SAMUEL CAMILO DA SILVA

# DESENVOLVIMENTO DE MATERIAIS BIODEGRADÁVEIS CONTENDO CASCA DE AVEIA E POLPA PELETIZADA CÍTRICA PRODUZIDOS POR EXTRUSÃO E INJEÇÃO TERMOPLÁSTICA

Londrina
2025

**Centro de Ciências Agrárias**

**Depto. De Ciência e Tecnologia de Alimentos**

**Programa de Pós-Graduação em Ciência de Alimentos**

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Tese apresentada ao Programa de Pós-Graduação em Ciência de Alimentos, nível Doutorado, da Universidade Estadual de Londrina, como requisito parcial à obtenção do título de Doutor em Ciência de Alimentos.

Orientador: Prof. Dr. Fábio Yamashita.

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Silva, Samuel Camilo da Silva.
DESENVOLVIMENTO DE MATERIAIS BIODEGRADÁVEIS CONTENDO CASCA DE AVEIA E POLPA PELETIZADA CÍTRICA PRODUZIDAS POR EXTRUSÃO E INJEÇÃO TERMOPLÁSTICA / Samuel Camilo da Silva Silva. - Londrina, 2025.
134 f.

Orientador: Prof. Dr. Fabio Yamashita Yamashita.
Tese (Doutorado em Ciência de Alimentos) - Universidade Estadual de Londrina, Centro de Ciências Agrárias, Programa de Pós-Graduação em Ciência de Alimentos, 2025.
Inclui bibliografia.

1. polibutileno succinato - Tese. 2. amido - Tese. 3. biodegradação - Tese. I. Yamashita, Prof. Dr. Fabio Yamashita. II. Universidade Estadual de Londrina. Centro de Ciências Agrárias. Programa de Pós-Graduação em Ciência de Alimentos. III. Título.

CDU 641.1

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Londrina, 19 de setembro de 2025.

## AGRADECIMENTOS

Primeiramente, agradeço a Deus, cuja graça me alcançou e que me capacita diariamente.

Gostaria também de agradecer o Programa de Pós-Graduação de Ciência e Tecnologia de Alimentos da Universidade Estadual de Londrina pelo apoio financeiro e educacional.

À minha esposa, Sarah, pelo amor, apoio incondicional, paciência, carinho e por nunca poupar esforços para me motivar e fortalecer durante esta caminhada.

Ao meu orientador, Professor Fábio, pela amizade construída ao longo desses seis anos, pelo apoio constante, pelos ensinamentos, pela paciência, pelos conselhos valiosos e por ser um verdadeiro exemplo de orientador e amigo.

Aos meus pais, Kenya e Fernando, pelo acolhimento, pelo esforço incansável em garantir minha formação e por sempre investirem em minha vida.

Aos meus irmãos e melhores amigos, Matheus e Davi, pelo companheirismo e apoio.

Aos meus sogros, Keila e Maycon, e à minha cunhada Rebeca, pela presença, incentivo e cuidado.

Aos amigos que me acompanharam em diferentes etapas desta trajetória. Às amizades construídas na UEL, que tanto acrescentaram ao meu aprendizado e crescimento pessoal.

Por fim, a todos que, de alguma forma, contribuíram para a realização deste trabalho, deixo meus mais sinceros agradecimentos.

SILVA, Samuel Camilo. **Desenvolvimento de materiais biodegradáveis contendo casca de aveia e polpa peletizada cítrica produzidos por extrusão e injeção termoplástica.** 2025. 142 p. Tese de Doutorado (Doutorado em Ciência de Alimentos) – Universidade Estadual de Londrina, Londrina/PR, 2025.


## RESUMO

O uso de polímeros derivados de fontes fósseis é amplamente difundido em diversos setores, mas sua baixa biodegradabilidade resulta na geração de grandes volumes de resíduos. Nesse contexto, biopolímeros renováveis e biodegradáveis, como o poli(butileno succinato) (PBS), têm sido investigados como alternativas sustentáveis, embora ainda apresentem elevado custo e limitações de desempenho. A incorporação de fibras naturais (FN) provenientes de resíduos agroindustriais, como a polpa cítrica (PC) e a casca de aveia (CA), surge como estratégia para reduzir custos, aumentar a biodegradabilidade e agregar valor a subprodutos de baixo aproveitamento econômico. Neste estudo, foram produzidas blendas injetadas de PBS e amido, nas quais o amido foi progressivamente substituído por diferentes concentrações de PC e CA (0–56% m/m). Os resultados mostraram que o aumento da fração de FN reduziu a resistência à tração e o alongamento na ruptura, devido às interações interfaciais limitadas com o PBS. Por outro lado, observou-se redução significativa no encolhimento pós-injeção (de 1,56% para 0,70% na CA e 0,84% na PC), evidenciando efeito de preenchimento e melhora na estabilidade dimensional. As formulações com maiores teores de FN apresentaram menor densidade (1,28 g/cm³ para CA e 1,32 g/cm³ para PC), atribuída à ausência de amido, que favorece maior coesão na matriz. Ensaios de biodegradação em solo indicaram mineralização superior a 50% após 150 dias, atendendo aos critérios da OECD 301B. A PC apresentou degradação mais acelerada, provavelmente devido à presença de pectina e polissacarídeos solúveis que intensificam a atividade microbiana. Esses resultados demonstram o potencial de PC e CA como reforços naturais em blendas biodegradáveis, ampliando suas aplicações em materiais sustentáveis.



**Palavras-chave:** Polibutileno Succinato; amido; biodegradação; fibras naturais; subprodutos.

SILVA, Samuel Camilo. **Development of biodegradable materials containing oat hulls and pelletized citrus pulp produced by extrusion and thermoplastic injection**. 2025. 142 p. Doctoral Thesis (PhD in Food Science) – State University of Londrina, Londrina/PR, 2025.

## ABSTRACT

The use of polymers derived from fossil resources is widespread across multiple sectors, but their low biodegradability generates significant amounts of waste. In this context, renewable and biodegradable biopolymers, such as poly(butylene succinate) (PBS), have been investigated as sustainable alternatives, although they still present high costs and performance limitations. The incorporation of natural fibers (NF) from agro-industrial residues, such as citrus pulp (CP) and oat hulls (OH), emerges as a strategy to reduce costs, enhance biodegradability, and add value to low-utilization by-products. In this study, injection-molded PBS–starch blends were prepared, with starch progressively replaced by different concentrations of CP and OH (0–56% w/w). Results showed that increasing NF content decreased both tensile strength and elongation at break, due to limited interfacial interactions with PBS. Conversely, significant shrinkage reduction was observed after injection molding (from 1.56% to 0.70% for OH and 0.84% for CP), indicating a filler effect and improved dimensional stability. Formulations with higher NF contents exhibited lower densities (1.28 g/cm³ for OH and 1.32 g/cm³ for CP), attributed to the absence of starch, which promotes matrix cohesion. Soil biodegradation tests indicated mineralization above 50% after 150 days, meeting OECD 301B criteria. CP degraded more rapidly, likely due to the presence of pectin and soluble polysaccharides that enhance microbial activity. These results demonstrate the potential of CP and OH as natural reinforcements in biodegradable blends, expanding their applications in sustainable materials.

**Keywords:** Poly(butylene succinate); starch; biodegradation; natural fibers; products.

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**SUMÁRIO**

# CAPÍTULO I – Introdução e estrutura da tese

## 1. Introdução

O uso de polímeros derivados de fontes fósseis tem sido essencial em diversos setores da sociedade, incluindo embalagens, bens de consumo, aplicações médicas e cosméticas, entre outros, impulsionando o crescimento de sua produção (AWASTHI et al., 2022; STOICA et al., 2020; KABIR et al., 2020). No entanto, essa produção em larga escala gera uma quantidade significativa de resíduos (400 milhões de toneladas anualmente – United Nations), uma vez que eles possuem baixa biodegradabilidade, sendo direcionados para aterros sanitários ou incinerados, gerando um impacto ambiental (KABIR et al., 2020). Brasil é o quarto maior produtor de resíduos plásticos no mundo com um milhão de toneladas por ano, reciclando apenas 24,5% do seu total (EMBRAPA, 2025). Além disso há muitos impactos quanto a poluição nos ecossistemas marinhos, pela contaminação por microplásticos pela cadeia alimentar de peixes e outros animais, nas águas doces e no solo, afetando a microbiota e pôr fim a saúde humana (EMBRAPA, 2025).

A crescente preocupação com a poluição plástica e a busca por alternativas sustentáveis têm impulsionado a pesquisa em materiais biodegradáveis e compostos poliméricos de origem renovável (GEORGE et al., 2020; BISWAS et al., 2022; IBRAHIM et al., 2019). Entre os diversos biopolímeros em estudo, o poli(butileno succinato) (PBS) se destaca por apresentar boas propriedades mecânicas, processabilidade em equipamentos convencionais de termoplásticos e potencial de biodegradação (RAFIQAH et al., 2021; XU; GUO, 2010). Entretanto, seu elevado custo e limitações no desempenho mecânico e térmico em algumas aplicações têm motivado o desenvolvimento de compósitos e misturas com adição de amido e fibras ou resíduos lignocelulósicos (MOCHANE et al., 2021; GHAZVINI et al., 2022; YUSOF et al., 2021). Nesse contexto, resíduos agroindustriais representam uma alternativa promissora, pois, além de reduzirem custos de formulação, agregam valor a subprodutos de baixo aproveitamento econômico, favorecendo a economia circular.

O Brasil é atualmente o maior produtor e exportador mundial de laranjas e suco de laranja (FAO, 2023). Trata-se de um produto de extrema importância econômica. A casca, as sementes e as laranjas descartadas são denominadas polpa cítrica (CP), o principal subproduto da indústria cítrica e um

subproduto destinado para alimentação de ruminantes devido ao seu alto teor de nutrientes e excelente digestibilidade (BAKR et al., 2020). Já a casca de aveia é rica em fibras lignocelulósicas, podendo atuar como reforço estrutural em matrizes poliméricas, enquanto a polpa cítrica contém elevado teor de pectina, celulose e hemicelulose, apresentando potencial como agente de modificação e compatibilização em blendas poliméricas. As cascas de aveia são utilizadas principalmente como biomassa para geração de eletricidade e vapor negligenciando seu potencial para outras aplicações de valor, como em blendas biodegradáveis (SILVA, CARVALHO, YAMASHITA, 2024). A baixa densidade, baixo custo e alta biodegradabilidade dessas fibras naturais podem ser atrativos em aplicações nas quais materiais mais leves e rígidos de alta descartabilidade são desejados, como revestimento de copos, canudos, colheres, bandejas descartáveis, ou mesmo para a indústria automotiva, de tecidos, entre outras (FERREIRA; MOLINA; PELISSARI, 2020; HUANG et al., 2018).

O amido é um dos biopolímeros mais estudados devido à sua ampla disponibilidade, baixo custo e biodegradabilidade (SURENDREN et al., 2022). Apesar dessas vantagens, seu uso em escala industrial é limitado por características intrínsecas, como elevada hidrofilicidade, baixa estabilidade térmica e propriedades mecânicas inferiores em relação a polímeros sintéticos (ZHANG et al., 2014; KUMARAN et al., 2020). A combinação do amido com poliésteres biodegradáveis, como o PBS, representa uma estratégia promissora, pois alia processabilidade e desempenho funcional, ao mesmo tempo em que reduz custos (RAFIQAH et al., 2021). Nesse contexto, fibras lignocelulósicas, como a casca de aveia, e resíduos ricos em polissacarídeos, como a polpa cítrica, podem contribuir não apenas como reforço estrutural, mas também como modificadores interfaciais, ampliando as propriedades mecânicas e funcionais das blendas (GHAZVINI et al., 2022; MOCHANE et al., 2021).

O presente estudo teve como objetivo produzir e caracterizar injetados termoplásticos de poli(butileno succinato) (PBS) com fibras naturais de casca de aveia (CA) e polpa cítrica (PC) em diferentes concentrações (0–56% m/m), variando-se também a fração de amido. Foram avaliados os efeitos das fibras sobre propriedades mecânicas, morfologia, estrutura, cristalinidade, densidade, cor, índice linear de contração, isotermas de sorção, entre outras características físico-químicas. Além disso, os injetados contendo CA e PC foram submetidos a ensaios de

biodegradação em solo, analisando-se parâmetros como perda de massa, teor de carbono orgânico total (TOC) de acordo com os critérios da OECD 301B, atividade microbiana do solo em amostras fumigadas e não fumigadas, isotermas de sorção, caracterização estrutural por microscopia de varredura eletrônica (MEV) e espectroscopia de infravermelho por transformada de Fourier (FTir).

## 2. Estrutura da Tese

Diante disso, a presente tese foi estruturada em três artigos científicos. O primeiro artigo aborda a produção e caracterização de compósitos injetados contendo PBS, amido e diferentes concentrações de casca de aveia. O segundo artigo apresenta formulações injetadas à base de PBS, amido e diferentes teores de polpa cítrica, avaliando suas propriedades físico-químicas e morfológicas. Por fim, o terceiro artigo investiga o comportamento de biodegradação dos compósitos desenvolvidos, buscando compreender o impacto da presença de diferentes resíduos agroindustriais na degradação ambiental dos materiais. Assim, este trabalho contribui para o avanço do conhecimento na área de polímeros biodegradáveis e na valorização de resíduos da indústria de alimentos, propondo formulações inovadoras que aliam desempenho tecnológico e sustentabilidade.

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# CAPÍTULO II – Revisão Bibliográfica

## 1. Polímeros

Polímero é toda macromolécula formada por unidades repetidas menores denominadas monômeros, que se ligam através de ligações ou interações químicas (FERNANDES, 2014). Os polímeros no século XX promoveram grandes mudanças tecnológicas por meio de sua utilização nas formas de borrachas, plásticos e fibras sintéticas, impactando diversos setores industriais (automotivo, eletrônico, embalagens etc.) (HAGE, 1998). Atualmente, estes polímeros continuam sendo essenciais para diversas áreas e novas aplicações, como na medicina, na agricultura, entre outros.

Um polímero pode ser de origem natural: celulose, proteína vegetal, animal ou de origem sintética: polietileno (PE), nylon, poliésteres, entre outros (FERNANDES, 2014). Eles também podem ser classificados quanto ao seu comportamento frente ao calor como termoplásticos, termoresistentes (termorrígidos) ou como elastômeros. Cada um desses apresenta características diferentes que definem a forma final de um produto (HSISSOU et al., 2021).

Os materiais termoplásticos são reconhecidos pela sua capacidade de serem moldados ou remodelados de maneira repetida em presença de calor, tornando-se fluidos e maleáveis sem que haja mudança em sua estrutura química (CALLISTER; RETHWISCH, 2020). Essa propriedade só é possível devido à ausência de ligações covalentes e à presença de cadeias lineares, unidas por forças intermoleculares fracas (ligações de hidrogênio ou Van der Waals) (CALLISTER; RETHWISCH, 2020). Entre os mais utilizados estão o polietileno (PE), polipropileno (PP), politereftalato de etileno (PET) e policloreto de vinila (PVC). Já os termorrígidos, uma vez processados termicamente em extrusão ou molde, não conseguem ser remodelados, uma vez que ocorre um processo de reticulação (*crosslinking*) das cadeias poliméricas. Isto promove uma estrutura tridimensional com alta resistência térmica, química e mecânica, contudo sem a capacidade de ser fundida novamente (STRONG, 2006). Exemplos de termorrígidos são os baquelite, resinas epóxi ou de poliésteres insaturados. Por fim, os elastômeros possuem a capacidade de sofrer grandes deformações sob força aplicada e conseguir retornar para sua forma original com as mesmas dimensões. Isto ocorre pois em suas cadeias poliméricas há a presença de longas cadeias com poucas ligações cruzadas, permitindo mobilidade e

resistência, sendo mais utilizadas em setores automobilísticos, ou em luvas, vedações etc. (CALLISTER; RETHWISCH, 2020; RODRIGUES; ROSA, 2015).

## 2. Biopolímeros

A utilização de polímeros não biodegradáveis tem sido essencial em várias áreas da sociedade, como embalagens, bens de consumo, aplicações médicas, cosméticas, entre outras, impulsionando o crescimento na produção destes materiais (AWASTHI et al., 2022; STOICA et al., 2020; KABIR et al., 2020). A baixa degradação é a grande desvantagem desta classe, uma vez que eles são simplesmente incinerados ou depositados em aterros sanitários (KABIR et al., 2020). Apesar do tratamento térmico ser a única forma de quebrar a cadeia polimérica destes materiais, o processo acaba por liberar componentes tóxicos para a atmosfera, como furanos, dioxinas, entre outros (KABIR et al., 2020). Por conta disso, a produção de plásticos biodegradáveis tem sido avaliada como uma alternativa para a substituição dos plásticos convencionais (GEORGE et al., 2020; BISWAS et al., 2022; IBRAHIM et al., 2019).

Os polímeros biodegradáveis também podem ser classificados quanto ao seu comportamento frente ao calor, sendo separados em elastômeros, termoplásticos ou termorrígidos (IBRAHIM et al., 2019; GEORGE et al., 2022; NIAOUNAKIS, 2015). Estes materiais podem ser quimicamente sintetizados, podendo ser obtidos de fontes renováveis ou não, sendo sua capacidade de degradação determinada pela sua estrutura química, natureza (cristalina ou amorfa), peso molecular, entre outros fatores (MTIBE et al., 2021; GEORGE et al., 2020). Dentro dessa classe de polímeros sintéticos biodegradáveis estão alguns mais conhecidos como o poliácido láctico (PLA), polibutileno succinato (PBS), poli(butileno adipato co-tereftalato) (PBAT), poli-hidroxialcanoatos (PHA) e poli(ε-caprolactona) (PCL).

Estes polímeros biodegradáveis não podem ser amplamente utilizados como os convencionais, apenas em aplicações específicas, devido a algumas limitações quanto ao custo, processabilidade, propriedades mecânicas, de barreira e térmicas, contudo, a adição de compatibilizantes pode melhorar a performance destes materiais (MUTHURAJ; MISRA; MOHANTY, 2018).

Polímeros de origem natural biodegradáveis podem ser obtidos de diferentes fontes vegetais (IBRAHIM et al., 2019; WESTLAKE et al., 2023). Neste contexto há uma valorização destes biopolímeros para aplicações na área de alimentos, medicina, impressões 3D e na agricultura (BALART et al., 2021; KUMARAN et al., 2020). A grande vantagem deste grupo é sua grande disponibilidade na natureza e baixo custo se comparado a outros materiais. Além disso, suas propriedades podem ser controladas de acordo com modificações químicas ou no processamento (FLÓREZ; CAZÓN; VÁZQUEZ, 2023).

O amido é distribuído em diferentes fontes vegetais (milho, mandioca, trigo, entre outras) e industrialmente é utilizado na forma de amido termoplástico (TPS). Durante o cisalhamento da extrusão, altas temperaturas e presença de um plastificante como o glicerol, o amido se torna um material termoplástico, ou seja, quando resfriado ele mantém sua forma moldada (FLÓREZ; CAZÓN; VÁZQUEZ, 2023; ZHANG; REMPEL; LIU, 2014; MÜLLER; PIRES; YAMASHITA, 2011). O amido também apresenta uma excelente biodegradação e é mais barato do que os polímeros convencionais e biodegradáveis, como o PE, o PP, o PBS e o PLA, mas apresenta ainda desvantagens como a hidrofilicidade e a fragilidade (DIYANA et al., 2021).

As fibras lignocelulósicas são componentes com potencial para aplicação, amplamente disponíveis na natureza, com baixa densidade e custo, além de garantirem em algumas aplicações propriedades mecânicas adequadas, além de serem totalmente biodegradáveis (ASYRAF et al., 2023). São encontradas principalmente em plantas lenhosas, sendo constituídas de frações de celulose (30-40%), 20-30% (hemicelulose) e 15-20% (lignina) (IBRAHIM et al., 2019). Podem ser adotadas como agentes de reforço, junto a outros biopolímeros devido às suas propriedades mecânicas, contudo apresentam muitas desvantagens como a absorção de umidade (hidrofílicas) e estabilidade térmica (ASYRAF et al., 2023; GALLOS et al., 2017; RANGAPPA et al., 2022).

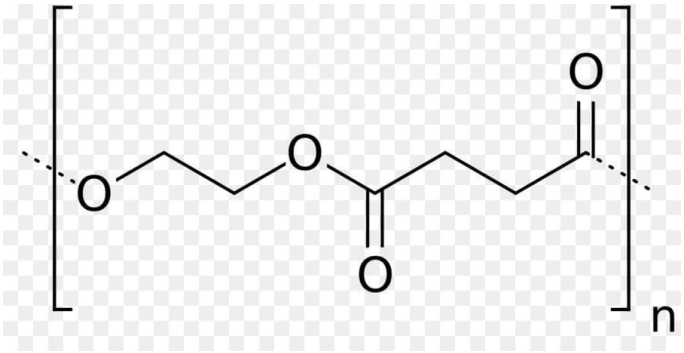
A quitina é um precursor direto da quitosana, sendo uma fibra insolúvel em água e encontrada principalmente no exoesqueleto de moluscos, crustáceos e insetos (JIMÉNEZ-GÓMEZ; CECILIA, 2020). Pesquisas com a quitosana têm sido desenvolvidas devido a algumas propriedades químicas, além de ser solúvel em ácido, possibilitando sua aplicação como biomaterial, aplicações farmacêuticas, entre outras (JIMÉNEZ-GÓMEZ; CECILIA, 2020). Já a pectina é obtida de frutas, por um grupo de polissacarídeos presentes nas paredes celulares das plantas, sendo

comumente descartada em indústrias de alimentos, não considerando seu potencial (IBRAHIM et al., 2019). Dentro dos constituintes da polpa cítrica, destaca-se a pectina, polissacarídeo complexo presente em teores que variam de 20-35% da matéria seca (SCHALOW et al., 2018).

## 2.1 Poli (succinato) de butileno (PBS)

Poliésteres alifáticos são materiais com um grande potencial para substituição de materiais fósseis, uma vez que possuem propriedades mecânicas e térmicas interessantes para aplicação em escala industrial, além de terem como principal característica sua capacidade de biodegradação. O poli (succinato) de butileno (PBS) é um biopolímero, da família dos poliésteres, termoplástico, obtido através de processos biotecnológicos, via policondensação do ácido succínico com o 1,4-butanodiol. É um dos polímeros emergentes no mercado para redução do impacto ambiental e substituição de plásticos fósseis não biodegradáveis, sendo composto por subunidades polimerizadas de succinato de butileno com repetições de unidades de $C_8H_{12}0_4$ (MOCHANE et al., 2021) (Figura 1).

**Figura 1 –** Poli (succinato) de butileno (PBS).



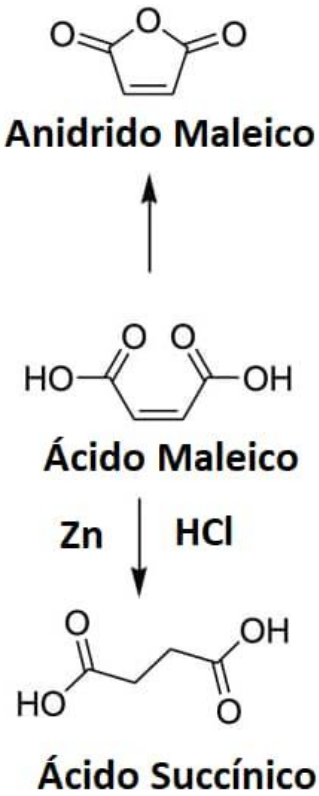

Fonte: Domínio público (2022).

A síntese do PBS se dá em duas etapas principais: (I) processo de esterificação direta por meio do diácido (ácido succínico com o 1,4-butanodiol e a (II) policondensação em alta temperatura. Primeira etapa é realizada na ausência de oxigênio evitando assim a oxidação dos produtos devido às altas temperaturas alcançadas (150 a 190°C). A policondensação em alta temperatura é realizada para formar o PBS de alta massa molecular polimerizando os oligômeros, sendo

necessária a presença de vácuo, removendo os coprodutos produzidos. As suas propriedades físicas, assim como a sua taxa de biodegradação, podem ser controladas de acordo com diferentes tipos de copolimerização e quantidades de monômeros (JIANG et al., 2017).

O método mais popular para obtenção do ácido succínico petroquímico utilizado na produção do PBS, é por meio da hidrogenação catalítica do ácido maleico ou de seu anidrido, conforme a Figura 2.

**Figura 2 –** Obtenção do Ácido Succínico.




Referência: Adaptado de Lou e colaboradores (2020).

O processo de hidrólise do anidrido maleico resultará na destruição das ligações simples do carbono com o oxigênio, obtendo-se o ácido maleico. Em seguida, o hidrogênio será adicionado ao meio, o que resultará no rompimento da ligação dupla carbono-carbono, completando a reação e obtenção do ácido succínico (XU; GUO, 2010; RAFIQAH et al., 2021). Já para o processo de fermentação na obtenção do ácido succínico, vários microrganismos (*Aerobiospirillum succiniciproducens, Actinobacillus succinogenes* e *Mannheimia succiniciproducens*) podem ser utilizados e já foram testados na produção do PBS, no entanto, cada um

deles e seus processos biotecnológicos de produção são muito mais caros se comparados ao processo de obtenção anterior (KASMI et al., 2018).

