**UNIVERSIDADE ESTADUAL DE MARINGÁ**
**CENTRO DE CIÊNCIAS AGRÁRIAS**
**Programa de Pós-Graduação em Ciência de Alimentos**

# BIODEGRADABLE FILMS BASED ON COMMERCIAL κ-CARRAGEENAN AND CASSAVA STARCH TO ACHIEVE LOW PRODUCTION COSTS

## CAMILA DE LIMA BARIZÃO

Maringá

2021

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Dissertação apresentada ao programa de Pós Graduação em Ciência de Alimentos da Universidade Estadual de Maringá, como parte dos requisitos para obtenção do título de mestre em Ciência de Alimentos.

Maringá

2021

Dados Internacionais de Catalogação-na-Publicação (CIP)
(Biblioteca Central - UEM, Maringá - PR, Brasil)

Barizão, Camila de Lima
B253b Biodegradable films based on commercial k-carrageenan and cassava starch to achieve low production costs / Camila de Lima Barizão. -- Maringá, PR, 2021.
47 f.: il. color., figs., tabs.

Orientador: Prof. Dr. Elton Gutendorfer Bonafé.
Coorientadora: Profa. Dra. Patrícia Salomão Garcia.
Dissertação (Mestrado) - Universidade Estadual de Maringá, Centro de Ciências Agrárias, Programa de Pós-Graduação em Ciência de Alimentos, 2021.

1. Polissacarídeos. 2. Embalagens de alimentos. 3. Biopolímeros. I. Bonafé, Elton Gutendorfer , orient. II. Garcia, Patrícia Salomão, coorient. III. Universidade Estadual de Maringá. Centro de Ciências Agrárias. Programa de Pós-Graduação em Ciência de Alimentos. IV. Título.

CDD 23.ed. 664.09

Márcia Regina Paiva de Brito - CRB-9/1267

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Dissertação apresentada à Universidade Estadual de Maringá, como parte das exigências do Programa de Pós-graduação em Ciência de Alimentos, para obtenção do grau de Mestre em Ciência de Alimentos.

Oscar de O. Santos Júnior
**Prof. Dr.** Oscar de Oliveira Santos Júnior

Paula F. Montanher
**Profa. Dra.** Paula Fernandes Montanher

Elton G. Bonafé
**Prof. Dr.** Elton Guntendorfer Bonafé
**Orientador**

Maringá – 2021

**Orientador**
Elton Gutendorfer Bonafé

**Co-Orientadora**
Patrícia Salomão Garcia

# BIOGRAFIA

Camila de Lima Barizão nasceu em 05 de janeiro de 1996 na cidade de Paranavaí-PR. Possui graduação em Bioquímica pela Universidade Estadual de Maringá. Tem experiência nas áreas de Polímeros e biopolímeros atuando principalmente nos seguintes temas: Desenvolvimento de filmes biodegráveis e Filmes biodegrádeveis ativos.

***Dedico***

*Dedico este trabalho a Deus, minha*
*familia e namorado, que são as*
*pessoas mais importantes*
*da minha vida.*

# AGRADECIMENTOS

Agradeço primeiramente a Deus, por ter me ajudado e guiado permitindo que eu chegasse até aqui.

Aos meus pais, que sempre estão do meu lado incentivando e auxiliando em tudo que podem, fazendo o possível para que eu tenha sempre o melhor, amo muito vocês.

A minha irmã querida, que me ajudou muito e sempre esteve ao meu lado ao longo da minha vida, mesmo estando longe físicamente. Você sem dúvidas é minha maior inspiração pra eu ir atrás dos meus sonhos, te amo muito.

Ao meu namorado lindo que sempre está comigo, me dando todo amor, apoio, incentivo e ajudando muito. Muito obrigada por nunca me deixar desistir, te amo demais.

Ao meu orientador, por todos os ensinamentos, suporte e compreensão ao longo desses dois anos, tudo isso foi muito importante para mim. Muito obrigada.

A minha coorientadora, que deu todo suporte inicial para comerçarmos a trabalhar nessa área, obrigada pelo conhecimento transmitido.

Ao pessoal do laboratório, que me auxiliaram tirando dúvidas e ajudando quando precisei. Obrigada.

Ao programa de Pós- graduação e todos os professores que eu tive, muito obrigada por compartilhar um pouco do conhecimento de vocês durante as disciplina, isto foi essencial para o meu desenvolvimento.

Finalmente, gostaria de agradecer a Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, CAPES pela bolsa concedida e ao Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq pelo apoio financeiro.

# APRESENTAÇÃO

Esta dissertação de mestrado está apresentada na forma de um artigo científico

## Biodegradable films based on commercial κ-carrageenan and cassava starch to achieve low production costs

Camila de Lima Barizão[b], Marina I.Crepaldi[b], Oscar de Oliveira S.Junior[b], Ariel C.de Oliveira[c], Alessandro F.Martins[a, c], Patricia S.Garcia[a], Elton G.Bonafé[a, b.]

[a] Laboratório de Materiais, Macromoléculas e Compósitos (LaMMAC), Universidade Tecnológica do Paraná (UTFPR), Apucarana, PR 86812-460, Brasil

[b] Analítica Aplicada a Lipídios, Esteróis e Antioxidantes (APLE-A), Universidade Estadual de Maringá (UEM), Maringá, PR 87020-900, Brasil

[c] Grupo de Materiais Poliméricos e Compósitos (GMPC), Departamento de Química, Universidade Estadual de Maringá (UEM), Maringá, PR 87020-900, Brasil

Este artigo foi publicado no International Journal of Biological Macromolecules em 15 de dezembro de 2020, tendo como DOI: https://doi.org/10.1016/j.ijbiomac.2020.09.150

# GENERAL ABSTRACT

**INTRODUCTION.** Conventional oil-based packaging is becoming a huge problem due their high degradation time, resulting in environmental pollution. Therefore, natural packaging, based on proteins and polysaccharides, with a short degradation time has been studied. The starch is one of the most used polysaccharides in biodegradable biofilms due to its capacity to form a continuous matrix, plenty, low cost, renewability and eco-friendly. Starch granules are gelatinized with a plasticizer (such as glycerol) excess water and temperature between 60º C and 100º C producing the thermoplastic starch (TPS). Despite nontoxic and biodegradable, the TPS films do not have good mechanical and barrier properties. Thus, TPS and different polymers blends (including synthetic polymers, such as polyvinyl alcohol; PVA) can produce films with improved features, suitable for use in food. Few studies have reported the starch and κ-carrageenan (linearly sulfated polysaccharide extracted from red algae) blends. The κ-carrageenan as a gelling agent, used in the production of the biodegradable films, for example, GENUGEL®. The GENUGEL® is a commercial product based on κ-carrageenan developed by CP Kelco and used as a thickener, stabilizer, gelling and texturizing agent in food applications. However, GENUGEL® was not used in biodegradable films or any mixture with starch, by the solvent evaporation method. The κ-carrageenan application is approved by Food and Drug Administration (FDA), and both (κ-carrageenan and GENUGEL®) can be used as food ingredients and in food packaging.

**AIMS.** Evaluate the effect of the incorporation of a commercial κ-carrageenan on the physicochemical properties of starch-based films for the first time. PVA and glycerol were used as plasticizers.

**MATERIALS AND METHODS.** Films were created from the casting method. Glycerol and PVA were dissolved in distilled water under magnetic stirring. Then, desirable κ-carrageenan and cassava starch contents were slowly added to the aqueous glycerol and PVA solution with magnetic stirring for 20 min. The mixture was heated to 90 °C for 30 min under magnetic stirring to prepare polymer blends and support starch gelatinization. After, the mixtures were added to the ultrasonic bath to remove air bubbles and then, transferred to Petri dishes to solvent evaporation. After the solvent evaporation, each film was peeled off the Petri dish and stored in an appropriate package at room temperature for further analysis. It was produced five different films at κ-carrageenan: starch weight ratios of 100:0 (100κ-c), 75:25 (75κ-c), 50:50 (50κ-c), 25:75 (25κ-c) and 0:100 (0κ-c). The thickness of films was analyzed by an electronic digital micrometer, while the mechanical properties were verified by a texturometer, where was evaluated the tensile strength (σ - MPa), elongation at break (ε - %), and Young's modulus (MPa) (Modulus of elasticity related to the stiffness). The Fourier transform infrared spectroscopy (FTIR) spectra of films and their precursors were also considered. In terms of thermal analysis, we realized the thermogravimetric (TGA/DTG) and differential scanning calorimetry (DSC). The physical-chemical films characteristics were also studied across moisture and water solubility, swelling degree (SD) and swelling kinetic, water and oil vapor permeability. The color and apparent opacity were studied by spectrophotometer.

