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Departamento de Ciência e Tecnologia de Alimentos
Programa de Pós-Graduação em Ciência de Alimentos

**DESENVOLVIMENTO DE MATERIAIS BIODEGRADÁVEIS A BASE DE AMIDO
TERMOPLÁSTICO, POLI (SUCCINATO DE BUTILENO) E POLI (ADIPATO CO-
TEREFTALATO DE BUTILENO)**

Natália de Camargo Lima Beluci

Londrina/PR

2023

NATÁLIA DE CAMARGO LIMA BELUCI

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Tese apresentada ao Programa de Pós-Graduação em Ciência de Alimentos da Universidade Estadual de Londrina - UEL, como requisito parcial para a obtenção do título de Doutora em Ciência de Alimentos.

Orientador: Dr. Fábio Yamashita

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BELUCI, Natália de Camargo Lima. **Desenvolvimento de Materiais Biodegradáveis a Base de Amido Termoplástico, Poli (Succinato de Butileno) e Poli (Adipato Co-tereftalato de Butileno)**. 2023. 97 p. Tese de Doutorado (Doutorado em Ciência de Alimentos) – Universidade Estadual de Londrina, Londrina/PR, 2023.

RESUMO

Os plásticos podem ser uma grande ameaça para o nosso ecossistema global, devido à sua baixa biodegradabilidade e falta de destinação apropriada, o que pode resultar em um acúmulo prejudicial no meio ambiente. Por essa razão, muitas pesquisas têm se concentrado no desenvolvimento de substitutos para os polímeros tradicionais, a fim de encontrar soluções sustentáveis para este problema. Assim, o objetivo deste trabalho foi produzir filmes com alto teor de amido termoplástico (ATP, 70% em massa) e diferentes proporções (30% em massa) de poli (succinato de butileno) (PBS) e poli (adipato co-tereftalato de butileno) (PBAT), com e sem presença de ácido cítrico (AC), por extrusão sopro em balão. O efeito dos polímeros e do AC nas blendas foi avaliado quanto à opacidade, cor, propriedades de tração, microscopia eletrônica de varredura (MEV), espectroscopia de infravermelho com transformada de Fourier (FTIR) e difração de raios-X (DRX), taxa de estiramento transversal (TIT), permeabilidade ao vapor de água (PVA), taxa de solubilidade (TS), isotermas de sorção de água, técnicas termogravimétricas. Em termos globais, os resultados obtidos pelas blendas ternárias (ATP/PBS/PBAT) foram melhores do que os obtidos pelas blendas binárias (ATP/PBS ou ATP/PBAT). Por exemplo, a amostra PBS/PBAT/ATP (20/10/70% m/m) alcançou o melhor equilíbrio entre dureza, ductilidade e resistência, com alongamento na ruptura de 32%, resistência à tração de 6 MPa e módulo de Young (MY) de 56 MPa. O AC atuou como um composto multifuncional, aumentando a resistência à tração e o alongamento na ruptura e diminuindo o MY para todos os filmes. A opacidade e o grau de cristalinidade dos filmes aumentaram de forma significativa, já para cor não houve diferença. O FTIR não indicou reações químicas entre os constituintes das blendas. O MEV demonstrou maior compatibilidade entre ATP/PBAT do que com ATP/PBS. Todas as amostras apresentaram TIT maior que 205%. As diferentes proporções de PBS e PBAT influenciaram significativamente o PVA dos filmes para os filmes sem AC. Todas as amostras tiveram PVA com ordem de grandeza similar a outros filmes com alto teor de amido (10^{-6} g m⁻¹ dia⁻¹ Pa⁻¹). O AC foi eficiente para diminuir o PVA das formulações de PBS/PBAT/ATP (15/15/70 e 20/10/70% em massa) em 25,2% e 24,7% em comparação com as formulações sem ácido. A TS variou de 19,0 à 20,1%, e diferentes proporções de polímeros ou a presença de AC não a influenciaram significativamente. Os materiais produzidos exibiram um aumento acentuado no teor de umidade de equilíbrio após atividade de água de 0,5, sendo sensíveis à umidade. Os filmes obtiveram boa estabilidade térmica, com temperatura máxima de decomposição próxima aos polímeros puros PBAT e PBS, ainda que fossem majoritariamente compostos por ATP. A estabilidade térmica das blendas não foi aumentada pelo AC, possivelmente devido ao baixo teor utilizado (0,1%). Este trabalho propôs um processo de fabricação viável que permite aumento de escala da produção de filmes biodegradáveis de ATP, PBS e PBAT. Os filmes exibiram propriedades adequadas para uso em embalagens, que teriam menor custo do que aquelas feitas com os poliésteres puros. Além disso, a inclusão de 0,1% de AC trouxe alterações positivas para maioria dos atributos avaliados.

Palavras-chave: poliéster; extrusão por sopro em balão; plástico biodegradável.

BELUCI, Natália de Camargo Lima. **Development of Biodegradable Materials of Thermoplastic Starch, Poly (Butylene Succinate), and Poly (Butylene Adipate-co-terephthalate)**. 2023. 97 p. Doctoral Thesis (Doctorate in Food Science) – Universidade Estadual de Londrina, Londrina/PR, 2023.

ABSTRACT

Plastics can be a major threat to our global ecosystem due to their low biodegradability and lack of proper disposal, resulting in harmful environmental accumulation. For this reason, many research efforts have focused on developing substitutes for traditional polymers to find sustainable solutions to this problem. Thus, the objective of this work was to produce films with high content of thermoplastic starch (TPS, 70 %wt) and different proportions (30 %wt) of poly(butylene succinate) (PBS) and poly(butylene adipate-co-terephthalate) (PBAT), with and without the presence of citric acid (CA), by blow extrusion. The effect of the polymers and CA on the blends was evaluated for opacity, color, tensile properties, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), blow-up ratio (BUR), water vapor permeability (WVP), solubility rate (SR), water sorption isotherm, and thermogravimetric techniques. Overall, the results obtained for the ternary blends (TPS/PBS/PBAT) were better than those obtained for the binary blends (TPS/PBS or TPS/PBAT). For example, the PBS/PBAT/TPS sample (20/10/70 wt%) achieved the best balance between hardness, ductility, and strength, with elongation at break of 32%, tensile strength of 6 MPa, and Young's modulus (YM) of 56 MPa. CA acted as a multifunctional compound, increasing tensile strength and elongation at break and decreasing YM for all films. The opacity and degree of crystallinity of the films increased significantly, while there was no difference in color. FTIR did not indicate chemical reactions between the constituents of the blends. SEM demonstrated greater compatibility between TPS/PBAT than with TPS/PBS. All samples showed BUR greater than 205%. The different proportions of PBS and PBAT significantly influenced the WVP of the films for the films without CA. All samples had WVP with an order of magnitude similar to other blends with high starch content (10^{-6} g m⁻¹ day⁻¹ Pa⁻¹). CA efficiently decreased the WVP of the PBS/PBAT/ATP formulations (15/15/70 and 20/10/70% by mass) by 25.2% and 24.7% compared to the acid-free formulations. SR varied from 19.0 to 20.1%, and different polymer proportions or the presence of CA did not significantly influence it. The materials produced exhibited a sharp increase in equilibrium moisture content after water activity of 0.5, being sensitive to humidity. The films obtained good thermal stability, with a maximum decomposition temperature close to pure PBAT and PBS polymers, although they were primarily composed of TPS. The thermal stability of the blends was not increased by CA, possibly due to the low content used (0.1%). This work proposed a viable manufacturing process that allows scaling up the production of biodegradable TPS, PBS, and PBAT films. The films exhibited suitable properties for use in packaging, which would cost less than those made with pure polyesters. In addition, including 0.1% of CA brought positive changes to most of the evaluated attributes.

Keywords: polyester; blown extrusion; biodegradable plastic.

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CAPÍTULO I – Introdução e Estrutura da Tese

1. Introdução

O plástico não biodegradável é um material versátil para uso industrial, comercial e doméstico devido às características como baixa densidade, custo acessível, alta durabilidade e resistência à umidade. Porém, uma de suas propriedades de maior destaque – a durabilidade – faz com que o plástico persista nos ambientes, gerando uma grande quantidade de resíduos e, conseqüentemente, problemas ambientais (PATEL *et al.*, 2022). O desenvolvimento de polímeros biodegradáveis como substitutos potenciais para polímeros não biodegradáveis de fonte não renovável é um campo emergente de pesquisa e desenvolvimento na área de embalagens, em especial para embalagens GRAS (*Generally Recognized as Safe* – Geralmente Reconhecido como Seguro).

Nos últimos anos, diferentes tipos de polímeros biodegradáveis têm recebido atenção para o desenvolvimento de novos materiais e para reduzir as preocupações ambientais (VINOD *et al.*, 2020). Atualmente existem muitos polímeros biodegradáveis comercialmente disponíveis, entre os quais se destacam os poliésteres, tais como poli (succinato de butileno) (PBS) e poli (adipato co-tereftalato de butileno) (PBAT) (GEORGE *et al.*, 2020).

O PBS é um poliéster alifático semicristalino obtido pela polimerização de butanodiol com o ácido succínico, ambos disponíveis a partir de recursos fósseis ou renováveis de base biológica (LIU *et al.*, 2009). Este poliéster é considerado uma das alternativas mais promissoras para a formulação de materiais biodegradáveis, devido resistência e tenacidade altas, baixa permeabilidade ao oxigênio e parâmetros de processamento que permitem seu uso em técnicas convencionais como moldagem por injeção e extrusão de filmes planos (FAHRNGRUBER *et al.*, 2020; MUTHURAJ; MISRA; MOHANTY, 2015). Além disso, o PBS pode fornecer uma barreira seletiva de O₂/CO₂ com uma taxa de transmissão de CO₂ 10 vezes maior que a do O₂ (SIRACUSA *et al.*, 2015). Com isso não há acúmulo de CO₂ na parte interna da embalagem, o que poderia ser interessante para produtos que respiram. No entanto, o PBS possui menores ductilidade, flexibilidade e biodegradabilidade que seus copolímeros, tais como o poli (succinato-co-adipato de butileno) (PBSA) (DE MATOS

COSTA *et al.*, 2020). Portanto, para melhorar essas características, pode ser misturado com outros poliésteres biodegradáveis, como o PBAT.

O PBAT é um copoliéster alifático-aromático, sintetizado comercialmente por policondensação entre butanodiol, ácido adípico e ácido tereftálico (JIAN; XIANGBIN; XIANBO, 2020). Além de ser altamente biodegradável, o PBAT possui excelente tenacidade e pode ser utilizado principalmente para extrusão de filmes e revestimentos (JAVADI *et al.*, 2010). Suas propriedades mecânicas são semelhantes às do polietileno de baixa densidade (PEBD) (NAGARAJAN; MISRA; MOHANTY, 2013) e derivam da unidade aromática na cadeia molecular (JIAN; XIANGBIN; XIANBO, 2020). Apesar disso, o PBAT apresenta fraca barreira ao oxigênio e ao vapor de água (LI *et al.*, 2018), o que poderia ser melhorado quando combinado com outros poliésteres como o PBS.

Embora esses polímeros possuam propriedades adequadas para que possam ser aplicados na produção de plástico biodegradável, não são comumente utilizados no dia a dia industrial devido ao seu alto custo em comparação aos polímeros convencionais (MUTHURAJ; MISRA; MOHANTY, 2014). O PBS custa cerca de 4,5 US\$/kg e o PBAT 4,1 US\$/kg, sendo pelo menos três vezes mais caro que o polietileno de baixa densidade (ROSENBOOM; LANGER; TRAVERSO, 2022), polímero amplamente utilizado para embalagens de alimentos. Deste modo, uma alternativa viável é misturá-los com amido, um polímero natural que pode produzir misturas com menores custos de fabricação e maiores taxas de degradação.

O amido possui boas propriedades filmogênicas, baixo custo em relação aos polímeros convencionais e fácil processamento em equipamentos utilizados pela indústria de plástico (BILCK; YAMASHITA; MARZANO-BARREDA, 2021). O amido apresenta compatibilidade com os processos de extrusão utilizados na fabricação de filmes convencionais e na presença de um plastificante, normalmente glicerol, produz um material com características termoplásticas, conhecido como amido termoplástico (ATP) (THUNWALL *et al.*, 2008; ZULLO; IANNACE, 2009). No entanto, sua natureza hidrofílica, fragilidade, alta sensibilidade à umidade e rápida degradação quando exposto ao ambiente limita seu uso como material apropriado para embalagens (WANG *et al.*, 2020).

Portanto, conforme relatado em outros estudos, a mistura de ATP com PBS e PBAT pode produzir materiais sustentáveis com propriedades aprimoradas desde

que tenham sua compatibilidade melhorada. Este problema pode ser contornado com o uso de um composto multifuncional, tal como o ácido cítrico, que pode atuar como compatibilizante, diminuindo a tensão interfacial entre os compostos, o que resulta em materiais com melhores propriedades mecânicas e de processabilidade (GARCIA *et al.*, 2014).

Blendas a base de PBAT e ATP tem sido extensivamente estudadas devido à sua capacidade de produzir produtos com propriedades apropriadas para a fabricação de filmes extrudados (BRANDELERO *et al.*, 2011; DA SILVA *et al.*, 2017; GARALDE *et al.*, 2019; NAYAK, 2010; WEI D. *et al.*, 2015). Já a mistura de PBS e ATP normalmente origina produtos adequados para serem moldados por injeção termoplástica ou por pressão (AZIMAN *et al.*, 2021; ZENG *et al.*, 2011). Alguns estudos também mostraram que é possível desenvolver uma mistura binária de PBAT/PBS para produzir materiais injetáveis (MUTHURAJ; MISRA; MOHANTY, 2014, 2017) ou filmes moldados por compressão ou por extrusão combinada com calandragem por rolo (DE MATOS COSTA *et al.*, 2020; NOBILE *et al.*, 2018). Estudos contendo misturas ternárias são menos comuns do que os mencionados acima; e, geralmente, seu escopo é limitado a misturas fundidas (WEI X. Y. *et al.*, 2021) ou moldadas por compressão (YAP *et al.*, 2020), que são técnicas mais estáveis e menos complexas em comparação com filmes produzidos por extrusão soprada.

Diante do exposto, o objetivo deste trabalho foi produzir filmes com alto teor de TPS (70% em massa) e diferentes proporções (30% em massa) de PBS e PBAT com e sem presença de ácido cítrico, por extrusão sopro em balão. O efeito dos polímeros e do AC nas blendas foi avaliado quanto à opacidade, cor, propriedades de tração, microscopia eletrônica de varredura, espectroscopia de infravermelho com transformada de Fourier e difração de raios-X, taxa de estiramento transversal, permeabilidade ao vapor de água, taxa de solubilidade, isotermas de sorção de água, técnicas termogravimétricas e de calorimetria exploratória diferencial.

2. Estrutura da Tese

A tese foi estruturada de forma que os capítulos possam ser lidos independentemente uns dos outros, embora alguns conceitos fundamentais estejam interconectados e adequadamente referenciados.

O conteúdo desta tese está organizado em seis capítulos. O capítulo I tem caráter introdutório acerca do conteúdo estudado e apresenta os objetivos e a estrutura da tese. No capítulo II, uma fundamentação teórica e uma revisão bibliográfica são reportadas ao estilo do estado da arte, contextualizando o tema de produção de materiais biodegradáveis a base de amido. O capítulo III apresenta de maneira detalhada a metodologia de produção dos filmes. Os resultados obtidos pelos métodos propostos são apresentados e discutidos no capítulo IV e V. O capítulo VI apresenta as conclusões gerais, bem como sugestões para trabalhos futuros e publicações científicas alcançadas ao longo do desenvolvimento da tese.

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CAPÍTULO II – Revisão Bibliográfica

1. Materiais Biodegradáveis

O primeiro plástico sintético foi produzido em 1907 por Leo Baekeland, revolucionando a indústria química, e servindo como base para o desenvolvimento de outros materiais. Apenas na década de 70, os polímeros biodegradáveis começaram a ser produzidos industrialmente. Com o crescimento exponencial da produção, aliada a falta de destinação apropriada e alta resistência à degradação, estima-se que em 2050 a quantidade de plásticos e peixes nos oceanos sejam as mesmas. Para piorar este cenário, a reutilização dos polímeros é baixa (~ 17% com ciclo repetido por no máximo três vezes), deste modo a maioria deles é descartada na natureza, causando um grande desequilíbrio no ecossistema global (OLIVER, 2020).

Mesmos em países com legislações consideradas mais severas em relação a preservação ambiental, tais como os países europeus, ainda existem poucas normas especificamente voltadas para a solução do problema dos plásticos. Em nível mundial, o Programa das Nações Unidas para o Ambiente desenvolveu, durante a reunião em Honolulu em 2011, o primeiro acordo global que visa reduzir, prevenir e gerenciar resíduos de plástico. Cientistas e organizações conservacionistas trabalham para aumentar a conscientização da sociedade em relação a este problema, bem como para encontrar soluções alternativas ao uso de plástico. À sociedade, de um modo geral, cabe reduzir o consumo de plásticos, em especial dos descartáveis, bem como pressionar as indústrias por materiais com caráter menos agressivo ao ambiente, e que conseqüentemente, afete menos a sua saúde (OLIVER, 2020).

Existe uma tendência de crescente interesse por pesquisas voltadas para substituição de polímeros sintéticos por biopolímeros naturais, visando diminuir os problemas dos polímeros à base de petróleo (GEORGE *et al.*, 2020). Através de avanços técnicos, os biopolímeros e seus compostos foram trazidos ao mercado devido ao desempenho semelhante ao dos polímeros sintéticos em termos de configuração e aplicações (GEORGE *et al.*, 2020). Comercialmente, os biopolímeros começaram a ocupar uma posição positiva nas indústrias, em especial na indústria de alimentos, mas retrocederam devido ao seu custo e ineficácia causada pelos processos de síntese, desenvolvimento e processamento posterior (KAWALKAR, 2014).

A atual economia do plástico também tem desvantagens que se tornam mais evidentes a cada dia. De acordo com a Ellen MacArthur Foundation, 95% do valor do material de embalagens de plástico, o que representa US\$ 80-120 bilhões anualmente, é perdido após um curto primeiro uso. Aliás, apenas 14% das embalagens plásticas são recolhidas para reciclagem; e ao considerar perdas adicionais de valor na triagem e reprocessamento, apenas 5% do valor do material é retido para uso posterior. Além disso, os plásticos reciclados são usados principalmente em aplicações de menor valor agregado e não são recicláveis novamente após o uso (REPORT, 2017).

O mercado de plásticos biodegradáveis apresentou forte crescimento nas últimas duas décadas. Em 2005, a produção do mercado global de plásticos biodegradáveis foi estimada em 94.800 toneladas e em 2010 o mercado atingiu 214.400 toneladas, o que representa uma taxa de crescimento anual composta (CAGR) de 17,7% durante o período 2005-2010 (JIAN; XIANGBIN; XIANBO, 2020). Apesar disso, o mercado de biopolímeros ainda tem pouca representatividade no tamanho do mercado global de plásticos, apenas US\$ 10,2 bilhões de 593,00 bilhões em 2021. Ainda assim, mostra uma tendência de crescimento maior (CAGR de 17,1% de 2022 a 2030) do que o tradicional mercado de plástico (CAGR de 3,7% no mesmo período). Essa tendência se deve ao esgotamento das fontes fósseis e ao crescimento esperado da população mundial, que deve chegar a 9 bilhões de pessoas em 2050 (ABIPLAST, 2020). Conseqüentemente, há uma forte demanda para projetar e melhorar os plásticos biodegradáveis para que não sejam apenas biodegradáveis, mas também atendam aos requisitos de propriedades esperadas para este material (JIAN; XIANGBIN; XIANBO, 2020).

Os biopolímeros podem ser enquadrados como sintetizados naturalmente, de forma química e de origem microbiana. Os polímeros naturais também podem ser classificados com base em suas estruturas químicas, como polissacarídeos, proteínas e poliésteres (UDAYAKUMAR *et al.*, 2021). Dentre os diversos tipos de materiais, se sobressaem o amido (polissacarídeo), o PBS e PBAT (poliésteres), cujo uso em conjunto pode superar as limitações de quando são aplicados separadamente para produção de polímeros biodegradáveis (ZENG *et al.*, 2011).