O PBS pode ser processado por moldagem por injeção, extrusão e sopro de filme usando equipamentos convencionais e pode ser utilizado para várias aplicações. Demonstra bom processamento, boas propriedades mecânicas (comparáveis ao PP e ao PE), flexível, excelente biodegradação no solo e na água e resistência térmica (RAFIQAH et al., 2021; XU; GUO, 2010). É cristalino com temperatura de fusão acima de 100°C, temperatura de transição vítrea (Tg) entre -45°C e -10°C e densidade de 1,25 g $cm^{-3}$ (MOCHANE et al., 2021). O PBS é comercializado como BioBPS™ (Mitsubishi Chemical), GsPLA e Bionolle (Showa Denko).

Possui diversas aplicações como sacos, frascos, filmes de recobrimento, além de servir como matriz para aplicações envolvendo aditivos antimicrobianos (YUSOF et al., 2021). No entanto, há algumas limitações relacionadas ao seu alto custo e propriedades de barreira (MOCHANE et al., 2021). Para diminuir o custo e ao mesmo tempo melhorar propriedades mecânicas, fibras de diferentes fontes (café, aveia, laranja, entre outros) podem ser incorporadas, mas devido às fracas interações entre as fibras naturais e o PBS, essa melhora é dificultada (GHAZVINI et al., 2022; MOCHANE et al., 2021). A adição de outros biopolímeros como o amido pode beneficiar algumas propriedades do próprio PBS em algumas aplicações alimentícias ou em outros setores (GUMEDE; LUYT; MULLER, 2018; YUSOF et al., 2021).

Em trabalho realizado por Yusof e colaboradores (2021) houve a produção de um filme de revestimento para produtos cárneos (filés de peito de frango) contendo PBS/Amido termoplástico como matriz polimérica, além de dois agentes antimicrobianos no meio, totalizando dez formulações. Os filés embalados com a formulação da blenda entre o PBS/Amido apresentaram crescimento microbiano menor se comparados com os filés embalados com filmes de PBS. As demais amostras embaladas com filmes contendo agentes antimicrobianos apresentaram resultados ainda melhores, revelando o potencial antimicrobiano da blenda PBS/amido por si só ou junto com outros aditivos.

Em relação à sua degradação, microrganismos do grupo *Fusarium solani* podem ser os maiores responsáveis na degradação do PBS, além de outras da

classe *Firmicutes* e *Proteobacteria*, que degradam tanto o PBS quanto o PHB e PCL (RAFIQAH et al., 2021).

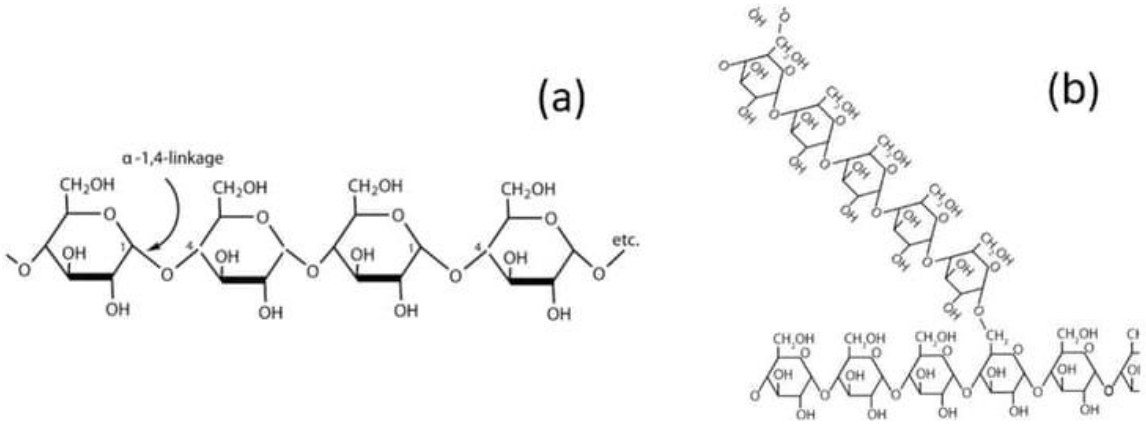
## 2.2 Amido

O amido é um homopolissacarídeo composto exclusivamente por unidades de D-glicose, sendo constituído por dois polímeros principais: amilose e amilopectina. A amilose é uma cadeia linear de resíduos de glicose unidos predominantemente por ligações glicosídicas α-(1→4), enquanto a amilopectina apresenta uma estrutura altamente ramificada, contendo tanto ligações α-(1→4) quanto α-(1→6), estas últimas responsáveis pelas ramificações laterais da molécula (CLIFTON; KEOGH, 2016; DENARDIM; SILVA, 2009). A biossíntese do amido ocorre nos plastídios de plantas superiores, especialmente nos cloroplastos das folhas, onde atua como reserva temporária de carboidratos. Durante o dia, é acumulado nos cloroplastos, sendo posteriormente degradado no escuro para a síntese de sacarose (DENARDIM; SILVA, 2009).

É encontrado na natureza como partículas parcialmente cristalinas, denominadas grânulos, estes que são insolúveis, contudo, possuem hidratação parcial em água em temperatura ambiente (PÉREZ; BERTOFT, 2010; HUBER; BEMILLER, 2019).

Em relação às cadeias presentes no amido, a amilopectina (Figura 3b) é altamente ramificada, possuindo ligações α-1,6 (ramificações), responsáveis por 4 a 7% do total de conexões entre as moléculas da glicose, estando presente em todos os tipos de amido (HUBER; BEMILLER, 2019).

**Figura 3 –** Representação da estrutura da amilose (a) e amilopectina (b).




Fonte: Adaptado de Smith (2024).

A amilose (Figura 3a) é um polímero linear composto predominantemente por unidades de α-D-glicopiranose unidas por ligações glicosídicas do tipo α-(1→4). Embora considerada uma molécula linear, pode apresentar um número reduzido de ramificações unidas à cadeia principal por ligações do tipo α-(1→6), as quais correspondem a aproximadamente 0,3% a 0,5% do total de ligações (DENARDIN; SILVA, 2009). O teor de amilose nos amidos varia entre 20% e 30% nos cereais, sendo, por exemplo, de 25% a 28% no milho e aproximadamente 17% na mandioca (WEBER; COLLARES-QUEIROZ; CHANG, 2009). A presença da amilose influencia significativamente a organização estrutural das duplas hélices nos grânulos de amido, afetando a densidade de empacotamento das cadeias de amilopectina e, por conseguinte, as propriedades físico-químicas do amido como um todo (DENARDIN; SILVA, 2009). Por sua vez, a amilopectina exibe uma estrutura altamente ramificada, em contraste com a conformação mais linear da amilose. Essa diferença estrutural tem impacto direto nas propriedades funcionais do amido, como solubilidade, gelatinização, viscosidade e retrogradação (DENARDIN; SILVA, 2009; HUBER; BEMILLER, 2019).

Em aplicações tecnológicas, filmes produzidos a partir de amido termoplástico com maior teor de amilose apresentam melhores propriedades mecânicas, como maior resistência à tração e alongamento na ruptura, além de melhor desempenho de barreira ao vapor de água (THAKUR et al., 2019). Apesar do potencial dos filmes de amido como revestimentos comestíveis, ainda persistem limitações quanto às suas propriedades mecânicas e de barreira. Fatores como temperatura de processamento, tipo e concentração de plasticizante, retrogradação,

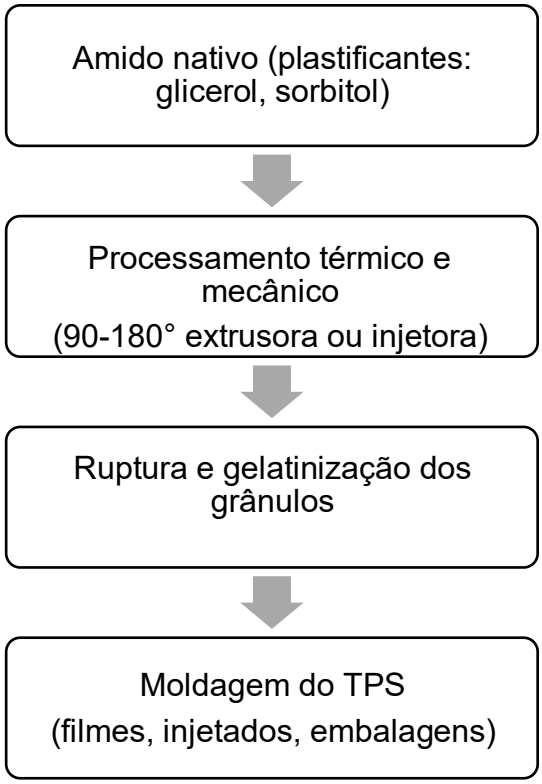
condições de armazenamento e formulação de blendas precisam ser mais bem compreendidos e otimizados para viabilizar sua aplicação em escala industrial (THAKUR et al., 2019).

## 2.3 Amido Termoplástico

O amido é amplamente distribuído na natureza, especialmente em fontes vegetais (milho, batata, cana de açúcar e mandioca), onde ele serve como fonte de reserva energética para plantas (ALDAS et al., 2025; KSHITIJ, et al., 2025). Devido a essa grande disponibilidade, seu custo é consideravelmente menor do que outros polímeros biodegradáveis, tornando-o favorável para aplicações em blendas com outros materiais, garantindo um material com uma taxa de biodegradação maior e de fonte renovável (SURENDREN et al., 2022; ALDAS et al., 2025; KSHITIJ et al., 2025). Porém, o amido apresenta limitações quanto à processabilidade, "scale-up" (produção em larga escala) e características hidrofílicas (compatibilidade com outros materiais hidrofóbicos é prejudicada), assim como muitos biopolímeros provenientes de resíduos agroindustriais (KSHITIJ et al., 2025; SHARMA; MUDHOO, 2011).

O amido na presença de altas temperaturas, cisalhamento (extrusão e injeção) e de um plastificante (glicerol, sorbitol, ácido cítrico, glicerina, água e outros açúcares), se tornando um material termoplástico (Figura 5), com a capacidade de fluir e ser processado como um plástico em processos de extrusão (AKRAMI et al., 2016; SHARMA; MUDHOO, 2011). Durante essas condições ocorre a destruição da estrutura semicristalina do amido e sua gelatinização completa, destruindo as ligações intermoleculares e reorganizando as cadeias poliméricas, garantindo assim as propriedades funcionais do amido termoplástico (AKRAMI et al., 2016; SHARMA; MUDHOO, 2011).

**Figura 4** - Obtenção do amido termoplástico.




Fonte: autoria própria (2025).

## 2.4 Fibras Lignocelulósicas

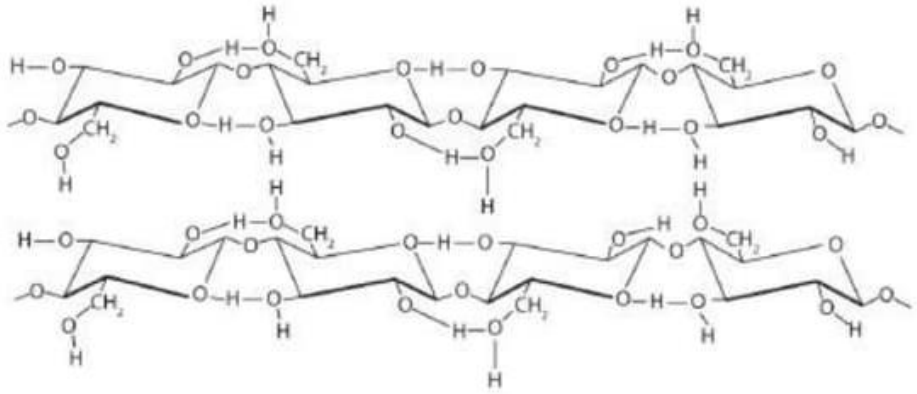
As fibras lignocelulósicas são componentes de origem vegetal, que estruturalmente podem ser divididas em três maneiras: celulose, hemicelulose e lignina. São carboidratos fibrosos mais abundantes do planeta, sendo encontrados nas paredes celulares das plantas, inclusive de cascas, sementes, bagaços, entre outros subprodutos não aproveitados pela cadeia agroindustrial (SCHELLER; ULVSKOV, 2010; ROWELL, 2005; SERGERS et al., 2024). Estima-se que aproximadamente 1 bilhão de toneladas de resíduos agrícolas por ano são descartados (resto de colheitas, subprodutos de processamento de alimentos) no mundo (PENG et al., 2023). Já no Brasil, a cadeia agroindustrial gera cerca de 291 milhões de toneladas em perdas em culturas como a da cana-de-açúcar, soja, milho e arroz, sem considerar possíveis aplicações para esses subprodutos (SIQUEIRA et al., 2022; PACHECO et al., 2023). Estes resíduos possuem em sua composição fibras lignocelulósicas naturais que podem ser adotadas como biopolímeros ou como material de reforço em blendas poliméricas, através de processos físicos como a

extrusão e a moagem, que podem garantir a obtenção de polímeros de alta qualidade com propriedades adequadas para variadas aplicações (PACHECO et al., 2023).

## 2.5 Celulose

A celulose (Figura 5) é um polímero de origem natural, de estrutura linear e formado por unidades repetidas de glicose ($C_6H_{10}O_5$), sendo sintetizada durante o processo de fotossíntese nos cloroplastos das células vegetais (SEDDIQI et al., 2021). Cada unidade monomérica pode formar ligações de hidrogênio intra- e intermoleculares, o que confere à celulose sua elevada cristalinidade e notável resistência à tração (SHANGHALEH; XU; WANG., 2018).

**Figura 5 –** Estrutura da celulose.



Fonte: MAP Organic Chemistry, Libretexts (2025).

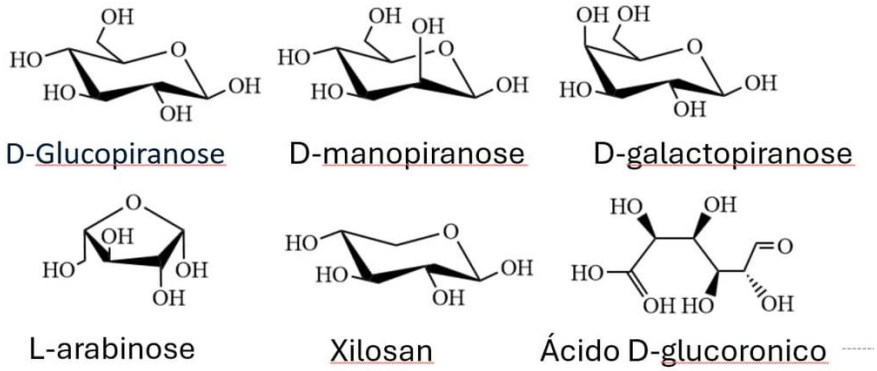
Essa organização molecular resulta em uma estrutura mais compacta e densa, característica essencial para suas propriedades mecânicas e estruturais. A celulose tem sido aplicada como biopolímero, por apresentar alta resistência mecânica, térmica, biodegradabilidade, baixa densidade, fonte renovável e de baixo custo, podendo ser utilizada na preparação de blendas com outros polímeros como agente de reforço, contudo, ainda apresenta limitações devido à sua hidrofilicidade e pobre adesão interfacial entre os componentes (PACHECO et al., 2023; LIU et al., 2021). Ayu e colaboradores (2020) produziram chapas utilizando PBS e cachos de frutas vazias e notou-se que a presença de fibras naturais como a celulose contribuiu para um aumento de 6% na resistência à tração. Também foi possível observar uma pobre adesão interfacial entre o PBS e as fibras naturais. Outro estudo (WANG et al., 2020) utilizou nanofibras de celulose aplicadas em blendas entre PLA/PBS. Houve

melhoras significativas na resistência mecânica uma vez que essas fibras conseguiram se dispersar melhor na fase contínua do PLA em relação ao PBS, contudo ainda os resultados são menores do que do PLA puro, contudo, os autores ressaltam que as características do PLA (rigidez) e do PBS (flexibilidade) junto com as nanofibras de celulose (reforço) geraram uma blenda biodegradável com performance mecânica adequada para possíveis aplicações.

## 2.6 Hemicelulose

A hemicelulose é composta por unidades monoméricas como pentoses, hexoses, galactose, glicose, entre outros (HE; LIU; ZHANG, 2024). Sua estrutura é formada por ligações glicosídicas com alto grau de ramificações. É um dos polissacarídeos em maior quantidade na natureza, estando presente nas paredes celulares das plantas (HE; LIU; ZHANG, 2024; ZHAO et al., 2020). Apesar de sua nomenclatura ser semelhante à celulose, ela apresenta algumas diferenças características estruturais como cadeias ramificadas e, por ser amorfa, resulta em uma estrutura menos resistente que a da celulose e mais facilmente degradável (ZHAO et al., 2020). Sua estrutura também apresenta ampla variedade de compostos glicosídicos (Figura 6). Além disso, ela apresenta taxas elevadas de biodegradação, biocompatibilidade e bioatividade, podendo ser adotada como filmes de revestimento, hidrogéis e como emulsificantes. Contudo, ela apresenta algumas desvantagens, como baixa resistência à tração, devido ao baixo peso molecular (ZHAO et al., 2020). Outro estudo (MENDES et al., 2023) avaliou a produção de filmes por casting contendo PLA e poli-hidroxibutirato (PHB), utilizando ácido acético e clorofórmio como agentes plastificantes. Notou-se que, conforme o aumento da concentração de hemicelulose nas blendas, piores eram as propriedades térmicas e menor era a cristalinidade, devido à falta de compatibilidade entre as fibras e os biopolímeros.

**Figura 6 –** Unidades glicosídicas da hemicelulose.



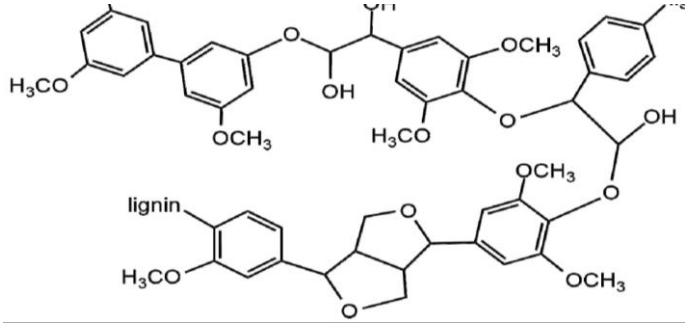

Fonte: Adaptado de Zhao et al. (2020).

## 2.6 Lignina

A lignina (Figura 7) é um dos polímeros biodegradáveis naturais mais abundantes do planeta, presente nas paredes celulares das plantas, representando cerca de 15-30% da biomassa vegetal seca, também sendo o único polímero aromático renovável do mundo (PACHECO et al., 2023). É característico por ser amorfo, tridimensional e altamente ramificado, sendo composto por unidades fenólicas, possuindo propriedades antioxidantes, biodegradabilidade e alta estabilidade térmica. Devido a isso, subprodutos ricos em lignina de indústrias que utilizam bagaço de frutas ou papel principalmente poderiam obter grande retorno financeiro além da diminuição do impacto ambiental ao aproveitarem desses resíduos, uma vez que estes subprodutos são de baixo custo (VÁSQUEZ-GARAY et al., 2021). Em blendas produzidas com PBS e lignina por extrusão e injeção termoplástica (DOMÍNGUEZ-ROBLES et al., 2020) foi observada uma queda na resistência à tração, conforme o aumento da concentração de lignina, porém o módulo de Young se manteve constante. Isto segundo os autores é justificado pela estrutura altamente aromatizada, que dificulta a lignina de atuar como um agente de reforço ou preenchimento dentro de blendas poliméricas, mantendo o material rígido apenas, porém mais frágil, contudo para aplicações médicas a lignina apresentou efeito antioxidante e antimicrobiano, o que pode possibilitar aplicações em setores específicos. Outro estudo (EWURUM; MCDONALD, 2025) investigou a aplicação do PBS variando as concentrações da lignina (0-45% do peso total) em extrusados em

forma de disco por meio de um processo de copolimerização e reações de grafitização. Novamente a lignina manteve o material rígido com perda de resistência à tração, porém com boa estabilidade térmica. Em concentrações maiores que 20-30% do peso total, ocorreu separação de fases e a blenda foi comprometida.

**Figura 7 -** Estrutura da lignina.



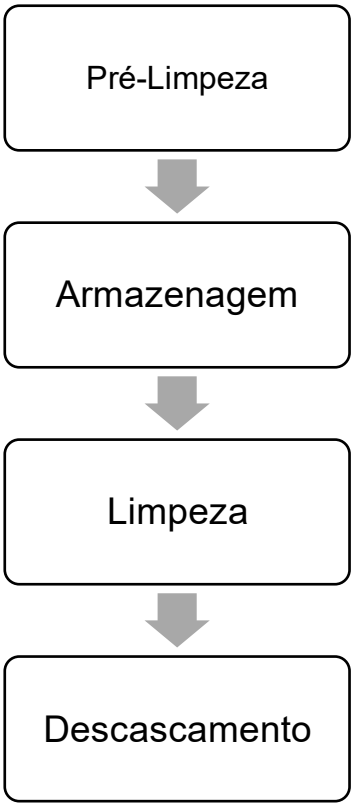

Autores: Vásquez-Garay (2021).

## 2.7 Casca de aveia

A aveia (*Avena sativa L.*) é um produto importante mundialmente, para consumo humano e principalmente como ração para gado, perdendo apenas para a soja em quantidade de proteína, sendo esse o maior fator para o declínio de sua produção nos últimos 70 anos (STRYCHAR; WEBSTER; WOOD, 2011). A utilização do grão como ração representa ainda cerca de 74% do uso da aveia de acordo com o Departamento de Agricultura dos Estados Unidos (USDA), contudo outras aplicações têm surgido em produtos alimentícios como: farinha de aveia, flocos de aveia, farelo, cereais matinais, justamente por ser uma boa fonte de vitaminas e minerais para consumo humano (CHAND et al., 2025; STRYCHAR; WEBSTER; de WOOD, 2011; ZHANG, et al., 2021). O grão de aveia é composto em média de 60% de amido, 14% de proteínas, 7% de lipídeos, além de possuir grande quantidade de β-glucanas, diferente de outros grãos (ZHANG et al., 2021). Apesar de seus benefícios e de sua composição, durante seu processamento há um grande descarte de sua casca. A casca de aveia é em volume o maior subproduto proveniente do processamento de moagem, variando de 25 a 36%. Em composição contém aproximadamente 4% de proteína, 5% de cinzas, 30-35% de fibra, 30-35% de pentosanas e 10-15% de lignina (). A moagem da aveia é um processo que consiste em separar materiais estranhos da aveia, assim como remover a casca, entre outras

funções. O processo até a obtenção da casca se dá pelas etapas de pré-limpeza, armazenagem, limpeza e descascamento (Figura 8). Durante o descascamento, o rotor irá impulsionar os grãos para a parede externa do descascador, colidindo com vários anéis de impacto, fazendo com que o grão se separe do casco (GIRARDET; WEBSTER, 2011).

**Figura 8 –** Etapas do processo de descascamento da aveia.




Referência: Adaptado de Girardet e Webster (2011).

É o subproduto mais versátil da aveia, sendo adotado como biomassa para geração de eletricidade e vapor, além de ser processado quimicamente produzindo um composto furfural, que pode servir para uma matéria prima renovável para plásticos e adesivos (PUKE; GODINA; BRAZDAUSKS, 2024.). Apesar de algumas aplicações terem sido encontradas, grande parte da casca de aveia é descartada em várias indústrias no processo de moagem da aveia, desconhecendo seu potencial. Em trabalho realizado por Debiagi e colaboradores (2010), foram produzidos péletes a partir de blendas de amido de mandioca, casca de aveia e bagaço de cana-de açúcar e glicerol. Notou-se que ao adicionar as fibras, elas agiram como um reforço para os compósitos, diminuindo o índice de solubilidade em água.

Outro trabalho realizado por Peixoto e colaboradores (2019) buscou avaliar a aplicação de fibra de casca de aveia com poliácido lático (PLA) e trimetafosfato de sódio (TMP) como agente compatibilizante na produção de injetados. Os autores afirmam que o trimetafosfato agiu como um agente de ligação cruzada, beneficiando a superfície interfacial do material, uma vez que fibras naturais apresentam poucas interações com a maioria dos polímeros, promovendo uma melhor adesão interfacial injetados mais densos; contudo, eles apresentaram perda de resistência mecânica (TRAN et al., 2015).

## 2.8 Polpa Cítrica

O Brasil é o maior produtor de laranjas no mundo (16,7 milhões de toneladas) de acordo com a FAO (Organização das Nações Unidas para Alimentação e Agricultura), e grande parte do seu uso é na indústria de sucos, onde elas são esmagadas para a extração do suco concentrado (RICCI; BITTAR, 2021). A casca, semente e laranjas descartadas são denominadas polpa cítrica, sendo o subproduto desta indústria cítrica.

Após as frutas serem esmagadas, é obtida uma massa, que passa por processos de secagem, até que se atinja uma massa seca (90%) adequada, posteriormente passando por um processo de peletização, obtendo-se a ração ou o pélete da polpa cítrica (RICCI; BITTAR, 2021). Esta peletização é favorável, pois reduz sua umidade, uma vez que o mesmo in natura sofria com a alta absorção de umidade, se degradando rapidamente em poucos dias quando transportada em longas distâncias ou mesmo quando armazenado, portanto, apesar de elevar o custo, a peletização é bem aceita no mercado (RICCI; BITTAR, 2021).