**RESULTS AND DISCUSSIONS.** Overall, κ-carrageenan: starch films showed excellent processability, handleability, and homogeneity. The films' thickness ranged from 150 to 190 μm. This finding can support packages for food applications. Small bubbles remained in the 100κ-c solution even after the treatment. It happens because the aqueous κ-carrageenan solution should

support a high viscosity due to the linear polymer structure and high molar mass, so, the bubbles do not escape from the blend. The moisture (MC) for κ-carrageenan: starch films was low and ranged from 2.52 to 3.74%. The MC increases as the starch concentration rise due to the higher density of hydroxyl groups on the starch molecules. The water solubility (WS) ranged from 39.22 to 62.86%. The 100κ-c, 75κ-c, and 50κ-c presented higher WS than the 25κ-c and 0κ-c. This was because the κ-carrageenan presents ionized sulfate sites stabilized by metallic ions. The SD results varied from 391.6 (0κ-c) to 2002% (100κ-c). The SD increases as the κ-carrageenan concentration raise because the κ-carrageenan solutions provide physical hydrogels at the presence of metallic ions. Therefore, they can absorb more water than the starch-based film (0κ-c). The film structures remained stable even after the maximum water gain in the kinetic curve profile. This result suggests that the films present stable networks due to the active association between the film precursors. The 100κ-c and 75κ-c were more permeable to water vapor than the 25κ-c and 0κ-c. The 50κ-c supported a WVP significantly lower than the WVP for 75κ-c ($p > 0.05$). Stiff structures (with low SDs) should promote low WVPs. The films displayed excellent visual appearance. The high values for L and WI, and low measures for E, suggest colorless films. The film opacity ranged from 0.67 to 0.88. The films with a higher amount of starch have greater opacity. The oil permeability was between 0.0033 and 0.0043 mm $m^2$ $d^{-1}$ for the κ-carrageenan: starch films, low oil permeability indicates that the oil molecules have difficulty in transposing the film, this is due to the hydrophobic groups of the precursors. As for mechanical, as the κ-carrageenan content increased, the tensile strength was higher. The films with the highest amount of κ-carrageenan had a higher Young's modulus, that is, they were more rigid, however, they had less elongation at break. The FTIR spectrum bands indicate films composed by PVA, glycerol, starch and κ-carrageenan. Thermogravimetric analyzes indicate that starch is more thermally stable compared to κ-carrageenan, so films with a higher amount of starch will be more stable at high temperatures. Films with the highest amount of starch (0κ-c and 25κ-c) show endothermic peaks on DSC analysis, while in the other films only exothermic peaks occurred. Endothermic peaks indicate the melting of the material and exothermic peaks to the degradation of the material; therefore, this result also indicates that films with higher amounts of starch are more thermally stable.

**CONCLUSION.** According to results obtained is possible conclude that the casting method was efficient for producing films from selected parameters. The κ-carrageenan: starch ratio was essential on mechanical, physical and chemical properties obtained. The addition of starch to the κ-carrageenan produced flexible films with high thermal stability. The presence of κ-carrageenan provided stiff films. Depending on the desired application, the film's traits can be modulated by tuning the κ-carrageenan: starch weight ratio in the polymer blend.

**Keywords: Polysaccharides; food packaging; Biopolymers.**

# RESUMO GERAL

**INTRODUÇÃO.** As embalagens convencionais originadas do petróleo têm se tornado um grande problema, visto que demoram muito tempo para se degradarem, o que pode gerar poluição ambiental. Assim, embalagens de origem natural, a base de proteínas e polissacarídeos, com curto tempo de decomposição vêm sendo estudadas. O amido é um dos polissacarídeos mais usados para o desenvolvimento dos novos biofilmes, devido ao seu potencial de formar uma matriz continua e também por sua abundância, baixo custo, por ser renovável e não tóxico. Quando os grânulos de amido são gelatinizados com um plastificante (como o glicerol) em excesso de água e a temperaturas entre 60º C e 100º C formam um termoplástico amido (TPS). Apesar de atóxicos e biodegradáveis, os filmes de TPS não apresentam boas propriedades físicas e de barreira. Assim, misturas de TPS e diferentes polímeros (incluindo polímeros sintéticos, como o álcool polivinílico; PVA) podem gerar filmes com características melhoradas, desejáveis para a aplicação em alimentos. Poucos estudos relataram a mistura de amido e κ-carragena, que é um polissacarídeo de estrutura linear sulfatada extraído de algas vermelhas. A κ-carragena possui capacidade de gelificação, podendo assim ser usada para a produção de filmes biodegradáveis, como é o caso do GENUGEL®. O GENUGEL® é um produto comercial de κ-carragena desenvolvido pela CP Kelco, utilizado como espessante, estabilizante, gelificante e agente texturizante em aplicações de alimentos. No entanto, GENUGEL® κ-carragena ainda não foi relatado em filmes biodegradáveis e nem em misturas com amido para formação de filmes pelo método de evaporação do solvente. O uso de amido e κ-carragena são aprovados pela Food and Drug Administration (FDA). Ambos podem ser usados como ingredientes alimentares e também em embalagens de alimentos.

**OBJETIVO.** O objetivo deste estudo foi avaliar o efeito da incorporação de uma κ-carragena comercial nas propriedades físico-químicas de filmes à base de amido de mandioca pela primeira vez. PVA e glicerol foram usados como plastificantes.

**MATERIAIS E MÉTODOS.** Os filmes foram produzidos pelo método de fundição. Glicerol e PVA foram dissolvidos em água destilada sob agitação magnética. Em seguida, os teores desejáveis de κ-carragena e amido de mandioca foram adicionados lentamente à solução aquosa de glicerol e PVA com agitação magnética. A mistura foi aquecida a 90ºC por 30 min sob agitação magnética para realizar a gelatinização do amido. Em seguida, as misturas foram levadas ao banho ultrassônico para remoção das bolhas de ar, transferidas para placas de Petri e colocadas em estufa para evaporação do solvente. Após a secagem, os filmes foram retirados das placas e armazenados em embalagens adequadas. Foram desenvolvidas cinco formulações de filmes variando as proporções de κ-carragena: amido 100: 0 (100κ-c), 75:25 (75κ-c), 50:50 (50κ-c), 25:75 (25κ-c) e 0:100 (0κ-c). Depois de prontos os filmes foram caracterizados. Avaliou-se a espessura por meio de micrômetro digital, enquanto as características mecânicas foram verificadas através de texturômetro, onde foram avaliados a resistência à tração (σ - MPa), alongamento na ruptura (ε -%) e módulo de Young (MPa) (Módulo de elasticidade em relação à rigidez do material). O espectro de infravermelho por transformada de Fourier (FTIR) dos filmes e de seus precursores também foram realizados. Quanto às análises térmicas, foram realizadas as análises termogravimétrica(TGA/DTG) e calorimetria de varredura diferencial (DSC). As caracteristicas fisico-químicas dos filmes também foram estudadas atraves de análises de umidade, solubilidade em água, grau de intumescimento, cinética de intumescimento, permeabilidade de vapor de água e permeabilidade de óleo. Um estudo da coloração e opacidade

foi realizado através de espectofotômetro.

**RESULTADOS E DISCUSSÃO.** Em geral, todos os filmes desenvolvidos apresentaram boa processabilidade, manipulação e homogeneidade. As espessuras variaram de 150 a 190 µm, o que pode ser considerado bom para uma possivel aplicação em alimentos. A formulação 100κ-c apresentou pequenas bolhas mesmo após o uso do banho de ultrassom. Isso ocorreu devido à estrutura linear e alta massa molar da κ-carragena produzir uma solução aquosa muito viscosa, impedindo assim que as bolhas escapassem da mistura. A umidade (MC) para os filmes de κ-carragena: amido foi baixa e variou de 2,52 a 3,74%. A MC aumentou com o aumento da concentração de amido devido à maior densidade de grupos hidroxila nas moléculas de amido. A solubilidade em água (WS) variou de 39,22 a 62,86%. Os filmes 100κ-c e 75κ-c apresentaram WS menores do que 50 κ –c, 25κ-c e 0κ-c, isso ocorre porque a κ-carragena foi estabilizada por ions metalicos deixando-a menos solúvel. Os resultados dos graus de intumescimento (SD) variaram de 391,6 (0κ-c) a 2002% (100κ-c). O SD aumentou à medida que a concentração de κ-carragena aumenta, isso porque as soluções de κ-carragena fornecem hidrogéis físicos na presença de íons metálicos. Assim, eles podem absorver mais água do que o filme à base de amido (0κ-c). As estruturas do filme permaneceram estáveis mesmo após o ganho máximo de água no perfil da curva cinética. Esse resultado sugere que os filmes apresentam redes estáveis devido à associação ativa entre os precursores dos filmes. O 100κ-c e o 75κ-c foram mais permeáveis ao vapor de água do que o 25κ-c e o 0κ-c. O 50κ-c suportou um WVP significativamente menor do que o WVP para 75κ-c ($p > 0,05$). Estruturas rígidas (com SDs baixos) devem promover WVPs baixos. Os filmes apresentaram excelentes aspectos visuais. Os altos valores de luminosidade e índice de brancura e as medidas baixas de coloração total indicam filmes incolores. A opacidade do filme variou de 0,67 a 0,88. Os filmes com maior quantidade de amido apresentaram maior opacidade. A permeabilidade ao óleo obteve resultados entre 0,0033 e 0,0043 mm $m^2$ $d^{-1}$, esses baixos valores indicam que o óleo tem dificuldade de transpor os filmes, isso se deve aos grupos hidrofóbicos dos precursores. Em relação às propriedades mecânicas, conforme o teor de κ-carragena aumentou maior foi à resistência à tração. Os filmes com maior quantidade de κ-carragena tiveram um maior módulo de Young, ou seja, foram mais rígidos, porém, tiveram menos alongamento na ruptura. O espectro de FTIR apresentou bandas que comprovaram que os filmes realmente são compostos por PVA, glicerol, amido e κ-carragena. As análises termogravimétricas indicam que o amido é mais estável termicamente se comparado com a κ-carragena, então os filmes com maior quantidade de amido serão mais estáveis em altas temperaturas. A análise de DSC indicou picos endotérmicos nos filmes com maior quantidade de amido (0κ-c e 25κ-c), nos demais filmes ocorreram apenas picos exotérmicos. Picos endotérmicos indicaram a fusão do material e picos exotérmicos a degradação do material, portanto, esse resultado também indica que os filmes com maiores quantidades de amido são mais estáveis termicamente.

