.6, 22.6, and 40.5° refer to the less crystalline regions of the polymer [69].

The sharp peaks observed in the diffractograms (**Figure 6(a)**) confirm the crystalline nature of sorbitol. The multiple peaks might be the result of a polymorphs formed due to the free rotation of C-C bonds [70].

Three different sorbitol concentrations were added to the films. **Figure 6(b)**, **(c)**, and **(d)** depict the obtained diffraction patterns presented by the films. Regardless of the percentage of sorbitol, the production of the films affected the crystallinity of both polymers because the relatively sharp peaks observed in **Figure 6(a)** were replaced by broad peaks in the subsequent diffractograms. The gelatinization step performed before the production of the films might justify this behavior. For starch, the gelatinization process inevitably leads to the destruction of its granular structure. It exposes the polymer chains that were entrapped inside the granule and, consequently, increases the amorphous character of the polymer.

For PVA, the initial dissolution in a good solvent (water) allows the chains to assume a relaxed state, which could lead to higher or lower degrees of organization. The broad peak observed for PVA₁₀₀CS₀S₁₅ in **Figure 6(d)** confirms the unpredictability of this chain reorganization.

The pure films (PVA₁₀₀CS₀S_z and PVA₀CS₁₀₀S_z) showed overall good compatibility with sorbitol at 30% w/w (**Figure 6(b)**) and 15% w/w (**Figure 6(d)**). For the aforementioned blends, sorbitol probably lost its crystalline structure. The absence of sharp diffraction peaks reinforces the previous statement. However, sharp peaks appeared were observed in the pure films prepared using 22.5% w/w of sorbitol (**Figure 6(c)**).

The overall results indicate that the crystallinity of the films increased by increasing the percentage of sorbitol in the blend, especially because the intensity of the peaks at 15 and 25° increased. Besides, these higher percentages of sorbitol led to well-defined peaks in the

diffractograms. Even though this crystallinity increase could indicate a higher degree of organization in the matrix, it is far more likely that it is the result of the exudation phenomenon observed in this work. The exudation indicates that sorbitol did not adhere into the matrix and was “expelled” to the surface of the films. The white regions observed in **Figure 8** evidence this phenomenon.

It should be reinforced that exudation was not observed immediately after the production of the films. As mentioned before, sorbitol was used as a plasticizer, decreasing the length of the hydrogen bonds formed between the polymers. The migration of sorbitol onto the surface of the films some time after their production suggests that, although all sorbitol molecules might have initially formed hydrogen bonds with the polymers, these polymer-sorbitol-polymer hydrogen bonds might have been replaced by polymer-water-polymer hydrogen bonds. It suggests that, (1) above 15% w/w of sorbitol, the polymer-sorbitol-polymer interaction loses its effectiveness, and, (2) for this particular blend, no structural gain comes from adding plasticizer at concentrations higher than 15% w/w.

Crystallinity increases after the addition of sorbitol to polymeric films were already reported in the literature. Ma, X., Qiao, C., Zhang, J., & Xu, J. (2018) [71], for example, used chitosan and sorbitol to produce films. They observed that higher amounts of sorbitol (up to 70%) led to films of higher crystallinity. However, the authors did not report exudation, suggesting the formation of strong and stable polymer-sorbitol-interactions. The same applies to the gelatin/sorbitol/citric acid-based films produced by Dai, H., Li, X., Du, J., Ma, L., Yu, Y., Zhou, H., ... & Zhang, Y. (2020) [72]. The authors reported a protective effect of sorbitol on the structure of gelatin when exposed to low citric acid concentrations, and the destruction of the gelatin/sorbitol interactions at high citric acid concentrations.

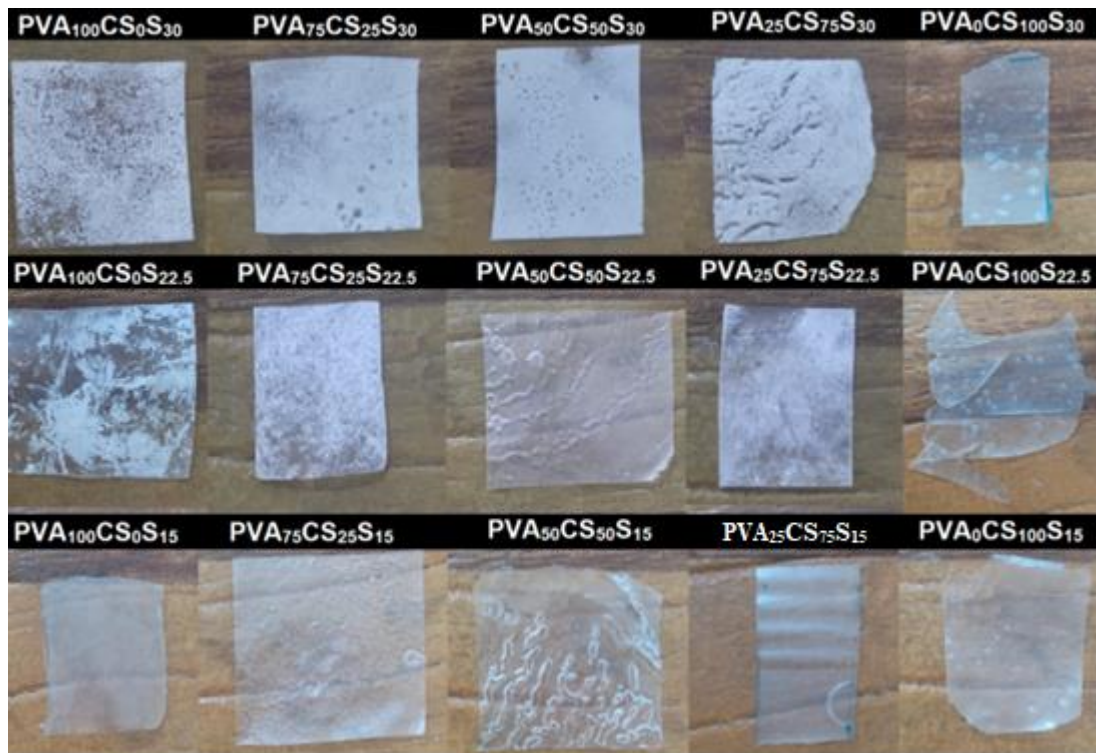


Figure 8: Exudation phenomenon in the films obtained, which are identified as $PVxCSySz$, with polyvinyl alcohol represented by PVA, cationic starch by CS and sorbitol by S. The subscripts x, y and z refer to the amount of polyvinyl alcohol, cationic starch and sorbitol respectively.