Os péletes de polpa cítrica são utilizados na alimentação dos ruminantes, sendo adotados em vários países europeus e nos Estados Unidos, com o objetivo de substituição do milho e de outros ingredientes, devido ao seu preço inferior; além disso, a polpa é benéfica para animais ruminantes e principalmente vacas em lactação (TIGRE, 2012; ASSIS et al., 2004). Em sua composição destaca-se a presença de pectina, que contém polímeros de ácido galacturônico, compondo a estrutura de sua parede celular, facilitando o processo de degradação do rúmen,

aumentando níveis de nitrogênio no intestino além da atividade celulolítica, gerando a alta digestibilidade da polpa (TIGRE, 2012).

Para vacas leiteiras, a pectina se torna benéfica, uma vez que seu produto final é o ácido acético, um precursor da gordura do leite, que acaba auxiliando ou mantendo os níveis de gordura do leite estáveis (ASSIS et al., 2004). Os peletes de polpa cítrica possuem cerca de 90% de matéria seca, 6,3% proteína bruta (matéria seca), 2,3% de lignina e 6% de amido (FEEDTABLES, 2022).

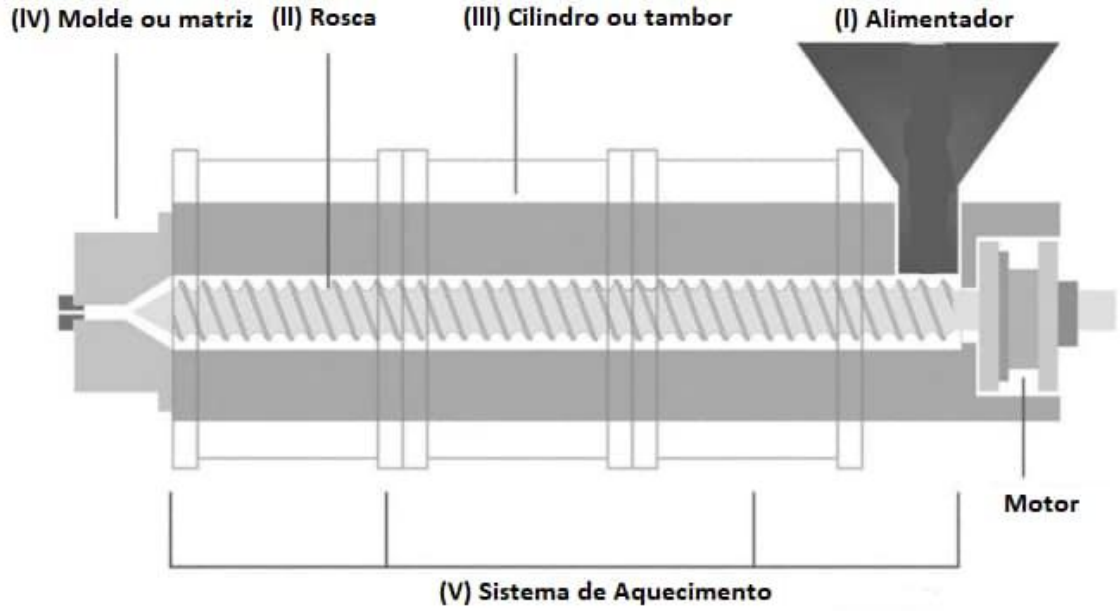
## 3. Extrusão termoplástica

A extrusão oferece uma vasta gama de produtos plásticos, sendo o processo de maior importância econômica para a obtenção de materiais plásticos. As linhas de extrusão são os maiores convertedores e podem ser consideradas o maquinário mais importante da indústria de plásticos (ROSATO, 2013). Os dois principais fatores que favorecem a utilização das extrusoras são sua grande versatilidade na produção de diferentes produtos e a outra é a capacidade de produção contínua (ROSATO, 2013). É o processo mais importante e antigo de transformação e moldagem de polímeros termoplásticos (LAFLEUR; VERGNES, 2014). O desenvolvimento da extrusora monorrosca é derivado do princípio de “Parafuso de Arquimedes”, sendo utilizada no princípio para produção de borrachas ou materiais impermeáveis e depois para polímeros (LAFLEUR; VERGNES, 2014). A tecnologia de extrusão tem sido amplamente utilizada não só para plásticos, mas para a área de alimentos, como no processamento de grãos e cereais em "snacks" de café da manhã, uma vez que esses produtos são ricos em amido, que expande na extrusão (MOUNT III, 2024).

Existem dois tipos principais de extrusoras: extrusoras de parafuso simples e de parafuso duplo (co-rotativas e contra-rotativas). Essas extrusoras variam amplamente em termos de diâmetro, comprimento e design. Tanto as extrusoras de rosca simples (monorrosca) quanto as duplas rosca são, por natureza, extrusoras com canal axial aberto, funcionando como bombas de fluxo por arrastamento (YACU, 2020). O desempenho dessas máquinas, ou o grau de enchimento, pode ser impactado pelo fluxo de pressão dentro da extrusora.

O processo (Figura 9) envolve o derretimento e homogeneização de materiais brutos da extrusora de rosca única, que rotaciona provocando cisalhamento e fusão desse material que acaba sendo direcionado ou forçado para uma saída, podendo ser um molde (injeção termoplástica, processo cíclico) ou matriz (processo contínuo), garantindo a forma desejada após o material ter sido resfriado e solidificado (LAFLEUR; VERGNES, 2014; GILES JR; MOUT III; WAGNER, 2004).

**Figura 9** - Extrusora monorrosca.




Fonte: Adaptado de Steel e colaboradores (2012).

Na Figura 9 são mostradas as cinco peças comuns encontradas em uma extrusora monorrosca (I- Alimentador; II- Rosca; III- Cilindro ou tambor; IV- Molde ou matriz; V- Sistema de Aquecimento). No alimentador (I) são colocados os polímeros ou a mistura preparada para ser extrusada, que é direcionada para a rosca (II). Este material introduzido no alimentador pode estar no formato de pó, grânulo ou pellet. O motor é responsável por garantir o movimento da rosca e o cisalhamento do material dentro do cilindro ou tambor (III). Durante a extrusão, a alta temperatura e o cisalhamento da rosca promovem a fusão e a homogeneização da mistura, que acaba sendo forçada para um molde ou para uma matriz (IV). A rosca de configuração "comum" possui um único movimento rotacional, sendo uma boa transportadora de granulados sólidos nas seções de alimentação, proporcionando uma fusão uniforme e mistura da maioria dos plásticos (GILES JR; MOUT III; WAGNER, 2004). Ela funciona movendo os grânulos sólidos ao longo do cilindro da extrusora por meio de

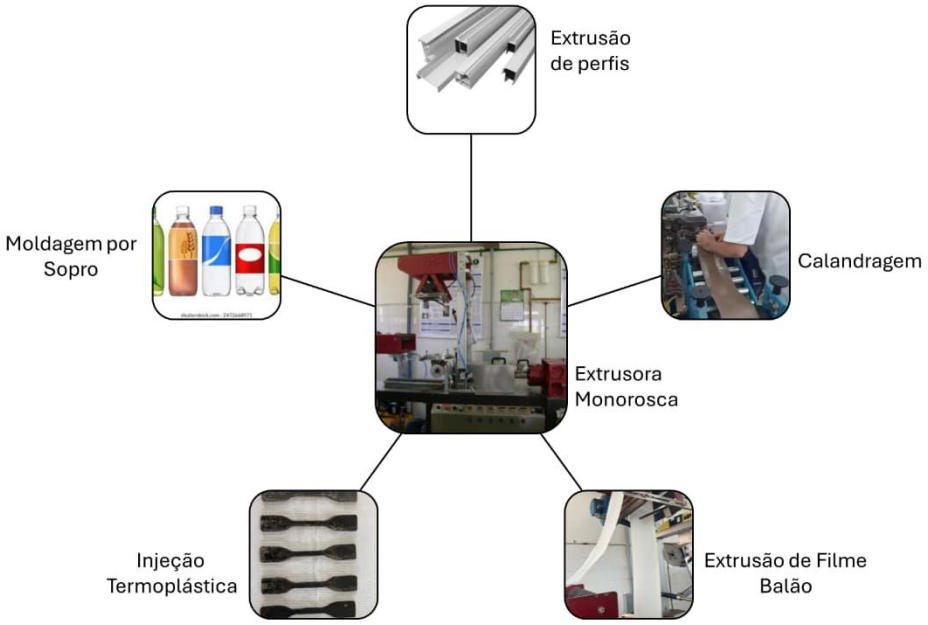
um movimento rotativo, e a fricção gerada pelo atrito com as paredes do cilindro e o calor externo ajudam a fundir o plástico. Entretanto, em casos em que uma mistura mais refinada precisa ser extrusada, pode-se empregar configurações mais complexas, como roscas de múltiplos estágios ou com barreiras, que otimizam ainda mais o processo (GILES JR; MOUT lll; WAGNER, 2004).

Existem alguns fatores que influenciam o processamento da extrusora monorrosca, como a pressão na matriz, a temperatura dentro das paredes do tambor/cilindro e a taxa de alimentação conforme a rosca é preenchida (MOUNT III, 2024). Uma das únicas limitações que podem ser atribuídas a este processo é a necessidade de homogeneizar os componentes antes do processamento, uma vez que sua capacidade de mistura com vários componentes pode ser reduzida (MOUNT lll, 2024). A Figura 10 mostra os principais produtos obtidos através da extrusão monorrosca.

A extrusão de perfis é um processo de fabricação utilizando seções transversais contantes, como perfis de alumínio, PVC, forçando um material aquecido através de uma matriz com formato desejado (perfis longos com a forma da abertura da matriz), sendo um processo rápido para produção de grandes volumes para aplicações na construção civil, bens de consumo, entre outros (ZHOU et al., 2021).

O processo de calandragem é um processo de conformação mecânica utilizando rolos/cilindros (calandras) que comprimem o material, deformando e definindo a espessura do composto (ROSATO; ROSATO, 1998). Normalmente é utilizada na fabricação de chapas metálicas, aço, alumínio e principalmente filmes plásticos com espessura adequada. Sua precisão, versatilidade e produção contínua são grandes vantagens.

**Figura 10 -** Produtos obtidos através da extrusora monorrosca.



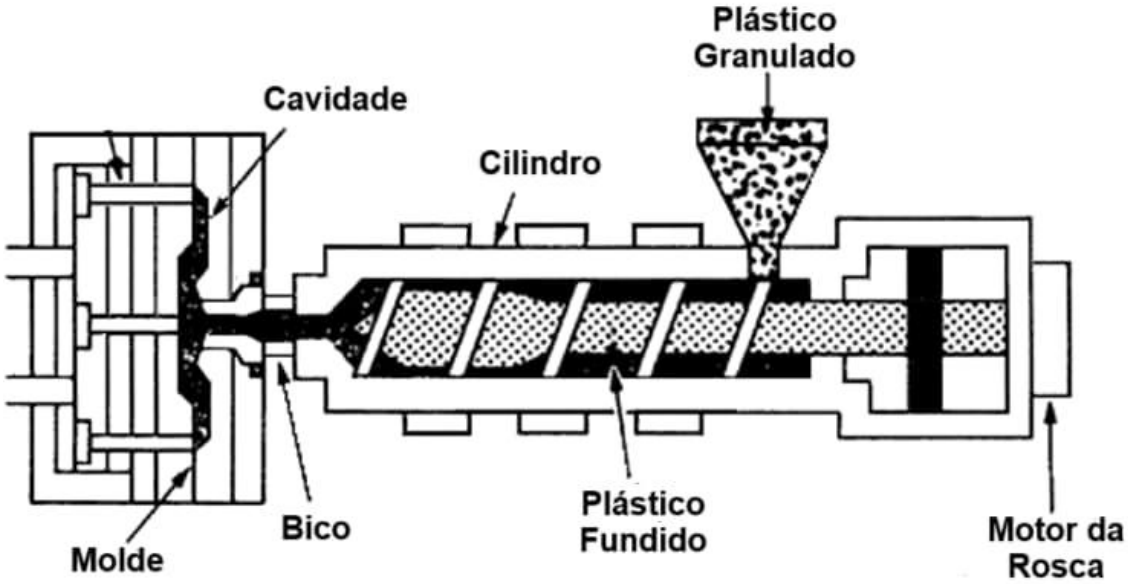

Fonte: Autoria Própria (2024).

A extrusão de filme balão é um processo reconhecido por fabricar filmes plásticos para aplicações em embalagens, sacolas plásticas e películas. É um método popular devido à sua flexibilidade, versatilidade e produção de filmes finos e uniformes com alta eficiência (GILES JR; MOUT III; WAGNER, 2004). A injeção termoplástica é um método comum para fabricação de peças, por meio da fusão de um material termoplástico e sua injeção em um molde, onde o material solidifica dentro da cavidade do molde. Após o resfriamento, a peça é removida, repetindo o mesmo ciclo. É um processo eficiente, com alta precisão, produzindo componentes de forma automatizada, como brinquedos, embalagens, eletrônicos, entre outros (GOODSHIP; MIDDLETON; CHERRINGTON, 2015). A moldagem por sopro é um processo que produz peças ocas de plástico, como garrafas, tanques e recipientes, por meio da expansão de um tubo plástico aquecido (pré-forma) dentro de um molde através de sopro de ar comprimido. Suas vantagens são a produção de produtos leves, duráveis e econômicos (BELCHER, 2011).

## 3.1 Injeção Termoplástica

O processo de injeção termoplástica é um método amplamente conhecido e desenvolvido na produção de materiais de diferentes áreas e bens de consumo, totalizando cerca de 32% de todo o plástico produzido mundialmente (GOODSHIP; MIDDLETON; CHERRINGTON, 2015; ROSATO; ROSATO, 2012). A injeção termoplástica é o processo responsável pela produção de variadas peças de plástico em grande escala. Consiste basicamente no aquecimento do material (este que possui a capacidade de ser fundido e moldado) que se torna fluido, e em seguida injetado através de um molde com temperatura mais baixa. Isto favorece a solidificação do material em um molde com o formato desejado. Pode ser adotada tanto para materiais termorrígidos quanto para termoplásticos (GOODSHIP; MIDDLETON; CHERRINGTON, 2015). O design da injetora (Figura 11) pode variar de acordo com tamanho, forma, quantidade, performance e custo do produto desejado.

**Figura 11 –** Injetora termoplástica com design comum.




Fonte: adaptado de Prototech Asia (2024).

O processo de injeção termoplástica envolve algumas etapas comuns (ROSATO; ROSATO, 2012):

1. Primeiramente, o material deve estar granulado (peletizado), e posicionado dentro do alimentador;

2. O material é fundido dentro do equipamento, se tornando fluído devido as altas temperaturas e cisalhamento por parte do cilindro/rosca;

3. O plástico fundido é injetado com um volume desejado e pressão através do bico, preenchendo a cavidade do molde, começando assim sua solidificação. O volume de plástico injetado pode variar entre 30 e 70% do volume presente na unidade de injeção.

4. Pós-enchimento, onde o material após ser injetado necessita de uma pressão por um tempo especificado para evitar refluxos ou defeitos durante a solidificação da amostra no molde;

5. Liberação da peça moldada, fechando ou abrindo o molde (cilindro) para iniciar um novo ciclo.

É um processo para produção de peças rígidas ou semirrígidas com tamanhos variados, onde a mesma unidade de peça pode ser criada milhares ou milhões de vezes em sucessão sendo esta alta repetibilidade a sua grande vantagem, além dos custos menores, baixo desgaste de equipamento para o processamento, alta produção e tempos menores de ciclo (ROGERS, 2015; ZHONG; LI 2005). Os termoplásticos representam cerca de 90% de todo o material injetado produzido, contudo, misturas com termorrígidos ou elastômetros podem ser realizadas (ROSATO; ROSATO, 2012). O tamanho de molécula, sua forma, distribuição, morfologia, cristalinidade são fatores que podem influenciar na processabilidade dos termoplásticos durante a injeção termoplástica (ROSATO; ROSATO, 2012).

O método proposto pela American Society for Testing (ASTM) D638 (2010) é útil para a realização de análises e ensaios de caracterização na determinação das propriedades de tração dos plásticos, disponibilizando dados em relação à tensão de tração, deformação e módulo de tração. Esta norma também é responsável por disponibilizar as formas, dimensões destes corpos de prova, assim como o condicionamento prévio para a realização das análises destes materiais. As duas formas utilizadas para a produção destes materiais são nos formatos "osso de cachorro" ou "gravata" (Figura 12) com dimensões pré-definidas em diferentes tipos e tamanhos. Por meio destes formatos é possível fazer os ensaios mecânicos, mais

comumente com um equipamento adequado como uma máquina universal de ensaios, que promoverá a ruptura do material.

**Figura 12 -** Corpos de prova produzidos pela injeção termoplástica.

Fonte: Autoria própria (2024).

## 3.2 Injetados Biodegradáveis

A extrusão normalmente é adotada anteriormente ao processo de injeção termoplástica, misturando todos os componentes da matriz e produzindo os granulados que são utilizados com a tecnologia de injeção (PACHECO et al., 2023). Existem muitas pesquisas utilizando a injeção termoplástica para materiais biodegradáveis ou que sejam provenientes de fontes vegetais (PACHECO et al., 2023; FELDMANN; FUCHS, 2016; MOCHANE et al., 2021). Geralmente a celulose, hemicelulose e lignina são adotadas como agentes de reforço, ou seja, são materiais incorporados na matriz com o objetivo de melhorar suas propriedades mecânicas (rigidez, durabilidade, resistência) (PACHECO et al., 2023; FELDMANN; FUCHS, 2016).

Existem algumas limitações quanto à utilização destes biomateriais no processo de injeção termoplástica, como a processabilidade, uma vez que estas fibras naturais em excesso podem reduzir o contato das superfícies com o biopolímero ou outro componente da blenda, prejudicando as propriedades mecânicas e a integridade do material (PACHECO et al., 2023). Outra grande desvantagem é a diminuição da resistência térmica se comparada com outros agentes de reforço como fibra de vidro (FELDMANN; FUCHS, 2016). Além disso, pode ocorrer um aumento da pressão durante o processo de injeção, provocando o entupimento do bico durante a injeção e gerando peças defeituosas.

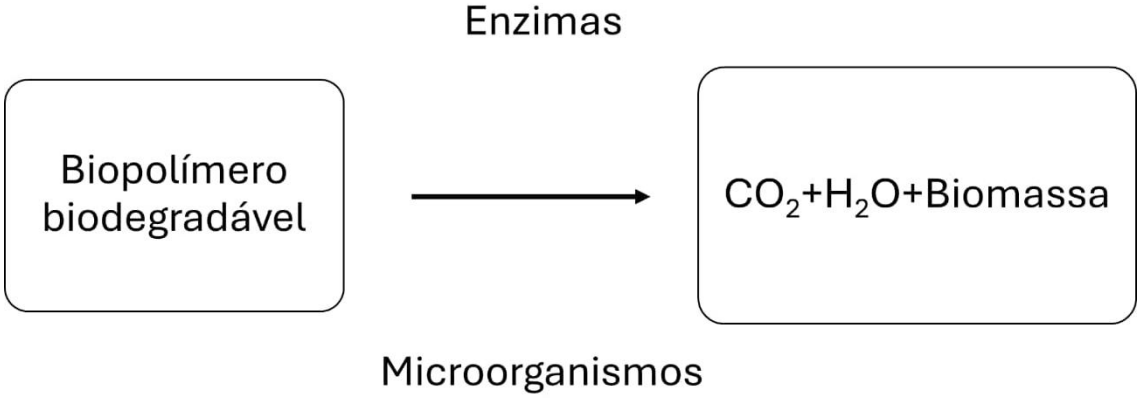
Na indústria alimentícia, estes biopolímeros provenientes de resíduos agroindustriais podem servir como bandejas, filmes, garfos e outros utensílios descartáveis que reduzem o impacto ambiental. Na indústria automotiva, esses materiais estão ganhando espaço como componentes leves e de fácil descarte ou reciclagem, alinhando-se às demandas por sustentabilidade no setor (PACHECO et al., 2023; MOCHANE et al., 2021). Além disso, blendas com amido são amplamente utilizadas em processos de extrusão e injeção termoplástica, contudo é necessária a modificação com glicerol (água, glicerol) para transformar o material em termoplástico, possibilitando sua processabilidade em processos contínuos como de extrusão (FELDMANN; FUCHS, 2016). PBS apresenta boa processabilidade em extrusão e injeção termoplástica, além da biodegradação e da flexibilidade que impulsionaram nos últimos anos o desenvolvimento de vários estudos utilizando o PBS em embalagens para alimentos ou bens de consumo rápido/descartável (BARLETTA et al., 2024). O processamento do PBS na injeção termoplástica pode ser influenciado pela quantidade de água residual, devido a isso, também é recomendada uma etapa de secagem anterior ao processamento, assim como controlar parâmetros como temperatura, velocidade da rosca e temperatura do molde (RAJGOND et al., 2024; BARLETTA et al., 2024).

## 4. Biodegradação

Biodegradação pode ser definida como processo de mineralização (Figura 14) do material orgânico através da ação de microrganismos (fungos, bactérias) que têm como produto dióxido de carbono ($CO_2$) e água ($H_2O$) em condições aeróbicas (POLMAN et al., 2021). Quase todos os polímeros convencionais

(poliésteres, polipropileno, poliestireno, polivinil cloreto) são resistentes à ação microbiana enquanto biopolímeros são degradados pelos mesmos (NAIR et al.,2017). A *American Society Standard for Testing Materials* (2019) define polímeros biodegradáveis como aqueles que se decompõem em ambientes aeróbicos naturais (compostagem) por meio de microrganismos capazes de metabolizar suas estruturas moleculares. A degradação dos biopolímeros ocorre na quebra ou cisão das cadeias principais ou secundárias das macromoléculas presentes no material em monômeros ou oligômeros.

**Figura 13 –** Processo de degradação enzimática




Fonte: Adaptado de Nair et al. (2017).

Esse processo naturalmente pode ocorrer por diferentes mecanismos como hidrólise por meio de reações com água (poliésteres biodegradáveis como PLA, amido termoplástico), oxidação com oxigênio ou radicais livres, ação enzimática (hidrolases, oxidorredutases) por parte de microrganismos, fotodegradação e degradação térmica por altas temperaturas (NAIR et al., 2017). O substrato (biopolímero degradado) é demasiado grande para ser absorvido, necessitando ser quebrado em moléculas menores. Quando isto ocorre, novos sítios ativos são formados no substrato para as enzimas dos microrganismos poderem formar substratos complexos, clivando uma parte do substrato e possibilitando que uma parte sua menor consiga ser absorvida para dentro do microrganismo (POLMAN et al., 2021). Ao mesmo tempo podem ocorrer outros processos de degradação como fotodegradação e reações de hidrólise em altas temperaturas ou condições ácidas ou básicas, influenciando na degradação enzimática (POLMAN et al., 2021). Fatores ambientais e outros parâmetros como umidade, T°, pH, salinidade, presença ou não

de oxigênio, assim como a presença de nutrientes também podem influenciar na degradação do polímero e possuem impacto crucial na população microbiana (NAIR et al., 2017). A adesão de microrganismos na superfície do plástico e a colonização são o passo inicial na degradação dos plásticos em solo (NAIR et al., 2017).

Tanto o amido quanto a celulose são os polissacarídeos mais abundantes do planeta e possuem muitas aplicações como biomateriais (SURENDREN et al., 2022). A degradação do amido ocorre principalmente pela ação da enzima α-amilase que promove a quebra de suas longas cadeias, resultando em frações menores que são quebradas por outras enzimas como β-amilase, glucoamilase e α-glucosidase (SURENDREN et al., 2022; JULINOVÁ et al., 2020; WARREN, 1996). Os principais produtores enzimáticos são o fungo *Aspergillus oryzae* e as bactérias *Bacillus circulans*, *Klebsiella pneumoniae e Bacillus stearothermophilus* (WARREN, 1996). Contudo, o fenômeno da retrogradação (processo em que o amido termoplástico reorganiza suas estruturas mais ordenadas e organizadas) pode diminuir a taxa de degradação do material devido ao aumento da cristalinidade do mesmo (LI et al., 2015).

Em relação ao PBS, Huang e colaboradores (2018) produziram compósitos utilizando PBS e fibra de cana de açúcar para avaliar a biodegradação da blenda enterrando as amostras em solo em 15, 30, 60 e 100 dias. Observou-se que, conforme o aumento dos ciclos de dias, maior era a degradação dos materiais, uma vez que a fração amorfa do PBS sofre hidrólise ao ter contato com o solo, ocorrendo a liberação de enzimas pelos microrganismos presentes, diminuindo as cadeias poliméricas do PBS em tamanhos menores, até sua desintegração total. Também notou-se que a blenda apresentou maior taxa de biodegradação em comparação com PBS puro, devido à presença dos grupos hidrofílicos das fibras da cana-de-açúcar, que absorvem inicialmente grande quantidade de umidade, aumentando a atividade microbiológica e, dessa forma, a área de contato do solo com o PBS, acelerando a hidrólise e desintegração do PBS. Autores (NOMADOLO et al., 2018) em análise de biodegradação também com PBS, avaliaram que a taxa de mineralização do mesmo aumentou devido à ação de enzimas que diminuíram o peso molecular da estrutura polimérica por meio da produção de produtos de hidrólise. A pobre adesão interfacial entre os componentes da blenda também pode contribuir para biodegradação conforme avaliado por Carvalho e colaboradores (2021) que produziram tubetes com

PLA, bagaço de mandioca e glicerol. Devido à incompatibilidade entre os componentes, o glicerol se tornou disponível para ser consumido pelos microrganismos, levando à degradação do material. Além disso, materiais contendo fibras naturais (bagaço) perderam mais peso que o biopolímero puro, o que foi observado em outros estudos também (HUANG et al., 2018; SHAIJU et al., 2020).