**CONCLUSÃO.** A partir dos resultados obtidos pode-se concluir que o método de fundição foi eficiente para a produção dos filmes a partir dos parâmetros utilizados. A razão entre κ-carragena: amido foi essencial para as propriedades mecânica, físicas e químicas obtidas. A adição de amido a κ-carragena produziu filmes mais flexíveis e mais estáveis termicamente. A presença de κ-carragena forneceu filmes mais rígidos. Portanto, dependendo da aplicação desejada pode-se alterar a razão dos polímeros para a produção do filme ideal.

**Palavras chaves: Polissacarídeos; embalagem de alimentos; Biopolímero**

# Biodegradable films based on commercial κ-carrageenan and cassava starch to achieve low production costs

Camila de Lima Barizão[b], Marina I. Crepaldi[a], Oscar de Oliveira S. Junior[b], Ariel C. de Oliveira[c], Alessandro F. Martins[a,c*], Patricia S. Garcia[a*], Elton G. Bonafé[a,b*]

[a]Laboratory of Materials, Macromolecules, and Composites (LaMMAC), Federal University of Technology – Parana (UTFPR), Apucarana, PR 86812-460, Brazil

[b]Analitycal applied in lipids, sterols, and antioxidants (APLE-A), State University of Maringá (UEM), Colombo avenue, Maringá, PR 87020-900, Brazil

[c]Group of Polymeric Materials and Composites (GMPC), Department of Chemistry, State University of Maringá (UEM), Maringá, PR 87020-900, Brazil

Corresponding author:

Laboratory of Materials, Macromolecules, and Composites (LaMMAC), Federal University of Technology – Parana (UTFPR), Apucarana, PR 86812-460, Brazil.

e-mail: eltonbonafe@utfpr.edu.br; p.salomaogarcia@gmail.com; afmartins@utfpr.edu.br

## Abstract

Biodegradable films have been a great alternative compared to non-renewable sources because of their cytocompatibility, biodegradability, and antimicrobial features. These properties may raise the food stuff shelf life, reducing costs and economic losses. Indeed, biodegradable films can also reduce the environmental pollution promoted by non-biodegradable conventional packs. For the first time, biodegradable films were produced by casting commercials *kappa*-carrageenan (κ-car) and cassava starch at different κ-carrageenan/cassava starch weight ratios. Physical, thermal, and mechanical properties were evaluated. Apparent opacity and color analyses suggest that the films present high transparency. The sample 0κ-c supported a film with high water solubility (39.22%) and a low swelling degree (391.6%). The lowest water vapor permeability (WVP) was observed for 50κ-c ($3.01 \times 10^{-8}$ g $(\text{Pa m s})^{-1}$). The oil permeability varied from 0.0033 to 0.0043 mm $\text{m}^2$ $\text{d}^{-1}$. The 100κ-c and 75κ-c films (high κ-carrageenan contents) had higher stiffness (19.23 and 25.88 MPa, respectively) than the 25κ-c and 0κ-c films with elongation at break (ε) of 21.60 and 67.65%, respectively. The thermal stability increased as the starch concentration raised in the blend. We produced low-cost biodegradable films from commercial polysaccharides. These films can be used as food packs.

**Keywords:** Polysaccharides; Food packaging; Biopolymers.

# 1 Introduction

Petroleum is a non-renewable resource widely used to produce plastics for conventional food packaging. This resource is harmful to the environment, mainly in aquatic media, due to low of biodegradability. In this context, alternative materials should be investigated [1,2]. Biodegradable products are great alternatives to petroleum-based plastics [3]. However, despite the positive features of biodegradable films and coatings, they represent only 5 to 10% of the plastics' current market. It occurs due to high production costs of packs.

Biodegradable materials can be used to develop packs, including cellulose, chitosan, pectin, starch, and proteins extracted from vegetable and animal sources [4]. Here, we highlight the starch, which is abundant, renewable, inexpensive, environmentally eco-friendly, and cytocompatible [5]. Biodegradable starch-based packs have been mainly created following the solvent evaporation approach (casting method) [6].

Starch comprises linear amylose and branched amylopectin structures. Amylose ($10^5$ g/mol) is composed of α-1,4 glucose units. This moiety supports the ability for film-forming. The amylopectin ($10^6$-$10^7$ g/mol) is formed of α-1,4 glucose units linked by β-1,6 bonds. The high molecular mass of amylopectin reduces the polymer chains' mobility in solution resulting in a high viscosity [6,7]. Hydroxyl groups on the starch are responsible for H-bonds that hold the starch chains together, promoting aqueous insolubility. However, thermoplastic starch (TPS) is formed as the starch granules are gelatinized with a plasticizer (like glycerol) in water excess at temperatures between 60 and 100ºC.

Starch-based films are often brittle and present weak mechanical properties [8]. Therefore, the TPS can be mixed with other polymers to produce blends with excellent mechanical traits after the solvent evaporation [7]. Polymer blending is a well-used strategy whenever a change or improvement of properties is necessary [9,10]. Starch-based films were created by blending starch with gelatin [11], lignocellulose nanofibers [3] chitosan [12], and biodegradable poly(vinyl alcohol) (PVA) [8,13–15]. PVA presents excellent features, including high tensile strength, flexibility, and thermal stability [16]. The association between PVA and starch can support films with appropriate mechanical properties for food packaging applications.

Few studies have reported about starch/κ-carrageenan blends. κ-Carrageenan has a linear sulfated structure obtained from red seaweed [17]. It is composed of D-galactose and 3,6-anhydro-D-galactose units linked by α-1,3 and β-1,4-glycosidic linkages [18]. κ-Carrageenan has gelling and film-forming features [19]. These traits allow producing biodegradable films [10,19–21]. GENUGEL® is a commercial product of κ-carrageenan developed by CP Kelco. It is applied as a thickening, stabilizing, gelling, and texturizing agent in food applications [22]. GENUGEL® κ-carrageenan was still not reported in biodegradable films. Also, it was not associated with the starch to provide blends and, thereby, films by the solvent evaporation method.

The use of starch and κ-carrageenan is approved by the Food and Drug Administration (FDA) [22,23]. Both can be used as food ingredients and also in food packs. In this study, we evaluated the effect of the incorporation of a commercial κ-carrageenan on the physicochemical properties of starch-based films for the first time. PVA and glycerol were used as plasticizers. The films were created following the casting approach. Infrared spectroscopy, and mechanical and thermal analyses characterized the films.

# 2 Material and Methods

## 2.1 Materials

Biodegradable films were produced with the commercial cassava starch, graciously donated by Indemil (Paranavaí, Brazil) and commercial GENUGEL® κ-carrageenan (277 kDa) gently donated by CP Kelco (Limeira, Brazil). Poly(vinyl alcohol) (PVA) (BASF, Germany) and glycerol (Dinâmica, Brazil) were used as plasticizers without previously purification steps.

## 2.2 Producing films

Films based on κ-carrageenan, cassava starch, PVA, and glycerol were created from the casting method as previously reported elsewhere with modifications [24]. Glycerol and PVA were dissolved in distilled water under magnetic stirring. Then, desirable κ-carrageenan and cassava starch contents were slowly added to the aqueous glycerol and PVA solution with magnetic stirring for 20 min. The mixture was heated to 90ºC for 30 min under magnetic stirring to prepare polymer blends and support starch gelatinization. After, the mixtures were added to the ultrasonic bath for 10 min (25ºC) to remove air bubbles, and then, the mixtures were transferred to Petri dishes (polystyrene plates with a diameter of 150 mm). The solvent evaporation was carried out at 40°C for 16 h. After the solvent evaporation, each film was peeled off the Petri dish and stored in an appropriate package at room temperature for further analysis. It was produced five different films containing 25 wt% glycerol and 25 wt% PVA concerning the polysaccharide concentration (wt%) in the blend. The films were prepared at κ-carrageenan: starch weight ratios of 100:0 (100κ-c), 75:25 (75κ-c), 50:50 (50κ-c), 25:75 (25κ-c) and 0:100 (0κ-c).

### 2.3 Moisture (MC) and water solubility (WS)

Moisture (MC) content and water solubility (WS) of the films was carried according to an experimental protocol reported elsewhere (*n* = 3) [25]. The moisture weight fraction (MC) was gravimetrically determined at 103°C for 24 h. The MC (%) was obtained through Eq. 1, using samples (2 × 2 cm) with $M_0$ of approximately 0.3 g

$$\mathrm{MC}\ (\%) = [M_0 - M_f/M_0]\ x\ 100 \qquad \textbf{(1)}$$

Where $M_0$ and $M_f$ correspond to the initial and final film masses, respectively.

For the WS test, films (2 × 2 cm) were dried at 103ºC for 24 h and weighed at 25$^{o}$C. After, the samples were added to 30 mL of distilled water (for 24 h at 25ºC and 100 rpm of shaking). Then, the swollen samples were dried in an incubator (103°C) for 24 h. After, the final dry mass ($M_f$) of the samples was determined at 25$^{o}$C. The WS was determined through Eq. 2

$$WS\ (\%) = [M_0 - M_f/M_0]\ x\ 100 \qquad \textbf{(2)}$$

Where $M_0$ is the initial mass of the film and $M_f$ is the final film mass determined after exposure to the distilled water for 24 h.