7.2 Morphological characterization

Scanning Electron Microscopy (SEM) analysis is used to study the surfaces of polymeric materials such as plastics, films, membranes, fibers and composites. The SEM results represented in **Figure 9** show that some films did not have a smooth and homogeneous surface, which could be an indication of the incompatibility between the three components of the formulation [33]. Since phase separation was not an issue for some of the films containing both polymers ($PVA_{50}CS_{50}S_{22.5}$, $PVA_{50}CS_{50}S_{15}$, and $PVA_{25}CS_{75}S_{15}$), it is likely that sorbitol was, indeed, the one precursor experiencing some sort of incompatibility. The observance of phase separation in all samples produced using 30% w/w of sorbitol and its absence in the films with 15% w/w of sorbitol reinforces the previous hypothesis.

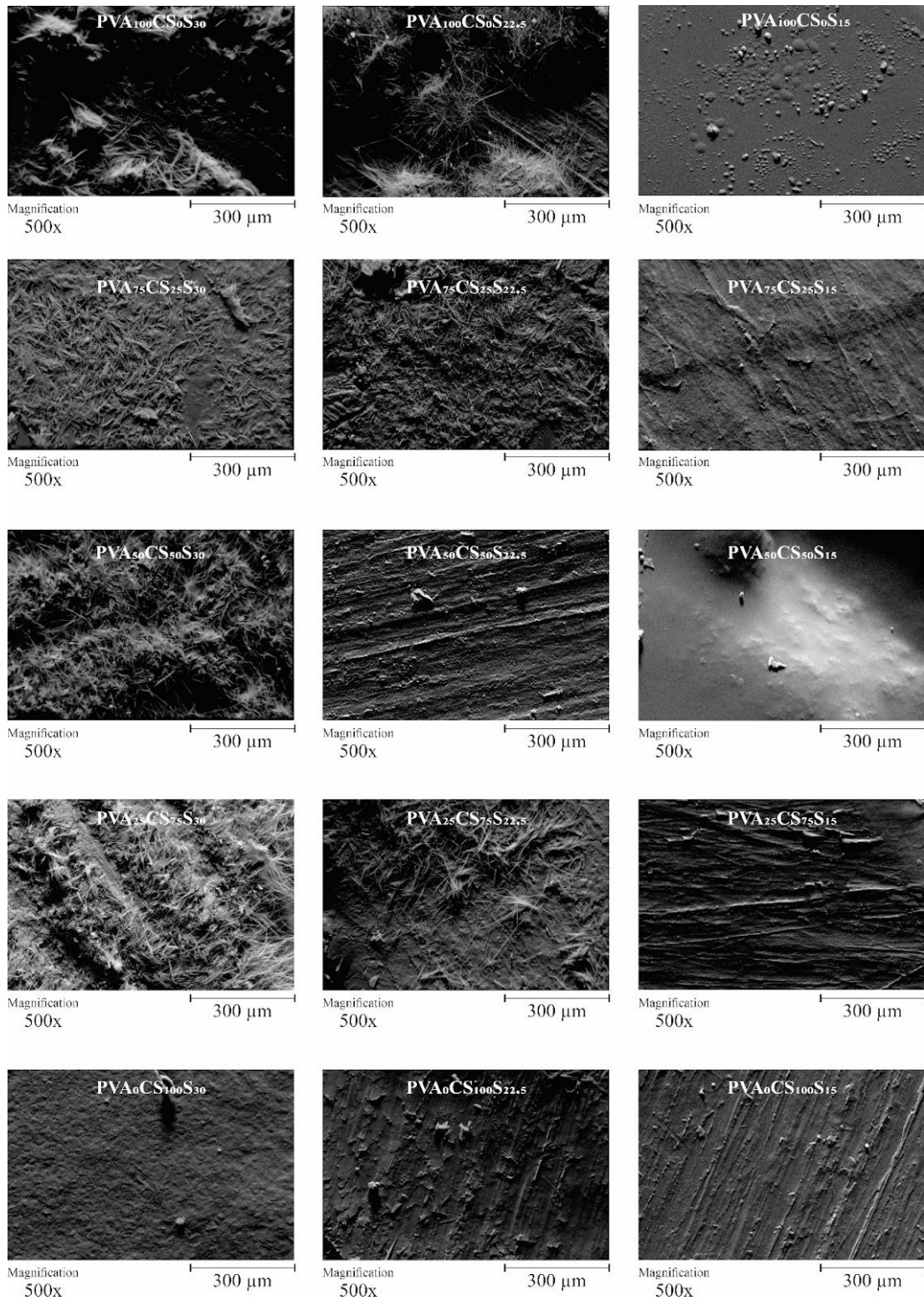


Figure 9. SEM micrographs of the produced films. They are identified as $PVAxCSySz$, in which PVA, CS and S refers to poly(vinyl alcohol), cationic starch, and sorbitol, respectively, and the sub-indexes x , y , and z specify, respectively, the amount of PVA, CS, and sorbitol ($z = 30, 22.5, \text{ or } 15\%$).

The films that did not show complete compatibility were the same ones that showed the phenomenon of exudation and thus higher peaks in the X-ray diffraction analysis. Therefore, the SEM

analysis corroborates the previous results and confirms that greater amounts of plasticizer do not affect the polymer matrix of the films in a permanent positive way.

7.3 Physical and mechanical Properties

The efficiency of biodegradable films for coating fruit in order to delay ripening depends mainly on physicochemical and mechanical properties, such as water vapor transmission rate (WVTR), solubility, Young's modulus, and thickness [17]. **Table 2** presents the results for the physical-chemical and mechanical parameters evaluated in this work.