De maneira geral, a mistura de poliésteres alifáticos com o amido na forma de amido termoplástico (ATP) pode melhorar o desempenho da blenda formada

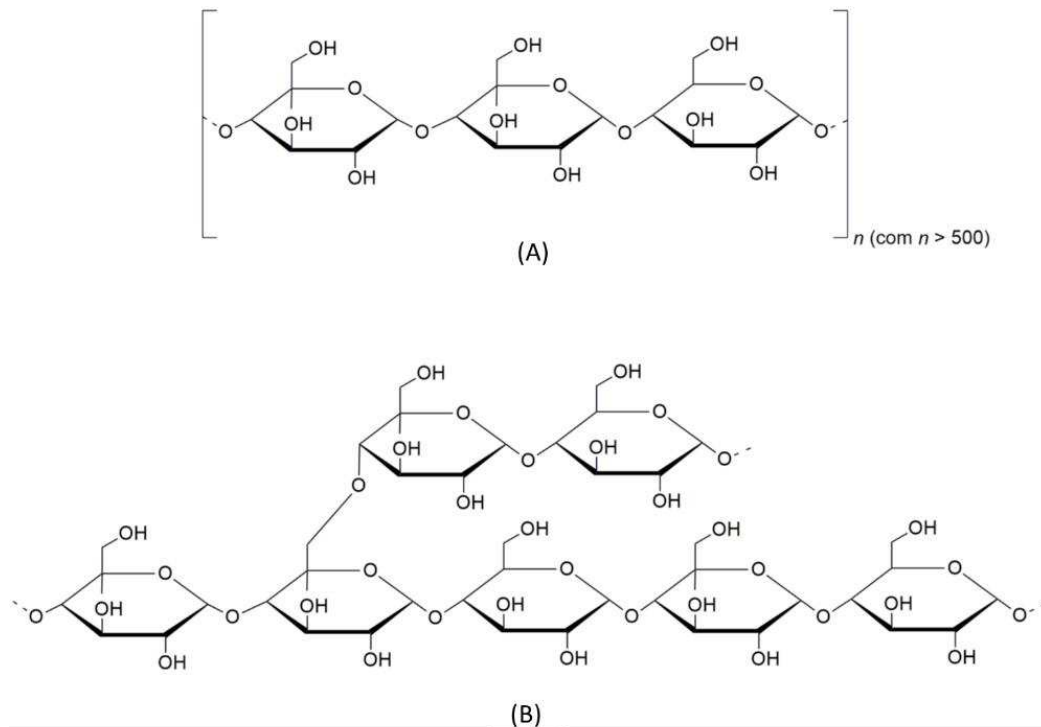
influenciando positivamente a biodegradabilidade, além de reduzir a dependência de recursos fósseis para a produção desses materiais poliméricos similares (ZENG *et al.*, 2011). Sendo assim, as seções seguintes apresentam uma revisão sobre cada um destes materiais.

1.1. Amido e Amido Termoplástico

O amido é um produto de origem vegetal pertencente a classe de compostos orgânicos carboidrato. As principais fontes comerciais deste polissacarídeo são provenientes de cereais (milho, arroz e trigo) e de raízes e tubérculos (mandioca e batata) (SIVAKANTHAN *et al.*, 2020). No Brasil, o milho é uma das fontes mais utilizadas para obtenção de amido. Isto se deve à alta disponibilidade deste cereal, da facilidade para estocagem pós-colheita, da sua melhor adaptação às condições climáticas do país, além da possibilidade de aproveitamento de praticamente todas as partes do grão (óleo, fibra, proteína e amido) (FOOD INGREDIENTS, 2015).

O amido é composto de um homopolímero de D-glicose, polímero predominantemente linear de amilose (ligações α -1,4 entre as unidades de glicose) e amilopectina altamente ramificada (ligações glicosídicas α -1,4 e α -1,6 nos pontos de ramificação) (BULATOVIĆ *et al.*, 2019). Em geral, o amido contém 20–25% de amilose e 75–80% de amilopectina, sendo as quantidades de amilose e amilopectina variáveis de acordo com a fonte botânica e do processo de extração do amido (ALCÁZAR-ALAY; MEIRELES, 2015). Lipídios e proteínas também estão presentes em pequenas quantidades. Normalmente, o amido com cristalinidade entre 20 e 40% é denominado como um polímero semicristalino. A região amorfa do amido contém amilose e os pontos de ramificação da amilopectina (KHAN *et al.*, 2017). A Figura 1 representa a estrutura química parcial do amido.

Figura 1. Estrutura química do amido – (A) amilose e (B) amilopectina.



Fonte: Autora (2021).

Além do mais, o amido é um polímero de baixo custo comparado com os polímeros convencionais e é totalmente biodegradável, o que justifica seu uso para produção de blendas poliméricas biodegradáveis. No entanto, sua temperatura de decomposição térmica é inferior ao seu ponto de fusão, devido às fortes interações de hidrogênio intra e intermoleculares (MA; YU; WAN, 2006), o que dificulta sua processabilidade (ORTEGA-TORO *et al.*, 2015). Por isso, o amido deve ser plastificado com compostos de baixa massa molecular, como os polióis, para que possa ser processado em equipamentos convencionais de produção de plásticos, formando o amido termoplástico. Essa transformação do amido nativo para ATP ocorre sob altas pressão e força de cisalhamento mecânico e temperatura moderada (BULATOVIĆ *et al.*, 2019).

Este processo destrói parcialmente a estrutura cristalina e enfraquece as interações de hidrogênio intra e intermoleculares no amido, gerando um material com boa processabilidade, tal como os polímeros convencionais (CARVALHO *et al.*, 2003). Os plastificantes ficam entre a cadeia do polímero, aumentando a flexibilidade e o movimento das cadeias, e também diminuem a temperatura de transição vítrea e de

fusão do polímero, levando a uma maior processabilidade do amido (KOCH, 2018). Para o processo de gelatinização eficaz do amido natural, é importante que a estrutura química dos plastificantes seja semelhante à dos polímeros (TUMWESIGYE; OLIVEIRA; SOUSA-GALLAGHER, 2016). Neste sentido, os plastificantes mais comumente usados são polióis, como glicol, sorbitol, açúcares e glicerol.

O glicerol é o plastificante mais popular entre os listados (TOGAS *et al.*, 2018). A adição de glicerol enfraquece as interações de hidrogênio interna da amilose e aumenta a fluidez da cadeia de amido, o que pode melhorar o alongamento na ruptura de materiais biodegradáveis a base ATP (AGHAZADEH *et al.*, 2018). Devido à sua natureza higroscópica, o ATP é caracterizado pela alta sensibilidade à umidade, apresentando propriedades mecânicas fracas (frágil e quebradiço) (YU; DEAN; LI, 2006). No entanto, o ATP tem baixa permeabilidade ao oxigênio e, portanto, pode potencialmente desempenhar um papel de barreira a este gás em embalagens biodegradáveis (BULATOVIĆ *et al.*, 2019).

O amido é abundante, renovável e biodegradável, além de ser mais barato que os polímeros convencionais. No entanto utilizar apenas amido, ainda que seja o termoplástico, produz materiais com características pouco competitivas frente aos polímeros convencionais, como polietileno e polipropileno (YU; DEAN; LI, 2006). Os filmes de ATP são hidrofílicos em comparação com filmes plásticos convencionais, e suas propriedades mecânicas e de barreira não são adequadas para produção e utilização em escala comercial. Para lidar com essas questões, uma das abordagens mais eficazes no desenvolvimento de novos materiais poliméricos é a mistura (blenda) de diferentes polímeros. Essa estratégia pode melhorar o desempenho do material para uma determinada finalidade desejada (BULATOVIĆ *et al.*, 2019).

Dessa forma, misturar ATP com outros polímeros biodegradáveis, em especial poliésteres alifáticos como o poli (succinato de butileno) (PBS) e poli (adipato co-tereftalato de butileno) (PBAT), pode reduzir custos, aumentar a velocidade de biodegradação e aumentar o conteúdo de base biológica (GADHAVE *et al.*, 2018). Isto permitiria produzir filmes biodegradáveis com melhores propriedades mecânicas, térmicas e de barreira, além de melhor processabilidade do que aqueles preparados apenas com ATP (BILCK; GROSSMANN; YAMASHITA, 2010; REN *et al.*, 2009).

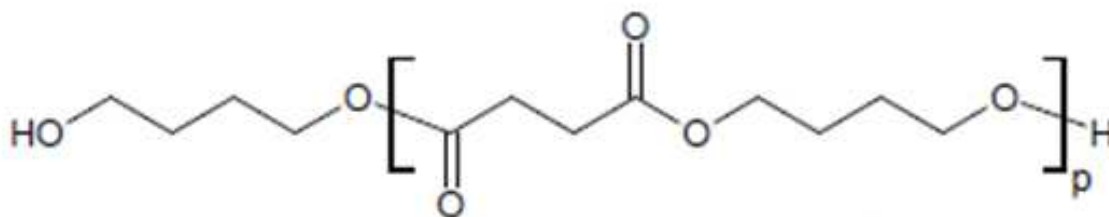
1.2. Poli (succinato de butileno) (PBS)

Nos últimos tempos, os poliésteres obtidos parcial ou totalmente a partir de matérias primas naturais, têm recebido uma atenção expressiva. Devido às suas características renováveis, o poli (succinato de butileno) (PBS) é um exemplo deles. Este biopolímero semicristalino é obtido pela polimerização de butanodiol com o ácido succínico, ambos disponíveis a partir de recursos fósseis ou renováveis de base biológica (LIU *et al.*, 2009).

Comercialmente, a produção de ácido succínico é feita através da hidrogenação do anidrido maleico a anidrido succínico, seguida de sua hidratação a ácido succínico. Existem duas rotas principais de síntese do ácido succínico. A primeira rota é a produção por eletrólise, enquanto a segunda rota é a fermentação por microrganismos usando matérias-primas renováveis, como amido, glicose e xilose (LUYT; MALIK, 2019). A síntese comercial de butanodiol é feita usando matérias-primas petroquímicas com vários métodos e técnicas industriais. Alguns desses métodos incluem o processo Reppe, a tecnologia de processo Davy e a rota do óxido de propileno Lyondell Basell (LUYT; MALIK, 2019). "Este composto também pode ser obtido por base biológica, sendo produzido pela redução catalítica do ácido succínico ou pela fermentação direta do açúcar (NIKOLIC; DJONLAGIC, 2001; XU; GUO, 2010).

O PBS é comumente sintetizado por policondensação em duas etapas: na primeira ocorrem reações de esterificação (ou transesterificação, no caso de dimetil succinato, DMS) com remoção de água (ou metanol). Enquanto a segunda etapa é conduzida à temperatura mais alta e sob pressão reduzida para remover butanodiol (geralmente um excesso de glicol de cerca de 10-20% é usado); assim o PBS de alta massa molecular é obtido (GIGLI *et al.*, 2012). A estrutura química unitária do PBS é mostrada na Figura 2.

Figura 2. Estrutura química parcial do PBS.



Este polímero apresenta um desempenho balanceado entre propriedades térmicas e mecânicas, além de uma boa processabilidade termoplástica (XU; GUO, 2010), juntamente com uma razoável resistência térmica e química (GALIANO *et al.*, 2018). Além disso, possui elevada flexibilidade e excelente resistência ao impacto (THURBER; CURTZWILER, 2020). Este poliéster é um termoplástico cristalino branco com ponto de fusão de cerca de 90-120 °C, semelhante ao do polietileno de baixa densidade (PEBD); temperatura de transição vítrea de -45 a -10 °C, entre a do polietileno (PE) e do polipropileno (PP); resistência à tração entre a do PE e do PP e rigidez entre a do PEBD e do polietileno de alta densidade (PEAD) (OJIJO; RAY, 2014; PARK *et al.*, 2006). Ademais, as ligações de ésteres presentes no PBS são hidrolisáveis e, portanto, mais suscetíveis à ação catalítica de microrganismos ou enzimas, o que pode resultar em um processo de degradação evidente a partir de 20 dias, dependendo das condições do ambiente (AYU *et al.*, 2018; FAHRNGRUBER *et al.*, 2020). Essas características tornam o PBS um polímero ambientalmente sustentável com potencial para produção de embalagens biodegradáveis (AYU *et al.*, 2018; GIGLI *et al.*, 2016).

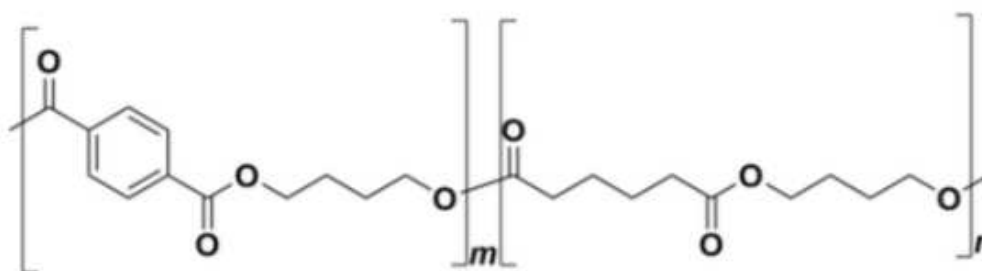
Um estudo realizado por Siracuas *et al.* (2015) mostrou que o PBS tem uma razão de seletividade muito alta de CO₂ e O₂, em que a taxa de transmissão do CO₂ é 10 vezes maior que a do O₂. Este fator poderia ser uma vantagem tecnológica para produtos com alta taxa de respiração, pois não haveria acúmulo de CO₂ na parte interna da embalagem.

Embora os materiais a base de PBS tenham boas propriedades mecânicas e de barreira, o PBS é mais caro que os polímeros convencionais, em torno de 3 a 7 vezes, e exibe uma taxa de biodegradação mais baixa em comparação com seus copolímeros por causa de sua alta cristalinidade (CAO *et al.*, 2002; CHRISAFIS; PARASKEVOPOULOS; BIKIARIS, 2005; MONTAUDO; RIZZARELLI, 2000; PAPAGEORGIOU; BIKIARIS, 2007). Neste sentido, o produto pode ser utilizado na formulação de blendas poliméricas, em especial com o ATP, a fim de superar estas limitações. Além do mais, o PBS é um polímero com rigidez e dureza moderadas, por isso também pode ser misturado com polímeros mais apropriados para formação de filmes, tal como o PBAT.

1.3. Poli (adipato co-tereftalato de butileno)

O poli (adipato co-tereftalato de butileno) (PBAT) é um copoliéster alifático-aromático, flexível e biodegradável que tem se destacado entre os numerosos copoliésteres alifáticos-aromáticos. Esse polímero é um dos mais promissores e populares com potencial de desenvolvimento em uma ampla gama de aplicações, pois apresenta uma combinação adequada entre excelentes propriedades e boa biodegradabilidade (JIAN; XIANGBIN; XIANBO, 2020). A Figura 3 apresenta a estrutura parcial do PBAT.

Figura 3. Estrutura química do PBAT.



Fonte: Autora (2021).

Comercialmente, este polímero é obtido por policondensação entre butanodiol, ácido adípico e ácido tereftálico, usando tecnologia e equipamentos convencionais de fabricação de poliéster. Compostos organometálicos à base de zinco, estanho e titânio podem ser usados como catalisadores de policondensação. A síntese de PBAT pode ser dividida em processo de pré-mistura, pré-polimerização e polimerização final (JIAN; XIANGBIN; XIANBO, 2020).

Um teste de compostabilidade foi realizado pela *Organic Waste System* (OWS) com PBAT, de acordo com os padrões EN 13432 e ASTM D6400. Como conclusão geral, pode-se afirmar que o material PBAT cumpre os critérios de avaliação de características do material, biodegradação, desintegração e qualidade do composto, que são descritos nestas normas. O PBAT pode, portanto, ser considerado totalmente compostável (JIAN; XIANGBIN; XIANBO, 2020).

Além de ser altamente biodegradável, o PBAT apresenta excelente tenacidade e pode ser usado principalmente para extrusão de filmes e revestimentos (JAVADI *et al.*, 2010). Ele se mostra mais flexível que a maioria dos poliésteres

biodegradáveis, como ácido polilático (PLA) e PBS. Suas propriedades mecânicas são semelhantes ao PEBD (NAGARAJAN; MISRA; MOHANTY, 2013) e derivam da unidade aromática na cadeia da molécula (JIAN; XIANGBIN; XIANBO, 2020). Em especial, o PBAT apresenta alta resistência à tração de até 32-36 MPa, um módulo de elasticidade de cerca de 20-35 MPa e tem grande flexibilidade, alcançado alongamento maior que 700% (DENG *et al.*, 2018; FERREIRA *et al.*, 2019).

O PBAT é um bom candidato para a fabricação de filmes biodegradáveis, no entanto possui barreira ao oxigênio e ao e vapor de água pouco eficientes; além de ser um polímero mais caro que os convencionais (REN *et al.*, 2017). Neste sentido pode ser combinado com outros polímeros, tal como o PBS e o ATP, para sanar estas deficiências e levar ao desenvolvimento de uma nova gama de materiais poliméricos biodegradáveis.

1.4. Blendas Poliméricas de ATP, PBS e PBAT

As propriedades do ATP, do PBS e do PBAT puros não são suficientes para ampla aplicação destes materiais como embalagens para utilização no cotidiano doméstico. Para que os polímeros a base de amido sejam comercialmente mais atraentes, os problemas relacionados a alta permeabilidade à água e as propriedades mecânicas insuficientes precisam ser resolvidos. Já o PBS e o PBAT têm custo mais alto que os polímeros convencionais e possuem propriedades mecânicas ligeiramente inferiores aos plásticos convencionais. Como consequência, o desenvolvimento de um mercado no qual estes materiais sejam vastamente comercializados somente será possível quando os custos de produção diminuírem e suas propriedades forem aprimoradas (JIAN; XIANGBIN; XIANBO, 2020). A Tabela 1 resume as vantagens e desvantagens gerais do ATP, PBS e PBAT aplicados a embalagens.

Tabela 1. Propriedades do ATP, PBS e PBAT aplicados a embalagens.

Material	Vantagens	Desvantagens	Tipo de Embalagem
ATP	<ul style="list-style-type: none">• Flexibilidade• Abundância natural• Custo acessível• Compostável• Biodegradável	<ul style="list-style-type: none">• Sensível à umidade• Alta viscosidade (quando fundido)• Alta fragilidade	<ul style="list-style-type: none">• Filmes• Plástico bolha• Folha• Espuma
PBS	<ul style="list-style-type: none">• Resistência• Biodegradável e compostável (EN 13432 e ASTM D6400)• Menor pegada de carbono (comparado com PEBD de petróleo - EN 16640)	<ul style="list-style-type: none">• Baixa processabilidade• Alto custo de produção• Baixa transparência	<ul style="list-style-type: none">• Filmes• Materiais moldados por injeção ou compressão• Misturas de polímeros para produção de compósitos
PBAT	<ul style="list-style-type: none">• Flexibilidade• Biodegradável e compostável (EN 13432 e ASTM D6400)• Menor pegada de carbono (em comparação com a sacola de PEBD à base de petróleo, ASTM D6866)	<ul style="list-style-type: none">• Baixa processabilidade• Alto custo de produção• Baixa transparência	<ul style="list-style-type: none">• Filmes• Misturas de polímeros para produção de compósitos

Fonte: Adaptado de Jariyasakoolroj, Leelaphiwat e Harnkarnsujarit, (2020).

Existem várias abordagens para resolver os problemas apresentados, sendo a mistura de materiais para formar uma blenda polimérica uma das mais simples e eficientes (JABEEN; MAJID; NAYIK, 2015). As blendas podem alcançar melhores resultados do que quando os polímeros são aplicados sozinhos, podendo haver redução dos custos, aumento da velocidade de biodegradação (GADHAVE *et al.*, 2018) e melhora na processabilidade do material (FORMELA *et al.*, 2018). Deste modo, a mistura de polímeros biodegradáveis, em especial do PBS e PBAT com ATP pode reduzir o custo de produção de filmes, mantendo um filme com alto teor de carbono de base biológica, reduzindo assim o impacto ambiental e melhorando a qualidade do produto (BAI *et al.*, 2021).

A mistura de PBAT com ATP já foi amplamente estudada e costuma gerar produtos com propriedades apropriadas para o desenvolvimento de materiais por extrusão termoplástica (BRANDELERO *et al.*, 2011; DA SILVA *et al.*, 2017; GARALDE *et al.*, 2019; NAYAK, 2010; REIS *et al.*, 2017).