### 2.4 Swelling degree and swelling kinetic

The swelling degree (SD%) was determined as reported elsewhere [22]. Dried films (0.20 g) were added to 30 mL of distilled water (24 h at 25 °C and 100 rpm of shaking). The SD% was determined in triplicate using the Eq. 3.

$$SD\ (\%) = [M_s - M_d/M_d]\ x\ 100 \qquad \textbf{(3)}$$

Where $M_s$ and $M_d$ are the mass of swollen and dried samples, respectively.

Swelling kinetics were performed according to a reported work [26]. The dried κ-carrageenan/starch samples (2 × 2 cm) were weighed (0.20 g) and immersed in 30 mL of distilled water for 24 h at 25°C with 100 rpm of shaking. The swelling kinetics were evaluated by measuring the film masses at different time intervals (after 1, 10, 30, 60, 120, 180, 300, and 600 min). The profile of the kinetic curves was determined by using the swelling degrees assessed at different time intervals through Eq. 4

$$SD\ (\%) = [M_t - M_0/M_0]\ x\ 100 \qquad \textbf{(4)}$$

Where $M_t$ and $M_0$ are the swollen film masses at desirable times $t$ (min) and the initial dry film mass at time $t = 0$ min, respectively.

## 2.5 Water vapor permeability

The water vapor permeability (WVP) was gravimetrically determined according to the ASTM E-96-(00) (2000) standard [24].

## 2.6 Oil permeability

The oil permeability was carried following the methodology reported by Yan and coworkers [27]. Films were cut and placed on the top of a small glass bottle containing 5 mL of soybean oil. The bottle was placed upside-down over a filter paper (previously weighed) and maintained in a desiccator for 48 h at 25ºC. The Po was determined through Eq. 5

$$Oil\ permeability = \Delta W\ x\ X/A\ x\ t \qquad \textbf{(5)}$$

Where $\Delta W$ is the difference of mass concerning the filter paper (g) determined before (dried sample), and after the analysis (after oil contact), $X$ is the film thickness (mm), $A$ is the exposition area ($m^2$), and $t$ is the analysis time (days).

## 2.7 Color and apparent opacity

The colors of the films were evaluated using a colorimeter (Minolta Spectrophotometer, CM- 3500D, Osaka, Japan) through of the lightness/brightness ($L^*$), redness/greenness ($a^*$) and yellowness/blueness ($b^*$) parameters. The equipment was calibrated following the manufacturer. The total color difference ($\Delta E$) and whiteness index ($WI$) were obtained through Eqs. 6 and 7.

$$\Delta E = \sqrt{(L^* - L)^2 + (a^* - a)^2 + (b^* - b)^2} \quad \textbf{(6)}$$

$$WI = 100 - \sqrt{(100 - L)^2 + a^2 + b^2} \quad \textbf{(7)}$$

Where $L^*$ (92.60), $a^*$(-0.92) and $b^*$(-2.24) were the white plate color parameters.

The apparent opacity was measured as previously described by Shojaee-Aliabadi and coworkers [28]. Samples films (approximately 10×40 mm) were added to a quartz cuvette and spectrophotometrically analyzed using a Thermo Fisher Scientific, Genesys 10-S model at 550 nm. A quartz cuvette without film was used as a control. The apparent opacity was determined by the Eq. 8

$$Apparent\ opacity = Abs_{550}/X \quad \textbf{(8)}$$

Where $Abs_{550}$ is the absorbance at 550 nm, and $X$ is the film thickness (µm).

## 2.8 Characterization

### 2.8.1 Thickness and mechanical properties

An electronic digital micrometer (0 – 25 mm with a resolution of 0.001mm/YST, model tech/YUANLS-H4024) was used to measure the film thicknesses. Fifteen random measurements were performed in the films, using areas of approximately 9.6 $cm^2$/3.5 cm of diameter.

A texturometer, model TA.TX2 plus (England) was used to perform the mechanical assays according to the ASTM D882-02 (2002) standard with some modifications [29,30]. We evaluated the tensile strength ($\sigma$ - MPa), elongation at break ($\varepsilon$ - %), and Young's modulus (MPa) (Modulus of elasticity related to the rigidity of the material). Five specimens for each sample (50 × 25 mm) were previously conditioned at 53 ± 2% relative humidity and saturated $Mg(NO_3)_2$ solution (25 ± 2°C) for 48 h. The test speed was 0.83 mm $s^{-1}$, and the initial distance between the grips was 30 mm.

### 2.8.2 Fourier-transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectra of the dried films were obtained in an Agilent infrared spectroscopy (Cary 630, USA). Prior, the films were triturated and dried with anhydrous calcium chloride salt for 1 week. Then, 3 mg of each film was pellet with 100 mg of KBr. The analysis was performed over the spectral range from 4000 to 400 $cm^{-1}$, with 4 $cm^{-1}$ resolution and 64 scans**.**

### 2.8.3 Thermal analysis

Thermogravimetric (TGA/DTG) analysis was carried out in a Shimadzu thermogravimetric apparatus (model TGA50, Japan) from 25 to 650°C at 10°C/min rate, under 50 mL/min argon purge. Differential scanning calorimetry (DSC) analysis was performed in a Shimadzu apparatus (model DSC60 Plus, Japan) at heating rate of 10 °C/min, from 20 to 300°C, under 50 mL/min argon purge.

## 2.9 Statistical analysis

The data were analyzed using PAST software Past [31], with analysis of variance and *Tukey's test* at a 5% significance level ($p \leq 0.05$) .

# 3 Results and discussion

## 3.1 Development and appearance of the films

In preliminary tests, we observe that κ-carrageenan: starch films containing glycerol (25 vol% regarding the whole polysaccharide weight in the blend) presented weak mechanical properties. Indeed, it was tough to remove these films from the Petri dishes. Then, PVA (25 wt% concerning the whole polysaccharide weight in the blend), a biodegradable polymer, miscible in aqueous starch-based solutions) was associated with the κ-carrageenan: starch: glycerol mixtures to improve the films' mechanical properties [23,27]. Overall, κ-carrageenan: starch films showed excellent processability, handleability, and homogeneity **(Figure 1)**. The films' thickness ranged from 150 to 190 µm. This finding can support packages for food applications.

Semi-refined carrageenan: ulvan (101 µm) [23] and κ-carrageenan: mulberry polyphenolic extract films (165 µm) [32] had lower thicknesses than the κ-carrageenan: starch films. On the other hand, potato starch: furcellaran: gelatin films incorporated with lavender essential oil showed a high thickness (200 µm) [11]. The film's thickness depends on the blend composition and polymer concentration [33]. K-Carrageenan, starch, and PVA are biodegradable polymers with predominant linear structures [13,18,23]. The film's thickness also relies on the polymer structure. Branched materials provide higher thickness than linear polymers. Also, a high polymer content in the blend increases the film's thickness [23].

Gómez-Aldapa and coworkers evaluated the effect of PVA on the physicochemical properties of starch-based films. The same authors observed that κ-carrageenan films present similar features even as different plasticizers (glycerol and sorbitol) were used [23,25]. Films with regular appearance were yielded by blending κ-carrageenan and corn starch, following the high-pressure homogenization approach [34].

In this study, the ultrasound bath played a significant role in removing bubbles from the polymer blends. However, even after the treatment, small bubbles remained in the 100κ-c solution **(Figure 1)**. It happens because the aqueous κ-carrageenan solution (3.0% wt/vol) should support a high viscosity due to the linear polymer structure and high molar mass (277 kDa). So, the bubbles do not escape from the blend.