Among the properties of biodegradable films, the analysis of the rate of vapor transmission allows assesses the ability of the films to prevent (or, at least, decrease) the loss of moisture content. Therefore, this analysis provides, among others, qualitative information regarding the arrangement of polymeric chains in the films, and the interaction between water and the polymeric matrix [73]. For fruit coating, low WVTR values indicate better protection against moisture loss and thus prevent dehydration, helping to keep fresh the harvested food [74].

As shown in **Table 2**, the WVTR values ranged from $(7.018 \pm 0.29) \text{ g h}^{-1} \text{ m}^{-2}$ (PVA₁₀₀CS₀S_{22.5}) to $(10.759 \pm 0.27) \text{ g h}^{-1} \text{ m}^{-2}$ (PVA₇₅CS₂₅S_{22.5}), and based on the statistical results, it was possible to observe that the films containing 15% w/w of plasticizer were statistically different to the ones containing 30% w/w of plasticizer, but statistically equal to the ones containing 22.5% w/w of sorbitol. Therefore, it is notable that the plasticizer has an effect on the polymeric chains of CS and PVA, with higher water affinity in films containing higher sorbitol percentages.

Table 2 - Water Vapor Transmission Rate (WVTR), solubility (%), Young's modulus (E; MPa), thickness (mm) and opacity (AU mm⁻¹) of the PVA_xCS_y matrices produced using different amounts of plasticizer (sorbitol; 15.0, 22.5, or 30.0%)*.

Analysis	Matrix	Amount of sorbitol (%)		
		15.0%	22.5%	30.0%
WVTR ($\text{g h}^{-1} \text{m}^{-2}$)	PVA ₁₀₀ CS ₀	$7.591 \pm 0.70^{\text{aAB}}$	$7.018 \pm 0.29^{\text{cAD}}$	$7.735 \pm 0.14^{\text{bCD}}$
	PVA ₇₅ CS ₂₅	$7.703 \pm 0.00^{\text{aAB}}$	$10.759 \pm 0.27^{\text{aAD}}$	$8.276 \pm 0.32^{\text{abCD}}$
	PVA ₅₀ CS ₅₀	$7.910 \pm 0.25^{\text{aAB}}$	$9.406 \pm 0.79^{\text{abAD}}$	$9.056 \pm 0.16^{\text{aCD}}$
	PVA ₂₅ CS ₇₅	$7.766 \pm 0.68^{\text{aAB}}$	$9.104 \pm 0.50^{\text{abcAD}}$	$9.135 \pm 0.50^{\text{aCD}}$
	PVA ₀ CS ₁₀₀	$8.340 \pm 0.32^{\text{aAB}}$	$7.591 \pm 0.70^{\text{bcAD}}$	$9.300 \pm 0.00^{\text{aCD}}$
Solubility (%)	PVA ₁₀₀ CS ₀	$94.602 \pm 1.205^{\text{aAB}}$	$96.205 \pm 0.405^{\text{aAC}}$	$94.880 \pm 2.680^{\text{aBC}}$
	PVA ₇₅ CS ₂₅	$94.167 \pm 1.179^{\text{aAB}}$	$90.958 \pm 0.623^{\text{bAC}}$	$69.050 \pm 3.370^{\text{bBC}}$

	<i>PVA₅₀CS₅₀</i>	58.590±1.430 ^{bAB}	63.340±0.263 ^{cAC}	57.050±0.389 ^{cBC}
	<i>PVA₂₅CS₇₅</i>	47.180±9.420 ^{bAB}	36.560±2.370 ^{dAC}	38.330±0.000 ^{dBC}
	<i>PVA₀CS₁₀₀</i>	0.000±0.000 ^{cAB}	0.000±0.000 ^{eAC}	0.000±0.000 ^{eBC}
<i>Young's Modulus (MPa)</i>	<i>PVA₁₀₀CS₀</i>	0.4515±0.0119 ^{bAB}	0.3579±0.0282 ^{aAC}	0.1626±0.0005 ^{aBC}
	<i>PVA₇₅CS₂₅</i>	0.3244±0.0695 ^{bAB}	0.2617±0.0021 ^{aAC}	0.5806±0.0941 ^{aBC}
	<i>PVA₅₀CS₅₀</i>	0.4430±0.0440 ^{bAB}	0.4890±0.2060 ^{aAC}	2.0800±1.1470 ^{aBC}
	<i>PVA₂₅CS₇₅</i>	3.0120±0.1900 ^{aAB}	0.5009±0.0677 ^{aAC}	0.5225±0.0503 ^{aBC}
	<i>PVA₀CS₁₀₀**</i>	–	–	–
<i>Thickness (mm)</i>	<i>PVA₁₀₀CS₀</i>	0.2220±0.0451 ^{aAB}	0.2400±0.0495 ^{bAC}	0.3220±0.0760 ^{aBC}
	<i>PVA₇₅CS₂₅</i>	0.2600±0.1091 ^{aAB}	0.2800±0.0600 ^{bAC}	0.2980±0.0460 ^{aBC}
	<i>PVA₅₀CS₅₀</i>	0.2640±0.0770 ^{aAB}	0.2980±0.0729 ^{abAC}	0.2100±0.0300 ^{bBC}
	<i>PVA₂₅CS₇₅</i>	0.2760±0.0503 ^{aAB}	0.2520±0.0327 ^{bAC}	0.2780±0.0259 ^{abBC}
	<i>PVA₀CS₁₀₀</i>	0.2960±0.0451 ^{aAB}	0.3820±0.0277 ^{aAC}	0.3640±0.0365 ^{aBC}
<i>Opacity (AU mm⁻¹)</i>	<i>PVA₁₀₀CS₀</i>	-	-	-
	<i>PVA₇₅CS₂₅</i>	1,4115	1,1750	2,5336
	<i>PVA₅₀CS₅₀</i>	2,0265	1,9094	2,7386
	<i>PVA₂₅CS₇₅</i>	1,4203	2,1706	2,9892
	<i>PVA₀CS₁₀₀</i>	-	-	-

*For each analysis, (mean ± SD)^{ab} that do not share the same letter are statistically different at 95% of significance. Lower case letters in the same column refer to the comparison of the different matrices produced using the same amount of plasticizer. Upper case letters in the same line refer to the comparison between a same matrix produced using different amounts of plasticizer (15.0, 22.5, or 30.0%).