Brandelero *et al.* (2011) estudaram diferentes métodos para produzir filmes por extrusão sopro em balão utilizando ATP e PBAT. O primeiro método (M1) consistia

em produzir filmes a partir de pellets de ATP (amido e glicerol) e extrudar novamente junto com pellets de PBAT (M1), já o segundo método (M2) consistia em extrudar os três componentes juntos (M2). O M1 resultou em filmes com melhores propriedades mecânicas quando a concentração de PBAT foi igual a 50%. Com o aumento da concentração de amido (> 50%), as blendas preparadas pelo método M2 resultaram em materiais que não tiveram perda das propriedades mecânicas. Assim, o M2 resultou em materiais com menor custo de processamento.

Em um outro trabalho, Ivanič, Kováčová e Chodák (2019) estudaram as propriedades de materiais produzidos com PBAT e ATP e plastificados com ureia (U-ATP) ou glicerol (G-ATP), via moldagem por compressão. O material produzido com U-ATP exibiu resistência à tração e módulo de elasticidade maiores do que o G-ATP e isso afetou as propriedades das misturas PBAT/ATP. A resistência à tração de misturas contendo 20% de ambos os tipos de ATP (G-ATP 4,3 MPa e U-ATP 7,7 MPa) foram substancialmente menores do que PBAT puro (19,1 MPa). Já a resistência para mistura com 50% de U-ATP (13,4 MPa) se aproximou do valor para PBAT puro, enquanto o mesmo conteúdo de G-ATP levou a uma diminuição da resistência (2,9 MPa). Em termos de alongamento na ruptura, as misturas de ATP/PBAT apresentaram redução do alongamento na ruptura de 985% do PBAT puro para 39% G-ATP e 76% U-ATP para mistura de 20%. O trabalho deu indicativos que os materiais produzidos com PBAT/U-ATP (50/50 %m/m) foram os que mais se aproximaram das características do PBAT puro.

Já a mistura de PBS com ATP normalmente gera produtos moldados por injeção ou por pressão (AYU *et al.*, 2018; AZIMAN *et al.*, 2021; ZENG *et al.*, 2011).

Utilizando a técnica de fundição e sopro, Aziman *et al.* (2021) fabricaram filmes de PBS, ATP e partículas de prata. Foram preparados filmes de PBS puro e filmes de misturas de PBS/ATP na proporção de 60/40 (% m/m). Para aumento do efeito antimicrobiano, diferentes quantidades de partículas de prata Biomaster (1,5% e 3%) foram incorporadas. O filme de PBS/ATP produzido com 3% de prata apresentou a melhor atividade antimicrobiana. A incorporação de prata aumentou a estabilidade térmica de filmes dos PBS puro e PBS/ ATP, bem como melhorou a cristalinidade e propriedades de barreiras dos filmes. Os autores consideram o método proposto como de fácil manuseio, o que permitiu controlar a interação entre os diferentes componentes para a geração de filmes com boa estrutura.

Ayu et al. (2018) investigaram o efeito da adição de cinco tipos de amido de mandioca modificados (A, B, C, D e E), sem transformá-los em termoplástico, diretamente em diferentes concentrações de PBS (40, 50 e 60% m/m), produzindo embalagens de alimentos via termoformagem, usando uma prensa aquecida. Verificaram que a inserção de amido de mandioca modificado em misturas de polímeros de PBS produziu melhores propriedades de resistência e estabilidade térmica em comparação ao amido puro. No entanto, com o incremento do teor de amido nas blendas observaram a deterioração das propriedades mecânicas para todos as blendas de amido/PBS testadas. De acordo com os autores, a baixa dispersão de moléculas de amido, má ligação interfacial e alto conteúdo de vazios foram os responsáveis pela redução destas propriedades. As moléculas de amido deslizam umas sobre as outras quando cargas de flexão são aplicadas, o que resultou na perda de capacidades de flexão. Dos cinco materiais testados, as misturas de amido A/PBS e amido B/PBS foram consideradas aplicáveis em embalagens de alimentos e materiais de recipientes de alimentos, pois obtiveram um bom alongamento de quebra e excelente capacidade de dobramento.

Em uma outra pesquisa, Li et al. (2013) desenvolveram um material biodegradável a base de amidos de milho ceroso (0% amilose) e normal (26% amilose) plastificados com glicerol (WTPS e NTPS, respectivamente) e misturados com PBS, usando a técnica de mistura por fusão. Os resultados mostraram que a plastificação e o processamento do amido de milho ceroso foram realizados mais facilmente do que o amido de milho normal. O índice de fluidez, propriedades de tração, resistência à água e estabilidade térmica das misturas PBS/ATP aumentaram com o aumento do teor de PBS (20 até 80% m/m). Além disso, em comparação com as misturas PBS/NTPS, a combinação de PBS/WTPS obteve melhor processabilidade, propriedades mecânicas superiores e maior resistência à água. Os autores concluíram que o PBS contribuiu para melhorar a resistência e extensibilidade, enquanto diminuiu a rigidez dessas blendas.

Apesar dos resultados positivos obtidos no desenvolvimento de blendas poliméricas de PBS, PBAT e ATP, problemas relacionados à baixa adesão entre os componentes ainda persistem (ZENG *et al.*, 2011), por isso algumas pesquisas utilizaram compatibilizantes para melhorar a interação entre os polímeros. Alguns ácidos multicarboxílicos, como maleico, cítrico e tartárico, agem como agentes de

hidrólise e de esterificação produzindo monoésteres, que na forma livre também podem atuar como plastificantes internos (GARCIA, P. S. et al., 2014).

1.5. Blendas Poliméricas ATP, PBS e PBAT com compatibilizantes

Os polímeros naturais, como o amido, possuem uma natureza hidrofílica, enquanto os poliésteres alifáticos, como PBS e PBAT, são hidrofóbicos. Por conta disso, a mistura desses componentes pode resultar em uma combinação termodinamicamente imiscível, o que pode causar baixa adesão entre os compostos e, conseqüentemente, levar a um desempenho mecânico insatisfatório. O processo de compatibilização é uma das formas de melhorar a incompatibilidade termodinâmica da mistura entre o poliéster/ATP (ZENG *et al.*, 2011). Os compatibilizantes são aditivos capazes de atuar na interface e melhorar a adesão entre as cadeias poliméricas e alguns autores já abordaram diferentes estratégias para a compatibilização de misturas de ATP/PBAT (CHANG; TRINH; MEKONNEN, 2021; OLIVATO *et al.*, 2012, 2013b).

Olivato et al. (2013) desenvolveram um filme por sopro em balão para produção de sacolas biodegradáveis à base de amido de mandioca e PBAT, usando ácido tartárico (AT) como compatibilizante. O AT melhorou a compatibilidade entre as fases poliméricas e resultou em blendas com estrutura mais homogênea e de matriz contínua, e também contribuiu para o aumento da resistência à tração e alongamento. De acordo com os autores, possivelmente o AT promoveu a reticulação e hidrólise ácida do amido, levando aos resultados obtidos. Os melhores resultados em termos de propriedades mecânicas e resistência à selagem por calor foram obtidos pela formulação de amido/PBAT (55:45, 88,2% m/m), glicerol (11,0% m/m) e AT (0,8% m/m). Assim, as sacolas plásticas biodegradáveis produzidas se mostraram competitivas com os sacos plásticos não biodegradáveis, atualmente comercializados para embalagem de produtos de baixo peso, que não requerem um material de alta resistência mecânica.

Em um outro trabalho, Chang, Trinh e Mekonnen (2021) desenvolveram filmes multifásicos e multicamadas compostos por ATP e PBAT, usando anidrido maleico (AM) como agente compatibilizante. O AM foi enxertado na estrutura do amido, substituindo seus grupos hidroxila, o que introduziu ligações éster que ficaram disponíveis para ligação covalente com PBAT. Além disso, os grupos de ácido

carboxílico livres promoveram reações de transesterificação interfacial com PBAT. Os filmes foram produzidos por meio de extrusão reativa, moldagem por compressão e processo de revestimento por imersão. O filme de ATP-AM/PBAT forneceu 86,8% de melhoria na barreira à umidade e 74,3% à barreira ao oxigênio, em comparação com o filme de ATP/PBAT, respectivamente. Os resultados obtidos evidenciaram que o agente compatibilizante melhorou as propriedades mecânicas e de barreira. No geral, todos os filmes produzidos alcançaram estabilidade térmica, resistência à tração e módulo aprimorados, enquanto a ductilidade melhorou apenas em altas concentrações de PBAT (> 50% m/m).

Algumas pesquisas também se concentraram em avaliar o efeito da compatibilização em blendas de ATP/PBS, visando diminuir a incompatibilidade entre os polímeros (FAHRNGRUBER *et al.*, 2020; SUCHAO-IN; KOOMBHONGSE; CHIRACHANCHAI, 2014; YIN *et al.*, 2015; ZENG *et al.*, 2011).

Zeng et al. (2011) preparam blendas de PBS e ATP com compatibilidade aprimorada por meio da extrusão reativa de PBS terminado em grupamento isocianato ($-N=C=O$) (RPBS - PBS reativo) com ATP. A fim de aumentar a miscibilidade entre ATP e PBS, o RPBS foi sintetizado primeiro e depois combinado com ATP. As blendas ATP/RPBS exibiram melhores propriedades mecânicas, com resistência à tração se aproximando do polietileno (PE) e polipropileno (PP), que foram notavelmente superiores às do ATP e aprimoraram com o aumento do teor de RPBS. Além disso, com o aumento do conteúdo de RPBS, houve aumento da hidrofobicidade e redução da absorção de água, permitindo a estes materiais serem utilizados em aplicações mais abrangentes. Após a mistura com 10% (m/m) de RPBS com ATP, a resistência à tração do filme foi aumentada em 10 vezes. Como o grupo isocianato reagiu com grupos hidroxila de amido e glicerol, a miscibilidade das duas fases foi melhorada.

Em uma outra pesquisa, Zhang et al. (2019) projetaram um novo elastômero de base biológica usando extrusão reativa para as misturas de amido, glicerol e ácido tartárico (ATP-AT). Em seguida, o ATP-AT foi extrudado com PBS (30:70 m/m) para fabricar biocompósitos. A resistência ao impacto do PBS/ATP-AT foi superior à do PBS puro. O mecanismo de tenacidade foi explorado através da análise das variações das propriedades para a matriz ATP-AT e PBS, e sua adesão interfacial. O AT reduziu a massa molecular do amido, e a viscosidade de cisalhamento do ATP foi benéfica para o ATP-AT se dispersar uniformemente na matriz de PBS.

Simultaneamente, o AT também atuou como agente de acoplamento, melhorando a compatibilidade do ATP/PBS. O ATP-AT diminuiu a capacidade de cristalização do PBS, evidenciando que as variações nas propriedades de cristalização da matriz de PBS não respondem à melhoria da resistência ao impacto do PBS/ATP-AT.

Mais recentemente, Fahrngruber et al. (2020) desenvolveram um filme plástico flexível por extrusão reativa à base de amido nativo, ATP, PBS e agentes compatibilizantes. Os autores aplicaram uma metodologia para desenvolver compatibilizantes a partir de amido nativo, ATP e PBS que foram denominados como amido-g-PBS e ATP-g-PBS. Os compatibilizantes (amido-g-PBS e ATP-g-PBS) foram obtidos via reação de conjugação em clorofórmio à temperatura ambiente entre grupos hidroxila de amido e grupos terminais de ácido carboxílico de PBS, usando o agente de conjugação N-N'-diciclohexilcarbodiimida (DCC), e como compatibilizante o amido nativo ou ATP enxertado com PBS. O ATP foi preparado a partir do amido nativo com adição de plastificantes (glicerol 13% m/m e ácido esteárico 2% m/m). O filme preparado com ATP-g-PBS como compatibilizante teve uma superfície de interação maior entre amilose/amilopectina - PBS e glicerol - PBS, o que permitiu uma melhor homogeneização do material produzido quando comparado ao filme produzido com amido-g-PBS. Isto resultou em um material com maior resistência mecânica, com potencial para substituir embalagens convencionais leves de uso único.

Outros trabalhos também avaliaram o desenvolvimento de uma mistura binária PBAT/PBS (DE MATOS COSTA *et al.*, 2020; MUTHURAJ; MISRA; MOHANTY, 2014, 2017; NOBILE *et al.*, 2018).

Muthuraj, Misra e Mohanty (2014) estudaram a mistura binária entre PBAT e PBS produzida via injeção. No estudo, a compatibilidade da mistura foi atribuída à reação de transesterificação, que foi confirmada por espectroscopia de infravermelho com transformada de Fourier. Houve uma melhoria na resistência à tração e alongamento na ruptura pela incorporação de PBAT em PBS, indicando que um bom nível de compatibilidade é alcançado entre os polímeros. As propriedades reológicas revelaram uma forte tendência de diluição por cisalhamento da mistura pela adição de PBAT em PBS. A morfologia das blendas revelou que ocorreu separação de fases nas blendas. O crescimento de esferulitas nas blendas foi altamente influenciado pela temperatura e composição de cristalização. Além disso, a presença de uma fase amorfa dispersa foi considerada um obstáculo ao crescimento de esferulitas, o que foi

confirmado por microscopia óptica de polarização. Além disso, o aumento da capacidade de cristalização do PBAT nos sistemas dá à mistura uma propriedade de resistência térmica equilibrada.

Em um estudo posterior, Muthuraj, Misra e Mohanty (2017) adicionaram fibras de Miscanthus a blenda de PBS/PBAT produzida por extrusão e injeção. Devido ao efeito de reforço das fibras, os módulos de tração, flexão e de energia armazenada dos compósitos aumentaram com o aumento do teor de fibra de 30 a 50% em massa. Houve uma redução acentuada na resistência à tração e resistência ao impacto após a incorporação das fibras na matriz da blenda PBS/PBAT. Essas reduções foram devidas à incompatibilidade entre as fibras e a matriz. Os pesquisadores também prepararam um compatibilizante composto da mistura PBS/PBAT funcionalizada com anidrido maleico (AM) para melhorar a compatibilidade entre as fibras e a matriz. Os compósitos preparados com 5% em massa deste compatibilizante funcionalizado com AM mostraram uma melhora significativa nas propriedades mecânicas. A análise morfológica dos compósitos apresentou boa interação fibra-matriz na presença de compatibilizante, enquanto os compósitos sem compatibilizante apresentaram interface pobre entre as fases. O comportamento pseudoplástico dos compósitos foi aumentado em comparação com a mistura PBS/PBAT pura. Este aumento foi atribuído ao reduzido emaranhamento da cadeia polimérica na presença de fibras.

Estudos contendo misturas ternárias (ATP/PBS/PBAT) são menos comuns do que os mencionados acima. Por exemplo, Yap et al. (2020) desenvolveram filmes por moldagem por compressão usando PBAT/PBS e ATP de arroz (60/40 % m/m). O desafio de incorporar grandes quantidades de amido, material de natureza hidrofílica, em PBS/PBAT hidrofóbico foi resolvido pela adição de plastificantes como glicerol e estearato de cálcio. Além disso, compatibilizantes como anidrido maleico e peróxido de dicumila foram usados para melhorar a miscibilidade entre o PBS/PBAT hidrofóbico e o material de enchimento hidrofílico. A formulação 24/36/40 (PBS/PBAT/ATP % m/m) apresentou resistência à tração de 14,2 MPa, módulo de elasticidade de 199,5 MPa e alongamento na ruptura de 15,4%, o que foi considerado adequado para a produção de produtos moldados como bandejas e canudos. Por fim, o biopolímero alcançou 97% de perda de massa após seis meses de teste de soterramento confirmando sua biodegradabilidade.

Wei, X. Y. et al. (2021) produziram uma mistura reativa ternária de PBS enxertado com glicidil metacrilato (PBS-g-GMA), amido plastificado com anidroxilitol tripalmitato e PBAT. Os autores fizeram dois esquemas experimentais, no primeiro fixaram o teor de ATP (30% em massa) e avaliaram a influência de diferentes concentrações de PBAT no sistema. No segundo, fixaram a razão de 1:1 PBAT:PBS-g-GMA e discutiram o impacto do ATP nas blendas. A inclusão de PBAT para as amostras contendo 30% em massa de ATP causou um aumento na resistência ao impacto e o aumento do teor de ATP diminuiu o módulo de Young. Para compensar a diminuição das propriedades mecânicas devido à adição de PBAT e reduzir o custo do compósito para torná-lo mais econômico a amostra 30/35/35 ATP/ PBAT/ PBS-g-GMA (% em massa) foi definida como sendo a mais balanceada.

Em suma, existem muitos estudos com materiais PBS/ATP e PBAT/ATP; no entanto, os estudos sobre as misturas PBS/PBAT/ATP são escassos e, geralmente, seu escopo é limitado a misturas fundidas ou moldadas por compressão, que são técnicas mais estáveis e menos complexas em comparação com filmes produzidos por extrusão em sopro balão. Por isso esta pesquisa concentrou esforços no desenvolvimento de uma blenda tripla que combine a alta ductilidade do PBAT, com a resistência à tração do PBS e a alta biodegradabilidade e baixo custo do ATP para desenvolver um material extrudado com propriedades balanceadas para a produção de filmes biodegradáveis com indicação para embalagens alimentícias.

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CAPÍTULO III: Produção de Filmes Biodegradáveis

1. Materiais

Para o desenvolvimento dos filmes biodegradáveis por extrusão termoplástica foram utilizados os seguintes materiais: amido de milho comercial nativo (Apti, Brasil), PBS (TK-BIO® PBS da Tiken), PBAT (TK-BIO® PBAT da Tiken), glicerol (Dinâmica, Brasil) como agente plastificante e como agente compatibilizante ácido cítrico (CA).

2. Métodos

2.1. Formulação e Produção dos Filmes Biodegradáveis

A Tabela 1 mostra as formulações de amido, glicerol, PBS, PBAT e ácido cítrico usadas para produzir filmes biodegradáveis. A relação poliéster/ATP (30/70%, m/m) foi definida com base no trabalho de Bilck, Yamashita e Marzano-Barreda (2021), enquanto a concentração de ácido cítrico foi definida em testes preliminares, que indicaram que mesmo em pequenas quantidades, a processabilidade e a fluidez do material foram melhoradas

Tabela 1. Composição das formulações dos materiais biodegradáveis.

Formulação	Concentração (g 100 g ⁻¹)				
	PBS	PBAT	Amido	Glicerol	Ácido Cítrico
PBS ₀ PBAT ₃₀	0,0	30,0	49,0	21,0	0,0
PBS ₁₀ PBAT ₂₀	10,0	20,0	49,0	21,0	0,0
PBS ₁₅ PBAT ₁₅	15,0	15,0	49,0	21,0	0,0
PBS ₂₀ PBAT ₁₀	20,0	10,0	49,0	21,0	0,0
PBS ₃₀ PBAT ₀	30,0	0,0	49,0	21,0	0,0
PBS ₀ PBAT ₃₀ CA	0,0	30,0	48,9	21,0	0,1
PBS ₁₀ PBAT ₂₀ CA	10,0	20,0	48,9	21,0	0,1
PBS ₁₅ PBAT ₁₅ CA	15,0	15,0	48,9	21,0	0,1
PBS ₂₀ PBAT ₁₀ CA	20,0	10,0	48,9	21,0	0,1
PBS ₃₀ PBAT ₀ CA	30,0	0,0	48,9	21,0	0,1

A produção do filme foi realizada em duas etapas utilizando uma extrusora monorosca (modelo EL-25, BGM, Brasil) com diâmetro de rosca de 25 mm e comprimento de rosca de 700 mm.

Primeiramente, pesou-se o glicerol e misturou com os poliésteres, em seguida o amido e ácido cítrico pesados e adicionados, todo processo de mistura foi feito manualmente. Em seguida essa mistura foi adicionada na extrusora seguindo o perfil de temperatura de 90/120/120/115 °C. A velocidade da rosca foi mantida em 40 rpm, e uma matriz com dois furos de 2 mm de diâmetro foi utilizada para produzir os perfis cilíndricos que foram cortados em granulador para formar pellets.

A segunda etapa consistiu em usar os pellets para fazer filmes. O perfil de temperatura foi de 90/120/120/130 °C nas quatro primeiras zonas de aquecimento e 135 °C na matriz de sopro em balão de 50 mm; a velocidade da rosca foi mantida em 40 rpm. A extrusora foi ajustada para produzir filmes com 100 – 150 µm de espessura. Os materiais foram mantidos em embalagens opacas lacradas até que as caracterizações fossem realizadas. A Figura 1 traz um esquema de como os filmes foram produzidos.