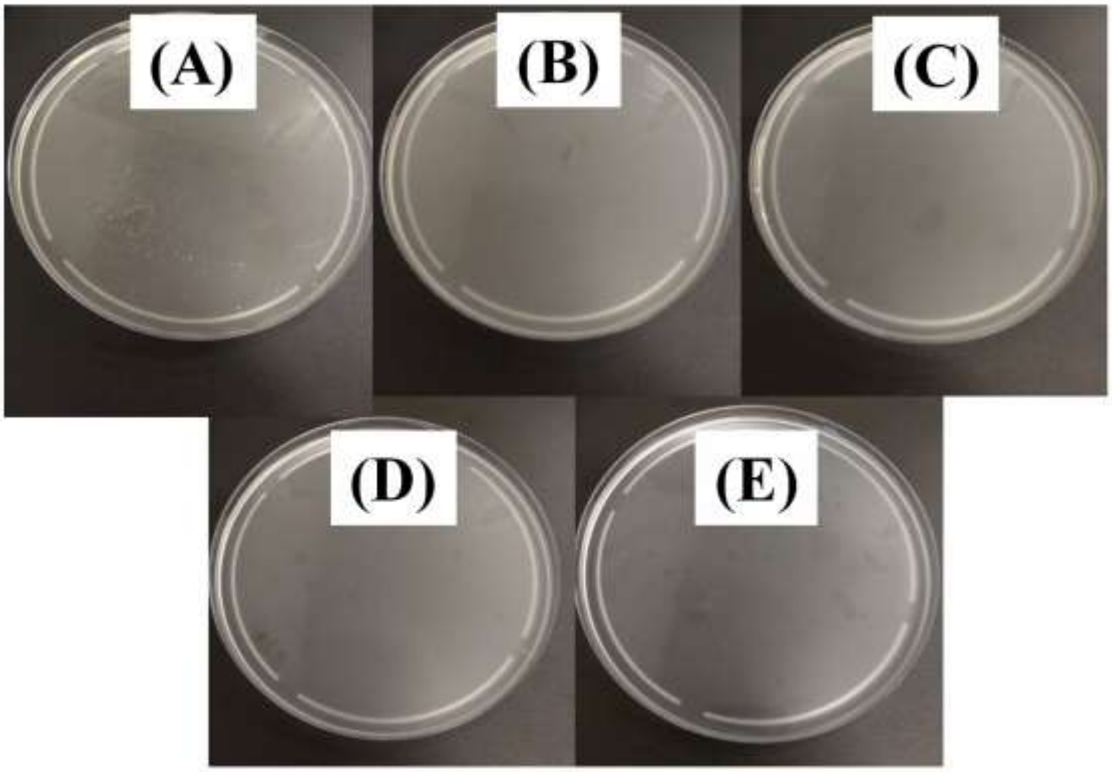
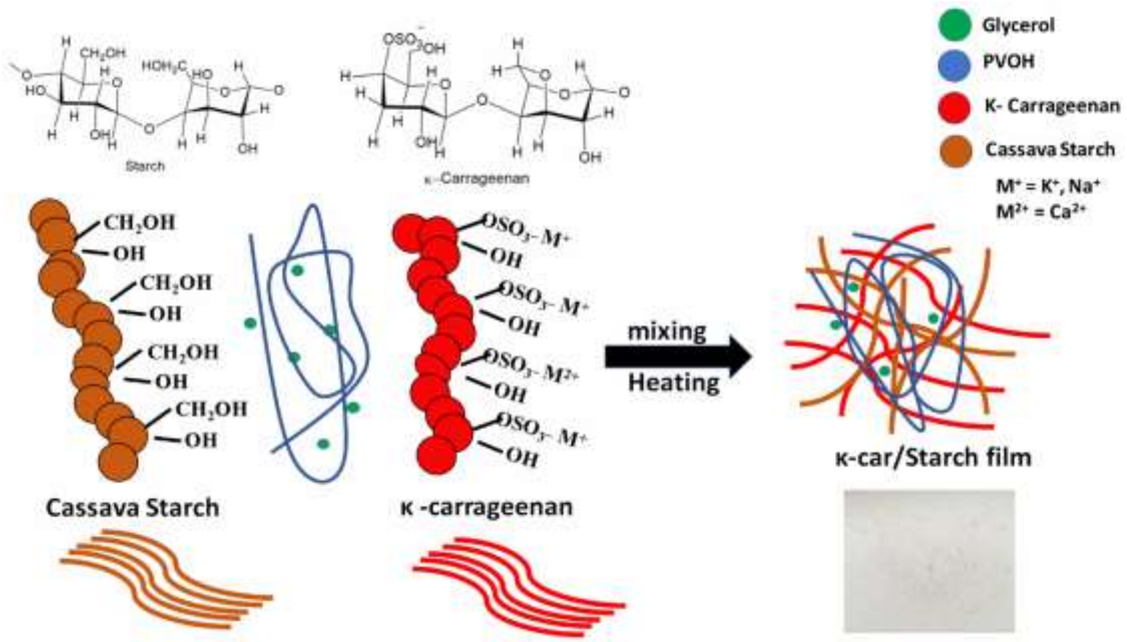


**Figure1.** Digital images of the κ-carrageenan: starch films: (A) 100κ-c, (B) 75κ-c, (C) 50κ-c, (D)25κ-c, and (E) 0κ-c.

CP Kelco kindly donated the commercial κ-carrageenan used in this study. It is used as a thickening, stabilizing, gelling, and texturizing agent in food industries [35]. The addition of metallic ions in the κ-carrageenan composition should improve these properties. A previous study showed that sodium (6.3 g/kg), potassium (216.1 g/kg), and calcium (12.5 g/kg) ions occur in this commercial κ-carrageenan [22]. These metallic ions stabilize the anionic κ-carrageenan chains [36] due to electrostatic interactions with the sulfate sites on the κ-carrageenan, facilitating the approximation of the polymer chains, and thereby, promoting films' stability. Also, the stabilization can be intensified by associating suitable glycerol [25] and PVA contents [15,37] to the aqueous κ-carrageenan and starch solutions (**Scheme 1)**. The film's stability depends on the intermolecular and intramolecular interactions established between the material chains, including H-bonds, dipole-dipole, ion-dipole, electrostatic, and hydrophobic forces [15,22].



**Scheme 1.** Formation scheme of κ-carrageenan: starch films.

### 3.2 Water solubility, moisture, swelling degree, and kinetic of water adsorption

The moisture (MC) for κ-carrageenan/starch films was low and ranged from 2.52 to 3.74% (**Table 1**). The difference between the moisture for 100κ-c and 75κ-c pair, as well as for 25κ-c and 0κ-c pair was not significant ($p < 0.05$). The MC increases as the starch concentration rise due to the higher density of hydroxyl groups on the starch molecules [15,37] compared to the κ-carrageenan and because metallic ions stabilize the anionic κ-carrageenan chains in the films. Polar hydroxyl groups on film components are responsible for inter- and intra-molecular H-bonds with water molecules [23]. Farhan and Hani reported high MC values between 8.8 and 14.5% wt/wt for κ-carrageenan films containing glycerol (20 to 30% wt/wt) [25]. Starch films containing glycerol (25% wt/wt) also had high moisture content (between 9 and 17 %) [38] mainly due to the high glycerol level in the film and presence of polysaccharides with sites available to interact with water molecules.

**Table 1.**
Physical properties of the films.

| **Formulation** | **MC%** | **WS%** | **SD%** | **Po (550/X)** | **WVP [$\times 10^{-8}$ g m (Pa m$^{2}$ s)$^{-1}$]** |
|---|---|---|---|---|---|
| **100κ-c** | 2.53 ± 0.09$^{a}$ | 39.22±0.56 | 2002±49.0 | 0.67±0.02$^{a}$ | 3.82 ± 0.74$^{a,b}$ |
| **75κ-c** | 2.52 ± 0.07$^{a}$ | 51.15±1.85 | 1762±30.0 | 0.68±0.02$^{a}$ | 4.48 ± 0.53$^{a}$ |
| **50κ-c** | 2.91 ± 0.03$^{b}$ | 60.42±4.92 | 1083±27.0 | 0.84±0.01$^{bcd}$ | 3.01 ± 0.37$^{b}$ |
| **25κ-c** | 3.69 ± 0.16$^{c}$ | 59.19±1.85 | 773.0±10.0 | 0.86±0.00$^{cd}$ | 3.84 ± 0.22$^{a,b}$ |
| **0κ-c** | 3.74 ± 0.14$^{cd}$ | 62.86±1.43 | 391.6±8.5 | 0.88±0.11$^{d}$ | 3.32 ± 0.04$^{a,b}$ |

MC (%): moisture content; WS (%): water solubility; SD (%): Swelling degree (%); Po: Apparent opacity; X is thickness (μm) of the film; WVP: water vapor permeability.
Results presented in mean ± standard deviation ($n$ = 3).
$^{a,b,c}$ Different letters in the same column indicate significant differences ($p \leq 0.05$).

The WS is a crucial parameter to evaluate the film's integrity in aqueous systems [3]. The WS ranged from 39.22 to 62.86% (**Table 1**). The 100κ-c, 75κ-c, and 50κ-c presented higher WS than the 25κ-c and 0κ-c. The commercial κ-carrageenan used in this study presents ionized sulfate sites stabilized by metallic ions (**Scheme 1**). These metallic ions support stability against solubilization at high levels of κ-carrageenan [39,40]. The WS increased from 39.22% (film 100κ-c) to approximately 60% (samples 50κ-c, 25κ-c, and 0κ-c). The starch is not soluble in aqueous solutions owing to the rearrangement of the hydrophobic starch chain segments in aqueous solutions [41], but starch-based materials can adsorb high water contents [42]. This fact can disrupt the film structure at a high starch concentration (**Table 1**).

The swelling degrees (SDs%) carried out in distilled water were statistically different ($p <$ 0.05, **Table 1**). The SD increase as the κ-carrageenan content in the blend is high. Indeed, the SD has a linear dependence ($R^2$ = 0.9985) with the κ-carrageenan concentration. The SD results varied from 391.6 (0κ-c) to 2002% (100κ-c, **Table 1**). The SD increases as the κ-carrageenan concentration raise because the κ-carrageenan solutions provide physical hydrogels at the presence of metallic ions. Hydrogel films can adsorb high water contents depending on the composition and experimental procedure used to create the films [29]. In this study, all samples containing κ-carrageenan are physical hydrogels; therefore, they can absorb more water than the starch-based film (0κ-c).

The highest swelling degree was reported for 100κ-c (sample without starch) due to the presence of stabilized sulfate groups on κ-carrageenan chains [43]. κ-Carrageenan stabilized by electrostatic interactions with metallic ions provide durable physical hydrogels with tridimensional structures [22]. These structures support water diffusion in the film matrices and, thereby, high SDs [44]. The addition of κ-carrageenan in the blends reduces the interactions between starch-starch chains, allowing expansion of the polymer networks and high SDs. The kinetic curves of water absorption are presented in **Figure 2**. The results agreed with the SDs findings, determined after 24 h of exposure to the distilled water. The water uptake reached 410 and 2200% between 120 and 180 min, except for 0κ-c that achieved the equilibrium state after 60 min. The maximum and minimum water gain was observed for 100κ-c and 0κ-c, respectively.