**It was not possible to perform the mechanical tests on the PVA₀CS₁₀₀ films due to brittleness presented by it.

The WVTR values observed in this work are four times smaller when compared to the values presented by Abdullah et. al. (2019) in a PVA/starch/glycerol blend [75]. This blend still reached lower WVTR values than the one made by Chowdhury et al. (2020). In their case, the pure PVA film had a WVTR of 54.24 g h⁻¹m⁻² [76]. It strongly suggests the blends from this work would be more effective in preventing losses of water through gas exchange processes.

Solubility is another important property for the production of biodegradable films. Some applications may even require insolubility in water to increase product integrity while, in other cases, solubilization in water before consumption of the product can be beneficial. [77]. For the present films, solubility values ranged from $(0.000 \pm 0.000)\%$ (PVA₀CS₁₀₀S_z) to $(96.205 \pm 0.405)\%$ PVA₁₀₀CS₀S_{22.5}).

The results suggest that the modification of starch with a quaternary amine drastically changes the water affinity of the polymer (at room temperature). The films with higher amounts of PVA, on the other hand, were more soluble. This behavior demonstrated the influence of PVA on the solubility of the films. Since, besides its affinity to water, this polymer also forms hydrogen bonds with the starch chains, it increases the flexibility of the films, facilitating water penetration [78].

The blends containing higher amounts of PVA were more soluble than the ones containing higher amounts of CS. However, the blend containing equal amounts of these polymers displayed intermediate solubility (almost 50% of solubility). It suggests the solubility observed in the films mostly comes from PVA. It could also indicate the formation of films containing PVA-rich and CS-rich regions. Both regions coexisted in the films because there was no phase separation. Nevertheless, it is not possible to establish how they were distributed in the matrix based on the solubility results, especially because the analysis was performed using a representative portion of the film. The relatively high standard deviation observed in this analysis supports this hypothesis.

The relationship between water solubility and the PVA/CS ratio was a positive factor for the preparation of the films, especially because the amount of these polymers could be adjusted to the required solubility for the desired application. Furthermore, it was found that films with the same amount of PVA/CS and different concentrations of plasticizer were statistically equal. Therefore, despite the differences in solubility caused by different amounts of sorbitol, the differences were not as expressive as expected. However, since statistical differences were observed in the samples produced using the same amount of sorbitol and different PVA/CS ratios, it is possible that sorbitol can only affect the polymeric arrangement in the film up to a limit. After this limit, no significant gain comes from increasing the amount of sorbitol.

The solubility of the films from this work was similar to those observed by Chowdhury et al., (2020). The authors found 100% solubility for their pure PVA film without plasticizer addition [76]. In regards to the solubility of films based on pure starch, the results from this work were also similar to the ones found by Mehayar and Han (2004). In their investigation, they found a solubility of 1.5% for pure starch films [79].

Thickness is also a parameter that affects the properties of films. When well-controlled, it leads to uniform materials and it also provides viable information for mechanical assays [77][80][81]. In this work, the thickness of the films ranged from (0.2100 ± 0.0300) mm

(PVA₅₀CS₅₀S₃₀) to (0.3820 ± 0.0277) mm (PVA₀CS₁₀₀S_{22.5}). Statistical analyses again indicated no significant difference between films when changing the plasticizer percentage. It suggests that the polymers assumed a favorable arrangement regardless of the amount of each polymer and plasticizer in the blend. However, as mentioned before, these results do not determine if the polymers were (a) homogeneously distributed throughout the matrix, (b) heterogeneously distributed but leading to similar thicknesses throughout the film, or (c) a mixture of both (a) and (b).

The thickness of the PVA_xCS_yS_z films was greater than the thickness of the films of starch and polyvinyl alcohol containing glycerol and sorbitol as a plasticizing agent and citric acid as an additive presented by Park et al., (2005) [82]. Park et al., (2005) found thickness values on average of 0.15mm for all their films, while the values found in this study ranged from 0.2100 to 0.3820.

In addition to the results of the physical properties of the films, **Table 2** also presents the results of the mechanical properties. Among the most studied mechanical properties of films the tensile strength, the elongation at break, and the modulus of elasticity (also called Young's modulus; E) stand out. These are usually evaluated by stress-strain tests [83][84].

A biodegradable film is considered efficient when it is resistant to the stresses that the product undergoes during the application, transport, and handling process [80]. Considering this, films based on pure starch have limitations because they tend to be more brittle than films based on synthetic polymers. Strong hydrogen interactions formed in gelatinized starch are responsible for this brittleness [85]. This problem can be overcome by incorporating a plasticizing agent that acts between the polymer chains, weakening the intermolecular forces and allowing them to increase their mobility [85]. Therefore, the mechanical properties of biodegradable packaging depend on the chemical composition of biodegradable polymers, and on the compatibility between polymers and plasticizers [86].

The calculated E values ranged from (0.1626 ± 0.0005) MPa (PVA₁₀₀CS₀S₃₀) to (3.0120 ± 0.1900) MPa (PVA₂₅CS₇₅S₁₅). Based on the statistical data, no significant differences were observed among the films containing different plasticizer percentages. Nevertheless, when evaluating the films with the same amount of plasticizer and different ratios of PVA and CS, the film PVA₇₅CS₂₅S₁₅ was statistically different from the other PVA_xCS_yS₁₅ films. These results confirm the synergistic effect of blending starch with PVA.

In terms of modulus of elasticity, these films behaved similarly to those observed in the work by Hosney et al., (2019). The author observed that films with higher amounts of PVA present lower values of Young's modulus. When developing a blend of 50% PVA and 50% starch, the Young's modulus increases about six times more than the film with 100% PVA [87].

In addition to all the aforementioned properties, opacity is also very important as it affects the acceptance of products by consumers [88]. Low and high opacity values indicate transparent and

opaque films, respectively [89]. In that study, opacity ranged from 1.1750 Abs/mm (PVA₇₅CS₂₅S_{22.5}) to 2.9892 Abs/mm (PVA₂₅CS₇₅S₃₀). In view of the results presented, the films with 30% w/w plasticizer are the least acceptable to be used in the coating of fruits, since they were the ones that presented the highest opacity values. On the contrary, films with 22.5% w/w and 15% w/w of plasticizer are the most suitable ones for coatings because they have lower opacity values.