Figura 1. Esquema para produção dos filmes.



Fonte: Autora (2023).

2.2. Caracterização dos Filmes

Os filmes produzidos tiveram suas propriedades investigadas por técnicas de caracterização como: opacidade, cor, propriedades de tração, microscopia eletrônica de varredura, espectroscopia de infravermelho com transformada de Fourier, difração de raios-X, taxa de estiramento transversal, permeabilidade ao vapor de água, taxa de solubilidade, isotermas de sorção de água, técnicas termogravimétricas. Essas técnicas serão descritas em detalhes nos capítulos IV e V.

Além disso, quando possível, os dados das caracterizações foram analisados por meio do software Statistica 7.0 (Statsoft Inc., Tulsa, EUA, 2004). O efeito da concentração dos polímeros (PBS/PBAT) dentro de cada grupo, com e sem ácido cítrico, foram avaliados com análise de variância (ANOVA) e teste de Tukey ao nível de significância de 5% ($p < 0,05$). Já o efeito do ácido cítrico foi avaliado, por meio de comparação entre os pares de amostras de composição similar com e sem ácido cítrico, pelo teste t ao nível de significância de 5% ($p < 0,05$).

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CAPÍTULO IV: Reactive Biodegradable Extruded Blends of Thermoplastic Starch and Polyesters

1. Introduction

Non-biodegradable plastic is a versatile material for industrial, commercial, and domestic use due to its low weight and cost, high durability, and resistance to humidity. However, one of its most prominent properties – durability – makes plastic persist in environments, generating a large amount of waste and, thus, environmental issues (PATEL *et al.*, 2022). A strategy to minimize these issues is manufacturing biodegradable polymers as potential substitutes for non-biodegradable ones. Vinod et al. (2020) published a review article approaching different types of biodegradable polymers that have received attention for developing new materials to reduce environmental concerns.

Among these commercially available biodegradable polymers, poly(butylene adipate-co-terephthalate) (PBAT) and poly(butylene succinate) (PBS) stand out (GEORGE *et al.*, 2020). Although they have good mechanical properties that may be applied to the production of biodegradable plastic, they are not commonly used in industrial day-to-day due to their high cost compared to conventional polymers. PBS costs about 4.5 US\$/kg and PBAT 4.1 US\$/kg, at least three times more expensive than low-density polyethylene (LDPE) (ROSENBOOM; LANGER; TRAVERSO, 2022), a polymer widely used for food packaging.

PBS is a semi-crystalline aliphatic polyester, considered one of the most promising alternatives for the formulation of biodegradable materials because of its high strength and tenacity, low oxygen permeability, and processing parameters that allow its use in conventional injection molding and flat film extrusion techniques (FAHRNGRUBER *et al.*, 2020; MUTHURAJ; MISRA; MOHANTY, 2015). Notwithstanding, PBS has lower ductility and biodegradability than its copolymers (DE MATOS COSTA et al., 2020); therefore, to improve these characteristics, it can be blended with other biodegradable polyesters, such as PBAT, which exhibit good thermal and mechanical properties (VROMAN; TIGHZERT, 2009), with a tensile strength comparable to LDPE (FERREIRA et al., 2019). This polymer can be used for film production, mainly by blown extrusion, due to its high flexibility and strength (MUTHURAJ et al., 2014; YU & LI, 2014). Despite these promising properties, these

polyesters have an uncompetitive cost in the polymer market, limiting their application. A viable alternative is to mix them with starch, a natural polymer that can produce blends with lower manufacturing costs and higher degradation rates.

Starch is a promising biopolymer to be blended with biodegradable polyesters, like PBS and PBAT, mainly due to its low cost, good film-forming properties, and compatibility with the extrusion processes used in manufacturing conventional plastic films of polyethylene or polypropylene (BILCK; YAMASHITA; MARZANO-BARREDA, 2021). In the presence of a plasticizer (usually glycerol), controlled pressure, shear, and heating conditions (90 to 180 °C), starch produces a material with thermoplastic characteristics, known as thermoplastic starch (TPS) (THUNWALL *et al.*, 2008; ZULLO; IANNACE, 2009). However, TPS's brittleness, hydrophilicity, and rapid degradation limit its commercial use (WANG *et al.*, 2020). Therefore, as reported in other studies, its blend with PBS and PBAT may produce sustainable materials with improved properties.

Biodegradable films using PBAT/TPS blends may be produced by blow-extrusion and commonly achieve good mechanical properties and processability (BRANDELERO *et al.*, 2011; DA SILVA *et al.*, 2017; GARALDE *et al.*, 2019; NAYAK, 2010; WEI, D. *et al.*, 2015) and PBS/TPS blends can be suitable to produce materials by thermoplastic injection (AZIMAN *et al.*, 2021; ZENG *et al.*, 2011). Furthermore, some researchers developed PBAT/PBS binary blends to produce materials by thermoplastic injection (MUTHURAJ *et al.*, 2014, 2017) or films by compression molded (DE MATOS COSTA *et al.*, 2020; NOBILE *et al.*, 2018). Studies containing ternary mixtures are less common than those mentioned above. For instance, (YAP *et al.*, 2020) developed films by compression molding using PBAT, PBS, and TPS. Wei X. Y *et al.* (2021) produced a ternary blend of PBS grafted with glycidyl methacrylate, starch plasticized with anhydroxylitol tripelargonate, and PBAT. There are plenty of studies with PBS/TPS and PBAT/TPS materials; however, reports on PBS/PBAT/TPS blends are scarce, and usually, their scope is limited to melted or compression-molded blends, which are more stable and less complex techniques compared to films produced by blown extrusion.

Due to the difference in polarity between polyesters and thermoplastic starch, the compatibility of a blend formed by them is low, so a multifunctional compound such as citric acid can be used as a compatibilizer to reduce the interfacial

tension between the compounds, improving the properties of the blend. The multicarboxylic structure of citric acid allows it to act as a plasticizer, crosslinking agent, or hydrolytic agent, depending on the interactions and reactions it can create with other constituents of the blends (GARCIA *et al.*, 2014).

This work aimed to develop PBAT/PBS/TPS biodegradable films by blown extrusion to develop blends with balanced properties between ductility, tensile strength, biodegradability, and low cost. The effect of the polymers and citric acid ratios in the blend was evaluated concerning opacity and color, tensile properties, scanning electron microscopy, Fourier-transform infrared spectroscopy, and X-ray diffraction.

2. Materials and Methods

4.1. Material

Native commercial corn starch (13 wt% moisture, 23 wt% amylose, 62 wt% amylopectin, 2 wt% ashes, lipids, and proteins) was purchased from Apti (Brazil). PBS (tensile strength ≥ 40 MPa and elongation at break $\geq 350\%$) and PBAT (tensile strength ≥ 25 MPa and elongation at break $\geq 400\%$) were both acquired from TK-BIO® - Tiken (China). Glycerol and citric acid at technical grade were purchased from Dinâmica (Brazil).

4.2. Production of the Biodegradable Films

Citric-acid-free films were prepared with TPS concentration fixed at 70 wt% (49 wt% starch and 21 wt% glycerol) and varying combinations of PBS and PBAT from 0 to 30 wt%. The films with citric acid were prepared using a concentration of 70 wt% TPS (48.9 wt% starch, 21 wt% glycerol, and 0.1 wt% citric acid), with the same variation in the concentration of polyesters. The nomenclature of materials without citric acid can be generically represented by PBS_xPBAT_y , where x and y indicate the amount of PBS or PBAT present, respectively. Similarly, the nomenclature of films with citric acid can be represented generically by PBS_xPBAT_yCA . The term TPS was not included in the nomenclature of the materials, as all films have it in the same concentration (70 wt%). The polyesters/TPS ratio was defined based on the work of Bilck, Yamashita and Marzano-Barreda (2021), while the concentration of citric acid

was defined in preliminary tests, which indicated that even in small amounts, the processability and fluidity of the material were improved.

Pellets and films were produced using a single-screw extruder (model EL-25, BGM, Brazil) with a screw diameter of 25 mm and a screw length of 700 mm. The components (PBS, PBAT, glycerol, citric acid, and corn starch) were mixed and pelletized with a barrel temperature profile of 90/120/120/115 °C from the feeding zone to the die zone and a screw speed of 40 rpm, using a die with two holes of 2 mm diameter. Subsequently, the extruded cylindrical profiles were pelletized and extruded to produce films. The pellets were processed with a barrel temperature profile of 90/120/120/130 °C in the four first zones and 135 °C in the 50-mm film-blowing die and a screw speed of 40 rpm. Feed and airflow rates were kept constant to maintain the thickness of the films around 100–150 µm. The films were stored in sealed aluminized packages until characterization analyses were performed.

4.3. Characterization of the Biodegradable Films

4.3.1. Opacity and Color

The apparent opacity and color of the biodegradable films were determined using a colorimeter (CR-400, Konica Minolta, Japan) with an illuminant D65 (daylight) and a visual angle of 10°, according to the methodology proposed by Olivato et al. (2017). Opacity (Y) was determined as the ratio of the opacity of the film over black (Y_b) and white (Y_w) standards, being represented on an arbitrary scale (0 to 100%), as indicated in Equation (1). Measurements were assessed at five different points in each film.

$$Y(\%) = \left(\frac{Y_b}{Y_w} \right) \times 100 \quad (1)$$

Under the same conditions, the color of each film was determined with the CIELab system represented by L (luminosity), a* (chromaticity, -a green, +a red), and b* (chromaticity, -b blue, +b yellow). The parameters ΔL*, Δa*, and Δb* are the differences in each CIELab value measured between the sample over a white pattern and the white standard. The total color difference (ΔE) was calculated using Equation (2). The total color difference (ΔE) was calculated using Equation (2).

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

4.3.2. X-ray Diffraction

X-ray patterns were obtained using a diffractometer (XPert PRO, Panalytical, Philips, Netherlands) with copper K α radiation ($\lambda=1.5406$ Å) operating at room temperature, 20 mA, and 30 kV. The scanned 2θ region ranged from 2.0° to 90.0° with 0.05° step and $0.05^\circ/\text{s}$ speed. The relative crystallinity index (RCI) was calculated as a function of the crystalline regions (CR) area and amorphous regions (AR) area, according to Equation (3).

$$\text{RCI (\%)} = \frac{\text{CR}}{\text{CR}+\text{AR}} \times 100 \quad (3)$$

4.3.3. Scanning Electron Microscopy

Scanning electron microscopy images of the biodegradable films (fracture and surface) was evaluated by an electron microscope (FEI Quanta 200, USA). The samples were cryofractured in liquid nitrogen, dried in a desiccator with calcium chloride ($\approx 0\%$ RH), and coated with gold (Sputter Coater BAL-TEC SCD 050, Germany). The film's images of the fracture and surface were taken at 1600x.

4.3.4. Fourier-Transform Infrared Spectroscopy

Before analysis, the specimens were ground and compressed into tablets with potassium bromide. FTIR spectrum of the films was analyzed using a vacuum spectrometer (Shimadzu, model IRPrestige-21, Japan) and in the wavenumber range from 4000 to 400 cm^{-1} at 2 cm^{-1} resolution and 16 scans.

4.3.5. Mechanical Properties

The tensile strength (σ , MPa), elongation at break (ϵ , %), and Young's modulus (YM, MPa) of the biodegradable films were determined using a Universal Testing Machine (EMIC, INSTRON, Brazil) fitted with a 50 kgf load cell, according to ASTM standard D882-18 (2018) with modifications. Ten specimens of each formulation were cut in the longitudinal direction (100 mm x 25 mm) and then tested. The crosshead speed was set at 0.8 mm/s, and the initial distance between the grips was 60 mm.

Before performing the tests, the films were placed in a desiccator for 72 h, keeping the temperature at $25 \pm 2^\circ\text{C}$ and the equilibrium relative humidity at $53 \pm 2\%$.

4.3.6. Statistical Analysis

The data were analyzed using Statistica 7.0 software (Statsoft Inc., Tulsa, OK, USA, 2004), with analysis of variance (ANOVA) and the Tukey test at 5% significance level ($p < 0.05$). The samples of the same composition with and without citric acid were compared in pairs by the t-test at 5% significance level ($p < 0.05$).

3. Results and Discussion

3.1. Opacity and Color Analysis

The evaluation of color and opacity provides information that allows making appropriate indications for the use of films. The films were flexible, easy to handle, and smooth to the touch, with a slightly yellowish color (Figure 1), which is common in extruded materials with high starch content (LIN *et al.*, 2021). All films presented thicknesses ranging from 100 to 150 μm . Table 1 shows the data related to the materials' apparent opacity and color.

Figure 1. Images of the biodegradable films.

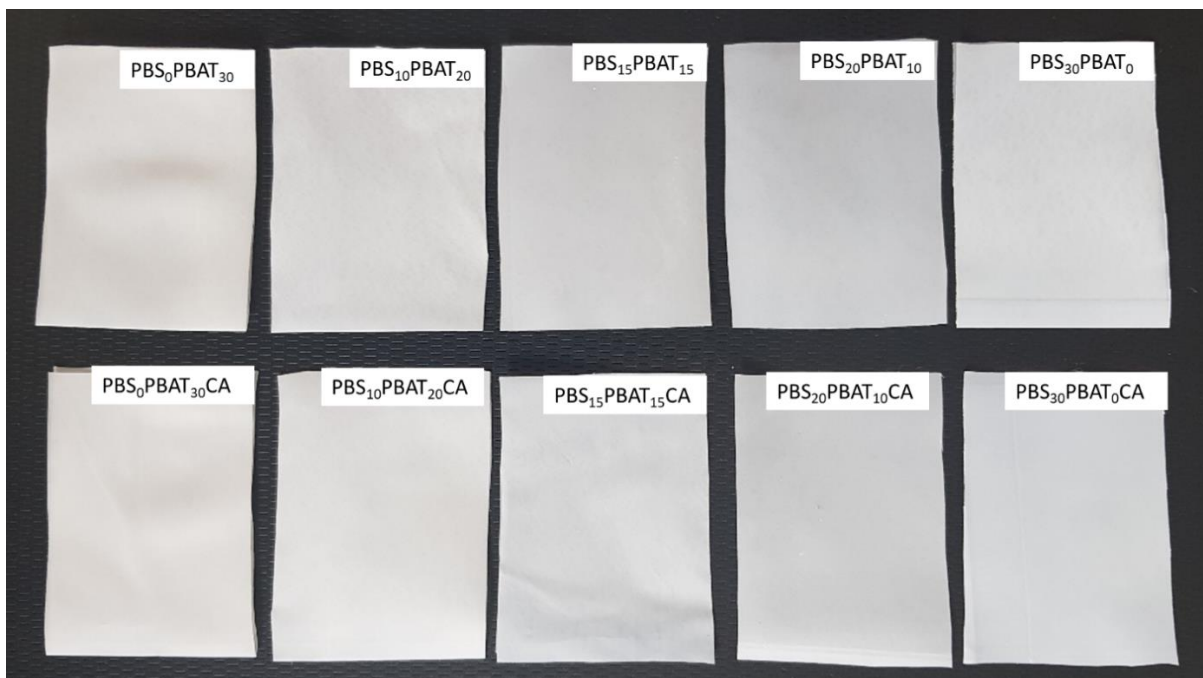


Table 1. Apparent opacity, color parameters, and total color difference of the films.

Film without citric acid		Film with citric acid	
Opacity (%)			
PBS ₀ PBAT ₃₀	53.77 ^{a,A} ± 0.36	PBS ₀ PBAT ₃₀ CA	55.78 ^{a,B} ± 0.76
PBS ₁₀ PBAT ₂₀	54.55 ^{a,C} ± 0.40	PBS ₁₀ PBAT ₂₀ CA	56.02 ^{a,D} ± 0.50
PBS ₁₅ PBAT ₁₅	55.37 ^{b,E} ± 0.61	PBS ₁₅ PBAT ₁₅ CA	56.64 ^{a,F} ± 0.43
PBS ₂₀ PBAT ₁₀	58.57 ^{c,G} ± 0.37	PBS ₂₀ PBAT ₁₀ CA	59.06 ^{b,G} ± 0.50
PBS ₃₀ PBAT ₀	62.40 ^{d,H} ± 0.25	PBS ₃₀ PBAT ₀ CA	63.10 ^{c,H} ± 0.86
Parameter a*			
PBS ₀ PBAT ₃₀	-1.55 ^{b,A} ± 0.18	PBS ₀ PBAT ₃₀ CA	-1.77 ^{b,A} ± 0.15
PBS ₁₀ PBAT ₂₀	-1.92 ^{a,b,B} ± 0.11	PBS ₁₀ PBAT ₂₀ CA	-2.03 ^{a,B} ± 0.12
PBS ₁₅ PBAT ₁₅	-2.12 ^{a,C} ± 0.39	PBS ₁₅ PBAT ₁₅ CA	-2.03 ^{a,C} ± 0.17
PBS ₂₀ PBAT ₁₀	-2.16 ^{a,D} ± 0.15	PBS ₂₀ PBAT ₁₀ CA	-2.03 ^{a,D} ± 0.17
PBS ₃₀ PBAT ₀	-1.94 ^{a,b,E} ± 0.16	PBS ₃₀ PBAT ₀ CA	-2.14 ^{a,E} ± 0.14
Parameter b*			
PBS ₀ PBAT ₃₀	4.89 ^{a,A} ± 0.41	PBS ₀ PBAT ₃₀ CA	5.06 ^{a,A} ± 0.35
PBS ₁₀ PBAT ₂₀	5.06 ^{a,B} ± 0.37	PBS ₁₀ PBAT ₂₀ CA	5.03 ^{a,B} ± 0.34
PBS ₁₅ PBAT ₁₅	4.93 ^{a,C} ± 0.36	PBS ₁₅ PBAT ₁₅ CA	4.95 ^{a,C} ± 0.53
PBS ₂₀ PBAT ₁₀	5.31 ^{a,D} ± 0.32	PBS ₂₀ PBAT ₁₀ CA	4.97 ^{a,D} ± 0.47
PBS ₃₀ PBAT ₀	5.51 ^{a,E} ± 0.68	PBS ₃₀ PBAT ₀ CA	5.60 ^{a,E} ± 0.42
Parameter L*			
PBS ₀ PBAT ₃₀	94.72 ^{a,A} ± 0.51	PBS ₀ PBAT ₃₀ CA	95.10 ^{a,A} ± 0.33
PBS ₁₀ PBAT ₂₀	95.36 ^{a,B} ± 0.27	PBS ₁₀ PBAT ₂₀ CA	95.14 ^{a,B} ± 0.29
PBS ₁₅ PBAT ₁₅	95.38 ^{a,C} ± 0.34	PBS ₁₅ PBAT ₁₅ CA	95.08 ^{a,C} ± 0.51
PBS ₂₀ PBAT ₁₀	94.88 ^{a,D} ± 0.30	PBS ₂₀ PBAT ₁₀ CA	95.13 ^{a,D} ± 0.40
PBS ₃₀ PBAT ₀	94.80 ^{a,E} ± 0.53	PBS ₃₀ PBAT ₀ CA	94.50 ^{a,E} ± 0.37
Total color difference (ΔE*)			
PBS ₀ PBAT ₃₀	1.42 ^{a,A} ± 0.59	PBS ₀ PBAT ₃₀ CA	1.55 ^{a,A} ± 0.41
PBS ₁₀ PBAT ₂₀	1.62 ^{a,B} ± 0.35	PBS ₁₀ PBAT ₂₀ CA	1.64 ^{a,B} ± 0.37
PBS ₁₅ PBAT ₁₅	1.64 ^{a,C} ± 0.46	PBS ₁₅ PBAT ₁₅ CA	1.61 ^{a,C} ± 0.61
PBS ₂₀ PBAT ₁₀	1.97 ^{a,D} ± 0.38	PBS ₂₀ PBAT ₁₀ CA	1.61 ^{a,D} ± 0.54
PBS ₃₀ PBAT ₀	2.08 ^{a,E} ± 0.79	PBS ₃₀ PBAT ₀ CA	2.31 ^{a,E} ± 0.52

Different lowercase letters in the same group of films (with and without CA) indicate a significant difference between the samples (Tukey's test, $p \leq 0.05$). Different capital letters between the two groups of samples represent a significant difference between each pair of samples (t-test, $p \leq 0.05$).