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## CAPÍTULO III - Potential biodegradable materials containing oat hulls, TPS, and PBS by thermoplastic injection


### Abstract

Fossil-origin plastics have raised great concerns due to their non-biodegradable nature. Biodegradable polymers can serve as an alternative to these materials; however, they are more expensive. The use of agro-industrial waste in blends with biopolymers can provide cheaper materials with improved properties. This study aims to develop low-cost biodegradable materials by extrusion and thermoplastic injection using oat hulls, polybutylene succinate (PBS), and starch. Six formulations with varying concentrations of oat hulls (0-56% w/w) were extruded using a single-screw extruder, and subsequently, the materials were produced through thermoplastic injection molding. The extrusion aligned the oat hull fibers, making the material dimensionally stable. The oat hulls enhanced stiffness and reduced material density compared to non-hull counterparts. Additionally, the oat hulls are a low-cost agro-industrial byproduct, and it is possible to produce biodegradable materials with up to 56% hulls and only 20% PBS. These biodegradable materials are environmentally friendly and non-toxic.


**Keywords**: Biodegradable Materials, blending, extrusion, natural fibers, mechanical properties.

## 1. Introduction

The escalating production of fossil-origin materials, currently amounting to 350 million tons annually, has sparked growing concerns due to their non-biodegradable nature and significant impact on the ecosystem (BRATOVIC, 2019). In response to these challenges, biodegradable polymers have emerged as a viable alternative to fossil-based materials. According to ASTM standard (2019), biodegradable polymers undergo decomposition in natural aerobic environments (composting) through the metabolic activity of microorganisms capable of metabolizing their molecular structures. Despite their potential, biodegradable polymers still face limitations compared to synthetic polymers, particularly in terms of mechanical properties, water vapor barriers, and production costs, making large-scale adoption challenging (SAMIR et al., 2022; RAI et al., 2021; ZHONG et al., 2020). The use of blends is well known for reducing material costs and improving specific properties (ZHONG et al., 2020; WU; MISRA; MOHANTY, 2021). Extensive research has investigated the incorporation of different components, such as starch (MALI; GROSSMAN; YAMASHITA, 2010) and fibers (MOCHANE et al., 2021; PRAVEENA et al., 2022), particularly agro-industrial residues or byproducts (SAMIR et al., 2022; ILYAS et al., 2022).

Polybutylene succinate (PBS) is a biopolymer from the family of polyesters that can be processed through injection or extrusion to produce rigid or flexible materials comparable to polypropylene/polyethylene. PBS presents excellent biodegradation properties in soil and water (ILYAS et al., 2022). Additionally, starch, which is widely available from diverse sources (corn, potato, and cassava), can also be effectively processed through injection or extrusion to produce biodegradable materials at a lower cost compared to petroleum-derived or aliphatic polyesters (BULATOVIC et al., 2021; JIANG et al., 2020; CHENG et al., 2021; LOPEZ-GIL et al., 2014; COMBRZYŃSKI et al., 2021). A significantly underutilized agro-industrial residue with high potential is oat hulls, a byproduct of oat milling processing, yielding approximately 25-36% during milling (PASCHOAL et al., 2015; GIRARDET; WEBSTER, 2011).

Despite their versatility, oat hulls are primarily adopted as biomass for generating electricity and steam (HOLTZAPPLE, 2003), overlooking their potential for other valuable applications, such as in biodegradable blends. The low density and

weight of these natural fibers can be attractive in applications where lighter and more rigid materials are desired, such as in the coating of cups, straws, spoons, single-use trays for some foods, in the automotive industry, tissue engineering, and marine industry, among others (FERREIRA; MOLINA; PELISSARI, 2020; HUANG et al., 2018).

Combining oat hull, PBS, and starch can ensure biodegradability, lower cost, and adequate material properties. This could lead to the production of new materials with numerous potential applications, such as single-use trays and food packaging, utilizing a by-product previously considered waste in the oats industry, while making it cheaper and more environmentally friendly. To do this, it is necessary to study the behavior of oat hulls at different concentrations to understand their effect as a fiber-reinforced agent. This study aims to develop low-cost biodegradable materials by extrusion and thermoplastic injection using oat hulls, PBS, and starch.

## 2. Materials and Methods

### 2.1 Material

The materials used in this study included corn starch (14% moisture) (APTI™, Brazil), glycerol (technical grade glycerin, Dinâmica, Brazil), polybutylene succinate (PBS) (TK-BIO®, China) (Table 1), and oat hull (SL-Alimentos, Brazil). Before material production, oat hulls were ground (Mill An 11, Brazil) and sieved (28 *mesh*) to enhance their homogeneity.

### 2.2 Production of Biodegradable Materials by Thermoplastic Injection

Preliminary tests were conducted using different concentrations of PBS, starch, and oat hulls to evaluate their processability in a pilot single-screw extruder (model EL-75, BGM, Brazil) and a pilot injector (AX16-III, AX-Plasticos, Brazil). Three formulations (T20: 20 PBS %-w/w; 44,8 Starch %-w/w; 24 Glycerol %-w/w; 11,2 Oat hulls %-w/w; T60: 20 PBS %-w/w; 22,4 Starch %-w/w; 24 Glycerol %-w/w; 33,6 Oat hulls %-w/w; T100: 20 PBS %-w/w; 0 Starch %-w/w; 24 Glycerol %-w/w; 56 Oat hulls %w/w.) were produced in a pilot single screw extruder (90/120/120/110°C) using a temperature profile from heating zone 1 to zone 4 at a screw speed of 40 RPM. After extrusion, they were processed in the pilot injector to produce a dog-bone-shaped specimen of type IV (ASTM, 2015). The temperature profile was set at 120/120/110°C

from the feeder to the nozzle. Based on the preliminary tests, it was decided to set the concentration of PBS and glycerol (plasticizer) constant and vary the concentrations of starch and oat hulls, as detailed in Table 1. All material was manually mixed and processed as described in the preliminary tests.

**Table 1 -** Formulation of biodegradable materials containing PBS, starch, and oat hulls

| Formulation | PBS (% - w/w) | Starch (% - w/w) | Glycerol (% - w/w) | Oat Hulls (% - w/w) |
|---|---|---|---|---|
| PBS | 100 | 0 | 0 | 0 |
| F0 | 20.0 | 56.0 | 24.0 | 0 |
| F20 | 20.0 | 44.8 | 24.0 | 11.1 |
| F40 | 20.0 | 33.6 | 24.0 | 22.4 |
| F60 | 20.0 | 22.4 | 24.0 | 33.6 |
| F80 | 20.0 | 11.2 | 24.0 | 44.8 |
| F100 | 20.0 | 0 | 24.0 | 56.0 |

### 2.3 Mechanical Properties

Mechanical tensile tests (Young's modulus, tensile strength, and elongation at break) were performed according to ASTM 638-14 (2015) using a universal testing machine (EMIC, model DL 2000, Brazil). Before analysis, the specimens were conditioned at room temperature, maintaining a relative humidity of 53 ± 2% for one week, as per the ASTM 638-14 (2015) standard procedures.

### 2.4 Scanning Electron Microscopy (SEM)

The microstructure images of the samples were captured using a scanning electron microscope (Philips, model FEI Quanta 200, USA). Before imaging, the specimens were subjected to cryogenic fracture by immersion in liquid nitrogen and metalized with a thin layer of gold using a metallizer [Bal-Tec, model SCD-050, Germany]. All samples were analyzed using a 20 kV voltage accelerator and 2000x magnification.

### 2.5 X-ray Diffraction (XRD)

The crystallinity of the biodegradable materials was determined using an X'PertPRO diffractometer (Panalytical, Philips, Netherlands) with Cu Ka radiation (λ = 1.5418 Å) operating at room temperature at 40 kV. The relative crystallinity index (RCI) was calculated as the ratio between the area of the crystalline region and the sum of crystalline and amorphous regions (Equation 1) (KÖKSEL; SAHBAZ; ÖZBOY, 1993)

$$\mathrm{RCI} = \frac{\mathrm{C_a}}{\mathrm{C_a + A_a}} = \frac{\mathrm{C_a}}{\mathrm{T_a}} \quad (1)$$

Where $C_a$ is the crystalline area, $T_a$is the total area, and $A_a$is the amorphous area.

### 2.6 Density

Density was calculated by weighing the mass and measuring the volume using a digital caliper (Starrett, Brazil). Five specimens from each formulation were placed in a desiccator for one week under a relative humidity of 53%. Then, the specimens were weighed and measured to obtain thickness, length, and width.

### 2.7 Linear Contraction Index (LCI)

After production, ten specimens from each formulation were measured using a digital caliper (Starrett, Brazil). These specimens were subsequently placed in desiccators at a relative humidity of 53% and a temperature of 25°C for one week. The linear contraction index (LCI) was determined using Equation 2 (ASTM, 2001).

$$\mathrm{LCI(\%)} = \left(\frac{\mathrm{Lcm - Lcp}}{\mathrm{Lcm}}\right) \mathrm{x100} \quad (2)$$

Where Lcm is the initial specimen length and Lcp is the length after one week.

### 2.8 Moisture Sorption Isotherms

Approximately 0.5 to 0.8 g of biodegradable material was placed in an Aquasorp isotherm generator (Decagon Devices, USA), and the experimental moisture sorption data were fitted by the Guggenhein-Anderson-de-Boer (GAB) model (Equation 3) using the Nonlinear Regression Module (Statistica Software 7.0, StatSoft, USA).

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

Where aw = water activity, $X_w$ = equilibrium moisture content (kg/kg dry solid), $m_0$ = monolayer moisture content (kg/kg dry solid), and C and k = GAB constants.

### 2.9 Color

The CIELab color parameters (L*, a*, and b*) of five specimens from each formulation were measured using a colorimeter (Minolta CR 400, Japan) with a visual angle of 10°, in accordance with ASTM D2244-09B (2010).

### 2.10 Statistical analysis

All data obtained were evaluated by analysis of variance (ANOVA) and Tukey's test at a 5% significance level ($p < 0.05$) using Statistica software, version 7.0 (StatSoft, USA).

## 3. Results and Discussions

### 3.1 Mechanical Properties

The results of the mechanical properties of the biodegradable materials are shown in Table 2.

**Table 2** - Mechanical properties of biodegradable materials produced by thermoplastic injection.

| Formulation | Tensile Strength (MPa) | Elongation at break (%) | Young's Modulus (MPa) |
|---|---|---|---|
| F0 | 1.8 ± 0.1$^{a}$ | 20.0 ± 1.3$^{a}$ | 13.8 ± 2.8$^{c}$ |
| F20 | 1.6 ± 0.1$^{ab}$ | 13.3 ± 0.9$^{b}$ | 15.9 ± 6.6$^{c}$ |
| F40 | 1.4 ± 0.1$^{bc}$ | 11.1 ± 1.3$^{c}$ | 22.6 ± 8.2$^{bc}$ |
| F60 | 1.2 ± 0.1$^{cd}$ | 08.3 ± 2.2$^{c}$ | 24.5 ± 10$^{b}$ |
| F80 | 1.1 ± 0.1$^{df}$ | 7.4 ± 0.6$^{de}$ | 17.9 ± 5.2$^{c}$ |
| F100 | 0.9 ± 0.1$^{f}$ | 6.5 ± 0.4$^{de}$ | 29.6 ± 6.6$^{a}$ |

*a,b,c,d,e Means in the same column with different letters represent a significant difference ($p \leq 0.05$) between the formulations, according to Tukey's test.

The F0 formulation had the highest tensile strength (1.8 MPa), approximately double that of F100 (0.9 MPa). The higher the oat hull concentration, the lower the TS, probably due to the limited interfacial adhesion between the oat hulls

and the polymeric matrix. The interaction between the polymeric matrix (PBS) and the oat hull is difficult due to the hydrophilic nature of the hull (MOHAMMED et al., 2015). According to Mochane *et al.* (2021), the hydrophilic characteristics of natural fibers may adversely affect interfacial adhesion, particularly when the polymeric matrix is hydrophobic, such as PBS, resulting in poor mechanical properties (KAMARUDIN et al., 2022; KHALID et al., 2021). Other factors, such as fiber length, fiber type, extraction process, and moisture absorption, can decrease the TS (KHALID et al., 2021).

According to Aydemir and Gardner (2020), in blends of polyhydroxybutyrate and polylactic acid reinforced with cellulose nanofibrils, increasing the fiber concentration did not improve the mechanical properties; instead, there was a greater agglomeration and clogging of the fibers within the matrix structure, which enhanced the stiffness and ductility of the material. Ayu *et al*. (2020) produced sheets of PBS, starch, and empty fruit bunch fiber (EFB). According to the authors, adding fiber fillers up to 8 wt% decreased the tensile and flexural strength due to a lack of interfacial adhesion and poor dispersion of the fibers in the PBS matrix. As the literature indicates, incorporating natural fibers into blends to improve mechanical properties can present some difficulties due to issues such as fiber dispersion, the formation of polar and nonpolar phases, varying fiber concentrations, and the extrusion process.

The F0 material had the highest flexibility, possibly due to its high thermoplastic starch content, which increases its elasticity. Thermoplastic starch (TPS), when combined with a plasticizer such as glycerol, exhibits increased flexibility by lowering its glass transition temperature (Tg), which can be beneficial for certain applications, including food packaging and films (KHAN et al., 2017; CALABIA et al., 2013). The material with 20% oat hull content (F20) had approximately 7% lower elongation than F0. Calabia *et al.* (2013) produced sheets of PBS and cotton fiber and reported a decrease in the elongation at break of approximately 8% in formulations containing fiber. This decrease in elongation was attributed to the reduction in PBS chain movement, leading to higher stiffness in the materials. Similarly, Yang *et al*. (2020) produced injected materials using bamboo fiber and polypropylene, and they found that as the fiber concentration increased, the elongation at break (%) decreased. This decrease resulted from difficulties maintaining fiber dispersion in the blend, which adversely affected material flexibility. The same occurred in this study, where the

material became stiffer and less flexible.

### 3.2 Scanning Electron Microscopy (SEM)

The images of the F0 material (Figures 3a and 3b) showed starch granules (circular shape) and a plasticized superficial area, characteristic of blends containing thermoplastic starch (AYU et al., 2018; LIU et al., 2015). Cracks were also observed due to the poor compatibility between PBS and starch, forming a heterogeneous phase (immiscible blend). Similar characteristics can create a strong bond, resulting in dimensional stability and improved mechanical and barrier properties (TAIB; JULKAPLI, 2019; RAJ et al.,2021).

The F20 (Fig. 3c, Fig. 3d), F40 (Fig. 3e, Fig. 3f), F60 (Fig. 3g, Fig. 3h), F80 (Fig. 3i, Fig. 3j), and F100 (Fig. 3k, Fig. 3l) materials' surface and fracture images showed oat hull fibers (cylindrical shape), most of which were agglomerated and aligned, possibly due to extrusion orientation. Many cavities and pores were also observed in the formulations containing oat hulls, which might explain the decrease in the mechanical properties of these materials. Similar observations were reported by Calabia *et al.* (2015) for PBS and cotton fiber composites and Ayu *et al*. (2021) for sheets containing empty fruit bunches, PBS, and starch. In both studies, the presence of long fibers and voids in the structure was observed, indicating weak interfacial adhesion.

Mechanical and barrier properties highly depend on the morphology status (MOCHANE et al., 2021; AYU et al., 2020). Some methods can improve the interfacial surface between the components, such as treatments with silanes, alkalis, or acetones, reducing incompatibility (ILYAS et al., 2022). However, the work aimed to produce biodegradable and nontoxic materials, and chemical or surface cleaning methods can harm the environment.

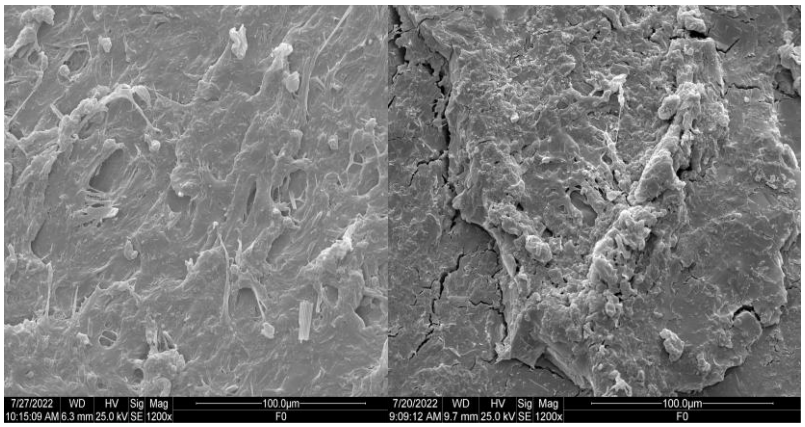



**Figure 1-** (a) F0 Formulation (100.0 µM); (b) F0 Fractured (100.0 µM)

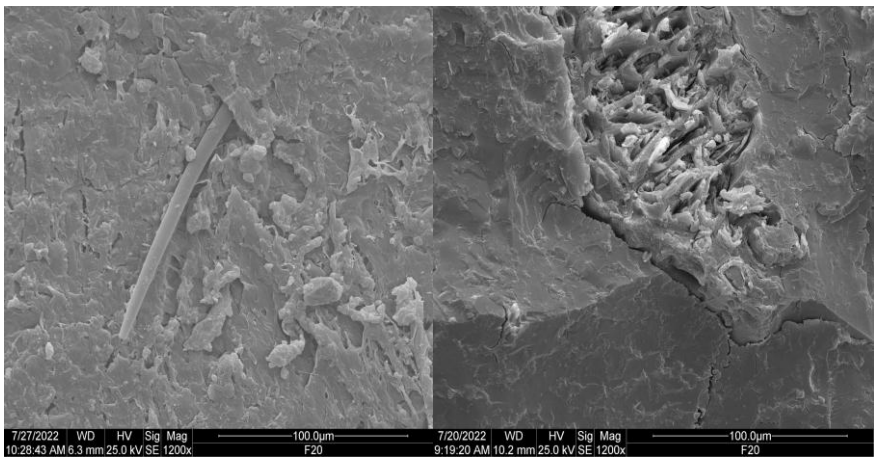



**Figure 2-** (a) F20 Formulation (100.0 µM); (b) F20 Fractured (100.0 µM)

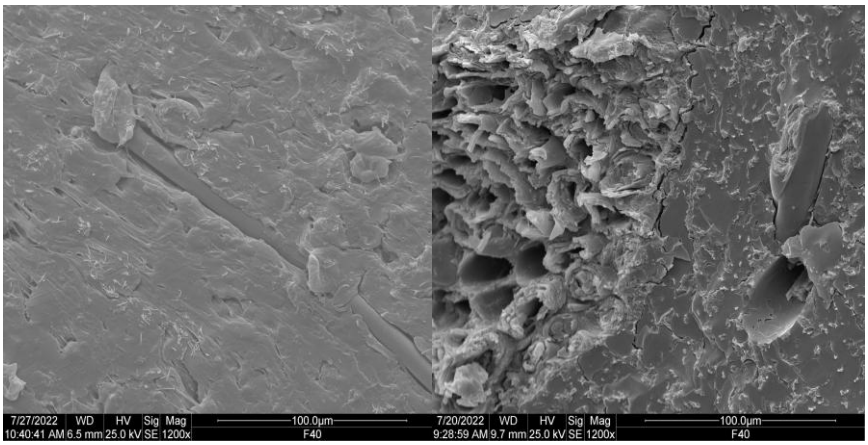



**Figure 3-** (a) F40 Formulation (100.0 µM); (b) F40 Fractured (100.0 µM)

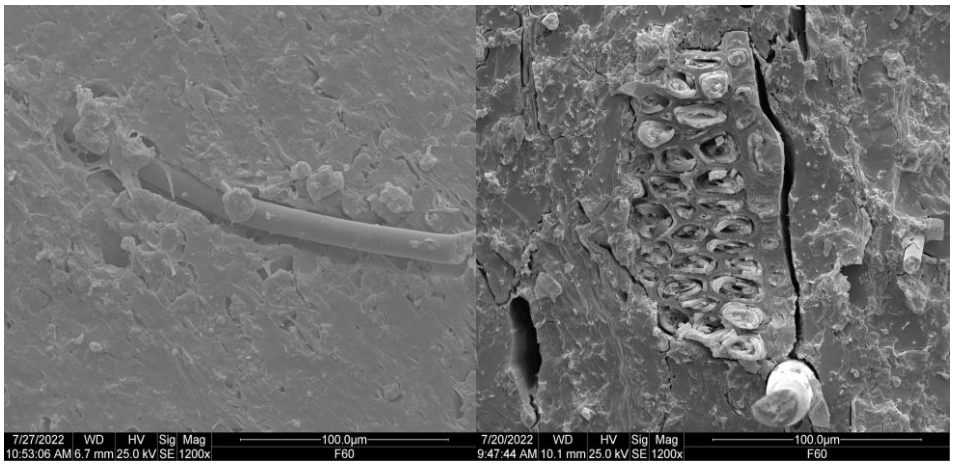



**Figure 4-** (a) F60 Formulation (100.0 µM); (b) F60 Fractured (100.0 µM)

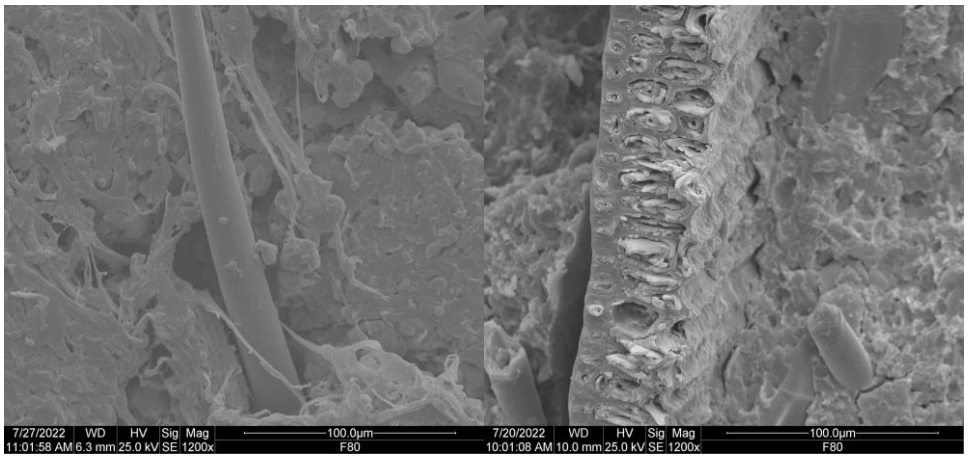



**Figure 5-** (a) F80 Formulation (100.0 µM); (b) F80 Fractured (100.0 µM)

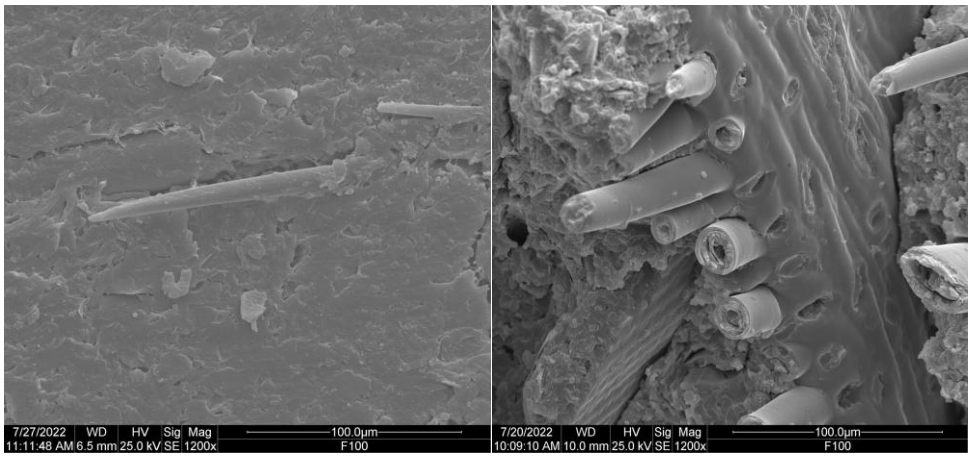
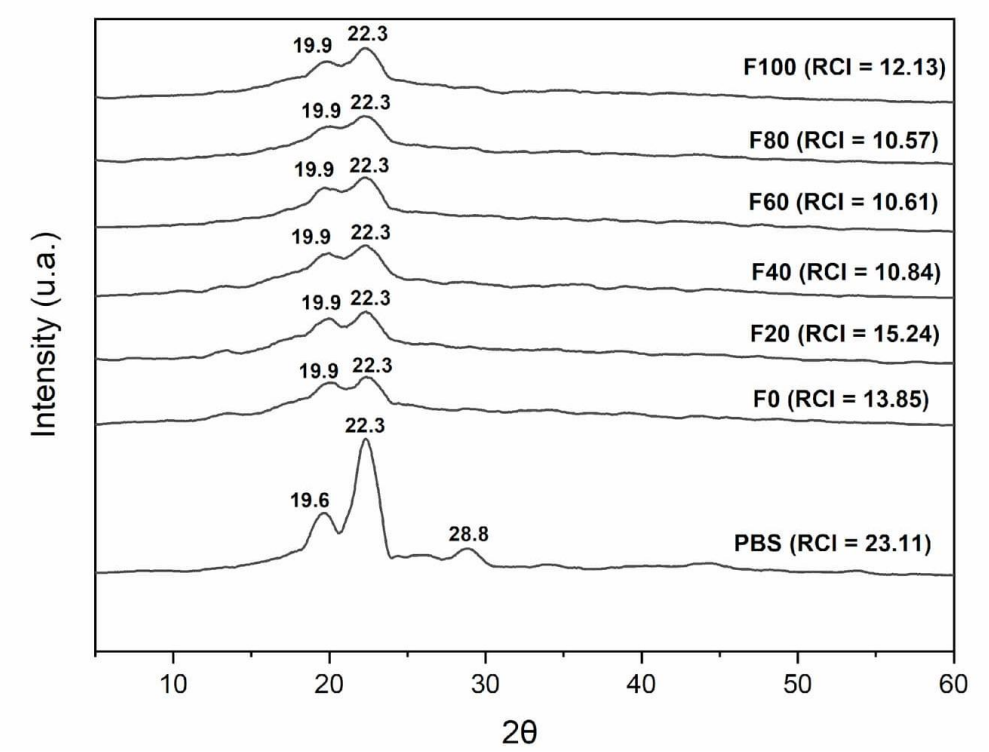



**Figure 6-** (a) F100 Formulation (100.0 µM); (b) F100 Fractured (100.0 µM)

### 3.3 X-ray Diffraction (XRD)

The X-ray diffractograms and the respective relative crystallinity index (RCI) of the biodegradable materials are presented in Figure 7.