Based on the results discussed above, the films with 15% plasticizer had the lowest WVTR values. As for the solubility, thickness, and Young's modulus analyses, the percentages of plasticizer did not show statistical differences. However, a statistical difference was observed in Young's modulus when working with 15% w/w of plasticizer. Therefore, based on these results, the film with PVA₇₅CS₂₅S₁₅ was chosen to perform the fruit coating. This choice was made based on the aforementioned characteristics, but also on the qualitative characteristic of this film, which was easily removed from the Teflon plate, and was resistant enough to maintain its apparent physical integrity while being removed from the plate.

7.4 Thermal stability

Thermogravimetric analysis (TG) determines the thermal stability of the material from its mass variation over temperature and the first derivative (DTG) provides information about the degradation behavior, as well as the temperatures at which the degradation rate is maximum [80]. **Figure 10** shows the thermal stability and degradation behavior of the PVA_xCS_yS₁₅ films, and **Figure S1** shows the thermal behavior of PVA, CS, and S.

PVA displays three thermal events in the thermogram. The first step refers to the loss of water molecules adsorbed onto the polymer chains. The degradation of PVA starts at the second step, which mostly involves elimination reactions, continuing on the third step, which is dominated by the breaking and cyclization of the chains [90]. Zheng Peng; Ling Xue Kong (2007) found similar degradation temperatures. However, in their case, the degradation occurred in distinct and well-defined curves (300 and 450°C and 450 and 550°C) [90].

Cationic starch, on the other hand, degrades in a single step, reaching its temperature of maximum degradation rate at ~300°C. It also has the step referent to water loss at ~100 °C. These results are similar to ones observed by Danilovas, Paulius Pavelas; Rutkaite, Ramune; Zemaitaitis, Algirdas (2014), who evaluated the degradation of cationic starches of different degrees of substitution [91]. The thermal degradation of sorbitol occurred in a single step, reaching the temperature of maximum degradation rate at ~400 °C, and led to the loss of 100% of the mass used in the analysis.

The films presented degradation behaviors dependent on the amount of each polymer in the blend. For instance, films with higher PVA amounts (**Figure 10(a)** and **(b)**) presented degradation

behaviors similar to PVA while the CS-rich ones (**Figure 10(d)** and **(e)**) resembled more the CS degradation behavior. However, even though the pure films (**Figure 10(a)** and **(e)**) display very similar thermal behaviors to the precursors, the incorporation of sorbitol still changed the thermal stability. For example, for PVA, the second degradation peak changed from a well-defined band to a broad and less intense band. It confirms the interaction between the polymers and sorbitol. Besides, the temperature of the maximum degradation rate of this second peak shifted from 436 °C for PVA (**Figure S1(a)**) to 460 °C in PVA₁₀₀CS₀S₁₅ (**Figure 10(a)**), confirming that the interaction not only occurred, but it increased the thermal stability of PVA as well.