There was a significant difference for CA-free films with more than 15 wt% PBS in their formulation, while for films with CA, only those with more than 20 wt% PBS differed from the others. This behavior indicates that the blend composition affected the opacity. . Apparent opacity of the films without CA ranged from 53.77 to 62.40% and with CA from 55.78 to 63.10%. These high opacities are characteristic of extruded materials with high starch content. During film processing, alignment and compaction of the molecules of its constituents occur, especially for starch, leading to the formation of crystalline areas, which increases the opacity of these films (FAKHOURY *et al.*, 2012; SOUSA; SOARES JÚNIOR; YAMASHITA, 2013). This behavior also occurred during the development of starch-based polymers with PBAT (DE CAMPOS *et al.*, 2019; SANTOS *et al.*, 2014; SHIRAI *et al.*, 2013). Besides, PBS is a more crystalline polymer than PBAT (DE MATOS COSTA *et al.*, 2020), then the opacity of the films tends to increase with the higher PBS content, as observed for both groups of samples.

The t-test reveals a significant difference between samples with and without citric acid for samples with up to 15 wt% PBS, indicating that adding citric acid tends to boost the materials' opacity. Citric acid can hydrolyze the amylopectin chains of starch, increasing the linearity of these molecules (GARCIA *et al.*, 2014). This higher molecular packing is responsible for enhancing films' opacity. Nevertheless, when comparing films with and without citric acid containing 20 or 30 wt% PBS, there was no significant difference between them, i.e., higher PBS content affects the films' opacity more than a small addition of citric acid. The higher opacity, due to the inclusion of citric acid and PBS fraction, agrees with the increase in the degree of crystallinity of the materials reported in XRD analysis.

Garcia *et al.* (2014) produced extruded blown films with 70 wt% TPS and 30 wt% PBAT without and with citric acid. The authors verified an increase in opacity from 54 to 77% after including citric acid in films (100 mm thickness); similar behavior was observed in this research. Also, Shirai *et al.* (2013) made materials with 59.49 wt% TPS, 40% wt% PBAT, 0.01 wt% citric acid, and 0.5 wt% magnesium stearate. They achieved 67% opacity for the film (100 mm thickness) even though the amount of TPS was lower than in this research, which may indicate that starch is the most critical component to raise the opacity. Although starch usually induces opacity in materials (FAHRNGRUBER *et al.*, 2020), partially opaque films can be good

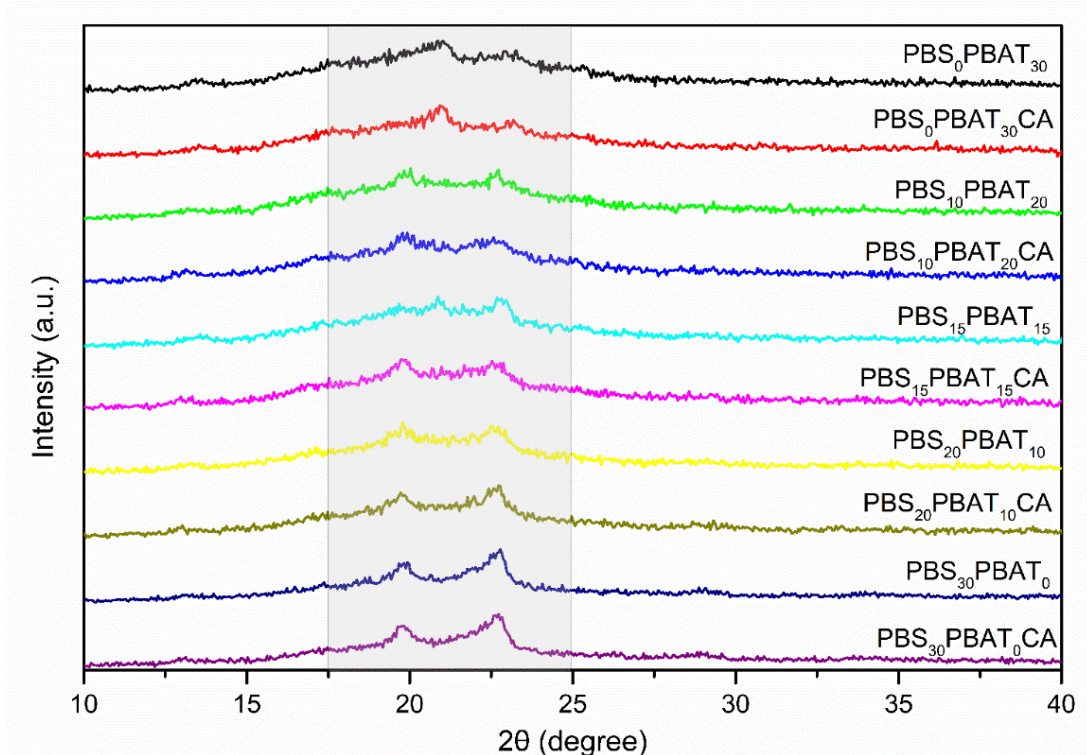
alternatives for packaging foods with some degree of photosensitivity, as they reduce the passage of light (HAN *et al.*, 2018).

Concerning the parameters of color, there was a significant difference only for a^* parameter, indicating different shades of green in films with and without citric acid (Table 1), which tended to be greener with higher PBS content. As for the parameters L, b^* , and ΔE^* , there was no significant difference between samples in each group, indicating that the films are perceived as equally luminous, yellowish, and with the same overall color, regardless of the blend composition. According to (ARRIETA *et al.*, 2014), human eyes cannot detect color differences when $\Delta E^* < 2$. Specifically, no color difference was perceived in this work for $\Delta E^* < 2.31$. The addition of citric acid does not generate noticeable changes in films of similar composition since, according to the t-test, there was no significant difference in the parameters of L, a^* , b^* , and ΔE^* for all pairs of samples compared to each other.

3.2. XRD Analysis

The diffractograms in Figure 2 are very similar in shape and show crystallinity peaks in the 2θ regions from 19.40° to 23.30° .

Figure 2. XRD patterns of the biodegradable films.



Each component displays crystallinity patterns in specific regions of the diffractogram. For example, corn starch typically shows peaks in 2θ at 15° , $22\text{-}23^\circ$, and a doublet at $17\text{-}18^\circ$ (ESMAEILI; PIRCHERAGHI; BAGHERI, 2017; VAN SOEST *et al.*, 1996). When corn starch is plasticized with glycerol, these peaks typically disappear or decrease after the extrusion process (FLOREZ; FAZELI; SIMÃO, 2019). PBS has characteristic peaks around 2θ at 20° , 22° , 23° , and 29° corresponding to the (020), (021), (110), and (111) planes, respectively (S. Wu *et al.*, 2017; Zhang *et al.*, 2019). Finally, PBAT shows diffraction peaks in the region of about 2θ at $16\text{-}17^\circ$, 20° , 23° , and 25° (GARALDE *et al.*, 2019). The diffraction peaks of each constituent of the blends have similar 2θ values. As a result, areas with overlapping peaks can be observed in the diffractogram, preventing attribution to a specific component. Therefore, the crystallinity of the films is due to the combined presence of different proportions of TPS, PBS, and PBAT.

Residual or induced crystallinity may appear after processing films with high starch content. The first occurs due to the non-rupture of the starch's granular structure, mainly caused by amylopectin, and classified as an A-type crystalline structure for corn starch. Its manifestation commonly occurred at $2\theta \sim 16.8^\circ$ and was not observed for any materials, although granules were observed in SEM. The second type happens due to the rapid recrystallization and alignment of the amylose chains and can be classified as V_A , V_H , and E_H -types according to the region where the peak appears (VAN SOEST; VLIEGENTHART, 1997). Thus, a peak in the region of $2\theta \sim 19.8^\circ$ can be associated with processing-induced crystallinity with V_H -type crystals (Mücke *et al.*, 2021; Olivato *et al.*, 2013), although they are not observed in the diffractograms due to overlap of peaks. Films with PBS in their composition also showed processing-induced crystallinity in the range of $2\theta \sim 20.5$ with V_A -type crystals (LI *et al.*, 2013), which was not observed for the sample without PBS in its formulation (PBS₀PBAT₃₀). Process-induced crystallinity is usual in the processing of starch-based extruded films, as also reported by Garalde *et al.* (2019), Li *et al.* (2013), and Santos *et al.* (2014). Table 2 presents the relative crystallinity index (RCI) of the films.

Table 2. Relative crystallinity index of the biodegradable films.

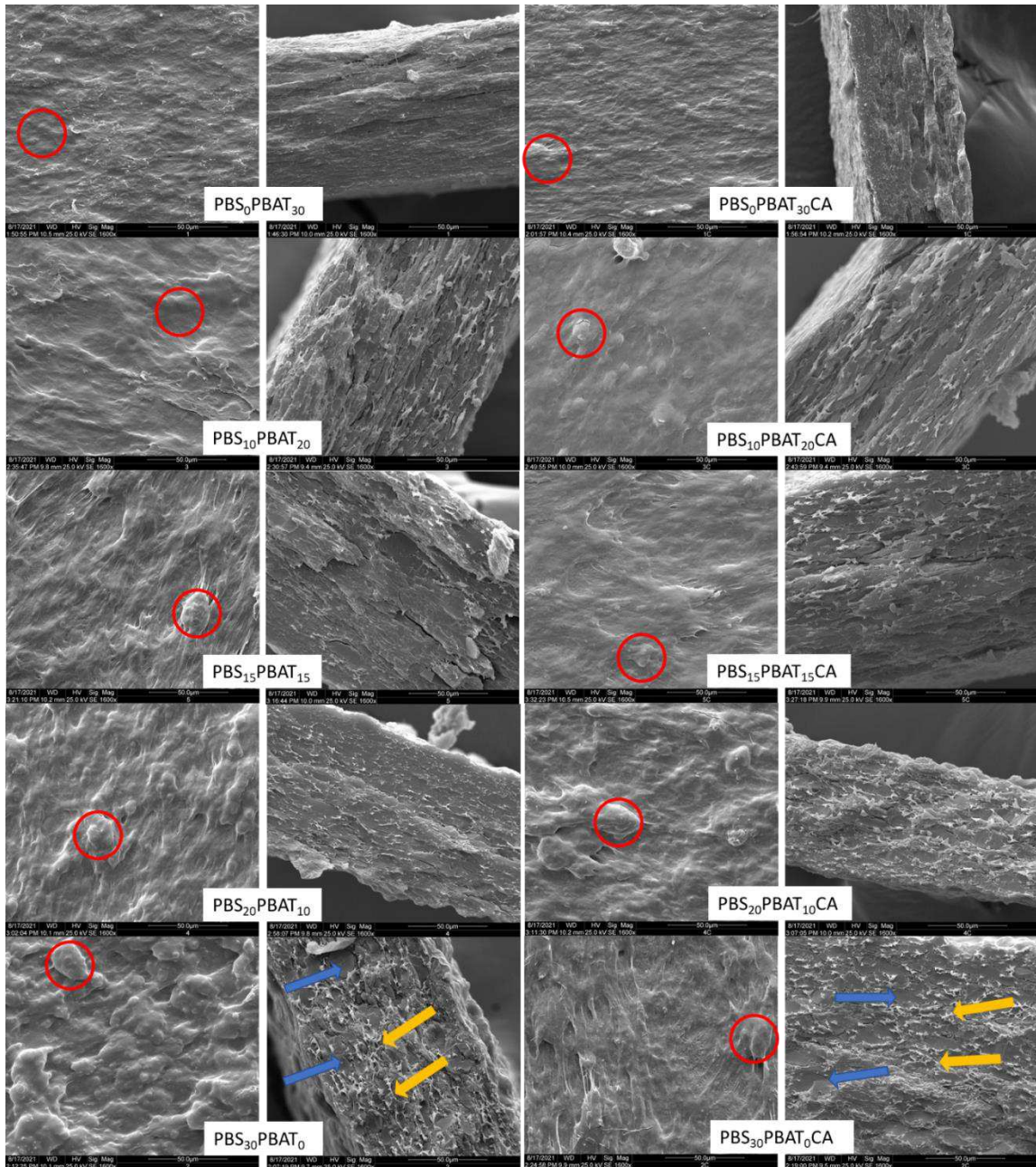
RCI (%)			
Film without citric acid		Film with citric acid	
PBS ₀ PBAT ₃₀	6.98	PBS ₀ PBAT ₃₀ CA	7.32
PBS ₁₀ PBAT ₂₀	7.30	PBS ₁₀ PBAT ₂₀ CA	9.06
PBS ₁₅ PBAT ₁₅	7.54	PBS ₁₅ PBAT ₁₅ CA	9.50
PBS ₂₀ PBAT ₁₀	8.95	PBS ₂₀ PBAT ₁₀ CA	10.12
PBS ₃₀ PBAT ₀	10.98	PBS ₃₀ PBAT ₀ CA	13.06

During film processing, alignment and interaction of the molecules of its constituents occur, especially for starch, leading to the formation of crystalline areas, which increases the opacity of these films (FAKHOURY *et al.*, 2012; SOUSA; SOARES JÚNIOR; YAMASHITA, 2013). This behavior also occurred during the development of starch-based polymers with PBAT (de Campos *et al.*, 2019; Santos *et al.*, 2014; Shirai *et al.*, 2013). Since PBS crystallinity is higher than PBAT, an increase in its fraction leads to an increase in the crystallinity of the films (DE MATOS COSTA *et al.*, 2020). As previously discussed, citric acid improves molecular interaction, which culminates in more crystalline materials (GARCIA *et al.*, 2014).

3.3. SEM Analysis

Figure 3 illustrates the surface and fracture micrographs of the biodegradable films without (columns 1 and 2) and with citric acid (columns 3 and 4).

Figure 3. SEM micrographs of the blends at 1600x magnification.



The films exhibited a non-porous and slightly rough surface structure due to the presence of intact starch granules (red circles), which is common in high starch content materials, as reported by De Campos et al. (2019) and Olivato et al. (2013). Internally, the material presented a partially cohesive structure with few cracks and fissures. However, to a greater or lesser extent, two phases were observed. These observations suggest that the films are partially homogeneous and have good structural integrity, which contributed to the excellent performance of the blends in terms of mechanical properties.

The film PBS₀PBAT₃₀ showed the most homogeneous surface with a fibrillar morphology, while two phases can be observed in PBS₃₀PBAT₀. Visibly, the interaction between PBS and TPS was lower than PBAT and TPS, which was also reported by Wei X. Y. et al. (2021) in their ternary blend of PBS grafted with glycidyl methacrylate, starch plasticized with anhydroxylitol tripelargonate, and PBAT. For example, in PBS₃₀PBAT₀ fracture, it is possible to see the matrix phase formed by thermoplastic starch (a denser region with well-defined contours - blue arrows) and the dispersed PBS phase (filaments whitish region - yellow arrows).

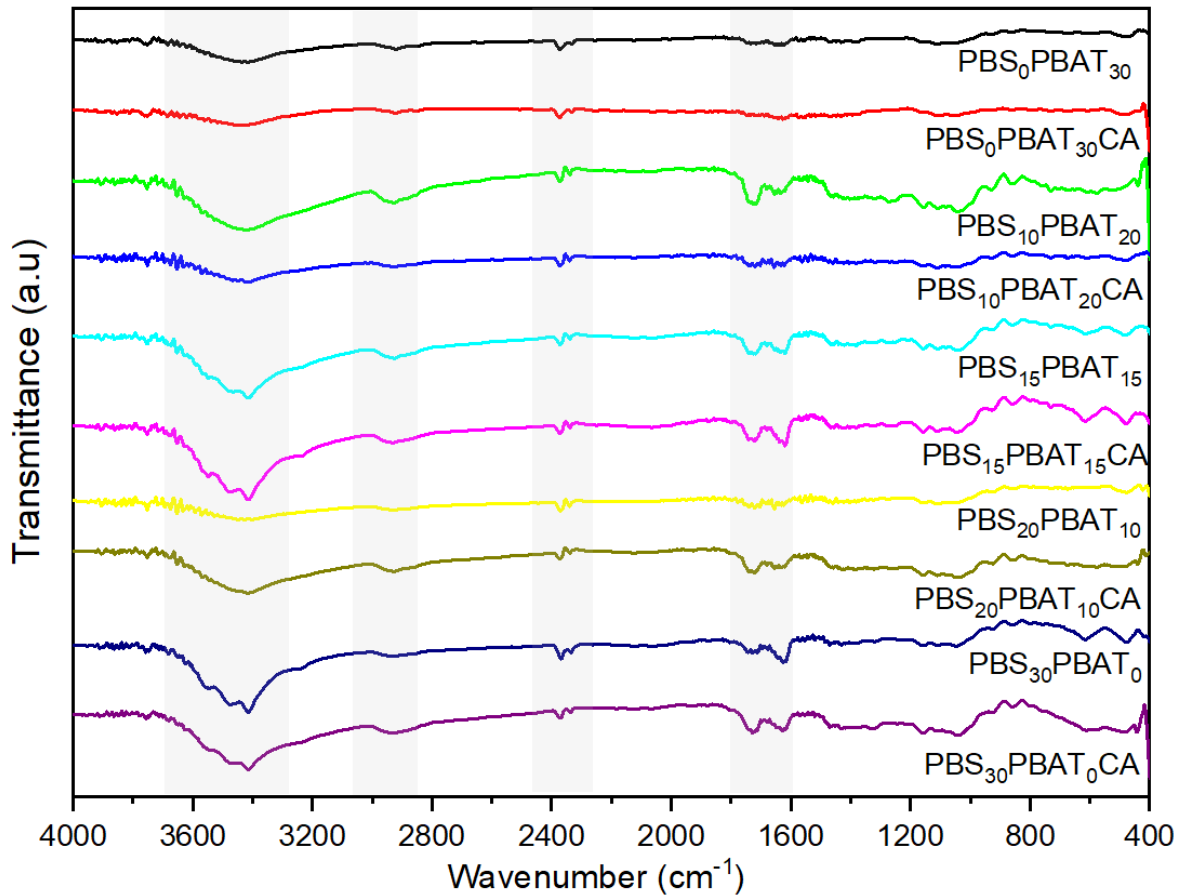
Although the PBS₃₀PBAT₀ sample presented lower interaction between its constituents, no significant difference occurred between this film and the other blends CA-free in terms of tensile strength. Among the materials composed of PBS and PBAT, the PBS₂₀PBAT₁₀ presented the most homogeneous morphology, which produced a film with balanced mechanical properties. Muthuraj et al. (2014) designed PBS/PBAT binary blends with high compatibility. The authors attributed these outcomes to the transesterification reaction due to residual catalysts in the homopolymer synthesis. This reaction formed an ester linkage between PBS and PBAT. The blend PBS/PBAT 70/30 wt% was reported to be the most compatible material. Besides, increased PBAT content over PBS decreased their compatibility, reducing the blends' tensile strength.

The citric acid smoothed the surface of the materials and made the internal structure more cohesive and with better interfacial adhesion, which positively influenced the mechanical properties of the films. These materials presented a more homogeneous and compact morphology due to the better compatibility between the TPS, PBAT, and PBS. CA grafts ester groups onto the starch chain, reducing its hydrophilicity and allowing better interaction with polyesters (GARCIA *et al.*, 2014). The use of citric acid to increase the miscibility of PBAT and TPS has been widely reported (BILCK; YAMASHITA; MARZANO-BARREDA, 2021; DE CAMPOS *et al.*, 2019; MÜCKE *et al.*, 2021; OLIVATO *et al.*, 2013). The incompatibility between PBS and TPS has also been improved with other compatibilizer agents such as tartaric acid (ZHANG *et al.*, 2019), reactive PBS (RPBS) with terminal NCO group (ZENG *et al.*, 2011), starch-g-PBS agent (SUCHAO-IN; KOOMBHONGSE; CHIRACHANCHAI, 2014) and maleic anhydride grafted PBS (rPBS) (YIN *et al.*, 2015). Overall, the same behavior profile reported for the samples without citric acid occurred for those with this acid.

3.4. FTIR Analysis

Figure 4 shows the FTIR spectra of the biodegradable films produced in this study.

Figure 4. FTIR spectra of the biodegradable films.