**Figure 7 -** X-ray diffractograms and relative crystallinity index (RCI) of the biodegradable materials




Two peaks (19.9° and 22.3°) were identified in all blend formulations, and the oat hull concentration did not influence the crystallinity of the materials. Hu *et al*. (2017) produced blends containing PBS and different types of cellulose, and all diffractograms showed reduced peaks, suggesting that the natural fibers used had low crystallinity. Liu *et al.* (2015) produced materials with starch, PBS, and ionic liquid; varying starch content did not modify the PBS crystalline phase.

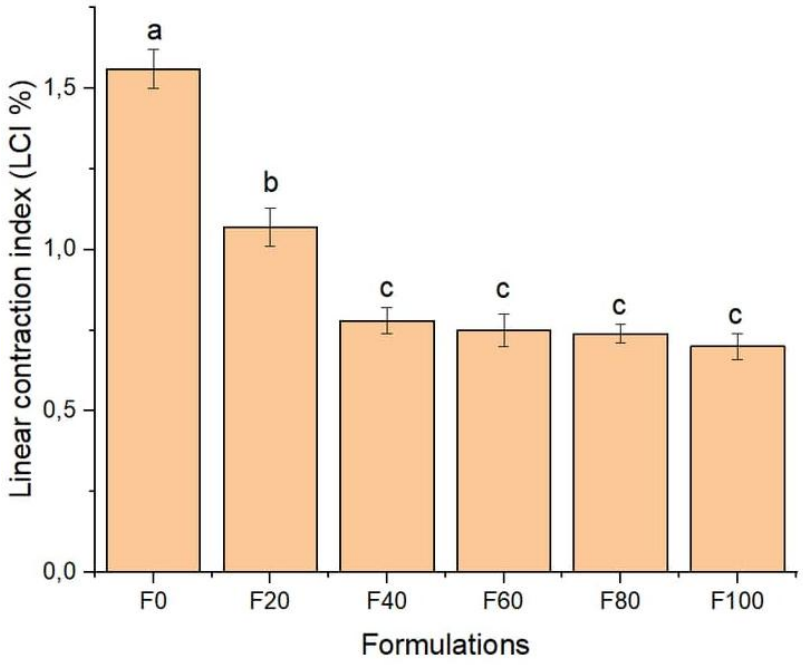
PBS showed peaks at approximately 19.6°, 22.3°, and 28.8°, and peaks near 19.5° and 22.5° are characteristic of the crystalline phase of PBS (ZHAO et al., 2020; XU et al.,2021). PBS also exhibited a larger peak at 22.3° compared to the other formulations, as the addition of starch, oat hulls, and glycerol impaired the crystallinity properties of PBS during the production/extrusion process of the materials. This same behavior was observed by Xu *et al*. (2021) for blends produced with PBS and corn starch, possibly due to starch particles obstructing PBS segments. The low

relative crystallinity indexes (RCIs) of the biodegradable materials containing starch, ranging from 10.57% to 15.24%, can be attributed to the destruction of the semicrystalline structure of starch during the extrusion process, leading to the formation of higher amorphous zones (PHETWAROTAI; POTIYARAJ; AHT-ONG, 2012).

### 3.4 Linear Contraction Index (LCI)

The linear contraction indexes (LCIs) of the biodegradable materials are presented in Figure 8. F0 (1.56%) and F20 (1.07%) had the highest LCI values. LCI of the other materials was not significantly different and ranged from 0.70 to 0.78%. Materials produced by injection molding can contract as they cool from a melted to a solid state under atmospheric pressure (KOWALSKA, 2007).

**Figure 8-** Linear Contraction Index (LCI) of the biodegradable materials




*a,b,c,d Means with different letters represent a significant difference ($p \leq 0.05$) between the formulations, according to Tukey's test.

Increasing the fiber concentration resulted in a lower contraction of the injected material because the fibers can act as fillers, i.e., occupying spaces in the blend structure and making it less capable of shrinking or expanding (SYKACEK et al.,

2009; MOUGIN; MAGNANI; EIKELENBERG, 2009). This can be advantageous since it avoids the appearance of marks on thicker parts of the materials, provides good geometrical stability, avoids deformation after injection, and reduces material shrinkage. The SEM analysis of the materials (item 3.2) with oat hulls showed that the fibers were oriented and agglomerated in a cylindrical shape, suggesting that these aligned and clogging fibers decreased the materials' LCI. The LCI can also be influenced by temperature, pressure, injection flow rate, equipment design, and material composition (KOWALSKA, 2007; ARÚJO et al., 2023).

### 3.5 Density

F100 had the lowest density, and the other formulations did not show significant differences (Table 4) due to the lower density of PBS compared to thermoplastic starch (TPS). Additionally, the high oat hull content in the F100 formulation contributed to decreased material density, as fibers have lower densities than TPS. One of the main advantages of incorporating natural fibers into polymeric structures is to reduce material density (MOCHANE et al., 2021; KANNAN & THANGARAJU, 2022; YUSOF et al., 2019). This can lead to applications where lighter and less flexible materials are desired, such as food packaging, single-trays, cups, and the automotive industry (FERREIRA; MOLINA; PELISSARI, 2020; HUANG et al., 2018). Aslan *et al.* (2018) produced composites of polypropylene and sisal fiber, fiberglass, and carbon fiber, and increasing sisal fiber concentration reduced the material's density. The density of the material decreases with the addition of natural fibers in the blend in most cases.

**Table 3** - Density of the biodegradable materials produced by injection extrusion.

| Formulation | Density (g 100g $g^{-1}$) |
|---|---|
| F0 | $1.34 \pm 0.02^{b}$ |
| F20 | $1.32 \pm 0.04^{b}$ |
| F40 | $1.35 \pm 0.04^{b}$ |
| F60 | $1.32 \pm 0.04^{b}$ |
| F80 | $1.35 \pm 0.03^{b}$ |
| F100 | $1.28 \pm 0.02^{a}$ |

*a,b,c Means with different letters represent a significant difference ($p \leq 0.05$) between the formulations, according to Tukey's test.

### 3.6 Moisture Sorption Isotherms

The Guggenheim-Anderson-de Boer (GAB) parameter values for the moisture sorption isotherms of the biodegradable materials are presented in Table 4.

**Table 4** - GAB model parameters of the moisture sorption isotherms of the biodegradable materials.

| Formulation | GAB Model Parameter | | | $R^2$ |
|---|---|---|---|---|
| | $m_0$ g 100 $g^{-1}$ | k | C | |
| F0 | 16.11 | 0.78 | 10.000 | 0.97 |
| F20 | 4.66 | 1.01 | 10.000 | 0.99 |
| F40 | 5.65 | 1.01 | 10.000 | 0.98 |
| F60 | 2.43 | 1.06 | 10.000 | 0.99 |
| F80 | 2.31 | 1.06 | 10.000 | 0.99 |
| F100 | 4.03 | 1.02 | 10.000 | 0.99 |

*Formulations containing F - Oat Hulls in different concentrations

The $m_0$ of the F0 material (16.11 g 100 $g^{-1}$) was the highest among all formulations, mainly due to its higher proportion of thermoplastic starch (TPS) and the absence of oat hull because TPS is known for its high hydrophilicity (MALI; GROSSMAN; YAMASHITA, 2010). As the oat hull content increased (F20, F40, F60, F80, F100), the $m_0$ values decreased compared with F0 material due to the reduction of TPS concentration in the blend. The F100 material had no starch in its composition and had an intermediary $m_0$ value between F0 and F80 because the oat hull is less hydrophobic than PBS but more hydrophobic than TPS. The k and C values were similar for all formulations.

### 3.7 Color

The CIELab color parameters L*, a*, and b* of the biodegradable materials are presented in Table 5.

**Table 5** - CIELab color parameters of the biodegradable materials.

| Formulation | L* | a* | b* |
|---|---|---|---|
| **F0** | 62.69 ± 0.27 | -2.71 ± 0.13 | 9.79 ± 0.26 |
| **F20** | 42.82 ± 0.47 | 4.09 ± 0.25 | 2.57 ± 0.31 |
| **F40** | 41.54 ± 0.74 | 3.17 ± 0.09 | 0.54 ± 0.29 |
| **F60** | 43.49 ± 1.91 | 2.62 ± 0.22 | 1.05 ± 0.92 |
| **F80** | 45.29 ± 3.50 | 2.47 ± 0.29 | 2.09 ± 1.97 |
| **F100** | 42.69 ± 2.03 | 2.84 ± 0.22 | 1.66 ± 1.29 |

The L* parameter is luminosity; a* red/green coordinate; b* yellow/blue coordinate

F0 had the highest luminosity (62.69), and the formulations containing oat hulls had lower values, ranging between 41 and 45. The decrease in luminosity can be attributed to the opaque nature of oat hulls, which can significantly influence the color parameters. For the a* parameter, F20 presented the highest value (4.09). The b* parameter of the F0 material (9.79) was higher than that of the others because it did not contain an oat hull in its formulation, only PBS and starch, resulting in a yellowish color.

In this study, all the materials with oat hulls had a brownish color. The oat hulls are composed of pentosans (30-35%) and protein (4%) (GIRARDET; WEBSTER, 2011), which are components that can contribute to the Maillard reaction during the extrusion process at high temperatures (90-110°C). This Maillard reaction could explain the color alteration observed in the materials with oat hulls.

## 4. Conclusions

Biodegradable materials, including oat hulls, starch, and polybutylene succinate, exhibited excellent processability during extrusion to produce pellets and during thermoplastic injection to produce dog-bone-shaped specimens. The extrusion aligned the oat hull fibers, making the material dimensionally stable, i.e., without the shrinkage observed in materials without fiber. Furthermore, incorporating oat hulls enhanced stiffness and reduced material density compared to non-hull counterparts.

These materials are suitable for producing lighter and stiffer materials for commercial applications, such as fast-food packaging and single-use items like trays, spoons, and cups. Additionally, the oat hulls are a low-cost agro-industrial byproduct, and it is possible to produce biodegradable materials with up to 56% hulls and only 20% PBS. Their potential for large-scale manufacturing is highlighted by their compatibility with existing equipment and processes in the plastics industry. For future projects, new studies using FTIR spectroscopy can be conducted to further understand the interactions between oat hulls, TPS, and PBS.

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## CAPÍTULO IV- Biodegradable materials of citrus pulp, starch, and polybutylene succinate produced by thermoplastic injection molding


### Abstract

Plastics from fossil sources have emerged as a significant concern at present. Biodegradable materials derived from renewable sources are an alternative to those derived from fossil sources for several purposes. This study investigates a novel approach to producing low-cost, biodegradable materials using citrus pulp (CP), polybutylene succinate (PBS), and starch through extrusion and thermoplastic injection molding. Six formulations with different concentrations of CP and starch (0-56% w/w) were produced. The biodegradable materials, regardless of the formulation, exhibited adequate mechanical properties for several purposes and excellent processability. Their densities are similar to those of polyethylene terephthalate (PET) and lower than those of polyvinyl chloride (PVC). They exhibit dimensional stability with a Linear Contraction Index (LCI) lower than 1%. No chemical reactions were detected in FTIR analysis, only interactions between components. These results are promising, as these biodegradable materials can be produced on a large scale at low cost, utilizing a by-product from the orange juice industry.


**Keywords:** Biopolymers, by-products, waste, orange, mechanical properties.

## 1. Introduction

Plastics from fossil sources have emerged as a significant concern at present. Despite their advantages (cheap, easy to process, low density, excellent mechanical properties, and chemical stability), these materials have a well-known environmental impact, including microplastic issues, which can be ingested by fish and other animals and ultimately end up in the human food chain. Biodegradable materials derived from renewable sources are an alternative to those from fossil sources, and they have the potential for various applications in the agriculture, pharmaceutical, medical, and food industries (WU; MISRA; MOHANTY, 2021; DOPPALAPUDI et al., 2014; ZHONG et al., 2020). However, they have disadvantages compared to conventional plastics, including lower chemical stability, higher costs, and lower processability (BIN, 2014).

Many alternatives have been explored to use biodegradable materials on a large scale, such as blends of high-cost biodegradable polymers like poly (lactic acid) (PLA), poly (butylene adipate co-terephthalate) (PBAT), and polybutylene succinate (PBS) with other components (BULATOVIC et al., 2021; ILYAS et al., 2022; DIN et al., 2020; BELUCI et al., 2023; BELUCI et al., 2024) to improve their properties, processability, and reduce cost. PBS is a biodegradable polymer for broader applications because it has mechanical properties comparable to polypropylene (PP) and polyethylene (PE), excellent processability, and can be extruded in an injection molder (ALIOTTA et al., 2021), but it is three to five times more expensive than petroleum-based plastics (PP or PE) (MOCHANE et al., 2021; RAFIQAH et al., 2021; MTIBE et al., 2023; BARRINO et al., 2023).

Many studies (FAHRNGRUBER et al., 2020; XEI et al., 2021; NAZRIN, SAPUAN, & ZUHRI, 2020; AYU et al., 2018, 2020) report that producing blends with starch and PBS is an effective way to create a new material at a reduced cost. Starch is widely distributed in nature and can be easily transformed into a thermoplastic material by extrusion with a plasticizer, such as glycerol (ZHANG et al., 2014; MÜLLER, PIRES, & YAMASHITA, 2012). Starch also exhibits excellent biodegradability and is less expensive than conventional and biodegradable polymers, such as PE, PP, PBS, and PLA; however, it still presents disadvantages, including high hydrophilicity and brittleness (DIYANA et al., 2021).

Brazil is currently the world's largest producer and exporter of oranges and orange juice (NEVES, 2024). It is a product of extreme financial importance. The peel, seeds, and discarded oranges are referred to as citrus pulp (CP), the primary low-cost by-product of the citrus industry. The CP is dried, pelletized, and used as a ruminant feedstock to partially replace corn and other high-cost ingredients (TIGRE, 2012; ASSIS et al., 2004). Other minor applications include the extraction of cellulose and nanocellulose (MANTOVAN et al., 2021) and the synthesis of synthetic carbons to remove heavy metals from water (LICONA-AGUILAR et al., 2022). Using CP as a fiber-reinforced agent in a PBS/starch blend can improve mechanical properties, decrease material density, and mainly reduce costs (MOCHANE et al., 2021; RAFIQAH et al., 2021; MTIBE et al., 2023). Enabling the production of CP blends on a large scale, using equipment such as extruders and injection molding machines, is a viable alternative to conventional plastics derived from fossil fuels. This approach would align with the growing focus on sustainable manufacturing practices and bio-based materials. This study explores a novel approach to producing low-cost, biodegradable materials using CP, PBS, and starch through extrusion and thermoplastic injection molding.

## 2. Materials and Methods

### 2.1 Material

Corn starch (14% moisture) (APTI™, Brazil), glycerol (Dinâmica, Brazil), polybutylene succinate (PBS) (TK-BIO®, China). Centesimal composition was determined according to the Association of Official Analytical Chemists (2009) for citrus pulp pellets (73% carbohydrates; 9% moisture; 6% protein; 1.6% lipids; 10% ash), and hemicellulose (15.47%), cellulose (19.40%), and lignin (15.86%) contents was determined according to Van Soest (1965) method. Citrus pulp pellets were donated by Citrusuco™ (Brazil). Before material production, citrus pulp pellets were ground (MA 680, Marconi, Brazil), and the particle size of CP (less than 150 μm) was determined using seven sieves (1000 μm - 150 μm).

### 2.2 Preparation of blends with CP, PBS, and starch

Preliminary tests were conducted with varying amounts of CP, PBS, and starch. Two formulations (P60: 20 PBS %-w/w; 22.4 Starch %-w/w; 24 Glycerol %-w/w; 33.6 CP %-w/w, and P100: 20 PBS %-w/w; 0 Starch %-w/w; 24 Glycerol %-

w/w; 56 CP %-w/w) were produced with a single-screw extruder (model EL-75, BGM, Brazil) with a two-hole die (2 mm diameter) at a temperature profile of 90/120/120/110 °C from zone 1 to zone 4, respectively, at a screw speed of 40 rpm. After being extruded, the material was pelletized and sent to the injection molding machine (AX-Plasticos, Brazil). To produce the specimens, the temperature profile was set at 120/120/110 °C from the feeder to the nozzle, using a dog bone-shaped mold (type IV) (ASTM D638-14, 2014). After preliminary tests, the concentrations of CP, PBS, and starch were established (Table 1). All formulations were produced according to preliminary test conditions.

**Table 1 –** Formulations containing PBS, starch, glycerol, and citrus pulp.

| Formulation | PBS (% - w/w) | Starch (% - w/w) | Glycerol (% - w/w) | CP (% - w/w) |
|---|---|---|---|---|
| $CP_0S_{56}$ | 20.0 | 56.0 | 24.0 | 0 |
| $CP_{11}S_{44}$ | 20.0 | 44.8 | 24.0 | 11.2 |
| $CP_{22}S_{33}$ | 20.0 | 33.6 | 24.0 | 22.4 |
| $CP_{33}S_{22}$ | 20.0 | 22.4 | 24.0 | 33.6 |
| $CP_{44}S_{11}$ | 20.0 | 11.2 | 24.0 | 44.8 |
| $CP_{56}S_0$ | 20.0 | 0.0 | 24.0 | 56.0 |

### 2.3 Scan electronic microscopy (SEM)

The samples were conditioned at 0% relative humidity for one week before analysis. The morphology of the cross-section (fracture) of the biodegradable materials was examined using a scanning electron microscope (Philips, model FEI Quanta 200, USA). The samples were fractured after immersion in liquid nitrogen (cryogenic fracture) and metalized with a thin layer of gold using a metallizer (Bal-Tec, model SCD-050, Germany). All samples analyzed used a 20kV voltage accelerator and 2000x magnification.

### 2.4 X-ray diffraction (XRD)

The samples were ground and conditioned at 0% relative humidity for one week before analysis. The relative crystallinity index (RCI) of the biodegradable materials was determined using an X'PertPRO diffractometer (Panalytical, Philips, Netherlands), equipped with Cu Kα radiation (λ = 1.5418 Å) and operating at 40 kV at room temperature. The RCI was calculated according to the crystalline and amorphous areas (Equation 1) (KÖKSEL; SAHBAZ; ÖZBOY, 1993).

$$RCI = \frac{C_a}{C_a + A_a} \quad 1)$$

Where $C_a$ is the crystalline area, and $A_a$ is the amorphous area.

### 2.5 Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectrometry analyses of the biodegradable materials were performed using the KBr pellet method in a Fourier Transform Infrared Spectrophotometer (Shimadzu, model IR Prestige-21, Japan). The biodegradable materials were triturated, mixed with KBr, and pressed at 784 N $m^{-2}$. Readings were taken in the spectral range of 400 to 4000 $cm^{-1}$, with a resolution of 4 $cm^{-1}$, and 16 scans.

### 2.6 Color Evaluation

The color analysis was conducted according to ASTM D2244-09b (2010), utilizing a Minolta CR-400 colorimeter (Japan) and a visual angle of 10°. The injections were placed on a white surface, and readings were taken using CIELab coordinates (L*, a*, and b*) in triplicate on five specimens of each formulation.

### 2.7 Mechanical Properties (Tensile Strength, Young's Modulus, and Elongation at Break)

Mechanical tensile tests (Young's modulus, tensile strength, and elongation at break) were performed using a Universal Testing Machine (EMIC, model DL 2000, Brazil) according to ASTM 638-14 (2014). As standard procedures, the specimens were conditioned at room temperature under 53 ± 2% relative humidity for one week.

### 2.8 Moisture Sorption Isotherms

The specimens were cut into small pieces, and 0.5 to 0.8 g was placed in an Aquasorp isotherm generator (Decagon Devices, USA). The dynamic method was used to determine the sorption isotherms. The moisture data and water activity were adjusted using the Guggenhein-Anderson-de-Boer (GAB) model (Equation 3) by non-linear regression using Statistica Software 7.0 (Statsoft, USA), where $X_w$ represents the equilibrium of moisture (g of water/g of dry mass), $m_0$ is the water content in the monolayer, k is the heat of sorption in the multilayer and C is the Guggenheim constant, representing the heat of sorption in the first layer in the sample.

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

### 2.9 Linear Contraction Index (LCI)

Ten specimens of each formulation were measured after the injection process with a digital caliper (Starrett, Brazil). The linear contraction index (LCI) was determined by Equation 4 (ASTM D955-00 2001).

$$LCI(\%) = \left(\frac{Lcm - Lcp}{Lcm}\right) x100 \quad 4)$$

Where: Lcm is the mold length (theoretical), and Lcp is the length of the specimen after contraction.

### 2.10 Density

Five specimens of each formulation were placed in a desiccator for one week at 53% relative humidity, then weighed and measured thickness, length, and width with a digital caliper (Starrett, Brazil) to calculate the volume.

$$Density(\%) = \frac{Weigth\ (g)}{Volume\ (cm^3)} \quad 5)$$

### 2.11 Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of the biodegradable materials were performed using a Shimadzu TGA-50 thermogravimetric analyzer (Japan). The

samples were heated from 25 to 600 °C at a heating rate of 10 °C $min^{-1}$ under an argon atmosphere (flow rate 50 mL $min^{-1}$). The thermal stability of the injected specimens was evaluated based on the TGA and DTG curves.

### 2.12 Statistical Analysis

All data obtained were evaluated by analysis of variance (ANOVA) and Tukey's test at a 5% significance level ($p < 0.05$) with Statistica software, version 7.0 (StatSoft, USA).