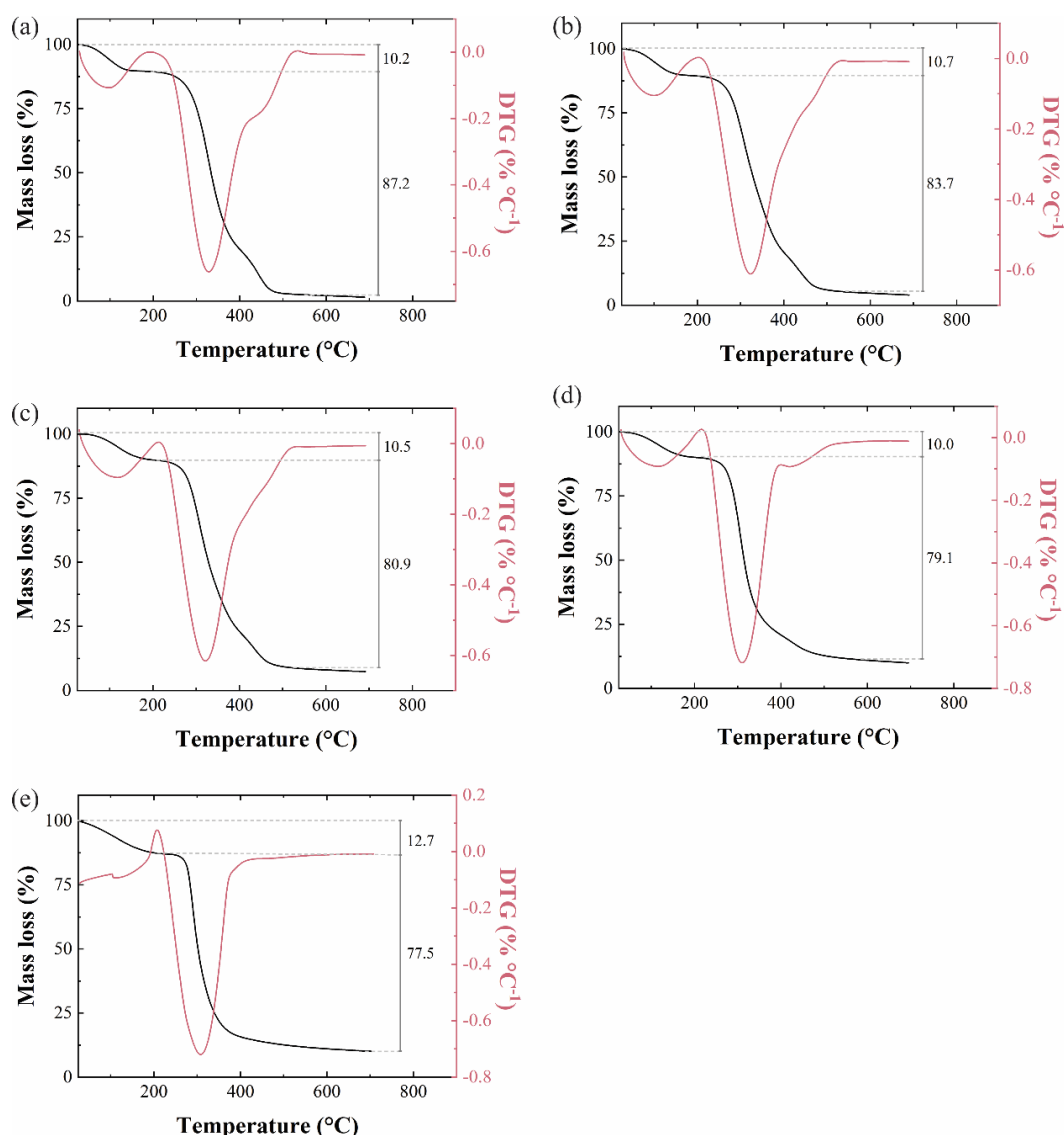


Figure 10. Thermal behavior of (a) PVA₁₀₀CS₀S₁₅, (b) PVA₇₅CS₂₅S₁₅, (c) PVA₅₀CS₅₀S₁₅, (d) PVA₂₅CS₇₅S₁₅, and (e) PVA₀CS₁₀₀S₁₅.

7.5 Coating performance in Barbados cherry

Biodegradable films have the function of improving food quality, protecting them from physical, chemical, and biological factors, which are responsible for food deterioration [92]. This work evaluated the efficiency of the film with the best performance so far (PVA₇₅CS₂₅S₁₅) in terms of mass preservation and physical-chemical parameters related to fruit senescence. For these analyses, divided into destructive and non-destructive, PVA₂₅CS₇₅S₁₅ was used as a coating rather than a film.

7.5.1 Non-destructive analysis

The quality of the fruits with and without the coating were evaluated in terms of mass variation and color changes. The loss of moisture during fruit storage indicates the acceleration of fruit aging, increases the rate of membrane disintegration, and promotes loss of cellular content. In addition, it allows wilting and loss of juiciness [17]. **Table 3** shows the mass loss of the acerolas in three days of storage.

Table 3 - The mass variation (g), vitamin C content (%), titratable acidity (CA%/100 g of fruit), soluble solids (°B), and harvest index (°B CA %/100 g of fruit) for the non-coated (control group) and coated Barbados cherries*.

Analysis	Experimental condition	Storage period (days)			
		0	1	2	3
Mass variation (g)	<i>Non-coated</i>	6.573 ± 1.007 ^{aABE}	5.884 ± 0.931 ^{aADG}	5.138 ± 0.907 ^{aCDI}	4.569 ± 0.971 ^{aFHJ}
	<i>Coated</i>	5.745 ± 1.022 ^{aABE}	5.301 ± 0.919 ^{aADG}	4.741 ± 0.841 ^{aCDI}	3.813 ± 1.265 ^{aFHJ}
Vitamin C (%)	<i>Non-coated</i>	1324.4 ± 19.9 ^{aACE}	931.7 ± 22.4 ^{aBDG}	741.5 ± 27.4 ^{aCDH}	1026.8 ± 82.2 ^{aFGH}
	<i>Coated</i>	1324.4 ± 19.9 ^{aACE}	1014.45 ± 2.49 ^{bBDG}	1158.9 ± 14.9 ^{bCDH}	649.0 ± 26.2 ^{bFGH}
Titratable acidity (CA %/100 g of fruit)	<i>Non-coated</i>	1.162 ± 0.046 ^{aACG}	1.094 ± 0.019 ^{aBEI}	0.8963 ± 0.0197 ^{aDFK}	0.8663 ± 0.0794 ^{aHJL}
	<i>Coated</i>	1.162 ± 0.046 ^{aACG}	0.958 ± 0.006 ^{bBEI}	0.9049 ± 0.0098 ^{aDFK}	0.5340 ± 0.0064 ^{bHJL}

<i>Soluble solids</i> (°B)	<i>Non-coated</i>	9.467 ± 0.057 ^{aACF}	10.00 ± 0.000 ^{aBEG}	9.866 ± 0.0577 ^{aDEH}	9.967 ± 0.0577 ^{aFGH}
	<i>Coated</i>	9.467 ± 0.057 ^{aACF}	9.800 ± 0.000 ^{bBEG}	10.00 ± 0.1000 ^{aDEH}	9.100 ± 0.265 ^{bFGH}
<i>Harvest Index</i> (°B CA %/100 g of fruit)	<i>Non-coated</i>	8.182 ± 0.320 ^{aACG}	9.145 ± 0.161 ^{aBEI}	11.01 ± 0.183 ^{aDFK}	11.57 ± 1.15 ^{aHJL}
	<i>Coated</i>	8.182 ± 0.320 ^{aACG}	10.223 ± 0.069 ^{bBEI}	11.05 ± 0.187 ^{aDFK}	17.04 ± 0.69 ^{bHJL}

* $(\text{Mean} \pm \text{SD})^{\text{aA}}$ that do not share the same letter are statistically different at 95% of significance. For each analysis, lower-case letters in the same column refer to the comparison between the different treatments (coated or non-coated) within the same storage day. Upper-case letters in the same line refer to the comparison of a same treatment throughout different storage days.

The control group showed a higher mass loss (compared to the coated fruit) since the first day. The higher slope of the non-coated fruit ($y_{\text{non-coated}} = (7.86 \pm 0.39)$) compared to the coated ones ($y_{\text{coated}} = (7.00 \pm 0.36)$) confirms the previous statement and suggests that the coating had a positive effect in terms of moisture preservation. However, this effect was not as evident as expected. The high solubility ($94.167 \pm 1.179\%$) and the low thickness (0.3244 ± 0.0695 mm) of this film (compared to the other PVA:CS ratios) might justify this behavior. In this case, the arrangement of the chains might have changed as water passed through the polymer layer, affecting the thickness of the coating.

It should also be reinforced that the shelf-life of the fruits evaluated in this experiment was short because the experiments were carried out without any refrigeration, it is, at room temperature. It probably favored the loss of moisture content throughout the storage days. However, it already suggests the coating would be minimally effective in slowing down the loss of moisture content even at room temperature, especially because most fruit are considered edible until losing 30% of their fresh mass. As seen in **Figure 11**, the coated fruit would take more than 4 days to lose that amount of fresh mass. This result suggests the coating would increase the shelf-life of acerolas in, at least, one day (if stored at room temperature).