All films had a broad band in the range from 3200 to 3600 cm^{-1} , which corresponds to the complex vibrational stretches associated with free, inter, and intramolecular bonded hydroxyl groups (O–H), as supported by the findings from Nordin et al. (2020) and Tarique et al. (2021). For $\text{PBS}_{30}\text{PBAT}_0$ and $\text{PBS}_{15}\text{PBAT}_{15}$ samples and their counterparts with citric acid, bands around 3545–3415 cm^{-1} represent the terminal hydroxyl group of PBS (FERREIRA et al., 2014). All films showed absorption bands around 2928 to 2931 cm^{-1} due to the C–H asymmetric stretching (EDHIREJ et al., 2017; NAZRIN et al., 2020). Peaks between 2331 to 2372 cm^{-1} are unusual and can appear due to CO_2 presence during the test (ABDULLAH et al., 2018) or gas trapped in the polymer matrix of the films.

Furthermore, the region ranging from 1711 to 1720 cm^{-1} describes the C=O stretching of ester groups of all materials components, except TPS (AYU *et al.*, 2018; YAO; CHEN; YE, 2017; ZHANG *et al.*, 2019). For PBAT and PBS, this absorption region (1711 to 1730 cm^{-1}) corresponds to the carbonyl groups of their amorphous fraction. For PBAT, these signals may be associated with specific interactions due to the conjugative effect between the phenylene aromatic groups and carbonyl groups of PBAT terephthalate residues (DE MATOS COSTA *et al.*, 2020). The peaks ranging from 1620 to 1655 cm^{-1} can be attributed to H₂O bending vibration caused by the water absorption of hydroxyl groups in starch molecules (ZHANG *et al.*, 2019). The region between 1157 to 1044 cm^{-1} is common to all components of the samples. The band at 1157 cm^{-1} belongs to C–O–C asymmetrical stretching and vibration, while the absorption band at 1109 cm^{-1} can ascribe the C–O(H) group (TARIQUE; SAPUAN; KHALINA, 2021) and at 1044 cm^{-1} represent the stretching vibration of CO at the ester bond (DA SILVA *et al.*, 2019). Specifically, for starch, the peak at 1044 cm^{-1} may also belong to D-glucopyranose (DUC; GIANG, 2021).

Regarding the effect of the citric acid in the films, the grafting of ester groups onto the starch chains may have occurred during the extrusion process of materials containing citric acid, although no new peak in the spectrum was observed. The presence of ester bonds in PBAT (GARCIA *et al.*, 2014) and PBAT polyesters hampers the visualization of other ester linkages. Finally, the FTIR analysis revealed that the individual compounds (starch, glycerol, PBS, PBAT, and citric acid) of blends had no substantial effect on the chemical structure of the films since there were no considerable changes in FTIR standards.

3.5. Mechanical Properties Analysis

The mechanical properties of the biodegradable films, tensile strength, elongation at break, and Young's modulus are in Table 3.

Table 3. Mechanical properties of the biodegradable films.

Film without citric acid		Film with citric acid	
Tensile strength (MPa)			
PBS ₀ PBAT ₃₀	5.01 ^{a,A} ± 0.73	PBS ₀ PBAT ₃₀ CA	5.41 ^{a,A} ± 0.41
PBS ₁₀ PBAT ₂₀	5.31 ^{a,B} ± 0.65	PBS ₁₀ PBAT ₂₀ CA	5.38 ^{a,B} ± 0.38
PBS ₁₅ PBAT ₁₅	5.03 ^{a,C} ± 0.66	PBS ₁₅ PBAT ₁₅ CA	5.35 ^{a,C} ± 0.38
PBS ₂₀ PBAT ₁₀	6.04 ^{a,D} ± 0.79	PBS ₂₀ PBAT ₁₀ CA	7.15 ^{b,D} ± 0.94
PBS ₃₀ PBAT ₀	6.14 ^{a,E} ± 0.25	PBS ₃₀ PBAT ₀ CA	7.42 ^{b,F} ± 0.69
Elongation at break (%)			
PBS ₀ PBAT ₃₀	198.53 ^{a,A} ± 31.27	PBS ₀ PBAT ₃₀ CA	275.71 ^{a,B} ± 36.69
PBS ₁₀ PBAT ₂₀	45.25 ^{b,C} ± 5.25	PBS ₁₀ PBAT ₂₀ CA	56.64 ^{b,D} ± 9.34
PBS ₁₅ PBAT ₁₅	43.17 ^{b,E} ± 2.65	PBS ₁₅ PBAT ₁₅ CA	48.04 ^{b,F} ± 2.77
PBS ₂₀ PBAT ₁₀	31.65 ^{b,G} ± 5.00	PBS ₂₀ PBAT ₁₀ CA	39.19 ^{b,H} ± 4.73
PBS ₃₀ PBAT ₀	23.16 ^{b,I} ± 2.79	PBS ₃₀ PBAT ₀ CA	33.87 ^{b,J} ± 5.67
Young's modulus (MPa)			
PBS ₀ PBAT ₃₀	19.65 ^{a,A} ± 2.71	PBS ₀ PBAT ₃₀ CA	20.06 ^{a,A} ± 2.67
PBS ₁₀ PBAT ₂₀	50.21 ^{b,B} ± 5.39	PBS ₁₀ PBAT ₂₀ CA	46.58 ^{b,B} ± 4.47
PBS ₁₅ PBAT ₁₅	50.18 ^{b,C} ± 5.95	PBS ₁₅ PBAT ₁₅ CA	47.35 ^{b,C} ± 6.54
PBS ₂₀ PBAT ₁₀	55.70 ^{b,c,D} ± 5.33	PBS ₂₀ PBAT ₁₀ CA	55.78 ^{c,D} ± 4.19
PBS ₃₀ PBAT ₀	62.44 ^{c,E} ± 8.05	PBS ₃₀ PBAT ₀ CA	58.54 ^{c,E} ± 8.92

Different lowercase letters in the same group of films (with and without CA) indicate a significant difference between the samples (Tukey's test, $p \leq 0.05$). Different capital letters between the two groups of samples represent a significant difference between each pair of samples (t-test, $p \leq 0.05$).

There was no significant difference in tensile strength for films without citric acid. However, as the PBS content increased, the tensile strength of blends also tended to increase because PBS is more resistant to tensile than PBAT (MUTHURAJ; MISRA; MOHANTY, 2014). This same phenomenon occurred for samples with citric acid, but they present a significant difference in this parameter. The films with the highest fraction of PBS – PBS₂₀PBAT₁₀CA and PBS₃₀PBAT₀CA – did not significantly differ and showed the highest tensile strength values (7.15 and 7.42 MPa, respectively).

Bilck, Yamashita and Marzano-Barreda (2021) formulated a film by blow extrusion with a similar composition to the PBS₀PBAT₃₀CA sample and achieved only

1.82 MPa of tensile strength, a value lower than all found in this work. YAP et al. (2020) developed films by compression molding with varying concentrations of PBAT/PBS (60 wt%) and TPS (40 wt%), and the tensile strength ranged from 10 to 14 MPa. The values are higher than those found in this work (5.01 to 7.42 MPa), probably due to two factors: the material production method is different, and the TPS content is lower than that used in our research. Usually, the higher the TPS content, the lower the tensile strength of the materials.

The films with citric acid generally had higher tensile strength than those without citric acid. During the extrusion process, citric acid loses two molecules of water, allowing it to react more easily with the hydroxyls of the starch, leading to the formation of monoesters that result in higher compatibility between the polymers of the blends (SIMÕES *et al.*, 2020). More compatible polymers have a better ability to transmit forces internally, which reflects higher tensile strength. However, statistically only the samples PBS₃₀PBAT₀ and PBS₃₀PBAT₀CA had a significant difference.

Thus, CA has more influence on tensile strength for higher PBS concentrations. PBS has a more linear chain than PBAT, being more accessible to interact with TPS in the presence of CA. The aromatic portion of PBAT probably hinders its interaction. Therefore, CA improves compatibility for higher PBS content because it can act as a coupling agent for TPS. Zhang et al. (2019) reported similar behavior; according to the authors, tartaric acid (TA) acted as a coupling agent and increased the compatibility of PBS/TPS, although it does not esterify with starch during extrusion. This effect enhanced the tensile strength of PBS/TPS-TA films due to the interactions between the starch and the PBS matrix.

The elongation at break of the biodegradable films differed only for the formulations with and without citric acid composed of 30 wt% PBAT (Table 3). In addition, the films PBS₀PBAT₃₀ and PBS₀PBAT₃₀CA had values much higher than the others (198.53 and 275.71%, respectively). PBAT materials are more flexible than PBS ones (DE MATOS COSTA *et al.*, 2020), so as the PBS fraction increases, there is a tendency to decrease the elongation at break for the blends. The elongation at break of the biodegradable films is like those reported by (ZENG *et al.*, 2011) for injected materials based on PBS with reactive terminal and TPS (24.3 to 46.6%) and is superior to those reported by (MÜCKE *et al.*, 2021) for extruded films based on PBAT and TPS with the addition of citric acid (187.76%).

The t-test indicated a significant difference for all pairs of samples with and without citric acid, and the citric acid increased the elongation at break for all films. According to Garcia et al. (2018), the monoesters formed by the reaction of citric acid with starch, besides acting as compatibilizers, can also act as internal plasticizers. These groups behave as flexible side chains, which decrease interactions between starch through steric hindrance. Thus, free volume rises, improving the elongation of materials with citric acid in their composition.

Films containing solely PBAT – PBS₀PBAT₃₀ and PBS₀PBAT₃₀CA – had the lowest Young's modulus (19.65 and 20.06 MPa, respectively), while samples containing only PBS, PBS₃₀PBAT₀, and PBS₃₀PBAT₀CA, presented the highest YM values (62.44 and 58.54 MPa, respectively). PBS inclusion in the blend formulation causes an abrupt increase in YM. According to ROBERTSON, (2013), pure PBS has a YM (645 MPa) much higher than PBAT (80 MPa), then a low addition of PBS in the blend already increases YM. Young's modulus of the biodegradable films was much lower than those of the pure polymers due to the high TPS content, which presents a low YM value (1.46 MPa) (ZENG *et al.*, 2011).

The outcomes in this work agree with the results of Bilck et al. (2021), who developed a similar blown film composed of TPS, PBAT, and CA (69.97/30/0.03 wt%) and reached a YM of 23.03 MPa. However, they are lower than those reported by Zeng et al. (2011), who made injected materials of TPS and different reactive PBS (70/30 wt%) and achieved YM from 97 to 472 MPa. These high values can be attributed to the manufacturing method and the type of PBS. The authors made modifications to turn the NCO terminal of PBS more reactive to be blended with TPS. Lastly, YAP et al. (2020) produced compression-molded blends made of PBAT, PBS, TPS, calcium stearate (CS), maleic anhydride (MA), and dicumyl peroxide (DP). They used a proportion of polyesters/TPS higher than in this research and got a YM of 134.38 MPa for PBAT/PBS/TPS/CS/MA/DCP (48/12/40/0.5/2/0.4 wt%) and 199.49 MPa for a sample with the same compounds at another proportion (36/24/40/0.5/2/0.4 wt%).

Finally, the t-test showed no significant difference between the pairs of samples, which indicated that citric acid does not interfere with the stiffness of materials with and without citric acid.

As the PBS/PBAT ratio increased, tensile strength and YM rose, and elongation at break decreased. It means a more resistant blend with lower ductility and

flexibility, which could meet the requirements for packaging food purposes. Considering the three properties together, the films PBS₂₀PBAT₁₀ and PBS₂₀PBAT₁₀CA were the ones that obtained the best balance between stiffness, ductility, and tensile strength.

The properties of these films can reach values close to the minimum tensile strength of commercial LDPE films (> 10 MB), although they have an elongation at break (> 200%) and Young's modulus (> 150 MPa) lower than theirs (OVERVIEW, 2022). Even so, the blends in this work have 70% by weight of TPS, a highly biodegradable and low-cost material, indicating that these films have good mechanical characteristics that meet the packaging requirements.

4. Conclusions

The current study used different ratios of PBS/PBAT/TPS with and without citric acid to investigate the effect on blown extruded films' physical, structural, and mechanical properties. Each component provided at least one feature of interest to the film; PBAT offers ductility, PBS contributes with strength, and the TPS provides high biodegradability and low cost. Films consisting of TPS and only PBS or PBAT showed less attractive mechanical characteristics than blends containing both polyesters. Citric acid was used as a compatibilizer agent, but its multicarboxylic nature allowed it to act as a plasticizer, crosslinking agent, or hydrolytic agent, depending on the interactions and reactions with other constituents of the blends. Citric acid increased tensile strength and elongation at break and decreased Young's modulus for all films. Opacity and degree of crystallinity were higher for films containing citric acid, and the colors were not significantly different, regardless of the blend composition. Although SEM analysis indicates higher compatibility between TPS and PBAT than with PBS, films with higher PBS content had higher tensile strength. Even though the FTIR analysis did not indicate chemical reactions between the blend's constituents, all films achieved a balance between hardness, ductility, and strength. In brief, the results of this research provide perspectives and direction for developing cost-effective biodegradable packaging with the potential to be produced on a large scale using conventional industrial equipment.

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CAPÍTULO V: Ternary Blends of PBS, PBAT, and TPS in the Production of Biodegradable Films by Extrusion Blow Molding

1. Introduction

Plastic is a material with high resistance to oxidation, which takes a long time for natural decomposition, causing accumulation and consequent environmental pollution (AYU *et al.*, 2018). The current plastic economy also has disadvantages that are becoming more apparent daily. According to the Ellen MacArthur Foundation, 95% of the value of plastic packaging material, or \$80-120 billion annually, is lost to the economy after a short first use. Incidentally, only 14% of plastic packaging is collected for recycling; and when considering additional value losses in sorting and reprocessing, just 5% of the material's value is retained for later use. Also, recycled plastics are primarily used in lower value-added applications and are not recyclable again after use (REPORT, 2017).

In this sense, biodegradable polymers have gained attention, as their sustainable proposal dialogues with the search for environmentally correct materials (MESSIN *et al.*, 2020). The biopolymer market has little representation of the global plastic market size, only \$10.2 billion of \$593.00 billion in 2021. Still, it shows a higher growth trend (compound annual growth rate (CAGR) of 17.1% from 2022 to 2030) than the traditional plastic market (CAGR of 3.7% from 2022 to 2030). This trend is due to the depletion of fossil sources and the expected growth of the world population, which should reach 9 billion people in 2050 (ABIPLAST, 2020).

Biodegradable polyesters, such as poly (butylene adipate-co-terephthalate) (PBAT) and poly(butylene succinate) (PBS), stand out among the commercially available biodegradable polymers that can be wholly or partially obtained from renewable sources (GEORGE *et al.*, 2020). PBS is a semicrystalline aliphatic polyester obtained by polymerizing butanediol with succinic acid, both available from fossil or bio-based renewable resources (LIU *et al.*, 2009). It has a balanced performance between thermal (elevated resistance) and mechanical (high strength and tenacity) properties and good chemical resistance (GALIANO *et al.*, 2018), in addition to attractive barrier properties (low oxygen permeability) (FAHRNGRUBER *et al.*, 2020). SIRACUSA *et al.* (2015) reported that PBS has a very high selectivity ratio of CO₂/O₂, where the transmission rate of CO₂ is ten times greater than that of O₂, which could

benefit the preservation of food inside the package, extending its shelf life (WU; MISRA; MOHANTY, 2021).

However, it has a lower biodegradability than its copolymers (DE MATOS COSTA *et al.*, 2020), additionally to lower ductility and flexibility (BELUCI *et al.*, 2023). PBAT is a viable alternative to remedy PBS deficiencies. This material is an aliphatic-aromatic copolyester, commercially synthesized by polycondensation between butanediol, adipic acid, and terephthalic acid (JIAN; XIANGBIN; XIANBO, 2020). Besides being highly biodegradable, PBAT has excellent toughness and can be used mainly for extruding films and coatings (JAVADI *et al.*, 2010). Its mechanical properties are like low-density polyethylene (LDPE) (NAGARAJAN; MISRA; MOHANTY, 2013) and derive from the aromatic unit in the molecule chain (JIAN; XIANGBIN; XIANBO, 2020). Despite this, PBAT presents poor oxygen and water vapor barrier (LI *et al.*, 2018), which could be improved by blending with polyesters such as PBS. Although combining these two polyesters benefits the new material, it would still be more expensive than conventional plastics, costing about three times more than LDPE (ROSENBOOM; LANGER; TRAVERSO, 2022).

Biodegradable materials composed of polyesters and starch are an alternative to make them economically competitive since starch is low-cost, abundant, biodegradable, and obtained from a renewable source (FAHRNGRUBER *et al.*, 2020). Starch is typically not used in raw form, as it is hydrophilic, making its mechanical properties sensitive to moisture content and challenging to process without plasticizing additives, in addition to the high degradation rate (YU; DEAN; LI, 2006). Therefore, starch needs to be plasticized to reduce intermolecular interactions and increase the processability of the blend (Liu *et al.*, 2015). Plasticizing occurs using heat, shear, and plasticizers such as glycerol, transforming starch into thermoplastic starch (TPS) (NAZRIN *et al.*, 2020). Furthermore, these polyesters have a high potential to form blends with TPS, but the production of high-quality materials is hampered by their low miscibility, caused by differences in viscosity and surface tension (LI *et al.*, 2013; SUCHAO-IN; KOOMBHONGSE; CHIRACHANCHAI, 2014). Polyesters are more hydrophobic and less polar than starch (BAI *et al.*, 2018), leading to phase separation and impairing the film's performance, which may require additives such as citric acid (ZHANG *et al.*, 2019).

Most studies focus on the production of PBAT/TPS materials (BRANDELERO; GROSSMANN; YAMASHITA, 2012; DA SILVA *et al.*, 2017; GARALDE *et al.*, 2019; NAYAK, 2010; WEI *et al.*, 2015) and PBS/TPS (AZIMAN *et al.*, 2021b; ZENG *et al.*, 2011), but only a few of them have investigated PBAT, PBS, and TPS blends. For instance, Wei et al. (2021) and Yap et al. (2020) developed ternary blends with melted and compression-molded techniques. Beluci *et al.* (2023) developed PBAT, PBS, and TPS extruded films, but they focused only on studying the mechanical and chemical properties of the material.

This work aimed to develop blends with a high concentration of TPS blended with PBS and PBAT, citric acid as a compatibilizing agent, and glycerol as a plasticizer, using a conventional industrial extruder. The films were investigated for their macroscopic appearance, blow-up ratio, water vapor barrier, solubility rate, water sorption isotherms, and thermogravimetric analysis.

2. Material and Methods

2.1. Material

Biodegradable films were produced using native commercial corn starch (Apti, Brazil), poly(butylene succinate) (PBS) (TK-BIO® PBS, Tiken, China), poly (butylene adipate-co-terephthalate) (PBAT) (TK-BIO® PBAT, Tiken, China), glycerol (Dinâmica, Brazil), and citric acid (Dinâmica, Brazil).

2.2. Manufacture of the Biodegradable Materials

The films were prepared with starch, PBS, PBAT, citric acid as a compatibilizing agent, and glycerol as a plasticizer, according to Table 1. The polyesters/TPS ratio and the amount of citric acid were defined based on the work of Beluci et al. (2023).

Table 1. Formulation of the biodegradable films.

Formulation	Concentration (g 100 g ⁻¹)				
	PBS	PBAT	Starch	Glycerol	Citric Acid
PBS ₁₀ PBAT ₂₀	10.0	20.0	49.0	21.0	0.0
PBS ₁₅ PBAT ₁₅	15.0	15.0	49.0	21.0	0.0
PBS ₂₀ PBAT ₁₀	20.0	10.0	49.0	21.0	0.0
PBS ₃₀ PBAT ₀	30.0	0.0	49.0	21.0	0.0
PBS ₀ PBAT ₃₀ CA	0.0	30.0	48.9	21.0	0.1
PBS ₁₀ PBAT ₂₀ CA	10.0	20.0	48.9	21.0	0.1
PBS ₁₅ PBAT ₁₅ CA	15.0	15.0	48.9	21.0	0.1
PBS ₂₀ PBAT ₁₀ CA	20.0	10.0	48.9	21.0	0.1
PBS ₃₀ PBAT ₀ CA	30.0	0.0	48.9	21.0	0.1

Film production was carried out in two stages using a single-screw extruder (model EL-25, BGM, Brazil) with a screw diameter of 25 mm and a screw length of 700 mm. The materials were weighted, mixed, extruded and pelletized in the first stage following the temperature profile of 90/120/120/115 °C. The screw speed was maintained at 40 rpm, and a matrix with two holes of 2 mm in diameter was used to produce the cylindrical strands that were then cut in a granulator to form pellets. The second step consisted in using the pellets to make films. The temperature profile was 90/120/120/130 °C in the four first heat zones and 135 °C in the 50-mm film-blowing die; the screw speed was kept at 40 rpm. The extruder has been adjusted to produce films with 100 – 150 µm of thicknesses. The materials were kept in opaque sealed packages until the characterizations were performed.