The film structures remained stable even after the maximum water gain in the kinetic curve profile. This result suggests that the films present stable networks due to the active association between the film precursors. Some samples showed a loss of mass between 100 and 600 min after the equilibrium state. As indicated by the WS test, the loss of mass should increase after 600 min of water exposure. Thawien and Manjeet prepared and studied the properties of starch: chitosan films. The authors justified that the loss mass happened due to the solubilization of chitosan in aqueous solutions of dilute acids [45].

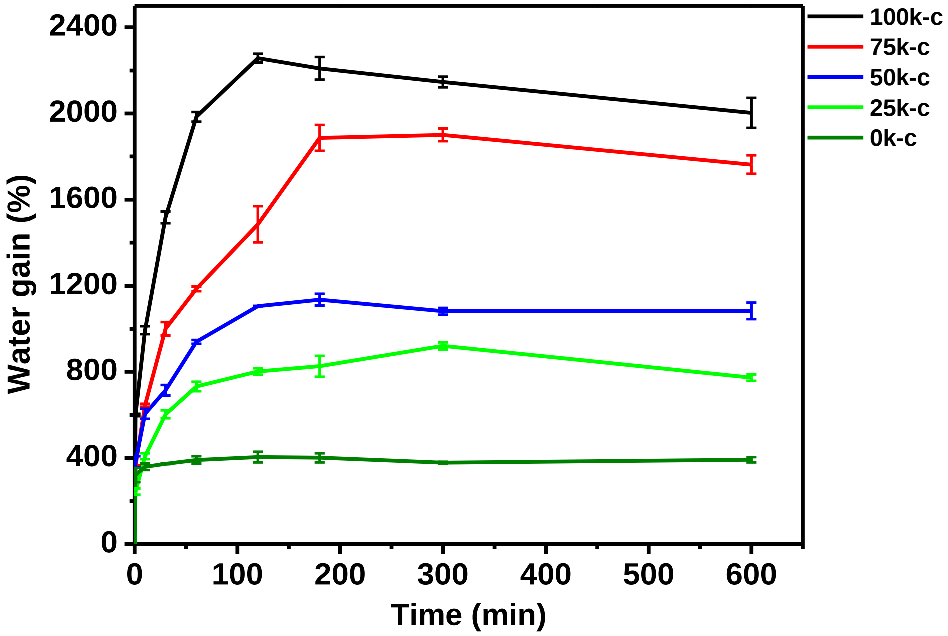


**Figure 2.** Swelling kinetic curves of the κ-carrageenan: starch films.

The SD findings reported here agreed with other results already published. Luchese and coworkers developed cassava starch-based films (incorporated with blueberry pomace) with SDs ranging from 240 to 280% [46]. Another study reported modified maize starch: essential oil films with SDs between 118 and 231% [47]. κ-Carrageenan-based composite films containing sulfur nanoparticles and grapefruit seed extract had SDs between 2900 and 3800% [48]. The commercial κ-carrageenan used here also supported a physical hydrogel with a high SD of approximately 3000% [22].

**Table 1** also presents the WVP results. The 100κ-c and 75κ-c were more permeable to water vapor than the 25κ-c and 0κ-c. The 50κ-c supported a WVP significantly lower than the WVP for 75κ-c ($p > 0.05$). Stiff structures (with low SDs) should promote low WVPs. This behavior can also be inferred by analyzing the opacity results (**Table 1**). The 50k-c presents the lowest WVP ($3.01 \times 10^{-8}$ g m (Pa m$^2$ s)$^{-1}$) and high opacity (absorbance of 0.85). Stiff structures suggest compact materials with high opacity and low WVP. The mechanical properties presented in the next section confirm these results.

The WVP and opacity results agreed with other reported findings. Garcia and coworkers produced cassava starch: poly(butylene adipate-co-terephthalate) films with and without sericin (a compatibilizer agent) by extrusion approach [30]. The WVP increases as the sericin concentration raise in the films because it supports stiff films. Roy and Rhim prepared carrageenan-based composite films with ZnO nanoparticles stabilized by melanin. The WVP varied from 1.22 to $1.58 \times 10^{-9}$ g m (Pa m$^2$ s)$^{-1}$ [49]. Saedi and coworkers prepared carrageenan: silver nanoparticles: halloysite composite films treated with sodium dodecyl sulfate. The WVP was between 1.31 and $1.84 \times 10^{-9}$ g m (Pa m$^2$ s)$^{-1}$ [50]. In this study, the association of κ-carrageenan and starch with hydrophilic PVA and glycerol materials support WVP 10-fold higher ($10^{-8}$ g m (Pa m$^2$ s)$^{-1}$) than the WVP of pure κ-carrageenan films reported elsewhere [49,50].

### 3.3 Color and opacity

The color is an essential parameter for producing edible films because it influences the appearance of the final material, compromising in consumer acceptance [20,51–53]. The lightness/brightness ($L^*$), redness/greenness ($a^*$), yellowness/blueness ($b^*$), ΔE, and WI color parameters of the different samples are presented in **Figure 3** (see the Supplementary Material **S.1** as well). The films displayed excellent visual appearance without the occurrence of deep coloration. The high values for L and WI, and low measures for E, suggest colorless films. No significant difference occurs in the $L^*$ parameter ($p < 0.05$). These features are positive points for commercial applications. However, $a^*$ and $b^*$ parameters were significantly affected ($p < 0.05$) by the κ-carrageenan: starch blend composition. The redness/greenness and yellowness/blueness are practically imperceptible for most consumers.

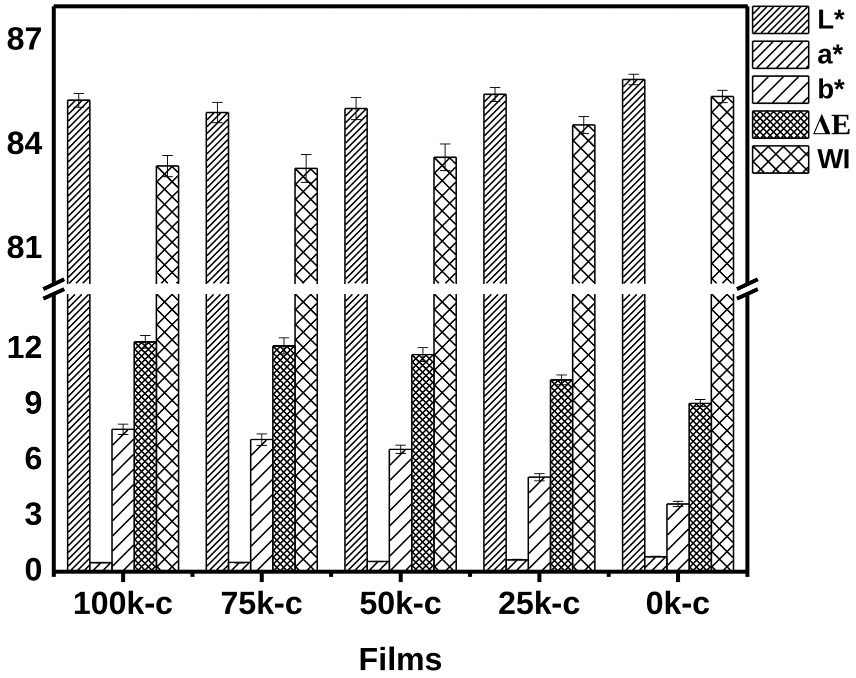


**Figure 3.** Color parameters $L^*$, $a^*$, $b^*$, ΔE, and WI of the κ-carrageenan: starch films. Lightness/brightness - L*; redness/greenness - a*; yellowness/blueness - b*; color difference - ΔE; whiteness index – WI.

Consumers well accept transparent packaging films. The film opacity (opposite property concerning the transparency) ranged from 0.67 to 0.88 (**Table 1**). The 50κ-c, 25κ-c, and 75κ-c have higher opacity than the 100κ-c and 75κ-c ($p < 0.05$). The films exhibited high transparency. Our results agreed with the findings reported by Domene-López and coworkers that showed a comparative study about the properties of starch-based films [7]. Also, tapioca starch films presented high opacity (2.78 – 3.15) [54]. The transparency relates to the amorphous arrangements in films composed of κ-carrageenan and starch [55].

### 3.4 Oil permeability

The oil permeability was between 0.0033 and 0.0043 mm $m^2$ $d^{-1}$ for the κ-carrageenan: starch films ($p < 0.05$). Low oil permeability indicates that the oil molecules have difficulty in transposing the film. High amounts of hydroxyl groups in the glycerol, PVA, and polysaccharides prevent the passage of oil molecules through the film due to weak interaction among hydrophilic moieties in the film precursors and hydrophobic oil. Soybean oil is mostly composed of fatty acids with average carbon chains of 18 atoms [56]. Carbonic chains preferably interact with hydrophobic moieties, resulting in low oil permeability.