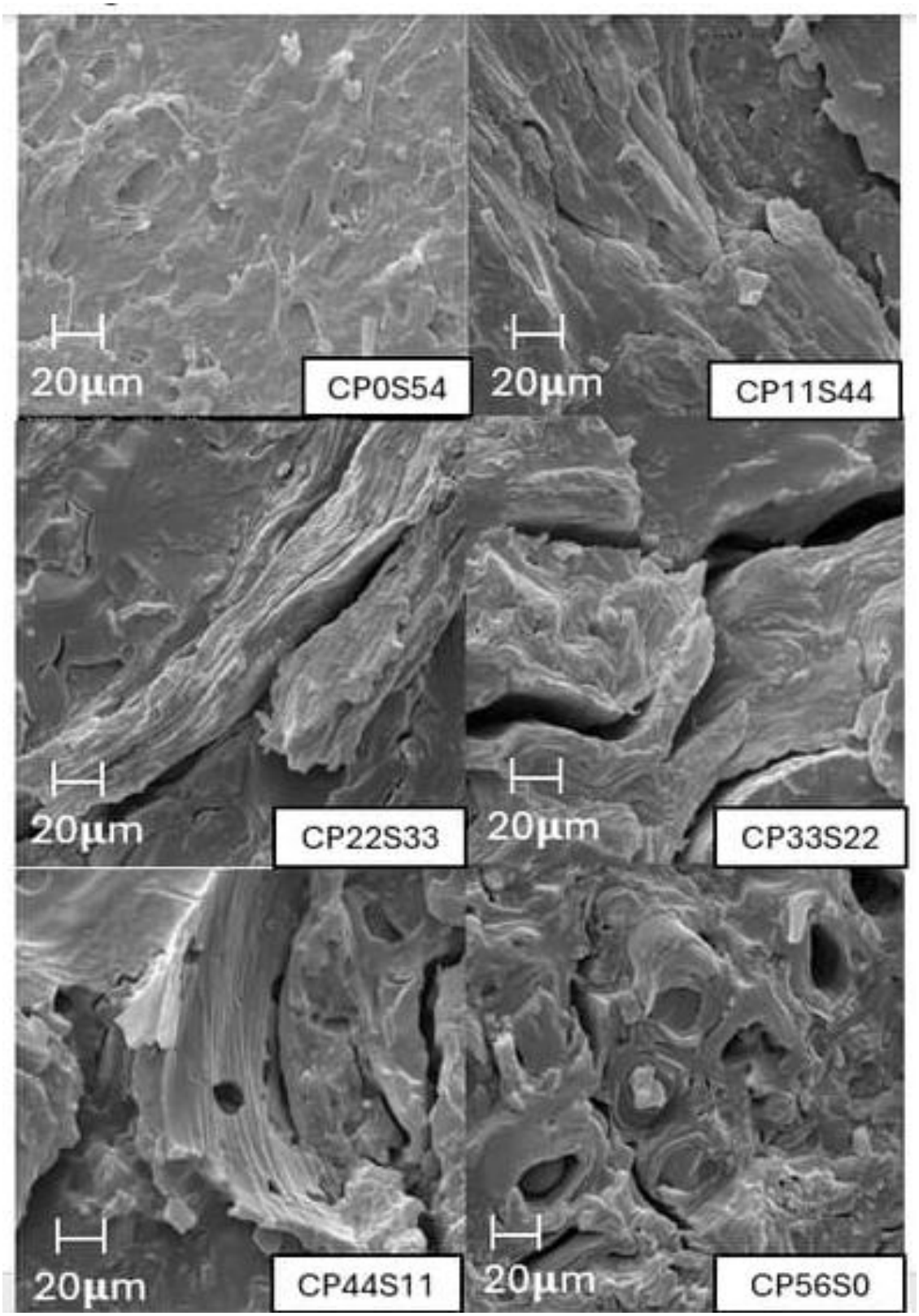
## 3. Results And Discussion

### 3.1 Scan Electronic Microscopy (SEM)

SEM analysis (Figure 1) depicted the morphologies of the cross-section (fracture) of the biodegradable materials produced by blending CP, starch, PBS, and glycerol as a plasticizer.

Formulation CP0S56 exhibited a smooth cross-section surface, indicating efficient blending of poly (butylene succinate) (PBS) and starch. All formulations containing CP showed cross-section surfaces with voids and cracks, and the higher the CP content, the more pronounced the voids and cracks. The non-homogeneity of these surfaces was due to the poor interfacial interaction between starch and CP and PBS, i.e., the CP-starch-PBS was an immiscible blend. This lack of interactions occurred due to the high cellulose (19.40%), hemicellulose (15.47%), and lignin (15.86%) contents in CP, which are incompatible with PBS. According to Fiore et al. (2016), the high moisture content in natural fibers, resulting from their hydroxyl groups, can impair the extrusion process. The moisture can lead to several issues during processing, including the formation of voids and cracks on the material, as the water vapor generated during extrusion creates pressure that compromises the material's integrity.

**Figure 1** - SEM images of the cross-section (fracture) of biodegradable materials



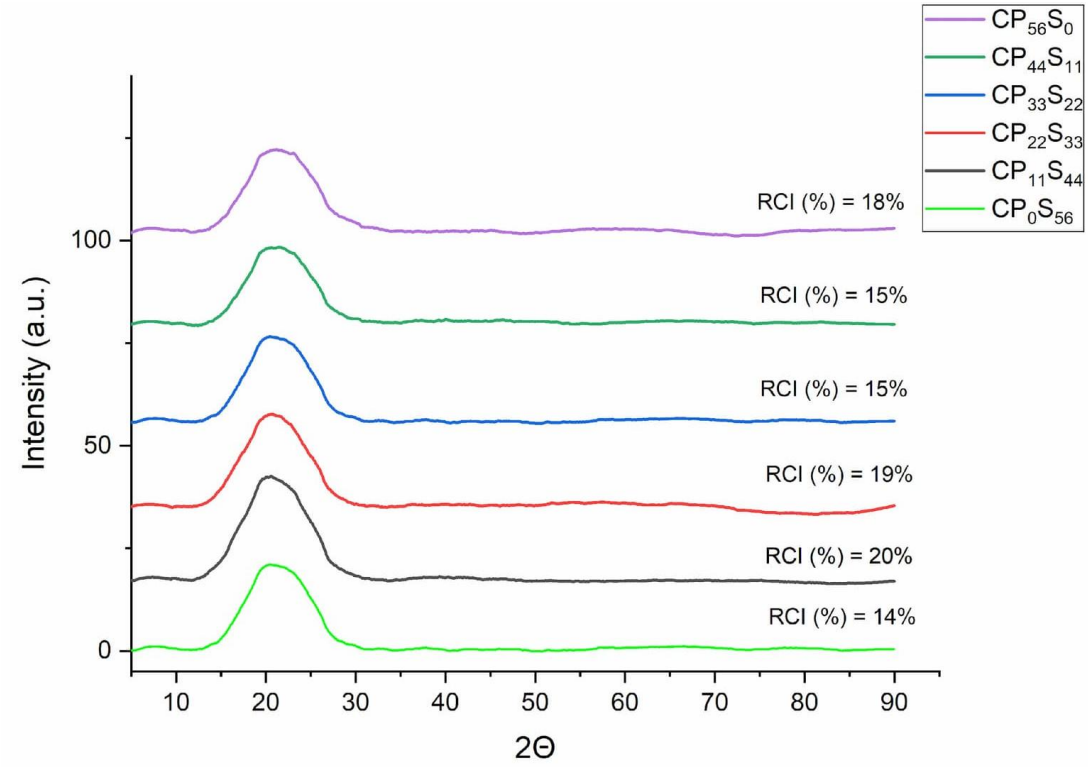

SEM images of biodegradable casting films made from orange peel (YARADODDI et al., 2022) showed a rough but uniform surface, as casting films

generally have more homogeneous surfaces than extruded materials. The SEM analysis reported by Ayu et al. (2018) showed that in blends of PBS and starch, the starch particles were not well dispersed within the PBS matrix. This poor dispersion led to weak bonding between the two phases of the blend. In another study (SOCCIO et al., 2023), SEM analysis of PBS/wheat flour blend films revealed a separation between the two phases due to a lack of compatibility between the wheat flour and PBS.

### 3.2 X-Ray Diffraction (XRD).

The X-ray diffractograms and the respective relative crystallinity index (RCI) of the biodegradable materials are presented in Figure 2.

**Figure 2 -** X-ray diffractograms and relative crystallinity index (RCI) of the biodegradable materials




All the formulations exhibited amorphous characteristics, with peaks that were not well-defined and located in the range of 22.6-22.9°, as all the components of the biodegradable materials have characteristic peaks in this range that overlap.

The crystalline phase of PBS exhibited characteristic peaks at 19.5° and 22.5° (ZHAO et al., 2020), while cellulose (CP) had peaks at 22.3° (SHEN,

GHASEMLOU, & KAMDEM, 2015).

Corn starch exhibited four characteristic peaks (15°, a doublet peak near 17-18°, 19.9°, and 23°) and is characterized by its A-type crystal structure. However, the thermoplastic extrusion process partially destroyed the semi-crystalline structure of TPS (ALTAYAN; AL DAROUICH; KARABET et al., 2021; LIU et al., 2015).

Mariño et al. (2015) conducted an XRD analysis of raw citrus waste, and they reported a similar diffractogram, with a peak that starts at 16.4° and becomes broader until it approaches the 22.4° peak, which corresponds to the cellulose peak.

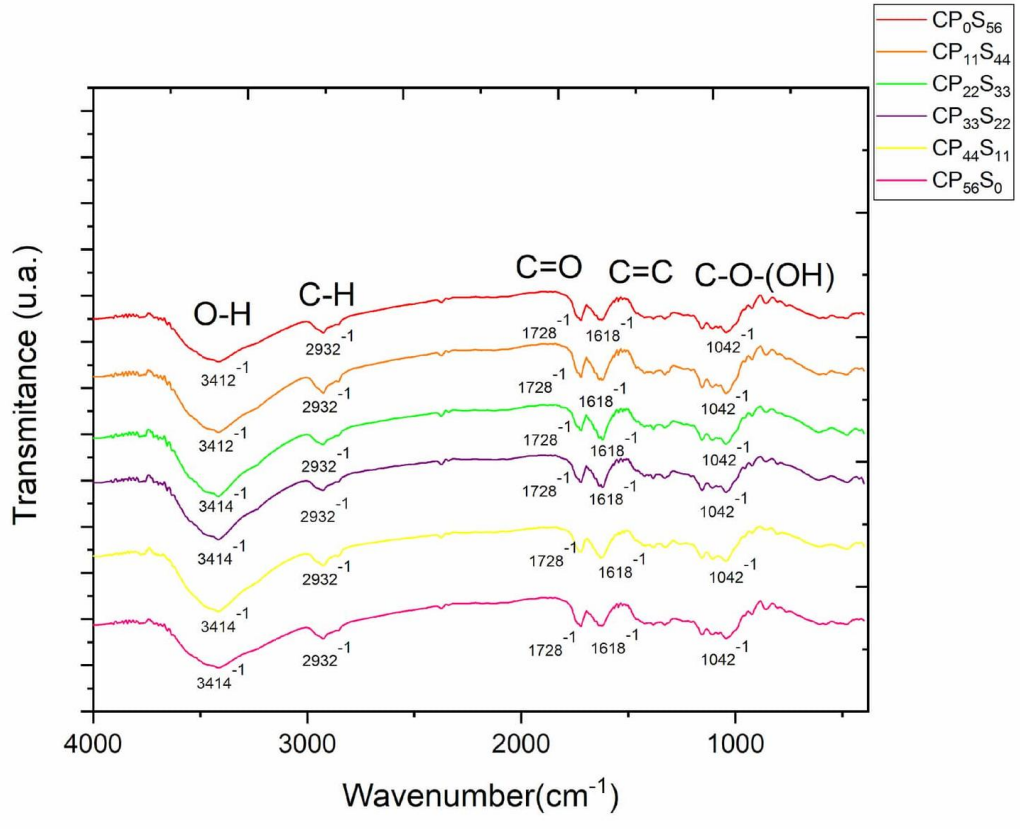
In another study (LIU et al., 2015), injection materials were analyzed by XRD, with PBS (80 wt.%), starch (20 wt.%), and varying the type of plasticizer (glycerol and ionic liquid), and only peaks at 19.4°, 21.5°, and 22.5°, characteristics of PBS, were identified, due to the high amount of PBS in the blend.

The relative crystallinity index (RCI) of all materials varied between 15% and 20%, but there was no correlation between the RCI and the CP content. According to Jin et al. (2014), the RCI (%) for pure and modified PBS was around 40-50%, whereas a thermoplastic starch film produced by casting had a value of around 30% (ISMAIL et al., 2014). The lower values (15-20%) were due to the amorphous areas, characteristic of the lignin and hemicellulose components present in the blends. In addition, the extrusion and plasticization of the starch contributed to reducing the RCI.

### 3.3 Fourier-Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the biodegradable materials are presented in Figure 3.

**Figure 3 -** FTIR spectra of the biodegradable materials containing CP




All the materials exhibited similar spectra despite their formulation. The broadband between 3600 and 3300 $cm^{-1}$ is related to O-H stretching vibrations (ALTAYAN; AL DAROUCH; KARABET, 2021). Native starch comprises amylose and amylopectin, and has hydroxyl groups with O-H bonds throughout its structure, forming various inter- and intramolecular bonds (HUBER; BEMILLER, 2019). During the extrusion process, the starch structure reorganizes, forming new hydrogen bonds.

The broadband between 3412 and 3414 $cm^{-1}$, which overlapped with O-H stretching vibrations, was due to the CP and starch. CP contains cellulose, hemicellulose, and lignin, which are composed of alkoxy groups and carboxy groups, among others, and are particularly abundant in the orange peel (YARADODDI et al., 2022).

Bands between 2939 - 2920 $cm^{-1}$ are related to C-H bonds present in orange peel due to their aliphatic characteristics (KAMSONLIAN et al., 2011; CYPRIANO; DA SILVA; TASIC, 2018). Yaradoddi et al. (2022) carried out an FTIR analysis on a film made with orange peel and found that alkoxyls (3353 $cm^{-1}$) and carboxylic acids (2920 $cm^{-1}$) were present.

Bands between 1728 and 1719 $cm^{-1}$ were related to C=O bonds from the PBS structure, and bands near 1050 $cm^{-1}$ were related to C-O-(H) bonds from starch since starch can leave traces of bonds for alkaline, aromatic, alkoxy, and ester compounds, among others (AYU et al. 2018).

The band around 1627 $cm^{-1}$ was attributed to the C=C stretching of double bonds (FERREIRA et al., 2020; CYPRIANO, DA SILVA, & TASIC, 2018). These bonds are present in aromatic components such as lignin.

The components of the biodegradable material remained unchanged chemically during the extrusion and injection processes, as no new bonds were detected. These results indicate that the PBS-starch-citrus pulp-glycerol blend is immiscible, with no chemical reaction, only physical interactions.

### 3.4 Color Evaluation

The color parameters (L*, a*, and b*) and the specimens are shown in Figure 4, and the CIELab color parameters are presented in Table 2.

**Figure 4 -** Visual aspect of the biodegradable materials

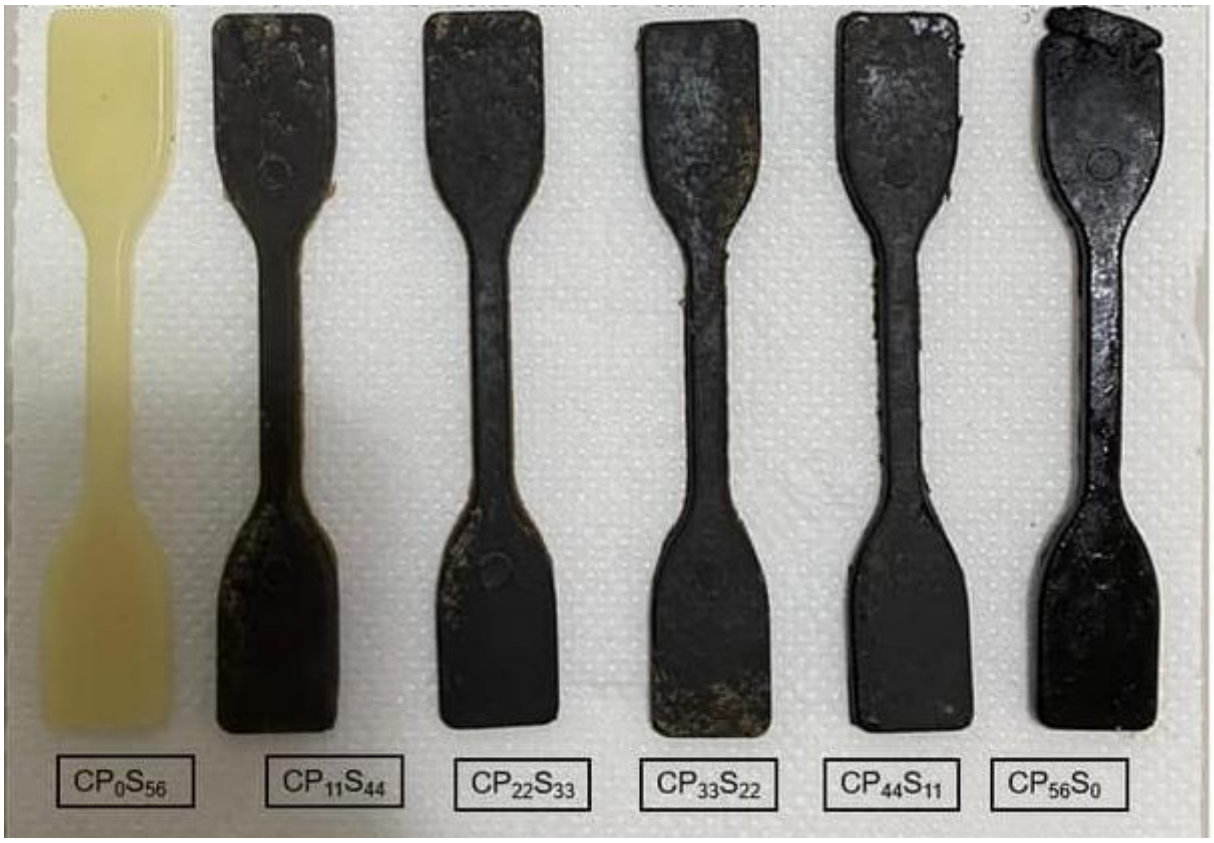


**Table 2 -** CIELab color parameters of the biodegradable materials.

| Formulation | L* | a* | b* |
|---|---|---|---|
| $CP_0S_{56}$ | 62.69 ± 0.27[a] | -2.71 ± 0.13a | 9.79 ± 0.26[a] |
| $CP_{11}S_{44}$ | 32.70 ± 0.36[b] | 1.65 ± 0.01b | 0.79 ± 0.16[b] |
| $CP_{22}S_{33}$ | 31.42 ± 0.74[b] | 1.40 ± 0.04b | 0.03 ± 0.16[b] |
| $CP_{33}S_{22}$ | 31.63 ± 1.91[b] | 1.35 ± 0.03b | 0.04 ± 0.07[b] |
| $CP_{44}S_{11}$ | 32.59 ± 3.50[b] | 1.44 ± 0.15b | 0.07 ± 0.08[b] |
| $CP_{56}S_0$ | 32.99 ± 2.03[b] | 1.66 ± 0.22b | 1.42 ± 1.02[b] |

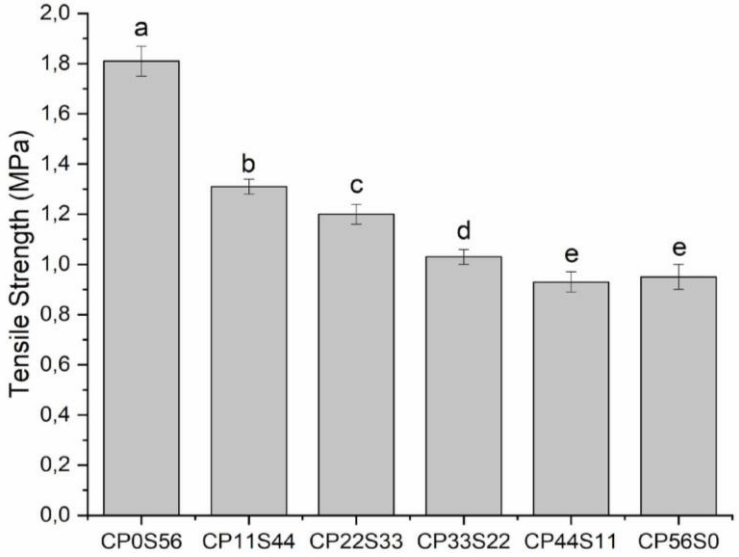
[a,b] Different letters represent a significant difference ($p \leq 0.05$) between the formulations, according to Tukey's test.

$CP_0S_{56}$ was the formulation with the highest L* and b* values. The $CP_0S_{56}$ formulation, due to the absence of CP and the greater presence of starch and PBS, showed greater luminosity and a yellowish hue, unlike the other formulations. All formulations differed from pure whitish crystalline PBS, which can reach values of L* close to 99.99 (FAJRAOUI et al., 2022; QUILES et al., 2020). The addition of starch and CP resulted in a considerable reduction in luminosity. The formulations showed a darker orange hue due to the presence of CP, which is naturally a darker fiber. In addition, caramelization, Maillard, and pyrolysis reactions may have occurred during the extrusion and injection of the materials, influencing the coloring of the materials (JEBALIA et al., 2019)

### 3.5 Mechanical Properties

The tensile strength (TS) of the injected materials is shown in Figure 5.

**Figure 5** – Tensile strength (TS) of the biodegradable materials



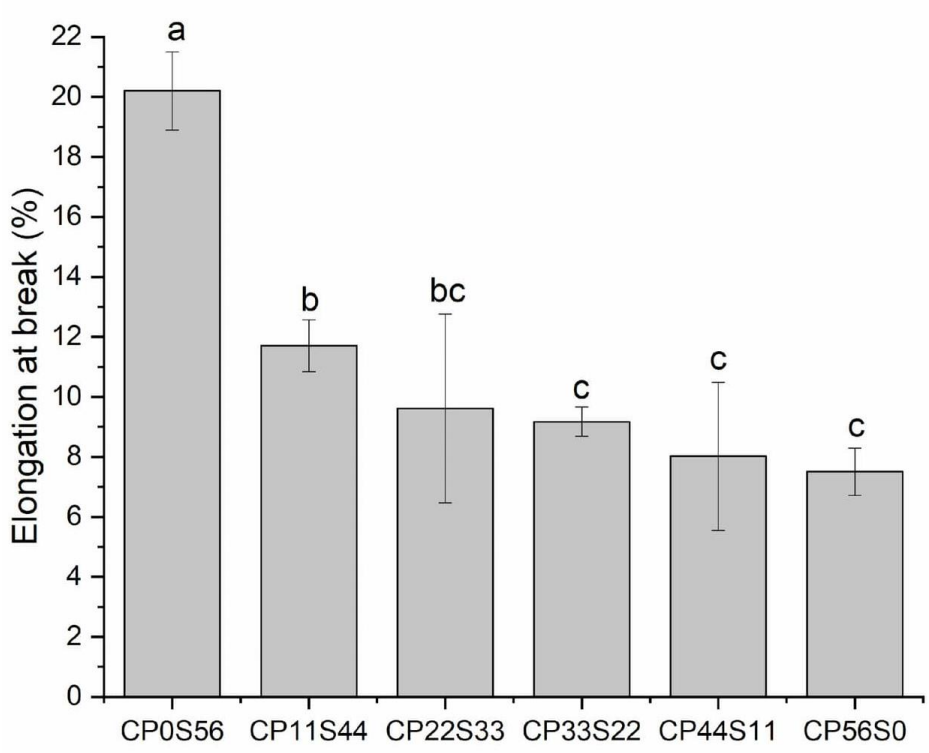
[a,b,c,d,e] Different letters represent a significant difference ($p \leq 0.05$) between the formulations, according to Tukey's test.

The formulation $CP_0S_{56}$ had the highest TS values (1.81 ± 0.06 MPa), followed by CP11S44 (1.31 ± 0.03 MPa), CP22S33 (1.20 ± 0.04 MPa), and CP33S22 (1.03 ± 0.03 MPa), which were approximately 27%, 33%, and 43% lower than $CP_0S_{56}$, respectively. The formulations $CP_{44}S_{11}$ (0.93 ± 0.04 MPa) and $CP_{56}S_0$ (0.95 ± 0.05 MPa) did not differ statistically and were 47% lower than $CP_{56}S_0$. There was a tendency for decreasing TS values, with CP concentration increasing because, as previously discussed (section 3.1), the pulp-starch-PBS formed an immiscible blend, and the higher the pulp content and the higher the non-homogeneity, impairing the material's mechanical properties and morphology (KUN; PUKÁNSKY, 2017; MOCHANE et al., 2021). This decrease in TS has been reported in several studies (NITHIKARNJANATHARN; SAMSALEE, 2022; FERREIRA; MOLINA; PELISSARIO, 2019; KU et al., 2011; GHAZVINI et al., 2022)

The materials with higher CP content (up to 56% w/w) had lower TS (0.95 ± 0.05 MPa), but these materials are still suitable for various uses, such as single-use trays for food packaging. Ferreira, Molina, and Pelissari (2019) produced single-use trays with cassava starch and different agro-industry wastes (malt bagasse, orange bagasse, corn husk, and sugarcane bagasse), varying the concentration of each residue (10, 20, and 30 w/w%), and all the formulations had TS ranging from 0.20 to 0.53 MPa. Expanded polystyrene (EPS) itself had a TS of less than 1 MPa (0.73 MPa).

The elongation at break (EAB) of the biodegradable materials is shown in Figure 6.

**Figure 6 –** Elongation at break (EAB) of the biodegradable materials




[a,b,c] Different letters represent a significant difference ($p \leq 0.05$) between the formulations, according to Tukey's test.

$CP_0S_{56}$ had the highest EAB (20.2 ± 1.3%), followed by CP11S44 (11.7 ± 0.86%), which did not differ statistically from CP22S33 (9.62 ± 3.15%). The materials $CP_{22}S_{33}$ to $CP_{56}S_0$ did not differ ($p > 0.05$), and their mean EAB was 8%, approximately 40% lower than $CP_0S_{56}$. There was a tendency towards a decrease in EAB as the concentration of CP increased (Figure 6).

Ghazvini et al. (2022) produced biodegradable materials by thermoplastic injection molding containing poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and coffee silver skin (CF). Blends containing only PBS/PLA were more flexible (15.7 ± 2.6 %) than formulations containing 20 wt.% CF (3.6 ± 0.3%) and 30 wt.% CF (2.7 ± 0.2%). Other authors (CALABIA et al., 2013; NITHIKARNJANATHAN; SAMSAILEE, 2022; NAGARAJAN; MOHANTY; MISRA, 2013; YANG et al., 2020; PIVSA-ART; PIVSA-ART, 2021) reported a similar trend, where blends of biopolymers with natural fibers became less flexible with the addition of natural fibers.