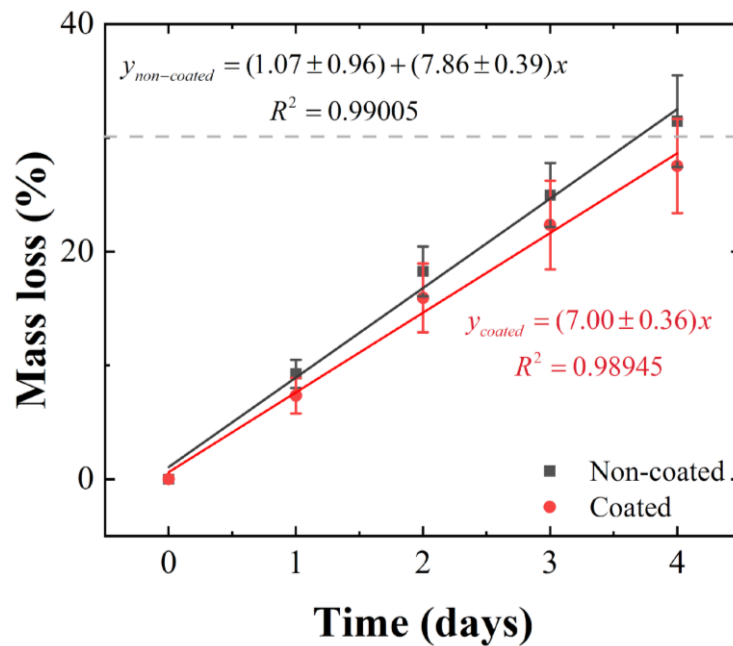


Figure 11. The percentage of mass loss of coated and non-coated acerolas throughout four days of storage at room temperature. The gray dotted line marks 30% of mass loss.

The color presented by the fruit during storage is also an important factor. Therefore, it is important to assess the effect of a coating on the color of the coated fruit. **Figure 12** provides a qualitative comparison of acerolas (coated and non-coated) on the third storage day. It is possible to notice that, visually, the non-coated fruit presented a darker red color compared to the coated one. The coated fruit is protected from the action of oxygen, which delays the oxidative processes responsible for changing the color of the fruit.



Figure 12. Visual comparisons between uncoated and coated fruit on the third day of storage.

The effect of applying the biodegradable coating on the acerolas in the colorimetry analysis was also verified through qualitative measurements carried out using the ImageJ software, where the levels of Red, Green, and Blue were evaluated. Based on the results presented in **Table 4**, it is observed that the non-coated and coated fruits had a significant difference in the red color on the

second day. For the green color, the fruits had statistical differences on the first day and for the blue color, they had no statistical differences over the three days. Therefore, the coating showed small but significant results for the two non-destructive analyzes carried out.

Table 4 - Qualitative color variation (according to the red, green, and blue (RGB) variation) for the non-coated (control group) and coated Barbados cherries*.

RGB values	Experimental condition	Storage period (days)			
		0	1	2	3
Red	<i>Non-coated</i>	145.9 ± 15.2 ^{aABE}	95.48 ± 3.180 ^{aADF}	83.17 ± 0.535 ^{aCDG}	74.5 ± 23.3 ^{aEFG}
	<i>Coated</i>	145.9 ± 15.2 ^{aABE}	129.55 ± 14.07 ^{aADF}	103.34 ± 3.56 ^{bCDG}	126.62 ± 2.53 ^{aEFG}
Green	<i>Non-coated</i>	29.13 ± 4.010 ^{aABE}	28.34 ± 1.200 ^{aACF}	24.43 ± 1.329 ^{aBDG}	33.79 ± 1.129 ^{aEFG}
	<i>Coated</i>	29.13 ± 4.010 ^{aABE}	37.64 ± 2.150 ^{bACF}	23.20 ± 1.500 ^{aBDG}	31.98 ± 11.46 ^{aEFG}
Blue	<i>Non-coated</i>	36.08 ± 4.790 ^{aABE}	42.50 ± 2.570 ^{aACG}	33.78 ± 0.752 ^{aBDH}	44.09 ± 4.27 ^{aFGI}
	<i>Coated</i>	36.08 ± 4.790 ^{aABE}	39.34 ± 1.088 ^{aACG}	30.51 ± 3.350 ^{aBDH}	42.94 ± 3.990 ^{aFGI}

*(Mean ± SD)^{ab} that do not share the same letter are statistically different at 95% of significance. For each analysis, lower-case letters in the same column refer to the comparison between the different treatments (coated or non-coated) within the same storage day. Upper-case letters in the same line refer to the comparison of a same treatment throughout different storage day

7.5.2 Destructive analyses

The quality of the fruits, without and with the coating, was also evaluated in terms of soluble solids, titratable acidity and vitamin C. The amount of vitamin C, it is, ascorbic acid, was monitored during the storage period of the fruits with and without the coating. The vitamin C content was supposed to decrease throughout the ripening process due to the action of ascorbate oxidase (a degradation enzyme) or due to its use as a respiratory substrate [93]. However, as shown in **Table 3**, the values of vitamin C initially decreased, but increased again on the last storage day. It suggests the fruit used for the analysis were in different stages of the ripening process.

According to the vitamin C results presented in **Table 3**, the treatments were statistically different since the first day of analysis. The results also suggest the coated fruit undergone a more homogeneous ripening process than the non-coated ones. The lower water loss experienced by the

coated fruit might justify this behavior. This result indicate that the coated fruit would probably need a longer period to reach senescence compared to the non-coated ones.

Titrateable acidity is another destructive analysis of great importance. It indicates the acidity of the fruit, which is related to the amount of organic acids in the fruit [17]. The amount of acid consumed during the fruit's respiratory process may be related to the rotting process [17]. TA is supposed to decrease as the fruit starts to ripe, and increase as the fruit rots [17]. This tendency was not observed in this work, reinforcing the hypothesis of fruits on different stages of ripening.