2.3. Characterization of Biodegradable Blends

2.3.1. Blow-up Ratio

The blow-up ratio (BUR, %) represents film elongation capacity and is calculated by the ratio between the film diameter (d_{film}) and die diameter (d_{die}), according to equation (1):

$$BUR(\%) = \frac{d_{film}}{d_{die}} \times 100 \quad (1)$$

The result was determined as the arithmetic mean of five random measures across the material.

2.3.2. Water Vapor Permeability

Water vapor permeability (WVP) was determined gravimetrically according to the ASTM E96/E96M-16 methodology with modifications. Measurements were performed in triplicate at a relative humidity (RH) gradient ranging from 33 to 64% ($\pm 3\%$) using saturated magnesium chloride and sodium nitrite solutions, respectively. This gradient covers the range of relative humidity that food products typically attain. Before analysis, the specimens were previously conditioned at 25 °C for 48 h at 53 \pm 3% RH, using a saturated magnesium nitrate solution. All measurements were performed in triplicate.

2.3.3. Soluble Ratio

Analysis was performed according to ASTM D570 (98/2018) standard method with modifications. Prior, the samples (25 mm x 38 mm) were dried at 50 °C in an oven (model TE-394/2 – Tecnal) for 24 h, before being weighed (w_0). Subsequently, they were immersed in distilled water (1:100 sample/water - w/w) and placed in an incubator (model TE 371/Tecnal) at 25°C for 24h. Then, the samples were dried at 50 °C for 24 h before being weighed again (w_1). The soluble ratio (SR) was obtained by equation (2) (ZENG *et al.*, 2011). All measurements were performed in triplicate.

$$\text{Soluble ratio } (\%) = \left[\frac{w_0 - w_1}{w_0} \right] \times 100 \quad (2)$$

2.3.4. Water Sorption Isotherms

The moisture sorption isotherms of the films were determined by the dynamic method. The films were cut into small pieces and conditioned at 0% RH with CaCl₂. The samples were analyzed in an isotherm generator (Aquasorp – Deagon Devices, USA), varying the water activity from 0.25 to 0.75, with a flow rate of 300

ml/min and a temperature of 25 °C, and the experimental data were modeled by the GAB model (Guggenheim-Anderson-de Boer) (equation 3).

$$X_w = \frac{C.k.m_0.a_w}{[(1 - k.a_w).(1 - k.a_w + C.k.a_w)]} \quad (3)$$

where X_w is equilibrium moisture (g H₂O/g dry matter), C is a Guggenheim constant (which represents the sorption heat of the first layer), k is a factor correcting properties of the multilayer molecules corresponding to the bulk liquid, m_0 is water content in the monolayer (g H₂O/g dry matter) and a_w is water activity (relative humidity/100). The GAB model parameters were determined by non-linear regression using Statistica 7.0 software (Statsoft Inc., Tulsa, OK, USA, 2004).

2.3.5. Thermogravimetric Analysis

The thermal stability of the films was determined by a thermogravimetric analyzer (model TGA-50 - Shimadzu, Japan). The samples were stored for 7 days in a desiccator with anhydrous CaCl₂ and then were heated from 25 to 500°C, with a heating rate of 10 °C min⁻¹, using an argon atmosphere (50 ml min⁻¹). The thermal stability of the films was evaluated based on the thermogravimetric (TG) curves and the respective derivative curves (DTG).

2.3.6. Statistical Analysis

The data were analyzed using STATISTICA 7.0 software (Statsoft Inc., Tulsa, USA, 2004), with analysis of variance (ANOVA) and the Tukey test at a 5% significance level. Each sample pair of similar composition, with and without citric acid, were compared by the t-test at a 5% significance level ($p < 0.05$).

3. Results and Discussion

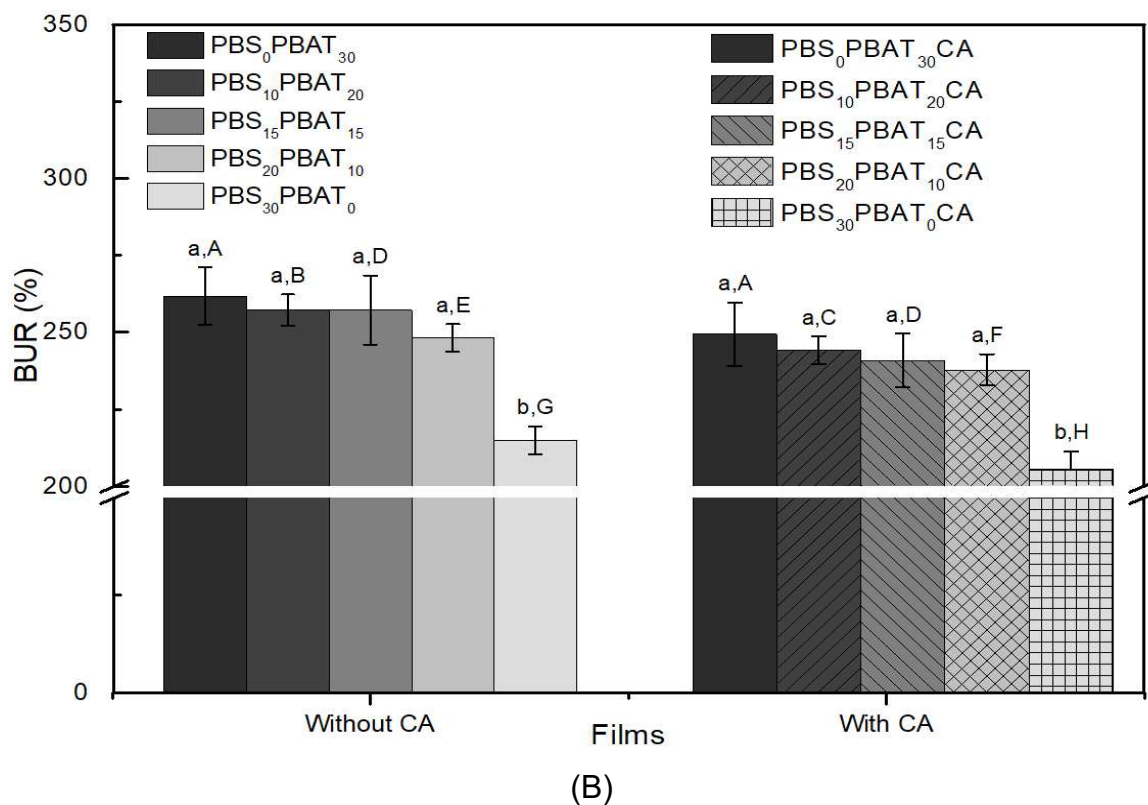
3.1. General Characteristics and Blow-up Ratio

Regarding the macroscopic appearance of the films, all samples were uniform (without visible cracks or bubbles), easy to handle, flexible, with a yellowish color, and soft to the touch. Figure 1 shows the extruder during film production (A) and the blow-up ratio (B) values.

Figure 1. Film production (A) and blow-up ratio (B).



(A)



Different lowercase letters in the same group of films (with and without CA) indicate a significant difference between the samples (Tukey's test, $p \leq 0.05$). Different capital letters between the two groups of samples represent a significant difference between each pair of samples (t-test, $p \leq 0.05$).

During extrusion, the airflow rate within the tubular film was kept constant so that the material had an average thickness of 100 to 150 μm . There was a significant difference between the BUR of the film containing 30 wt% PBS and the others. PBS₃₀PBAT₀ and PBS₃₀PBAT₀CA samples presented the lowest BUR (214.9% and 205.5%, respectively). This behavior occurred because the elasticity of PBAT is higher than that of PBS. Therefore, less elastic materials have a lower BUR rate.

Each pair of samples (films with and without citric acid-CA) was compared by t-test to verify the CA influence on BUR. Films CA-free had BUR from 214.9 to 261.8%, while films with CA had BUR from 205.5 to 249.3%. The samples PBS₁₀PBAT₂₀, PBS₂₀PBAT₁₀, PBS₃₀PBAT₀, and their counterparts with citric acid differed significantly on BUR when adding citric acid. Probably the CA had cross-linked with the starch, increasing the stiffness of the materials (SORNSUMDAENG; SEEHARAJ; PRACHAYAWARAKORN, 2021; XU *et al.*, 2015), which may have caused the lower BUR of these materials.

The BUR values obtained in this work were lower than those reported by Garcia et al. (2014) for films produced with PBAT/TPS/CA, which had a BUR of 530%, probably because of the higher PBAT content (40 wt%) and the absence of PBS.

3.2. Barrier Properties and Solubility

The films' water vapor permeability (WVP) and soluble ratio (SR) are in Table 2.

Table 2. WVP and SR properties of the films.

WVP ($\times 10^6$) ($\text{g m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$)			
PBS ₀ PBAT ₃₀	3.60 ^{a,A} \pm 0.54	PBS ₀ PBAT ₃₀ CA	2.98 ^{a,A} \pm 0.49
PBS ₁₀ PBAT ₂₀	2.52 ^{b,B} \pm 0.13	PBS ₁₀ PBAT ₂₀ CA	2.49 ^{a,B} \pm 0.43
PBS ₁₅ PBAT ₁₅	3.37 ^{a,C} \pm 0.05	PBS ₁₅ PBAT ₁₅ CA	2.52 ^{a,D} \pm 0.08
PBS ₂₀ PBAT ₁₀	3.44 ^{a,E} \pm 0.06	PBS ₂₀ PBAT ₁₀ CA	2.59 ^{a,F} \pm 0.31
PBS ₃₀ PBAT ₀	3.55 ^{a,G} \pm 0.61	PBS ₃₀ PBAT ₀ CA	3.72 ^{a,G} \pm 0.33
SR (%)			
PBS ₀ PBAT ₃₀	19.19 ^{a,A} \pm 0.10	PBS ₀ PBAT ₃₀ CA	19.31 ^{a,A} \pm 0.09
PBS ₁₀ PBAT ₂₀	19.92 ^{a,B} \pm 0.47	PBS ₁₀ PBAT ₂₀ CA	19.62 ^{a,B} \pm 0.37
PBS ₁₅ PBAT ₁₅	19.48 ^{a,C} \pm 0.95	PBS ₁₅ PBAT ₁₅ CA	19.98 ^{a,C} \pm 0.33
PBS ₂₀ PBAT ₁₀	19.38 ^{a,D} \pm 0.69	PBS ₂₀ PBAT ₁₀ CA	20.10 ^{a,D} \pm 0.04
PBS ₃₀ PBAT ₀	19.01 ^{a,E} \pm 0.13	PBS ₃₀ PBAT ₀ CA	20.07 ^{a,E} \pm 0.52

Different lowercase letters in the same group of films (with and without CA) indicate a significant difference between the samples (Tukey's test, $p \leq 0.05$). Different capital letters between the two groups of samples represent a significant difference between each pair of samples (t-test, $p \leq 0.05$).

WVP ranged from 2.52 to $3.60 \times 10^{-6} \text{ g m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$ for films without acid citric (CA) and from 2.49 to $3.72 \times 10^{-6} \text{ g m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$ for films with CA. The PBS₁₀PBAT₂₀ film differed significantly from the other samples in the group without CA, its WVP being the lowest among the materials. This behavior indicates that the film with 10 wt% PBS and 20 wt% PBAT provides the least sensitive film to water vapor. As for the films with CA, no significant differences were verified, indicating that the proportions of PBS and PBAT did not influence the WVP, probably due to the high TPS content (70 %wt) and the presence of CA since it reduced the WVP of almost all

samples compared to their counterparts without the compatibilizer. Even so, films with high starch content generally are poor water vapor barriers due to their hydrophilic nature. Using glycerol as a plasticizer increases the polymeric matrix's affinity with water, contributing to the high WVP values (OLIVATO *et al.*, 2013).

According to Lumdubwong (2019), the WVP of plasticized starch-based films varies from 3.38×10^{-7} to $3.02 \times 10^{-3} \text{ g m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$, which is consistent with the results in this work. Also, similar values were reported by other researchers. Brandelero *et al.* (2011) developed biodegradable extruded film with high TPS content (65/35 TPS/PBAT %wt) by two methods and reported WVP from 6.0 to $49.2 \times 10^{-6} \text{ g m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$. Olivato *et al.* (2013) reported WVP from 55.6 to $76.0 \times 10^{-6} \text{ g m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$ for films formulated with PBAT and TPS (70/30 wt%). Fahrngruber *et al.* (2020) developed an extruded film based on TPS and PBS (50/50 wt%) with WVP of $5.7 \times 10^{-6} \text{ g m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$.

Films with CA had lower WVP than those without CA (although statistically, only the PBS₁₅PBAT₁₅CA and PBS₂₀PBAT₁₀CA samples differ from their non-CA counterparts). The WVP of the films PBS₁₅PBAT₁₅CA and PBS₂₀PBAT₁₀CA was 25.2% and 24.7% lower than the WVP of the PBS₁₅PBAT₁₅ and PBS₂₀PBAT₁₀, respectively. The esterification reaction grafts ester groups onto the starch chain, which decreases the WVP (SELIGRA *et al.*, 2016), as these partially hydrophobic groups make it difficult for water vapor molecules to diffuse through the polymeric matrix. This behavior of reducing WVP when citric acid is added to blends has also been reported by Garcia *et al.* (2014) in films based on TPS/PBAT (64.4/35.6 wt%) with and without citric acid (5.81×10^{-6} and $3.47 \times 10^{-6} \text{ g m}^{-1} \text{ day}^{-1} \text{ Pa}^{-1}$, respectively).

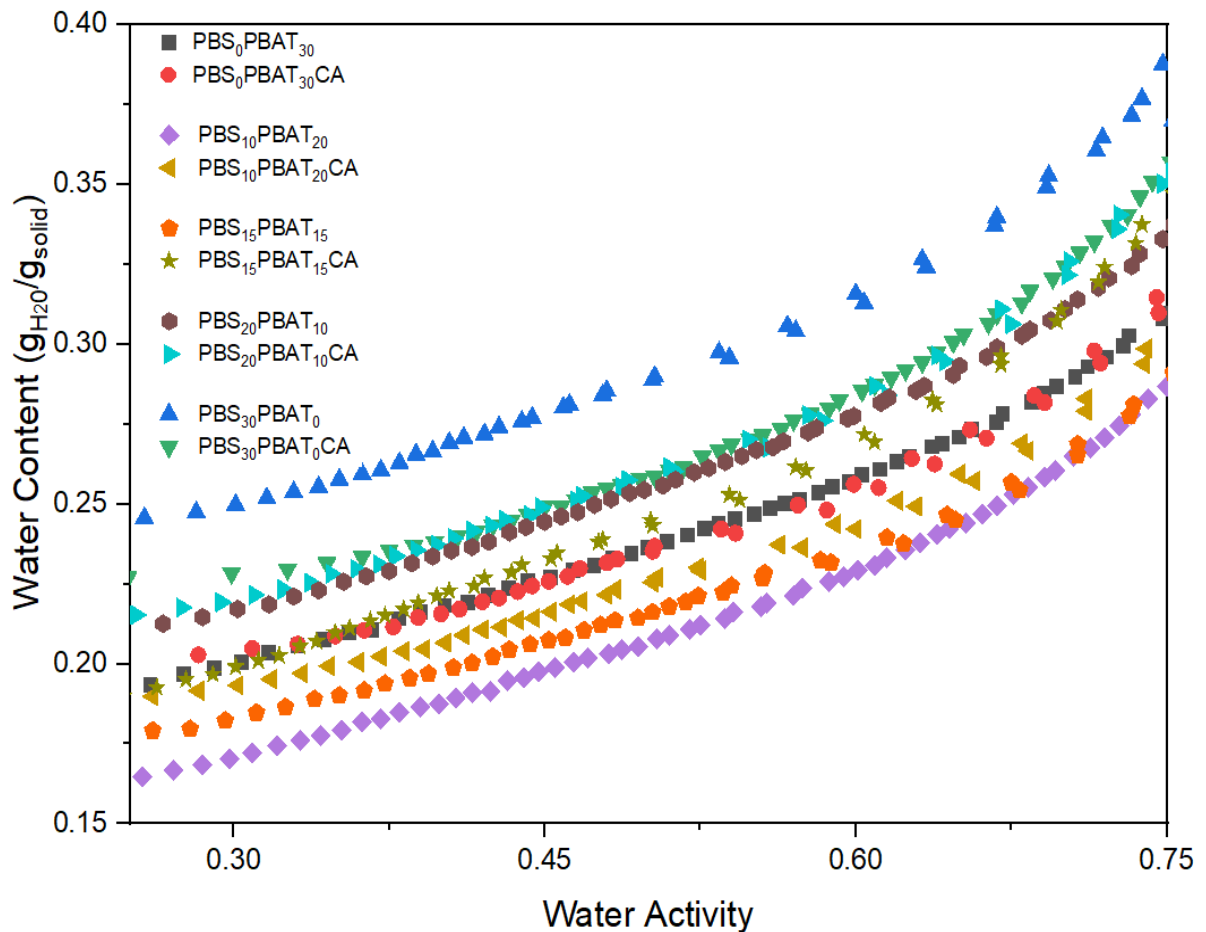
The soluble ratio (SR) ranged from 19.01 to 19.92% for films without CA and 19.31 to 20.10% for films with CA. In both cases, there were no significant differences between the samples of each group, which indicates that CA did not influence the SR of these materials. PBS and PBAT are hydrophobic and insoluble in water (KHATSEE *et al.*, 2018), then the high content of TPS is the leading cause of the pronounced solubility of these materials (BRANDELERO; GROSSMANN; YAMASHITA, 2012). The glycerol modifies the three-dimensional molecular organization of starch, reducing the intermolecular attraction forces and increasing the system's free volume and molecular mobility, which leads to a less dense polymer, facilitating the permeation of water in its structure and its solubilization (BILCK *et al.*,

2015; SOTHORNVIT; KROCHTA, 2000). These behaviors are consistent with similar biodegradable blends of TPS/PBS (ZENG *et al.*, 2011) and TPS/PBAT (MÜCKE *et al.*, 2021). The t-test demonstrated no significant differences between each pair of samples, indicating that citric acid did not influence the solubility parameter of these materials.

3.3. Water Sorption Isotherms Analysis

Figure 2 shows the water sorption isotherms (WSI) curves of typical hydrophilic materials, such as films with a high starch content, as reported by Bilck *et al.* (2021), Olivato *et al.* (2011), and Santos *et al.* (2014).

Figure 2. Experimental data of water sorption isotherms.



The equilibrium moisture content of the films increases gradually with the relative humidity, and this increased proportion became more pronounced from water activity of 0.5, indicating that these materials are susceptible to moisture. According to

Santos et al. (2014), films with less water uptake indicate a more stable polymer matrix; thus, the most stable formulation is PBS₁₀PBAT₂₀ (as also confirmed by WVP analysis), while the PBS₃₀PBAT₀ sample is the least stable. Film stability is intricately linked to lower WVP and SR values. Although differences were observed between the materials in the sorption isotherm patterns, it was not possible to relate them to SR since there was no statistical difference in this analysis. The parameters adjusted to the GAB model can be seen in Table 3.

Table 3. GAB model parameters of the isotherms.

Samples	m_o (g _{H2O} /g _{solid})	K	C (x 10 ⁴)	R ²
PBS ₀ PBAT ₃₀	0.1628	0.6208	2.048	0.9982
PBS ₀ PBAT ₃₀ CA	0.1621	0.6285	2.073	0.9760
PBS ₁₀ PBAT ₂₀	0.1560	0.6222	2.322	0.9808
PBS ₁₀ PBAT ₂₀ CA	0.1354	0.6922	2.130	0.9968
PBS ₁₅ PBAT ₁₅	0.1578	0.7061	2.193	0.9939
PBS ₁₅ PBAT ₁₅ CA	0.1433	0.6885	2.102	0.9630
PBS ₂₀ PBAT ₁₀	0.1759	0.6204	2.082	0.9965
PBS ₂₀ PBAT ₁₀ CA	0.1758	0.6494	2.102	0.9889
PBS ₃₀ PBAT ₀	0.2017	0.6139	2.155	0.9894
PBS ₃₀ PBAT ₀ CA	0.1730	0.6692	2.059	0.9888

The GAB model is considered the most versatile available in the literature for sorption isotherms of food products for water activities up to 0.85, which include starch-based films (BARRETTO *et al.*, 2019; BASHA *et al.*, 2021). This model represents experimental data with a correction coefficient greater than 0.97 for all films.