The Young Modulus (YM) of the materials did not differ statistically, with an average of 14 ± 6 MPa. The higher the pulp content, the more fragile the material because the YM remained constant. Hence, both TS and EAB lowered proportionally with higher pulp content.

### 3.6 Moisture Sorption Isotherms

The Guggenheim-Anderson-de-Boer (GAB) parameters of the biodegradable materials' moisture sorption isotherms are presented in Table 3.

**Table 3 -** GAB model parameters of the biodegradable materials' moisture sorption isotherms.

| Formulation | GAB Model Parameter | | | $R^2$ |
|---|---|---|---|---|
| | $m_0$ g 100 $g^{-1}$ | k | C | |
| $CP_0S_{56}$ | 16.11 | 0.78 | 10.000 | 0.97 |
| $CP_{11}S_{44}$ | 4.69 | 1.02 | 10.000 | 0.96 |
| $CP_{22}S_{33}$ | 5.65 | 0.95 | 10.000 | 0.96 |
| $CP_{33}S_{22}$ | 4.45 | 1.02 | 10.000 | 0.99 |
| $CP_{44}S_{11}$ | 6.47 | 0.96 | 10.000 | 0.98 |
| $CP_{56}S_0$ | 6.51 | 0.94 | 10.000 | 0.98 |

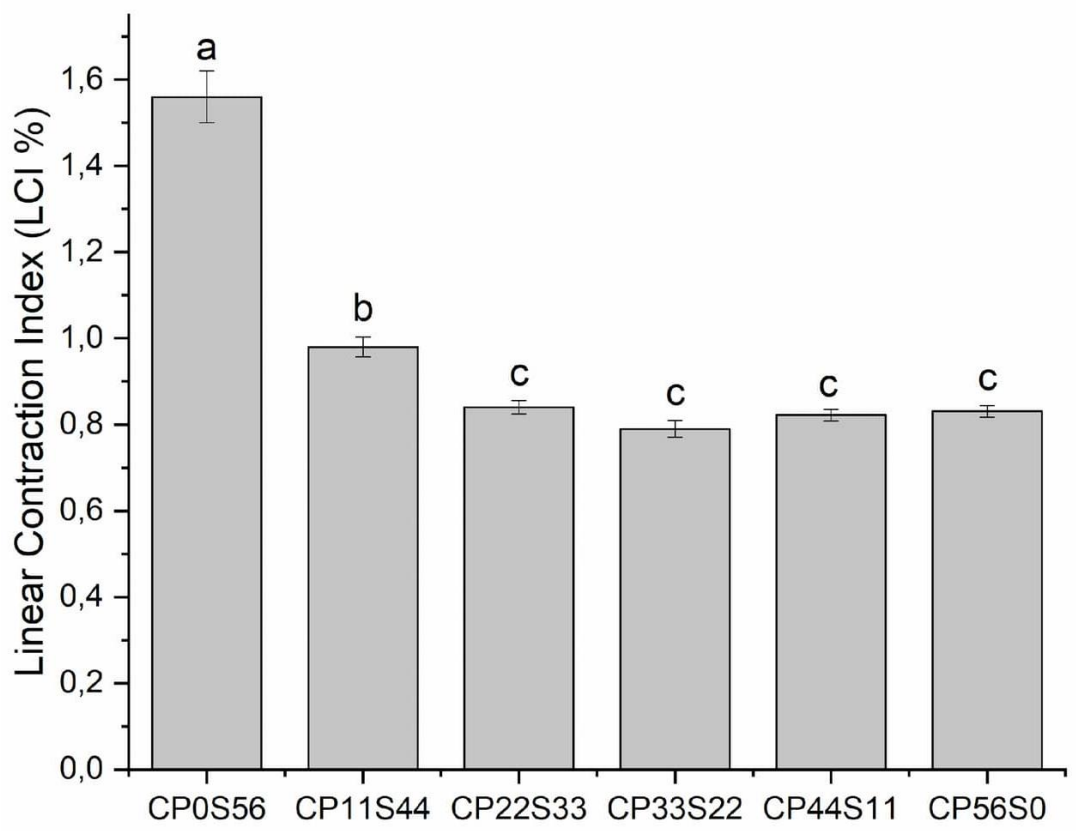
The behavior of the materials under different humidity conditions was investigated through sorption isotherms, and the GAB model was adjusted. The k and C GAB model parameters were similar for all formulations except for $CP_0S_{56}$. Values of k below 1.0 indicate that water in the inner layers of the material is less adsorbed than in the monomolecular layer (VAN DER BERG; BRUIN, 1981). The $CP_0S_{56}$ had the highest m0 value (16.11 g 100 $g^{-1}$), followed by the other formulations containing CP, which ranged from 4.45 to 6.51 g 100 $g^{-1}$, indicating that CP impaired water sorption at the starch sites. However, the materials remain hydrophilic overall, as the k values were close to 1.0 due to the presence of voids and cracks observed in the SEM images (immiscibility between PBS-starch-CP). Cellulose, like starch, has several hydroxyl groups (OH) that can form hydrogen bonds with water both on the surface and inside the material (MOCHANE et al., 2021). Depending on the use, it is essential to understand the material's affinity with water, particularly for applications in

agriculture, such as seedling bags, tubes, and hydrogels, as well as in food packaging (SILVA et al., 2024; SIMÕES et al., 2020).

### 3.7 Linear Contraction Index (LCI)

The linear contraction index (LCI) of the biodegradable materials is presented in Figure 7.

**Figure 7-** Linear contraction index (LCI) of the biodegradable materials




[a,b,c] Means with different letters represent a significant difference ($p \leq 0.05$) between the formulations, according to Tukey's test.

$CP_0S_{56}$ (1.56 ± 0.06%) was the formulation with the highest LCI, followed by CP11S44 (0.98 ± 0.02%) and the other formulations (on average, 0.84%). Materials with higher CP content had lower LCI and, consequently, better dimensional stability due to the high CP fiber content. Fibers are well-known reinforcements, as they can act as fillers in polymer blends, enhancing the dimensional stability of materials (MOCHANE et al., 2021; WU, MISRA, & MOHANTY, 2021; KUN & PUKANSKY, 2017). During the injection stage, the fibers are carried by the flow, and

their direction varies according to the stress or force they are subjected to, orienting themselves parallel or perpendicular to the direction of the injection flow (OUARHIM et al., 2020).

Dimensional stability is desired for injection-molded materials because higher LCI is detrimental when it is desired to obtain homogeneous materials with precise dimensions (KC et al., 2016; MOHAMED et al., 2018).

Santos et al. (2015) produced injected materials of high-density polyethylene (HDPE) and wood fiber, and they reported that materials containing 40 wt.% of fiber had the most significant reduction in shrinkage by volume due to changes in the crystallinity of the thermoplastic matrix and greater alignment and orientation of the fibers in the structures. Another study (TAN et al., 2013) with polypropylene and coir fiber had similar results. Increasing coir fiber content reduced shrinkage considerably due to changes in the crystallinity matrix after injection.

### 3.8 Density

The densities of the biodegradable materials $CP_0S_{56}$, $CP_{11}S_{44}$, $CP_{22}S_{33}$, $CP_{33}S_{22}$, and $CP_{44}S_{11}$ did not differ between them and ranged from 1.34 to 1.36 g $cm^{-3}$. These values are similar to those reported for polyethylene terephthalate (PET) (~1.36 g $cm^{-3}$) and lower than those for polyvinyl chloride (PVC) (~1.40 g $cm^{-3}$).

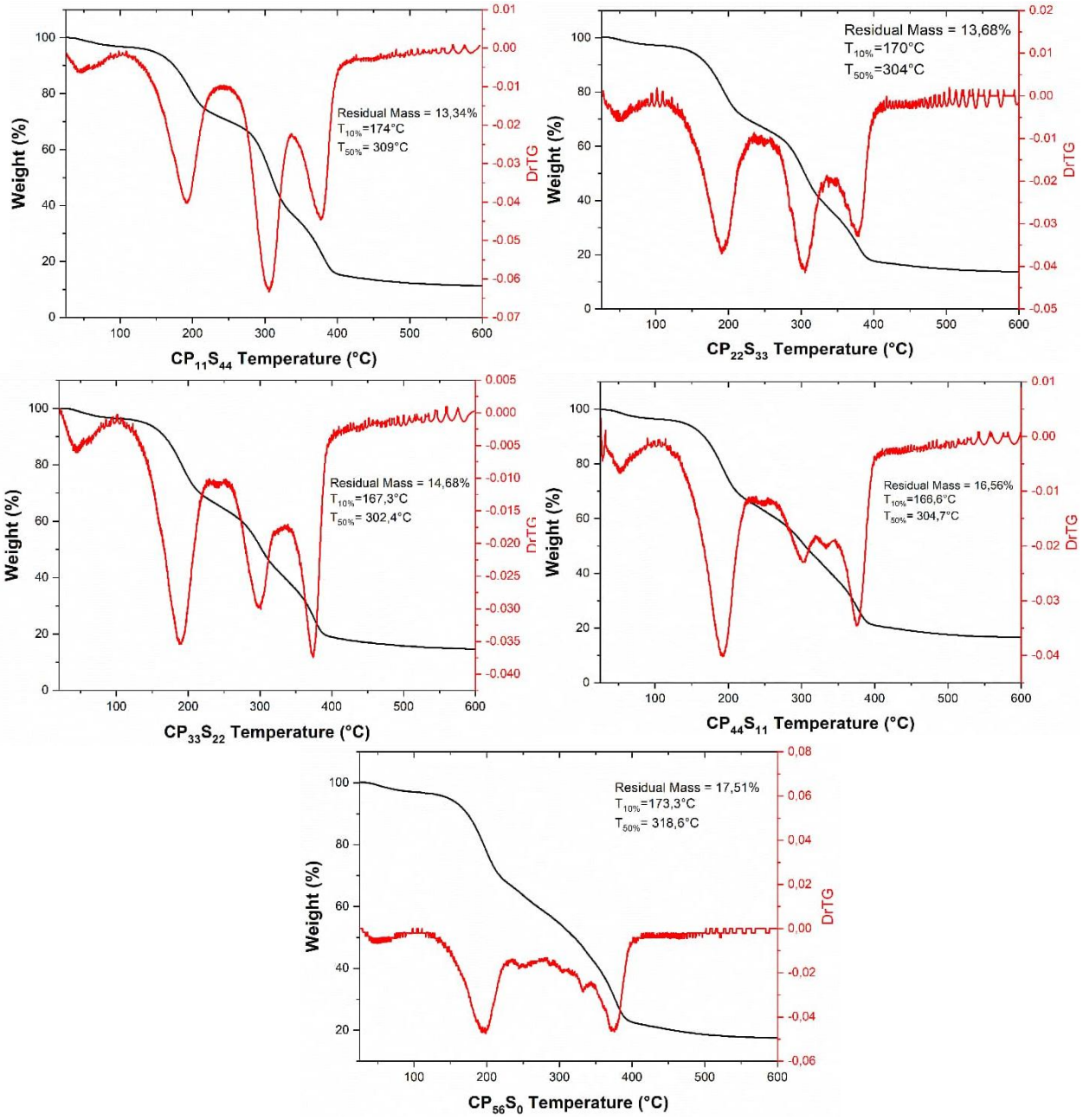
The $CP_{56}S_0$ formulation had the lowest density (1.32 g $cm^{-3}$) and differed statistically from the others, probably due to the absence of starch. Starch interacts with other components of the blend, resulting in greater cohesion and, consequently, increasing the density. Nazrin, Sapuan, and Zuhri (2020) produced biodegradable materials using poly(lactic acid) and thermoplastic starch through compression molding. The authors reported that the higher the starch concentration, the higher the materials' density (1.46 g $cm^{-3}$), while pure PLA showed the lowest density (1.26 g $cm^{-3}$).

One of the advantages of using natural fibers, apart from their low cost and biodegradability, is their low density. This behavior is particularly interesting for materials that need to be both lightweight and resistant, such as single-use trays in the packaging industry, packaging cups, spoons, straws, and others (FERREIRA; MOLINA; PELISSARI, 2019; YARADODDI et al., 2022; MOCHANE et al., 2021).

### 3.9 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) and its derivatives (DTG) of the biodegradable materials are presented in Figure 8.

**Figure 8 -** TGA and DTG of the biodegradable materials




According to the TGA and DTG curves of the biodegradable materials, there were three major temperature transitions, except for $CP_{56}S_0$, which had just two transitions. The slight transition between 80-150°C for all samples occurred due to the

removal of moisture from starch and CP (HUANG et al., 2021; LAM et al., 2016; SOARES, SCREMIN, & SOLDI, 2005).

The first weight drop, observed at 180-200 °C, was due to the degradation of CP constituents, such as cellulose and hemicellulose, into smaller components, including $CO_2$ (LAM et al., 2016; YARADODDI et al., 2022). Huang et al. (2021) also observed this behavior with pectin-rich dietary fibers prepared with citrus peel.

The second weight drop at 300-340 °C was due to starch degradation (SOARES; SCREMIN; SOLDI, 2005), which involved the breakage of C-C, C-H, or C-O bonds in the PBS/Starch matrix (AYU et al., 2018). As materials containing higher CP content and, consequently, lower starch, this drop became less defined, and for P100, which did not have starch, this drop disappeared.

The third weight drop at 350-370 °C was due to PBS degradation, as it is more thermally stable than the other components of the blends (AYU et al., 2018).

Regarding parameter T10%, the temperature at which a 10% loss of mass occurred, formulation CP11S44 (174 °C) had the highest value, with a decrease in T10% as the CP concentration increased. However, formulation CP56S0 (173.5 °C) had the second-highest T10%. The same trend was observed for T50%, the temperature at which a 50% loss of mass occurred, but $CP_{56}S_0$ (318.6 °C) was the formulation with the highest T50%, followed by $CP_{11}S_{44}$ (309 °C). The increase of T50% for the $CP_{56}S_0$ formulation was due to the absence of starch, which degrades within the 300-340°C range, resulting in a slight increase in T50%.

$CP_{56}S_0$ (17.51%) had the highest residual mass after reaching the plateau (close to 600 °C), followed by $CP_{44}S_{11}$ (16.56%), $CP_{33}S_{22}$ (14.68%), $CP_{22}S_{33}$ (13.68%), and $CP_{11}S_{44}$ (11.34%), i.e., the higher the CP content, the higher the residual mass, probably due to the higher amount of lignin which can have its degradation between the ranges of de 50-700 °C, which highlights its good thermal stability (AYU et al., 2020; LOPEZ-VELAZQUEZ, et al., 2013).

## 4. Conclusion

Biodegradable citrus pulp, PBS, and thermoplastic starch blend materials were produced by extrusion and thermoplastic injection with excellent

processability. The biodegradable materials, independent of the formulation, presented adequate mechanical properties for several uses and a low cost, as both citrus pulp and starch are cheaper than PBS and even other conventional polymers, such as PE or PP, particularly the citrus pulp. Their densities are similar to those of polyethylene terephthalate (PET) and lower than those of polyvinyl chloride (PVC). They exhibit dimensional stability with a linear contraction index of less than 1%. These results are promising, as these biodegradable materials can be produced on a large scale at low cost, using a by-product from the orange juice industry.

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## CAPÍTULO V- Influence of Oat Hulls and Citrus Pulp on the Biodegradation of PBS-Based Composites


### Abstract

The large-scale production of petroleum-based polymers generates considerable environmental waste due to their low biodegradability. Blending polybutylene succinate (PBS) with natural fibers (NF), such as oat hulls (OH) and citrus pulp (CP), offers a sustainable strategy to reduce costs and enhance biodegradation. In this study, two PBS/starch/NF formulations were produced via injection molding and characterized through mass loss (%), FTIR, SEM, microbial biomass carbon (MBC-C), moisture sorption isotherms, and ready biodegradability tests. Both formulations exhibited over 50% mass loss after 150 days in soil and met the OECD 301B criteria for ready biodegradability. Notably, CP-containing composites degraded faster than OH-based ones, likely due to pectin and soluble polysaccharides that stimulate microbial activity and nutrient availability. These results demonstrate that incorporating NF, particularly OH and CP, is an effective approach to accelerate the biodegradation of PBS-based biopolymers, supporting their application in sustainable materials.


**Keywords:** Biopolymers, biodegradability, natural fibers, injection molding, ready biodegradability.

## 1. Introduction

The use of polymers derived from fossil sources has been essential in several sectors of society, including packaging, consumer goods, medical and cosmetic applications, among others, driving the growth in their production (AWASTHI ET AL., 2022; STOICA ET AL., 2020; KABIR ET AL., 2020). However, this large-scale production generates a significant amount of waste, estimated at 400 million tons annually (United Nations) (OLSEN, 2024). The major drawback of these polymers lies in their low degradability, as they are typically incinerated or disposed of in landfills (KABIR ET AL., 2020). Consequently, the development and production of biodegradable plastics, or biopolymers, have been increasingly investigated as promising alternatives to conventional plastics (GEORGE; VENUGOPAL, 2022; BISWAS et al., 2022; IBRAHIM ET AL., 2019).

Biopolymers can rapidly degrade within the environment in which they are found, contributing to ecosystem maintenance and being environmentally friendly (CASTRO-DOMINGUEZ et al., 2025). Polybutylene succinate (PBS) is an aliphatic, biodegradable, and thermoplastic polyester with mechanical properties comparable to polypropylene and polyethylene. Moreover, its biodegradability and processability make it a sustainable alternative to plastics derived from fossil fuels. It can be combined with natural fiber (NF) to lower costs and improve mechanical properties and biodegradability (MOCHANE et al., 2021). Many studies have been conducted on the application of NFs in blends with biopolymers, aiming to serve as reinforcing agents, reduce costs through the utilization of by-products, and enhance biodegradability (MCKAY et al., 2024).

Brazil is widely recognized for its production and export of fruits, grains, and flours. This sector generates a rich variety of by-products containing NF with great potential for reuse in other applications, among which citrus pulp (CP) and oat hull (OH) are among the most notable. Pelletized CP is primarily used as feed for ruminants due to its high nutrient content and excellent digestibility (BAKR et al., 2020). OH is an abundant lignocellulosic by-product obtained during the processing of oats for human consumption. They consist mainly of cellulose, hemicellulose, and lignin, with lower amounts of residual starch, proteins, and phenolic compounds (SCHMITZ, NORDBERG KARLSSON; ADLERCREUTZ; 2020). Due to its high fiber content and low digestibility, OH is generally not used directly in human diets but is instead applied

in biomass and energy production (SCHMITZ; NORDBERG KARLSSON; ADLERCREUTZ, 2020; CORTIVO et al., 2018). Their low cost, availability, and renewable nature make both CP and OH attractive raw materials for applications in bio-based industries while enhancing the biodegradability.

This study aims to develop and characterize biodegradable injection-molded materials produced from blends of PBS, corn starch, CP, and OH. The incorporation of these agro-industrial by-products seeks to reduce production costs and potentially enhance the biodegradability of the final products.

## 2. Materials and methods

### 2.1 Materials

To produce the biodegradable materials for this study, corn starch (14% moisture) (APTI, Brazil), glycerol (Dinâmica, Brazil), and polybutylene succinate (PBS) (TK-BIO, China) were used.

Citrus pulp pellets (CP) were donated by Citrosuco (Brazil), and oat hulls (OH) by SL-Alimentos (Brazil). The centesimal composition of the CP and OH was determined according to the Association of Official Analytical Chemists (2009). The contents of hemicellulose, cellulose, and lignin were determined according to Van Soest (1965). The CP composition was 73% carbohydrates; 9% moisture; 6% protein; 1.6% lipids; 10% ash; 15 % hemicellulose; 19 % cellulose; 15 % lignin), and the OH was 80% carbohydrates; 9% moisture; 4% protein; 2% lipids; 3% ash; 31% hemicellulose; 27% cellulose; and 19% lignin.

Before material production, CP and OH were grounded (MA 680, Marconi, Brazil), and the particle size for both (less than 150 µm) was determined using seven sieves (1000 µm - 150 µm). The reagents used for the analyses were chloroform (Synth™, Brazil), potassium sulfate (Dinâmica, Brazil), potassium dichromate (Dinâmica, Brazil), sulfuric acid (Synth, Brazil), orthophosphoric acid (Êxodo Científica, Brazil), diphenylamine 1% (Êxodo Científica, Brazil), ferrous ammonium sulfate (Synth, Brazil).

### 2.2 Production of the Specimens

Two formulations were produced according to Table 1. The ingredients were weighed, mixed, and fed into a single-screw extruder (model EL-75, BGM, Brazil) at a temperature profile of 90/120/120/110 °C (zone 1 to 4, respectively) with a two-hole die (2 mm diameter), with a screw speed of 40 rpm. The pellets were injected into a dog bone mold (Type IV, ASTM D638-14, 2014) using a thermoplastic injector (AX-PLÁSTICOS, Brazil) at a temperature profile of 120/120/110 °C from the feeder to the nozzle.

**Table 1 -** Formulations containing OH and CP.

| Formulation | PBS (% - w/w) | Starch (% - w/w) | Glycerol (% - w/w) | OH (% - w/w) | CP (% - w/w) |
|---|---|---|---|---|---|
| CP | 20.0 | 33.6 | 22.4 | 0 | 22.4 |
| OH | 20.0 | 33.6 | 22.4 | 22.4 | 0 |

### 2.3 Biodegradability Test

For the biodegradability test of the materials, injected specimens (Type IV, ASTM D638-14, 2014) were cut in half, weighed, and placed in polyester bags (70 x 90 mm). Each bag was then placed inside a round polyethylene pot with a lid (120 mm x 120 mm x 78 mm). In each pot, 500 g of soil from the State University of Londrina, prepared with sand (2:1 sand: soil), covered the samples. The test was performed in quintuplicate for each storage time, including the control that contained only soil. The materials were analyzed after 15, 30, 45, 90, and 150 days. The pots were placed on a BOD at 25 °C, as shown in Figure 1. After each time, the test specimens were removed from the bags, carefully cleaned with a brush to remove dirt, and placed in an oven at 105 °C for 24 hours to determine the mass loss. Pictures were taken after each removal to assess the integrity of the materials. Soil moisture was kept to approximately 70% during the experiment.

**Figure 1-** Biodegradation test

### 2.4 Extract preparation

After each storage time, 5 g of soil from each pot was placed in an oven at 105 °C to determine moisture content. Approximately 20 g of soil was weighed into 125 mL Erlenmeyer flasks for both fumigated and non-fumigated samples. The flasks designated for fumigated samples were placed in a desiccator containing a Petri dish with approximately 5 mL of chloroform for 24 hours in the dark. Non-fumigated samples were kept in the dark under the same conditions without chloroform. After this period, the desiccator was opened and placed in a fume hood to allow volatile compounds to evaporate. Then, 50 mL of extractant solution (0.5 M $K_2SO_4$) was added to each Erlenmeyer flask, and the flasks were placed on a shaker at 175 rpm for 1 hour. The contents were then transferred to Falcon tubes and centrifuged at 2500 rpm for 10 minutes. The supernatant was filtered (Whatman filter) and stored in a freezer at -18 °C.

#### 2.4.1 Determination of Microbial Biomass Carbon (MBC) in Fumigated and Non-Fumigated Samples

The microbial biomass carbon (MBC) was determined using the chloroform fumigation–extraction method described by Vance et al. (1987), with adaptations based on oxidizable carbon titration using potassium dichromate. The correction factor (K = 0.33) was applied according to Sparling and West (1988). Filtered extracts (fumigated and non-fumigated) were analyzed in triplicate by adding potassium dichromate and concentrated sulfuric acid, followed by heating for 30 minutes. After cooling, orthophosphoric acid and diphenylamine indicator were added, and the solution was titrated with ammonium ferrous sulfate until a green endpoint was

observed. Carbon concentration (C) and microbial biomass carbon (MBC) were calculated according to Equations 1 and 2.

$$\mathrm{C}\left(\frac{\mu g\ C}{g\ soil}\right) = \frac{(\mathrm{V2}-\mathrm{V1}) * \mathrm{N} * 0.003 * 50}{8 * \mathrm{W}} \text{ x } 1{,}000{,}000 \quad (1)$$

V2 = volume of ammoniacal ferrous sulfate solution used in the blank

V1 = volume of ammoniacal ferrous sulfate solution used in the sample

N = corrected normality of the ammoniacal ferrous sulfate solution

50 = total volume of the extract

0.003 = milliequivalent (meq) factor of carbon

8 = aliquot volume of the extract used

W = weight of the soil sample with corrected moisture content

$$\mathrm{MBC\text{-}C} = \frac{(\mathrm{Cn}-\mathrm{Cnf})}{\mathrm{K}} \quad (2)$$

Cf = carbon from the fumigated sample

Cnf = carbon from the non-fumigated sample

K = correction factor (0.33) (*Sparling & West,1988)*

**2.5 Fourier-transform infrared spectroscopy (FTIR)**

Fourier Transform Infrared (FTIR) spectroscopy was carried out on the biodegradable materials using the potassium bromide (KBr) pellet technique. Samples were finely ground, homogenized with KBr, and compressed under a pressure of 784 N $m^{-2}$ to form translucent pellets. The spectra were acquired using a Shimadzu IR Prestige-21 spectrometer (Japan), operating within a wavenumber range of 4000 to 400 $cm^{-1}$, at a resolution of 4 $cm^{-1}$ and with 16 accumulative scans per sample.