Soluble solids indicate the amount of sugar and other compounds such as acids, vitamins, amino acids and some pectin in the fruit. Therefore, fruits suitable for consumption or industrial processing must have high SS values [94]. When performing the analysis of total solids (SS), it was observed that the non-coated fruits had an increase in SS on the first day, but on the second day, they showed a decrease. This occurs because, throughout the maturation of the fruit, the SS initially increase and subsequently decrease due to the consumption of sugar in the respiratory processes [42]. Therefore, the non-coated fruits showed a decrease in SS on the second day of storage. This increase followed by a decrease in SS indicates the fruit reached senescence. For the coated fruits, the increase in SS occurred until the second day of storage and the decrease began only on the third day. Therefore, the coating showed positive results on the fruit because the period of fruit senescence was increased by one day. It agrees with the mass loss and vitamin C content results.

Blends based on PVA and CS are not very common reported as fruit coating in the literature. However, several papers have already assessed the effectiveness of PVA and chitosan-based coatings. For example, the PVA and carboxymethyl chitosan film produced Elbarbary et al., (2023) preserved (unaltered) the physical-chemical characteristics of sweet oranges for 56 days. The higher resistance of the fruit itself might justify the preservation for longer times (comparing the oranges to acerolas).

The results presented in this work confirm the suitability of the PVAxCSySz films (especially PVA₇₅CS₂₅S₁₅) for food coating purposes. It is still necessary to assess the efficiency of this film under refrigerated conditions, and its effectiveness in preventing damages during the transportation and processing of the fruit. However, these analyses are still prospects of this work.

8. CONCLUSION

This work evaluated the effect of the percentage of sorbitol on the properties of biodegradable films based on PVA and cationic starch. FTIR and XRD analyses confirmed the formation of physical interactions between PVA, CS, and sorbitol. However, although the plasticizer was compatible with both polymers, the polymer/sorbitol interactions became less stable when the concentration of sorbitol increased from 15 to 22.5 and 30% w/w, leading to exudation. The observance of sharper peaks in

the diffractograms strongly supported the exudation hypothesis, plus, SEM micrographs confirmed the presence of crystals on the surface of the films containing higher percentages of sorbitol.

Despite exudation, higher percentages of sorbitol did not improve the performance of the films up to significant levels. Apart from WVTR, which led to significant differences at 95%, the performance of the films was statistically equal (at 95%) in all of the other assessed parameters (Young's modulus, solubility, opacity, and thickness). Therefore, the performance of this blend as a coating for acerolas was assessed using the film that was easier to remove from the Teflon plate, and maintained its apparent integrity in the process. The chosen film was composed by 75% of PVA, 25% of CS and 15% of S.

As a coating, PVA₇₅CS₂₅S₁₅ decreased the loss of moisture content, preserved the bright red color of the fruit and slowed down the ripening process of acerolas, ensuring their survival for one more day than the control. This result becomes even more relevant considering the fruit were stored at room temperature. Therefore, PVA₇₅CS₂₅S₁₅ is suitable for fruit coating purposes. However, assessing its effectiveness in preventing damages during the transportation and processing of the fruit are still prospects of this work.

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10. SUPPORT INFORMATION

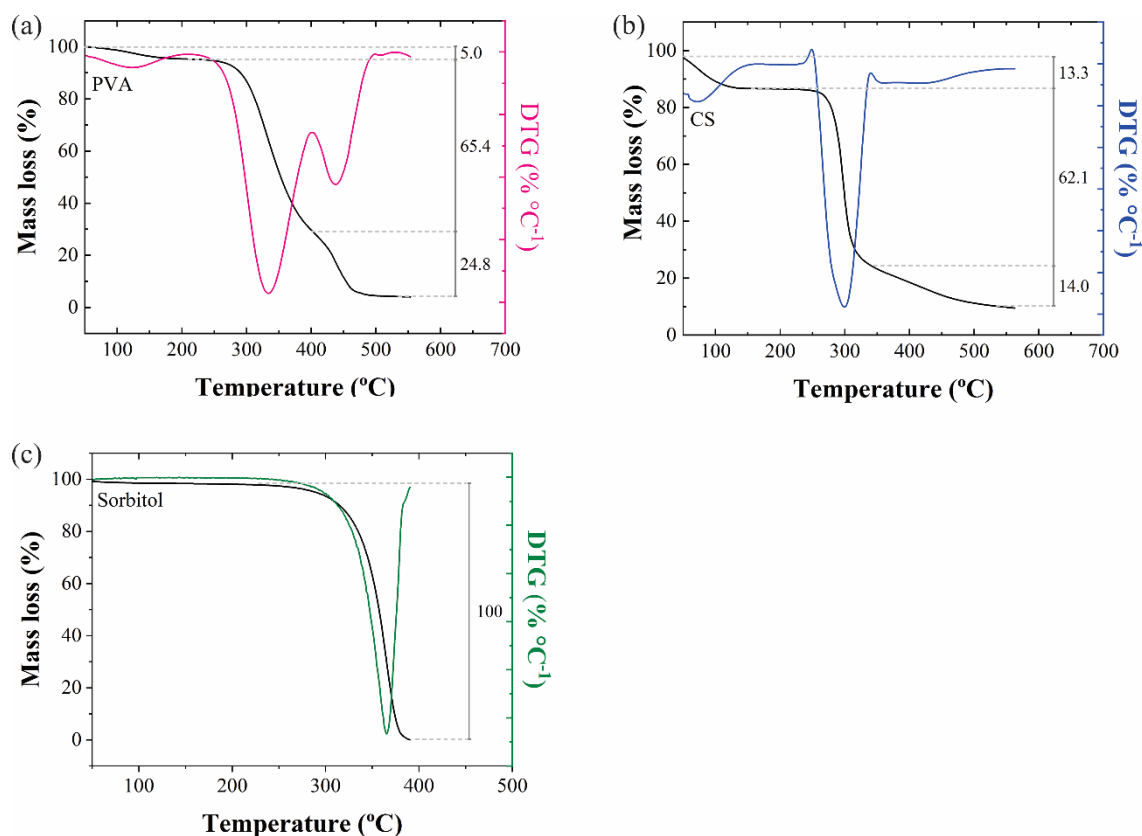


Figure S1. Thermogravimetric profile and first derivative (DTG) of (a) PVA, (b) CS, and (c) sorbitol.

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