κ-Carrageenan/glycerol films provided low oil permeability between 0.37 and 0.97 g mm $m^{-2}$ $d^{-1}$) [25]. On the other hand, oxidized and acetylated corn starch films presented high oil permeability (0.3 to 1.5 g mm $m^{-2}$ $d^{-1}$). Depending on the glycerol content into the film, it can significantly increase the free volume into the material, favoring the oil permeability due to the high film flexibility [27]. In this study, the films were prepared with the same concentration of plasticizer (glycerol and PVA); therefore, the difference in films' physical property may not be attributed to the plasticizer's content. Therefore, the physical features are impacted by the κ-carrageenan: starch weight ratio in the blend.

### 3.5 Mechanical properties

The mechanical properties play an essential role in the film's applicability. The results of the tensile strength (σ - MPa), elongation at break (ε - %), and Young's modulus (Σ - MPa) are presented in **Table 2**. High σ occurs as the κ-carrageenan content rises in the blend (σ = 19.23

MPa for 100κ-c and σ = 25.88 MPa for 75κ-c with no statistical difference between the results). The σ for 75κ-c is significantly ($p < 0.05$) higher than the σ found for the other films containing starch (σ between 6.53 and 17.29 MPa). Compared to the other films, the 0κ-c is significantly less resistant and stiff (see Young's modulus in Table 2). The 100κ-c and 75κ-c have the highest Young's modulus ($p < 0.05$), while the 100κ-c presents the lowest elongation at break (ε = 4.36%). On the other hand, 0κ-c is more flexible (ε = 67.65%) than the other films (**Table 2**).

**Table 2**
Mechanical properties of the films.

| **Formution** | **σ (MPa)** | **ε (%)** | **Σ (MPa)** |
|---|---|---|---|
| **100κ-c** | $19.23 \pm 3.58^{a,b}$ | $4.36 \pm 0.90^{c}$ | $59.64 \pm 9.53^{a}$ |
| **75κ-c** | $25.88 \pm 2.55^{a}$ | $8.41 \pm 1.71^{c}$ | $27.03 \pm 8.64^{b}$ |
| **50κ-c** | $17.29 \pm 2.43^{b,c}$ | $26.37 \pm 1.18^{b}$ | $5.30 \pm 0.58^{c}$ |
| **25κ-c** | $12.10 \pm 2.36^{c,d}$ | $21.60 \pm 4.12^{b}$ | $4.83 \pm 0.40^{c}$ |
| **0κ-c** | $6.53 \pm 0.66^{d}$ | $67.65 \pm 7.05^{a}$ | $1.23 \pm 0.01^{c}$ |

σ (MPa): tensile strength; ε (%): elongation at break; Σ (MPa): Young's modulus;
Results presented in (mean ± standard deviation); $n = 5$;
$^{a,b,c}$Different letters in the same column indicate significant differences ($p \leq 0.05$).

The σ and Young's modulus significantly increase at high κ-carrageenan contents (**Table 2**). The commercial κ-carrageenan chains are stabilized by metallic ions [22,57]. These cations are "physical crosslinking agents" for κ-carrageenan, promoting films with high stiffness [54]. The σ reduced from 38.2 MPa (ε = 5%) to 5.6 MPa (ε = 53%) as the glycerol (25% wt/wt) was added to the film.  A high ε occurs because the glycerol decreases the intramolecular interactions between starch-starch chains, increasing polymer chain mobilities [38]. High σ and Young's modulus imply low elongation at break [58].

### 3.6 Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the films are presented in **Figure 4**, while the FTIR spectra of the precursors are shown in **Figure S2** (Supplementary Material). The band at 1730 and 1650 cm$^{-1}$

are associated with the C=O bonds (of non-hydrolyzed poly(vinyl acetate) moieties and carboxylic acids on proteins), and $H_2O$ bending [59] and stretching of C=O bonds of amides, respectively. X-ray photoelectron spectroscopy confirmed that proteins should comprise the commercial κ-carrageenan structure supplied by the CP Kelco [22].

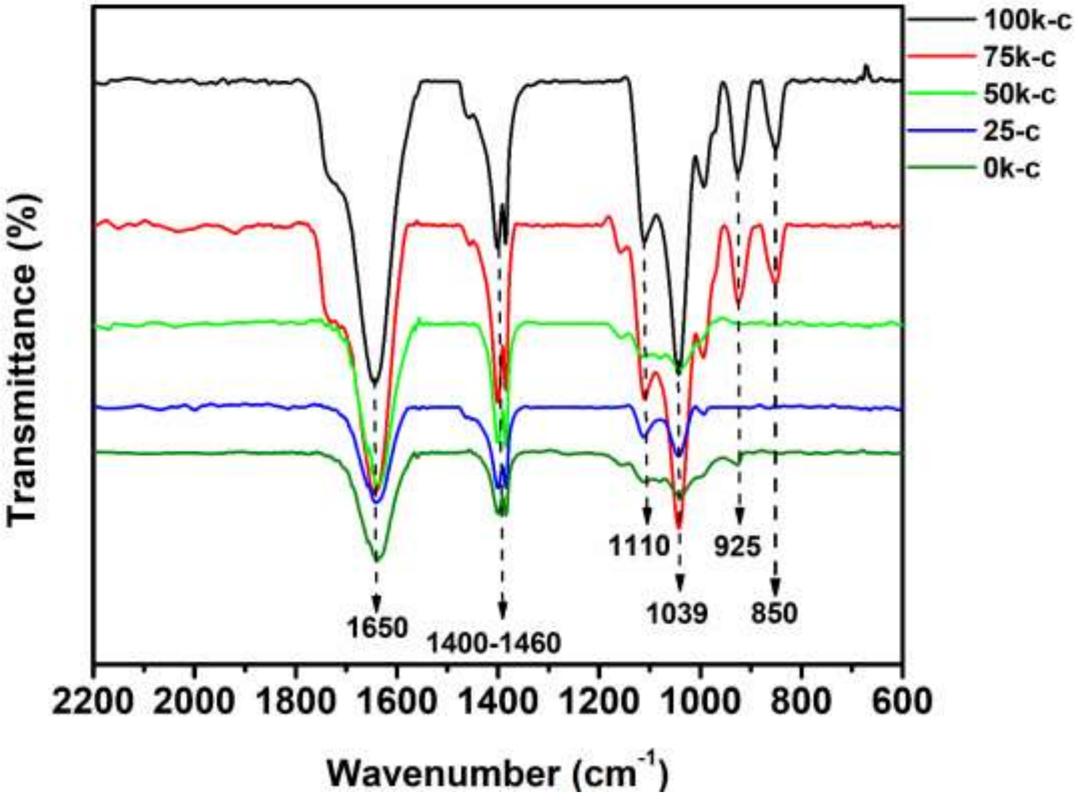


**Figure 4.** FTIR spectra of the films.

The bands between 1400 and 1460 $cm^{-1}$ are mainly ascribed to the stretching of $C-O-H$ and C=O bonds found on commercial polysaccharide and PVA chains. The band at 1110 $cm^{-1}$ (mostly related to the stretching of $C-O-H$ bonds on secondary alcohols) and bands between 950 and 1050 $cm^{-1}$ (assigned to the stretching of $C-C-H$ and $C-OH$ bonds, respectively) occur due to the polysaccharide, PVA and glycerol structures. Other bands at 925 $cm^{-1}$ (assigned to the 3,6-dehydrated galactose repeat unit) related to the stretching of $C-O-C$ bonds and 850 cm$^{-1}$ (ascribed to the galactose-4-sulfate repeat unit) assigned to the stretching of $C-O-S$ bonds take place due to the presence of starch and κ-carrageenan in the films, respectively. The FTIR findings confirm that the films are composed of κ-carrageenan, starch, PVA, and glycerol [20,25,60–62].

### 3.7 Thermogravimetric analysis

Thermogravimetric analysis (TGA) evaluated the thermal stability of the polysaccharides and films. Thermograms are indicated in **Figure 5**. The loss of water (linked through H-bonds with the polymers and glycerol) and volatile compounds occurs between 80 and 110ºC [12]. The thermal events between 200 and 400ºC are attributed to the decomposition of the materials [63]. Compared to these outcomes, edible native cassava starch-based films supported similar TGA profiles [61].

The first derivate of the TGA curves provides inflection points where the rate of degradation is the highest. The inflection points in the films DTG curves occur in the temperature range of the inflection points indicated in the DTG curves for the κ-carrageenan (210ºC) and starch (334ºC) films (**Figure 5**). The inter- and intra-molecular H-bonds established between starch macromolecules support its high thermal stability. Therefore, the thermal stability of the films reduces as the κ-carrageenan content raise in the blend. Medina Jaramillo and coworkers reported this behavior. They studied the thermal stability of edible cassava starch films containing yerba mate extract. The addition of the extract reduced the thermal stability of the films [60].