Monolayer moisture content (m_o) is essential for polymeric materials' microbiological, physical, and chemical stability and is related to their hygroscopicity and hydrophilicity, and it indicates the maximum amount of water absorbed in a single layer per gram of dry film (DE OLIVEIRA PIZZOLI *et al.*, 2017). The samples with pure polyesters and TPS present m_o of 0.2017 g_{H2O}/g_{solid} for PBS₃₀PBAT₀ and 0.1628 g_{H2O}/g_{solid} for PBS₀PBAT₃₀, which could indicate that the dispersion of PBAT in the TPS was less homogeneous than in the blend of PBS/TPS, allowing more starch to be available to bind the water. Furthermore, after the inclusion of citric acid (CA), there

was a decrease in the m_0 value of 0.1730 $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{solid}}$ for $\text{PBS}_{30}\text{PBAT}_0\text{CA}$ and 0.1621 $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{solid}}$ for $\text{PBS}_0\text{PBAT}_{30}\text{CA}$, indicating that CA improved the dispersion of pure polymers in the starch matrix. This same behavior was observed for all samples.

The other blends had m_0 values unrelated to the proportions of the polymers. These differences in monolayer values may be related to the availability of starch-binding sites. In each group, the samples with the lowest values of m_0 were $\text{PBS}_{10}\text{PBAT}_{20}$ (0.1560 $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{solid}}$) and $\text{PBS}_{10}\text{PBAT}_{20}\text{CA}$ (0.1354 $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{solid}}$), indicating a lower water sorption capacity, representing more stable materials (in agreement with the WVP analysis). Possibly, this ratio of PBS/PBAT allowed a more homogeneous distribution in the starch matrix when compared to single polymers distributed in TPS. The high amount of TPS in the materials is responsible for the water absorbed on the monolayer. The results of this work were superior to other authors who produced extruded films with TPS and PBAT (BRANDELERO *et al.*, 2011; SHIRAI *et al.*, 2013). The results of TPS/PBS films and tertiary blends were not compared with other authors because this study is unprecedented.

Parameter k is related to the sorption heat of water vapor in the multilayer and provides a measure of interactions between molecules in the multilayer with the adsorbent. The blends produced with the individual polymers ($\text{PBS}_0\text{PBAT}_{30}$ and $\text{PBS}_{30}\text{PBAT}_0$) and the $\text{PBS}_{20}\text{PBAT}_{10}$ sample had the lowest k values (0.6208, 0.6139, and 0.6204, respectively); all other formulations had higher k values. The closer this parameter is to 1, the characteristics of the water molecules are closer to those of pure water; for instance, the lower the difference between the energy associated with the sorption heat of the multilayer and the condensing heat of pure water (BAPTESTINI *et al.*, 2017). According to Enrione *et al.* (2007), the more sorbed molecules are structured in multilayers, the smaller the value of k . Films containing CA had higher k values than films without this compatibilizer, except for the $\text{PBS}_{15}\text{PBAT}_{15}\text{CA}$ sample (0.6885), indicating that this sample has more water vapor sorbed in the multilayers compared to a similar sample without CA ($\text{PBS}_{15}\text{PBAT}_{15}$ – $k = 0.7061$). Even so, in this work, the k values appear independent of the films' composition, as Mali *et al.* (2005) reported.

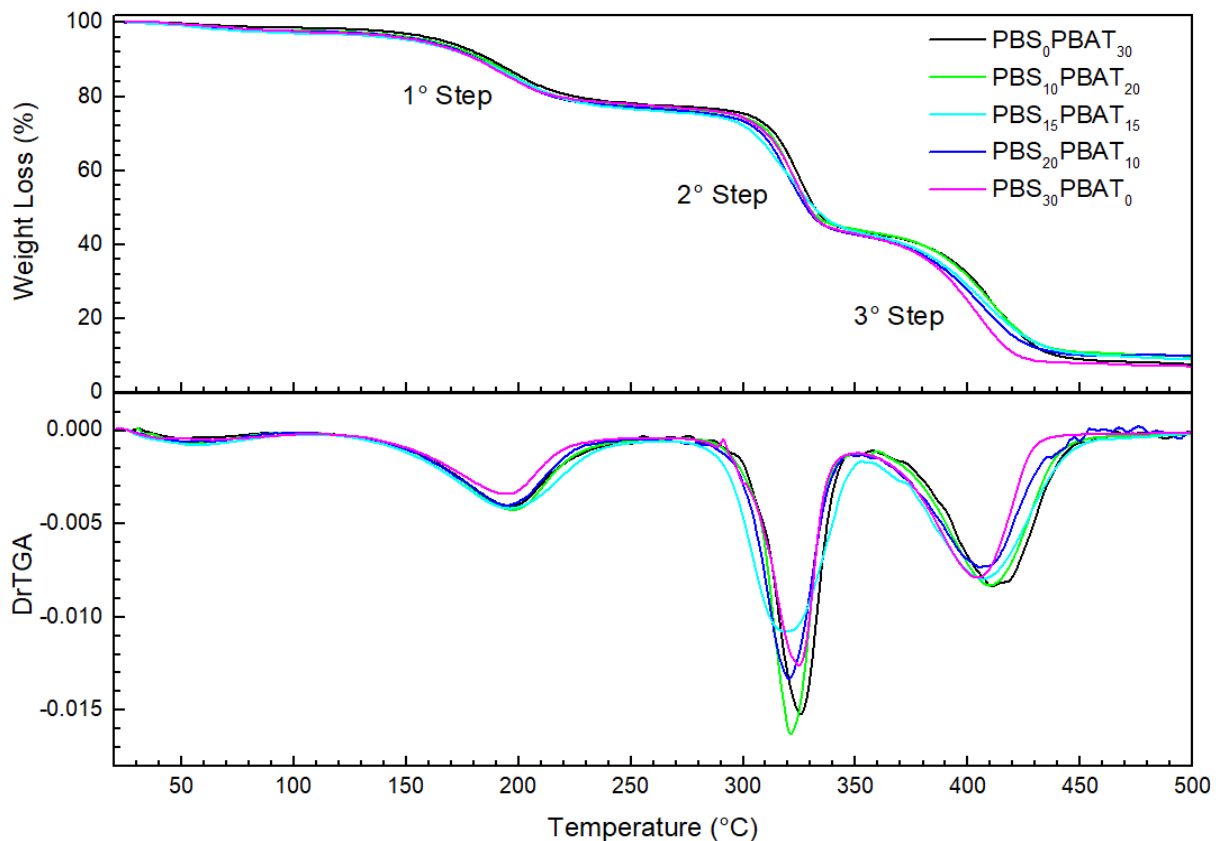
Parameter C is associated with the difference in chemical potentials between the upper and monolayer layers. If constant C is larger than 2, the GAB model should yield a sigmoidal shape characteristic of hydrophilic materials (DE OLIVEIRA ROMERA *et al.*, 2012) with the point of inflection (BASHA *et al.*, 2021). The sigmoidal

shape could not be seen in Figure 2, as the equipment does not work appropriately for extremes of water activity. The higher the C value, the higher the binding energy of the water molecules in the monolayer with the sorption sites on the film surface (BAPTESTINI *et al.*, 2017). This parameter has the same order of magnitude for all samples, which indicates that water is strongly absorbed in the active sites of the polymer matrix (SABERI *et al.*, 2016), regardless of its composition.

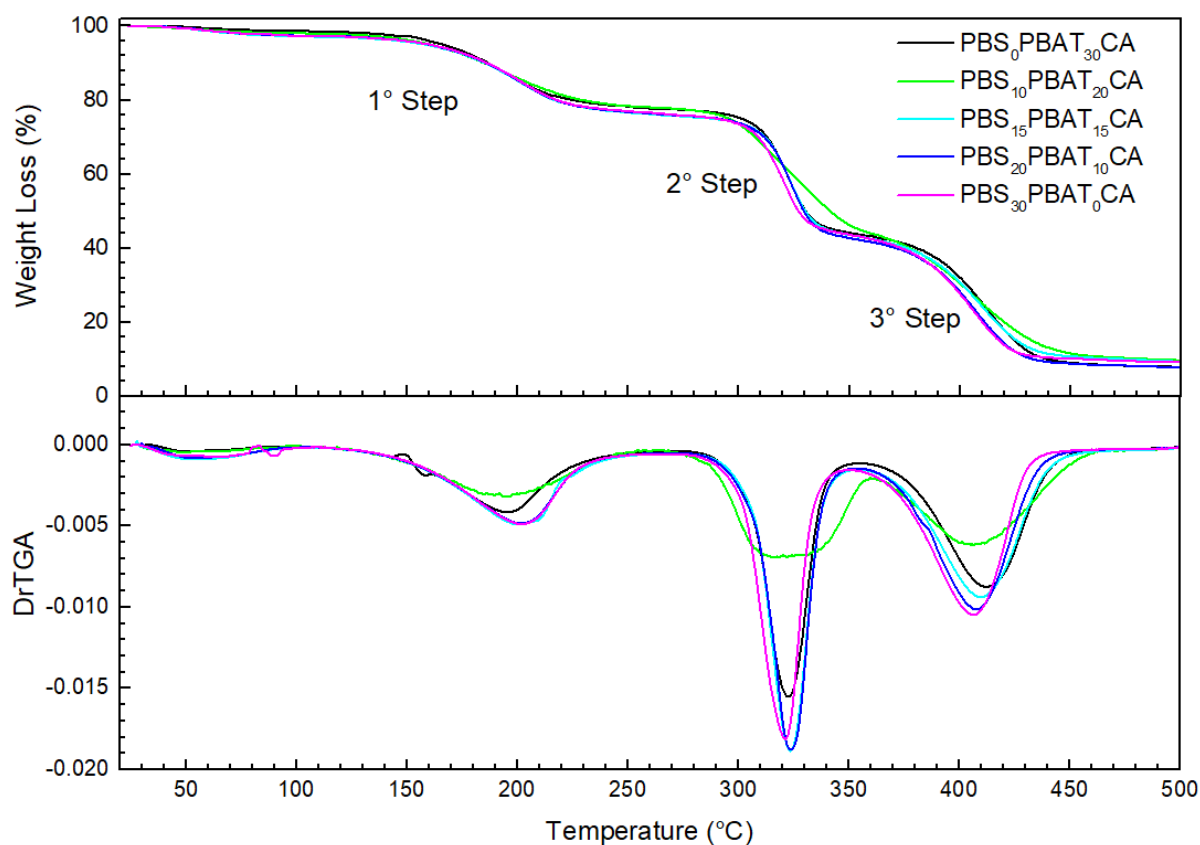
3.4. Thermal Stability

Thermogravimetry (TGA) and its derivatives (DrTGA) allow evaluation of the thermal stability of blends, showing at which temperature the degradation of its constituents occurs and the loss of mass related to thermal events. Figure 3 illustrates the films' thermograms (TGA and DrTGA), and Table 4 depicts the thermal stability data of the blends.

Figure 3. Thermogravimetric analysis of the blends – (A) samples without citric acid and (B) with citric acid.



(A)



(B)

Thermograms showed three main thermal events that can be observed for all samples. The first event relates to the vaporization of residual water bound to the polymer matrix and glycerol volatilization (ESMAEILI; PIRCHERAGHI; BAGHERI, 2017), occurring between 138-240 °C and 133-247 °C for the blends without and with CA, respectively. The water loss starts at 25 °C and goes until the beginning of the first crucial thermal event, so there is a slight mass loss in this range. The second event relates to starch degradation (TARIQUE; SAPUAN; KHALINA, 2021), occurring between 288-349°C and 285-357 °C for blends without and with CA, respectively. The last event is related to the degradation of PBS, PBAT (DE MATOS COSTA *et al.*, 2020; LEAL *et al.*, 2019), and carbonaceous materials from the previous event (AZEVEDO *et al.*, 2017) and occurred between 358-450 °C for blends without CA and 362-458 °C for blends with CA. Blends made from the combination of these two polymers had only one degradation peak in this range, as both have similar degradation temperatures (PBS at 405 °C and PBAT at 413 °C) (MUTHURAJ; MISRA; MOHANTY, 2014).

The blends had an intermediate degradation profile characteristic of the combination of their constituents: TPS, PBS, and PBAT. Despite the high content of TPS in the samples, they presented a maximum decomposition temperature close to PBAT and PBS pure polymers, indicating materials with good thermal stability.

Table 4. Thermogravimetric parameters of the films.

Sample	T _{10%} (°C)	Thermic Event	Range of decomposition temperature (T _{onset} - T _{endset})	Maximum weight loss (%)	Peak decomposition temperature (°C)	Residual mass (500°C)
PBS ₀ PBAT ₃₀	187	1°	143-238	18.7	196	7.7
		2°	298-346	31.4	325	
		3°	371-449	32.3	415	
PBS ₁₀ PBAT ₂₀	185	1°	145-229	18.6	198	9.7
		2°	301-340	28.8	322	
		3°	368-443	30.7	411	
PBS ₁₅ PBAT ₁₅	180	1°	138-240	19.0	197	9.0
		2°	288-349	31.0	321	
		3°	361-450	31.7	407	
PBS ₂₀ PBAT ₁₀	182	1°	146-228	17.8	196	9.9
		2°	298-341	26.0	322	
		3°	358-437	30.6	410	
PBS ₃₀ PBAT ₀	182	1°	140-228	17.5	194	7.1
		2°	297-341	30.9	325	
		3°	365-433	32.3	405	
PBS ₀ PBAT ₃₀ CA	185	1°	138-234	18.6	195	7.8
		2°	299-340	30.9	323	
		3°	373-447	32.4	413	
PBS ₁₀ PBAT ₂₀ CA	185	1°	133-247	18.8	195	9.7
		2°	285-357	32.3	324	
		3°	362-458	33.0	405	
PBS ₁₅ PBAT ₁₅ CA	185	1°	154-233	17.6	202	9.5
		2°	303-340	28.1	324	
		3°	367-442	30.3	410	
PBS ₂₀ PBAT ₁₀ CA	185	1°	147-235	18.4	201	8.0
		2°	300-341	29.9	324	
		3°	368-439	31.2	411	
PBS ₃₀ PBAT ₀ CA	186	1°	150-234	18.1	200	9.2
		2°	298-337	28.4	322	
		3°	362-434	31.4	408	

$T_{10\%}$ represents the temperature at which the material lost 10% of its initial mass. This measure can evaluate at which temperature the material's thermal degradation started, and, together with the degradation start temperature (T_{onset}) of each event, it is possible to verify which blend is more thermal stable. Samples $\text{PBS}_0\text{PBAT}_{30}$ and $\text{PBS}_0\text{PBAT}_{30}\text{CA}$ were slightly more stable than the others, as they presented high values of $T_{10\%}$ and T_{onset} considering the second and third cycles. The results suggest that films produced only with PBAT are slightly more stable than those produced only with PBS, as reported by De Matos Costa et al. (2020) and Muthuraj et al. (2014).

De Campos et al. (2019), Garcia et al. (2014), and Mücke et al. (2021) reported that the addition of CA increases the thermal stability of starch-based blends due to the cross-linking that this carbohydrate undergoes. In this study, CA did not have the same effect, probably because of the low proportion used (0.1%). CA also seems not to have influenced the mass loss in each thermal event, approximately 18%, 30%, and 31% for stages 1, 2, and 3, respectively. Also, the values of $T_{10\%}$ for samples with acid did not vary much, being between 185-186°C. Probably, the CA improved the compatibility between the blend components, causing the initial mass loss to be concentrated in a narrower temperature range. CA did not influence the residual mass at 500 °C, which ranged from 7.1 to 9.9 for the films CA-free and 7.8 to 9.7 for the films with CA.

4. Conclusions

Biodegradable films produced with high starch content and blended with PBS and PBAT presented a water vapor barrier and thermal properties more suitable for food packaging than those containing starch and only one of the polyesters. The citric acid at a low concentration (0.1%) did not notably improve the properties of the films, indicating new research possibilities testing higher concentrations and other compatibilizers. This research indicates that it is possible to develop low-cost biodegradable packaging that can be produced on a large scale using conventional industrial equipment. This could represent a solution to the growing demand for more sustainable and environmentally friendly packaging, which could mitigate the environmental impact of traditional packaging.

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CAPÍTULO VI: Conclusões, Produção Científica e Sugestão para Pesquisas

1. Conclusões Gerais

Nos últimos anos houve um aumento expressivo na atenção dada aos polímeros biodegradáveis. Isso se deve à sua proposta sustentável, que está em consonância com a busca por materiais mais amigáveis ao meio ambiente e em conformidade com a legislação ambiental cada vez mais rigorosa. Além disso, espera-se que, na próxima década, o mercado de biopolímeros se expanda mais rapidamente do que o mercado tradicional de plásticos.

Neste sentido, o presente estudo desenvolveu filmes poliméricos a partir de blendas ternárias de ATP, PBS e PBAT, com e sem ácido cítrico como compatibilizante, via extrusão sopro em balão e investigou o efeito da proporção dos constituintes nas propriedades dos materiais formados.

De maneira geral, as blendas ternárias compostas por ATP e diferentes teores de PBS e PBAT apresentaram propriedades físicas, químicas, mecânicas, térmicas e de barreira mais adequadas para filmes do que as binárias contendo ATP e apenas um dos poliésteres. Cada componente forneceu pelo menos um recurso de interesse aos filmes, por exemplo: o PBAT ofereceu ductilidade, o PBS contribuiu com resistência e o ATP proporcionou maior biodegradabilidade e redução de custo. O ácido cítrico foi utilizado como agente compatibilizante, mas sua natureza multicarboxílica permitiu que ele atuasse como plastificante, reticulante ou hidrolítico, dependendo das interações e reações com outros constituintes das blendas. Este ácido teve um efeito positivo para a maioria das propriedades avaliadas. Por exemplo, aumentou a resistência à tração e o alongamento na ruptura de todos os filmes e diminuiu a permeabilidade ao vapor de água de alguns filmes. Para a taxa de solubilidade e cor dos materiais, o ácido cítrico não apresentou diferenças significativas nas respostas. Além disso, a estabilidade térmica das blendas não foi aumentada pelo uso deste composto, possivelmente devido ao baixo teor utilizado (0,1%).

Considerando o conjunto de propriedades avaliadas, o filme que apresentou melhores resultados, especialmente em termos de propriedades mecânicas e de barreira, foi aquele composto por PBS/PBAT/TPS (20/10/70% em

massa) com adição de ácido cítrico. Apesar da sensibilidade a umidade, estes filmes poderiam ser boas alternativas para formulação de embalagens de alimentos.

Em síntese, os resultados deste estudo oferecem orientação e direcionamentos para o desenvolvimento de embalagens biodegradáveis acessíveis, que têm potencial para serem produzidas em grande escala com o uso de equipamentos industriais convencionais.

2. Produção Científica

Na busca dos objetivos estipulados, esta pesquisa visa contribuir cientificamente para promover o conhecimento dos processos de produção de filmes biodegradáveis a base de ATP, PBS e PBAT via extrusão sopro em balão, usando a mesma tecnologia empregada para produção de filmes convencionais de polietileno ou polipropileno.

O capítulo IV foi publicado na forma de artigo científico (BELUCI, N.C.L. *et al. Reactive biodegradable extruded blends of thermoplastic starch and polyesters. Carbohydrate Polymer Technologies and Applications*, v. 5, p. 100274, 2023) e o capítulo V será submetido para publicação em revista da área.

3. Sugestões para Pesquisas Futuras

Com base em todo o trabalho realizado, as seguintes sugestões são apresentadas para futuras pesquisas:

- Investigar o comportamento de blendas com teores mais elevados de ATP (superiores a 70% m/m), combinadas com os poliésteres PBS e PBAT.
- Estudar os efeitos da utilização de outros compatibilizantes, além do ácido cítrico, nas características dos filmes produzidos.
- Analisar o efeito da adição de fibras nas propriedades dos materiais.
- Investigar o efeito da adição de celulose e seus derivados nas propriedades das blendas, especialmente nas características de barreira.
- Avaliar a biodegradabilidade dos materiais desenvolvidos.
- Aplicar os materiais como embalagens flexíveis para alimentos.
- Testar a utilização dessas blendas na produção de produtos injetáveis ou prensados.