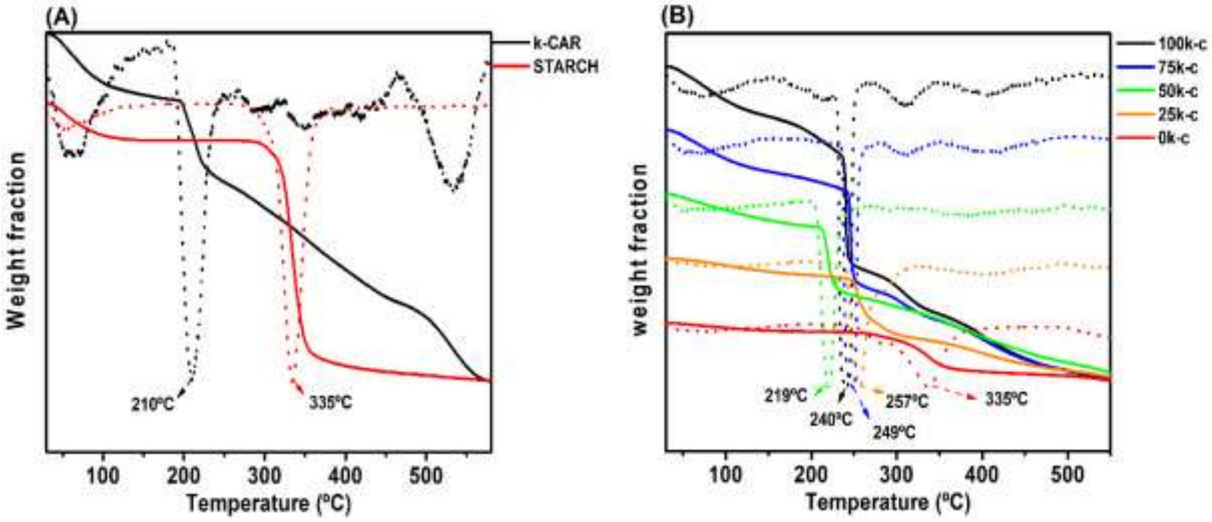


**Figure 5.** TGA and DTG curves of the polysaccharides (A) and films (B).

### 3.8 Differential scanning calorimetry

The DSC curves of the polysaccharides and films are presented in **Figure 6**. The thermograms of the pure starch and films (0κ-c and 25κ-c) with high starch contents show endothermic peaks at 290 ºC, and 234 ºC, respectively. No endothermic peaks occur in the DSC profiles of the κ-carrageenan and films containing high κ-carrageenan contents (100κ-c, 75κ-c, and 50κ-c). DSC profiles of other κ-carrageenan-based materials displayed similar behavior compared to the 100κ-c, 75κ-c, and 50κ-c DSC profiles [20,60]. Exothermic events are attributed to material degradation [12]. Endothermic peaks occur owing to the melting of semi-crystalline starch structures [60]. The semi-crystalline arrangement of the starch and starch-based films is related to the high density of H-bonds established between the starch chains [64].

The films were created at the same concentration of glycerol and PVA. Therefore, the thermal behavior of the films depends on the κ-carragennan: starch weight ratio in the blend. The DSC profiles also indicate more thermal stable films at a high starch content. Therefore, the endothermic peak in the 25κ-c DSC curve suggests that the semi-crystalline starch structure is disrupted by the κ-carrageenan [65]. Starch and κ-carrageenan-based films with similar thermal behavior were also reported elsewhere [12,20,60,66].

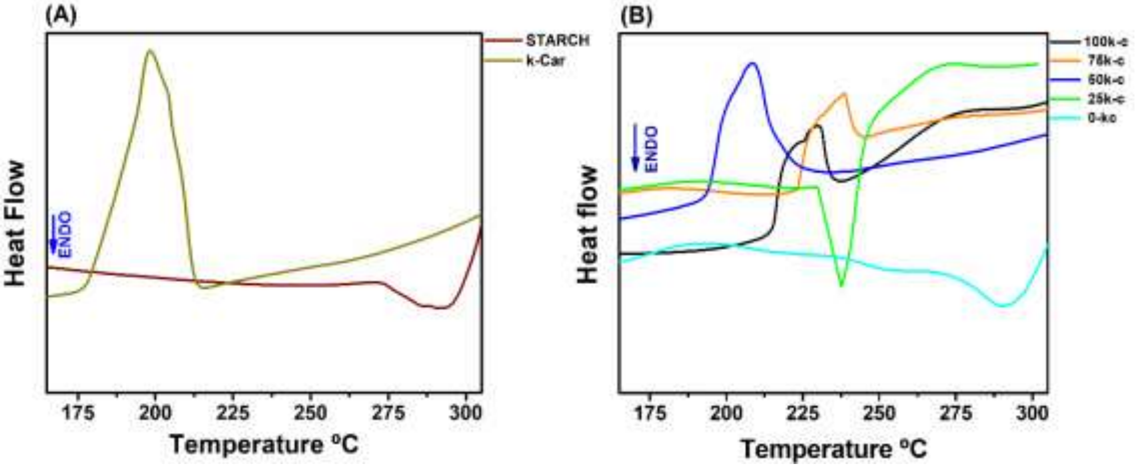


**Figure 6.** Differential scanning calorimetry (DSC) curves of the polysaccharides (A) and films (B).

## 4 Conclusion

The casting method is efficient for producing films of cassava starch, PVA, glycerol, and κ-carrageenan at different κ-carrageenan: starch concentrations. The κ-carrageenan: starch weight ratio played a critical role in the mechanical, physical, and chemical properties of the films. The low WVP occurred at κ-carrageenan: starch ratio equal to 1. Depending on its features, a film can be selected for the desired application. For example, fresh bread must be stored in packaging that allows moisture to escape, preventing fungi and molds' growth. The addition of starch to the κ-carrageenan, PVA, and glycerol produced more flexible films with high thermal stability. The presence of κ-carrageenan provided stiff films. Depending on the desired application, the film's traits can be modulated by tuning the κ-carrageenan: starch weight ratio in the polymer blend.

## Acknowledgments

The authors thank the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) agency (Brazil) for the Master fellowship destined to the Camila de Lima Barizão. E. G. Bonafé and A.F. Martins thank the “National Council for Scientific and Technological Development – CNPq” for financial support (protocols 420675/2018-3 and 0008678964988973). The authors thank the Fundação Araucária, State University of Maringá (Complex of Research Support Centers – COMCAP), and Federal University of Technology-Paraná by the Support in the Multi-User Laboratory LAMAP.

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**S1.**

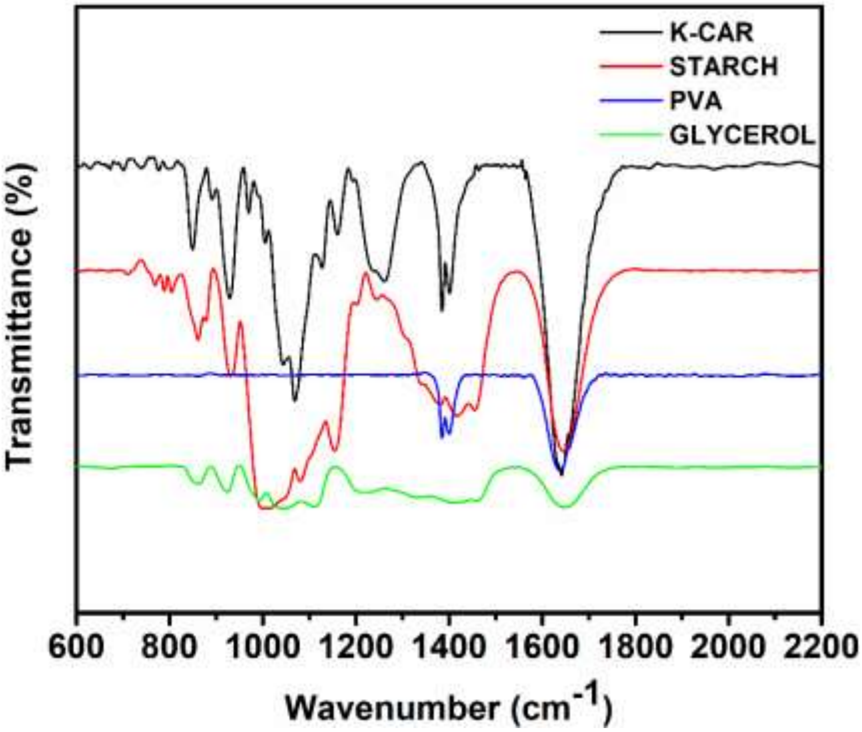
Color parameters of κ-carrageenan: starch films.

| Formulation | L | a | b | ΔE | WI |
|---|---|---|---|---|---|
| **100κ-c** | 85.29±0.20$^{a}$ | 0.49±0.02$^{a}$ | 7.69±0.28$^{a}$ | 12.40±0.34$^{a}$ | 83.40±0.30$^{a}$ |
| **75κ-c** | 84.94±0.29$^{a}$ | 0.49±0.02$^{ab}$ | 7.13±0.31$^{ab}$ | 12.18±0.43$^{a}$ | 83.33±0.40$^{a}$ |
| **50κ-c** | 85.06±0.32$^{a}$ | 0.55±0.02$^{b}$ | 6.61±0.23$^{b}$ | 11.72±0.37$^{a}$ | 83.65±0.38$^{a}$ |
| **25κ-c** | 85.46±0.20$^{a}$ | 0.64±0.02$^{c}$ | 5.09±0.19$^{c}$ | 10.35±0.26$^{b}$ | 84.58±0.24$^{ab}$ |
| **0κ-c** | 85.90±0.15$^{a}$ | 0.81±0.03$^{d}$ | 3.66±0.14$^{d}$ | 9.09±0.20$^{c}$ | 85.41±0.18$^{c}$ |

Lightness/brightness (L*), redness/greenness (a*), yellowness/ blueness (b*) parameters total color difference (ΔE) and whiteness index (WI);

Results presented in (mean ± standard deviation) – n = 3;

a,b,c Different letters in the same column indicate significant differences ($p \leq 0.05$) according to Tukey's test.



**S2.** FTIR spectra of the film components.