### 2.6 Scan Electronic Microscopy (SEM)

Before analysis, the samples were stored under 0% relative humidity conditions for seven days. The cross-sectional morphology of the biodegradable materials was examined using scanning electron microscopy (SEM) with a Philips FEI Quanta 200 microscope (USA). To obtain the fracture surfaces, the samples were submerged in liquid nitrogen and subsequently broken (cryofracture). A thin gold coating was applied using a sputter coater (Bal-Tec SCD-050, Germany) to enhance conductivity. Imaging was conducted at an accelerating voltage of 20 kV and a magnification of 2000×.

### 2.7 Moisture Sorption Isotherms

The samples were sectioned into smaller portions, and between 0.5 and 0.8 g of each was analyzed using an Aquasorp isotherm analyzer (Decagon Devices, USA) under the dynamic vapor sorption method. Moisture content and water activity data were modeled using the Guggenheim-Anderson-de Boer (GAB) equation (Equation 3), fitted by non-linear regression through Statistica Software version 7.0 (Statsoft, USA). In the GAB model, *Xw* represents the equilibrium moisture content (g $H_2O$/g dry matter), $m_0$ corresponds to the monolayer moisture content, *C* is the Guggenheim constant (related to the sorption heat of the first layer), and *k* refers to the sorption heat of the multilayer.

### 2.8 Ready Biodegradability Test

The analysis was performed by the environmental analysis laboratory Umwelt Biotecnologia Ambiental (Blumenau, Brazil). The biodegradability test of the samples followed the OECD Guideline 301B for the Testing of Chemicals. For this assessment, Total Organic Carbon (TOC) was measured according to the SMEWW Method 5310 B (APHA; AWWA; WEF, 2017), and Total Suspended Solids (TSS) were determined according to the SMEWW Method 2540 D (APHA; AWWA; WEF, 2017). A viable microbial source (inoculum) was required to promote the biological degradation of the samples. The inoculum was collected from an activated sludge system of a printing facility located in Blumenau (Brazil) in August 2023. A reference substance (analytical grade soluble starch) was used to verify the functional capacity of the activated sludge in parallel with the sample tests, ensuring test validity. For the ready biodegradability test, two test reactors were inoculated with 20.63 mL of a 10 g/L sample solution (TOC = 1162.8 mg/L) in 1.2 L of medium, aiming to reach a final

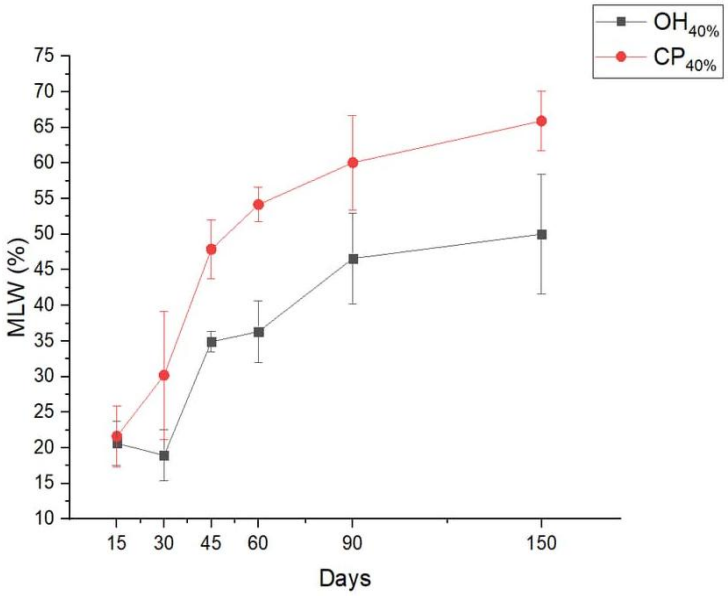
concentration of 20 mg C/L in each reactor. A substance is considered readily biodegradable if it reaches ≥ 60% biodegradation within 28 days and surpasses 10% degradation within a 10-day window.

## 3. Results And Discussion

### 3.1 Biodegradability in Soil

The mass loss of the biodegradable materials during the experiment is presented in Figure 2.

**Figure 2-** Mass loss during the biodegradation test of biodegradable materials.




$OH_{40\%}$ is the formulation containing oat hulls, starch, and PBS, while $CP_{40\%}$ is the formulation containing citrus pulp, starch, and PBS.

A consistent weight loss was observed throughout the test duration for both $OH_{40\%}$ and $CP_{40\%}$. During the first 15 days, both formulations exhibited a weight loss of approximately 20%, which remained statistically similar until 30 days. At this stage, all specimens were in the initial phase of degradation, remaining structurally intact. From day 30 onwards, some specimens began to show fragmentation, especially those of the $CP_{40\%}$ formulation.

After 45 days, both materials presented a statistically significant difference in mass loss compared to the 15- and 30-day cycles; however, $OH_{40\%}$ exhibited a lower degradation than $CP_{40\%}$ (approximately 35% and 47%, respectively),

and this trend continued at 60, 90, and 150 days. OH contains a higher proportion of cellulose, hemicellulose, and lignin compared to CP, which may hinder microbial and enzymatic penetration.

In contrast, the higher carbohydrate content of CP likely contributed to a more accelerated initial degradation. CP is widely used in ruminant nutrition due to its high energy content and easy digestibility, attributes linked to its abundance of soluble carbohydrates. According to Bakr (2020), CP contains between 10% and 40% pectin and approximately 54% water-soluble sugars. This substantial fraction of pectin and soluble polysaccharides contributed to the accelerated biodegradation of the polymeric matrix by providing readily available substrates for microbial metabolism. The higher lignin content may also have contributed to the lower weight loss observed for the OH sample. Stocker et al. (2024) investigated the effect of lignin content on the biodegradation of cellulose nanofibers derived from *Pinus*. According to the authors, increasing lignin content significantly reduced the degradation rate; fibers with 35% lignin achieved only 5.7% biodegradation after 14 days, while those with 20% lignin reached 20.8% in the same period because, in lignocellulosic systems, lignin forms covalent bonds with cellulose and hemicellulose, generating lignin–carbohydrate complexes that hinder enzymatic action by cellulase and β-glucosidase. Similarly, Vikman, Mikkelson, and Rautkoski (2024) utilized paper fibers (a byproduct of the paper industry) in a biodegradation test (ISO 17556) and reported that higher lignin content resulted in reduced degradation rates in both soil and aquatic environments.

Both CP and OH contributed to PBS degradation because PBS can be degraded through its amorphous regions by microbial enzymes, while starch undergoes degradation by enzymes such as α-amylase (HUANG et al., 2021; SURENDREN et al., 2022; JULINOVÁ et al., 2020; WARREN, 1996). PBS and sugarcane fiber, which were then buried in soil for 15, 30, 60, and 100 days. It was observed that the PBS sample showed degradation of only 2.5%, whereas the other samples containing natural fibers exhibited degradation of 15–20% over the 100-day period. According to the authors, this behavior was attributed to the hydrophilic groups of natural fibers, which enhance microbial activity in the materials. In comparison with the present study, a mass loss of approximately 20% was already observed after just 30 days for both OH and CP samples, due to the higher content of natural fibers (22.4% - w/w compared to 15% – w/w sugarcane fibers). Motloung et al. (2024) reported the

same trend, where PBS also showed no mass loss after 90 days of soil burial, and that the addition of chitin increased mass loss by up to 10%.

From the early days of analysis, a change in the coloration of the materials was observed (yellowish to orange tones) (Figure 3), which may indicate surface colonization by fungi or bacteria, whose metabolites (or pigments) can alter the material's color. During the assay, darkening of the samples was also observed, possibly associated with the degradation of starch and natural fibers by fungal activity. The same behavior was observed in film samples containing polylactic acid (PLA) and PBS, where, after 12 months, noticeable color changes occurred due to the action of microorganisms on the material's surface, which altered the pH and induced changes in the morphology of the samples (SLEZAK et al., 2023).

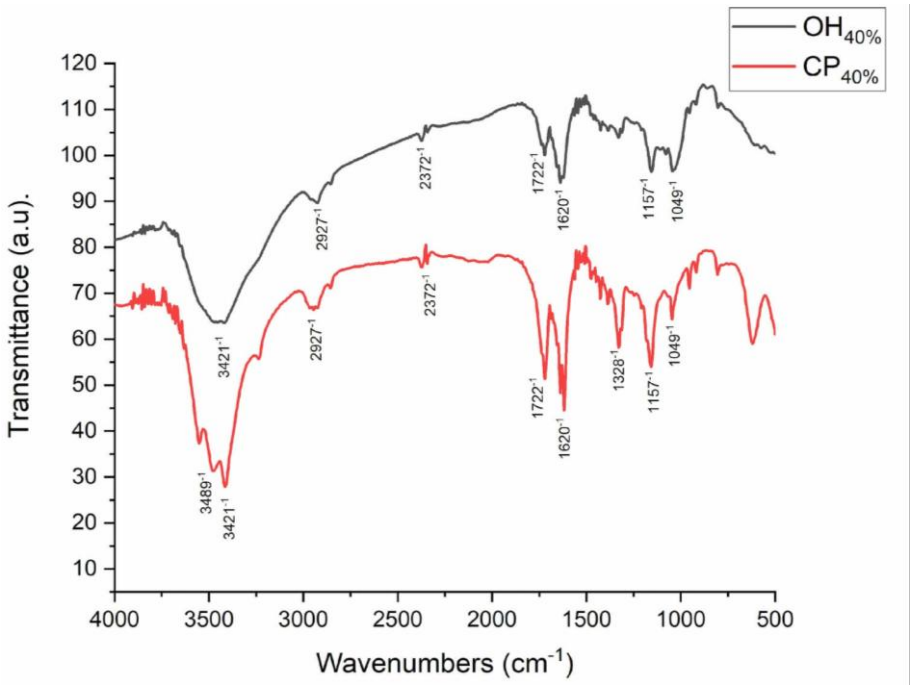
**Figure 3 –** Specimens of the biodegradable materials collected after each cycle of days.


$OH_{40\%}$ is the formulation containing oat hulls, starch, and PBS, while $CP_{40\%}$ is the formulation containing citrus pulp, starch, and PBS.

### 3.2 Fourier-transform infrared spectroscopy (FTIR)

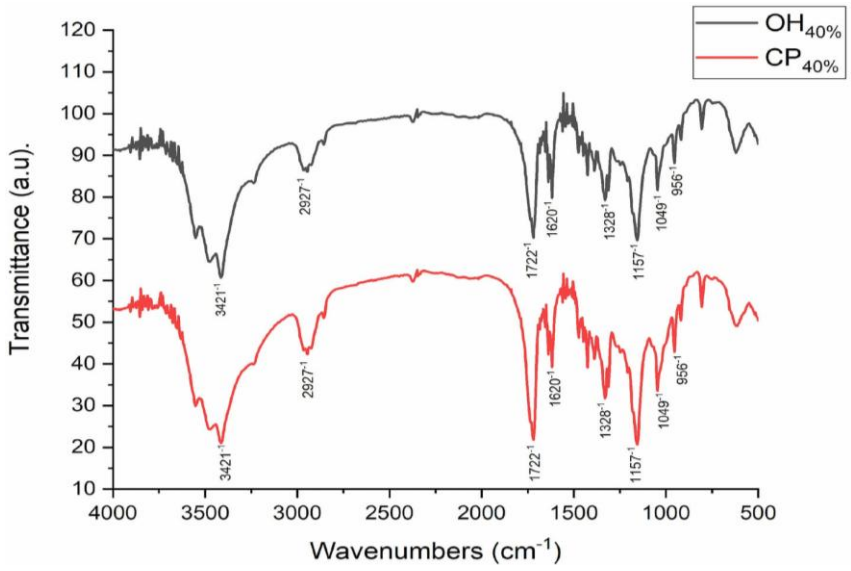
Figures 4, 5, and 6 show the FTIR spectra of the specimens after 30, 90, and 150 days of biodegradable test for both formulations.

**Figure 4 -** FTIR after 30 days



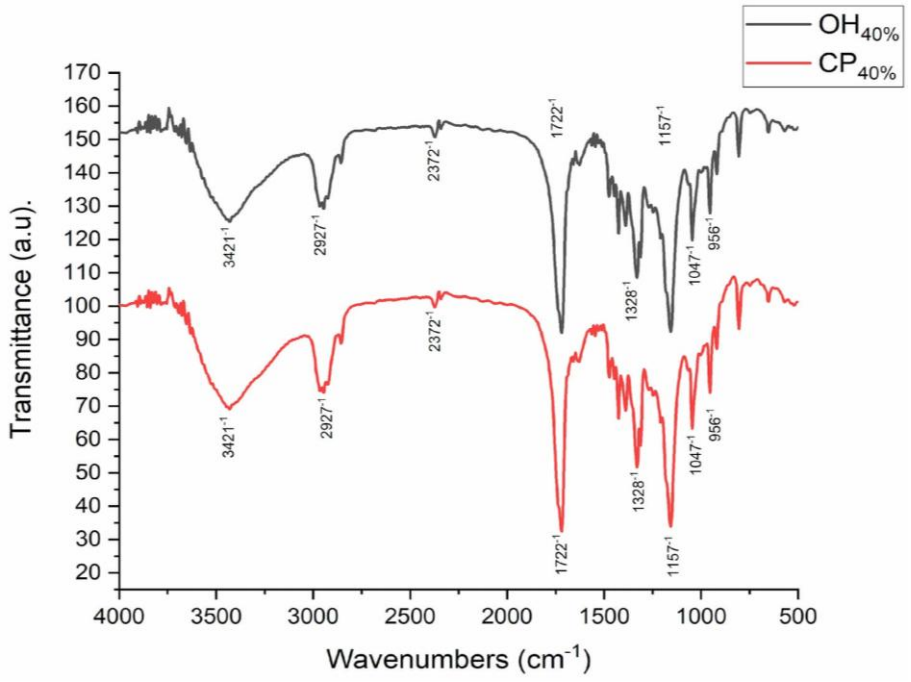

$OH_{40\%}$ is the formulation containing oat hulls, starch, and PBS, while $CP_{40\%}$ is the formulation containing citrus pulp, starch, and PBS.

**Figure 5-** FTIR after 90 days




$OH_{40\%}$ is the formulation containing oat hulls, starch, and PBS, while $CP_{40\%}$ is the formulation containing citrus pulp, starch, and PBS.

**Figure 6-** FTIR after 150 days




OH40% is the formulation containing oat hulls, starch, and PBS, while CP40% is the formulation containing citrus pulp, starch, and PBS.

After 30 days, peaks were observed in the 3200–3400 $cm^{-1}$ region, which are attributed to O–H stretching vibrations characteristic of starch structures (amylose and amylopectin) and natural fibers such as hemicellulose, cellulose, and lignin (YARADODDI et al., 2022). As the degradation period progressed (90 and 150 days), the intensity of this band decreased due to the microbial breakdown of these structures.

The peak observed near 2927 $cm^{-1}$, which ranged between 2925–2930 $cm^{-1}$, can be attributed to C–H stretching vibrations of methylene groups (C-H) (aliphatic chains), present in PBS and biodegradable materials containing PBS. The peak remained present throughout all degradation cycles, indicating the presence of PBS even after 150 days (BARRINO et al., 2023). Another characteristic band of PBS appears near 1720 $cm^{-1}$, corresponding to ester carbonyl (C=O) stretching in its structure ($[–O–(CH_2)_4–CO–O–(CH_2)_2–CO–]_n$), producing strong absorption in the 1715–1735 $cm^{-1}$ region (BARRINO et al., 2023; SHI et al., 2018). It is worth noting that this band became more intense and defined over time, possibly due to the degradation of other more labile components (starch, OH, and CP).

The nearby band at 1620 $cm^{-1}$ is attributed to aromatic C=C bonds, mainly from lignin (FERREIRA et al., 2020; CYPRIANO, DA SILVA, & TASIC, 2018), and the absence of this band after 150 days indicates the breakdown of lignin structure. The increase in intensity of the bands at 1328 and 1157 $cm^{-1}$, assigned to C–C–O and C–O–C ester groups in the PBS structure (PLATNIEKS et al., 2019; TOKIWA et al., 2009) indicate the faster degradation of simpler natural components (starch, glycerol, natural fibers) by microorganisms, while PBS remained in the material after the end of the experiment.

PBS exhibits a significant crystalline fraction that is less accessible to water and microbial enzymes, which limit enzymatic hydrolysis, due to the greater resistance of aliphatic ester bonds compared to the glycosidic bonds found in starch or natural fibers. PBS may take weeks or even months to fully degrade, with degradation time varying depending on the soil type and the presence of specific enzymes (TOKIWA et al., 2009; HUANG et al., 2018).

### 3.3 Scan Electronic Microscopy (SEM)

SEM images of the biodegradable materials containing CP and OH are shown in Figures 7 and 8, respectively. In both samples, the presence of glucose units was initially observed, which are characterized by their spherical or irregular shapes and heterogeneous distribution within the matrix (CHAKRABORTY et al., 2020; DANIEL et al., 2014). Over time, both samples exhibited a reduced presence of these spherical structures, which may indicate the early microbial degradation of starch.

**Figure 7-** SEM micrographs for the CP formulations. (a) surface (b) fractured

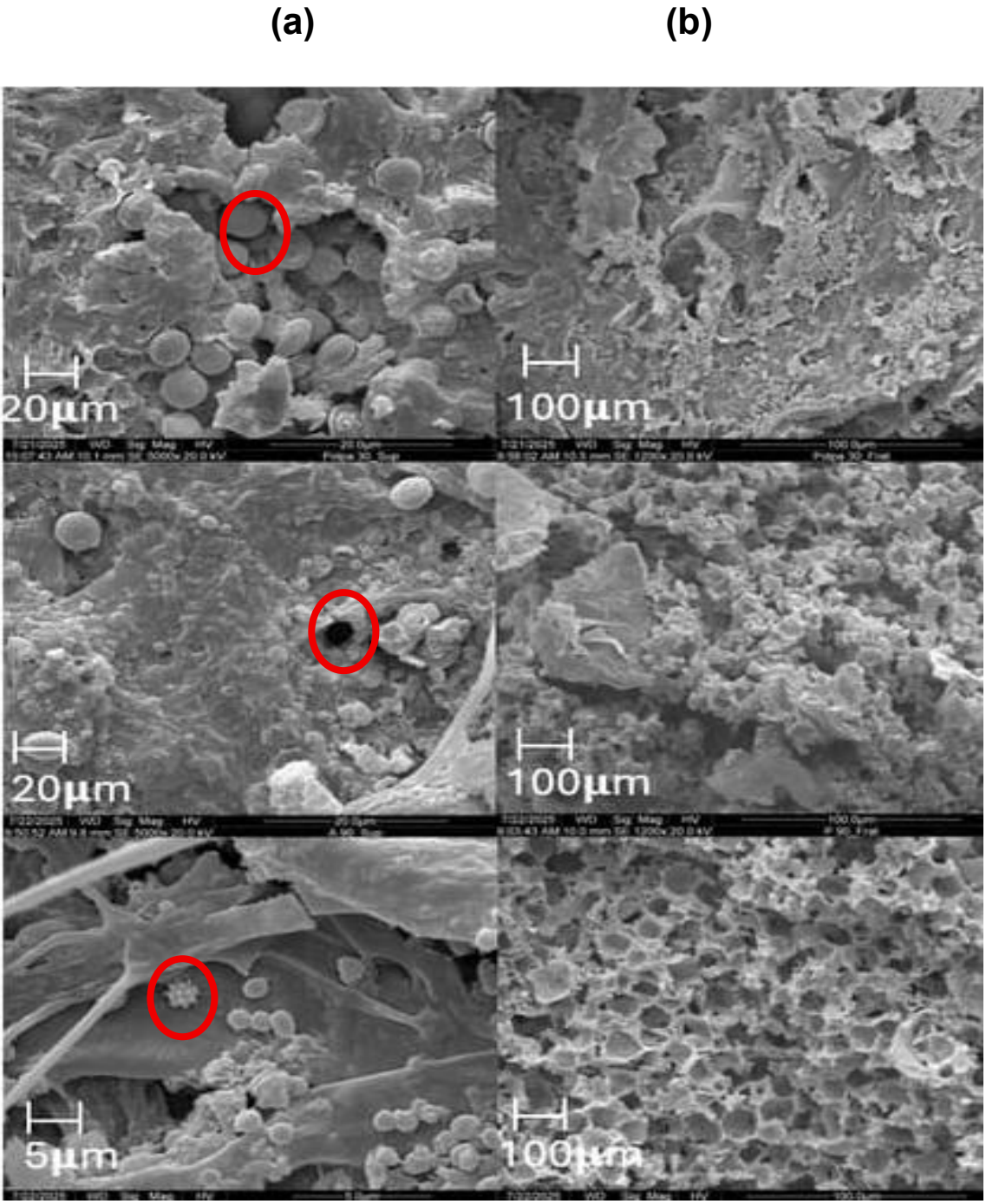
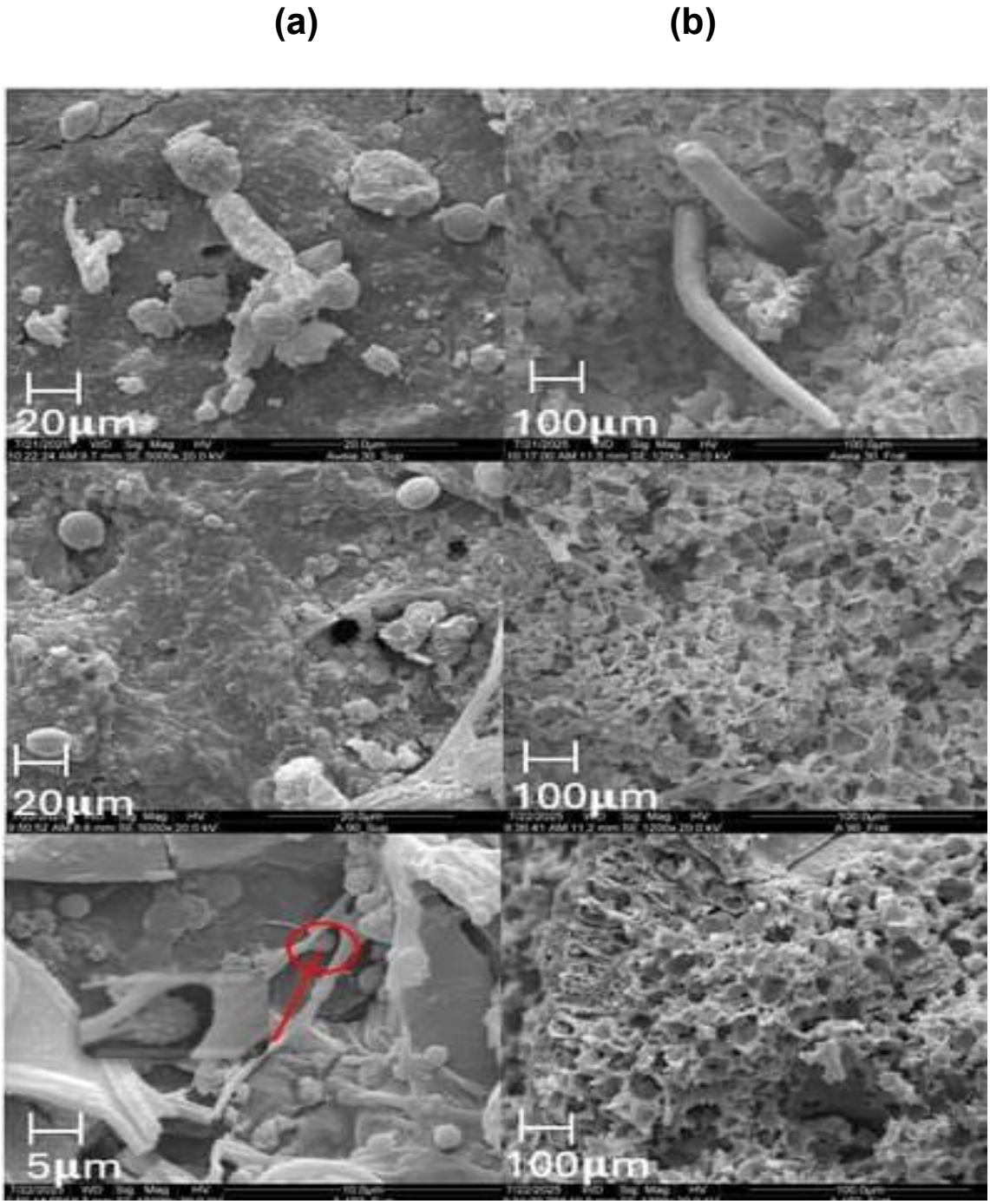


**Figure 8-** SEM micrographs for the OH formulations. (a) surface (b) fractured




Natural fibers characteristic of OH were also identified in Figure 7b (SILVA et al., 2024). However, as degradation progressed, these fibers were no longer visible, and only highly roughened and damaged surfaces remained. These results are consistent with the FTIR analyses (Section 3.2), which showed that both the starch structures and natural fibers were progressively degraded throughout the cycles, leaving predominantly PBS as the remaining component.

Additionally, the morphological incompatibility observed by SEM, characterized by interfacial gaps and poor dispersion of the starchy filler, facilitated microbial colonization and degradation, and promoted water diffusion and enzymatic access to the polysaccharide domains, thereby accelerating the overall biodegradation process in soil (SLEZAK et al., 2023).

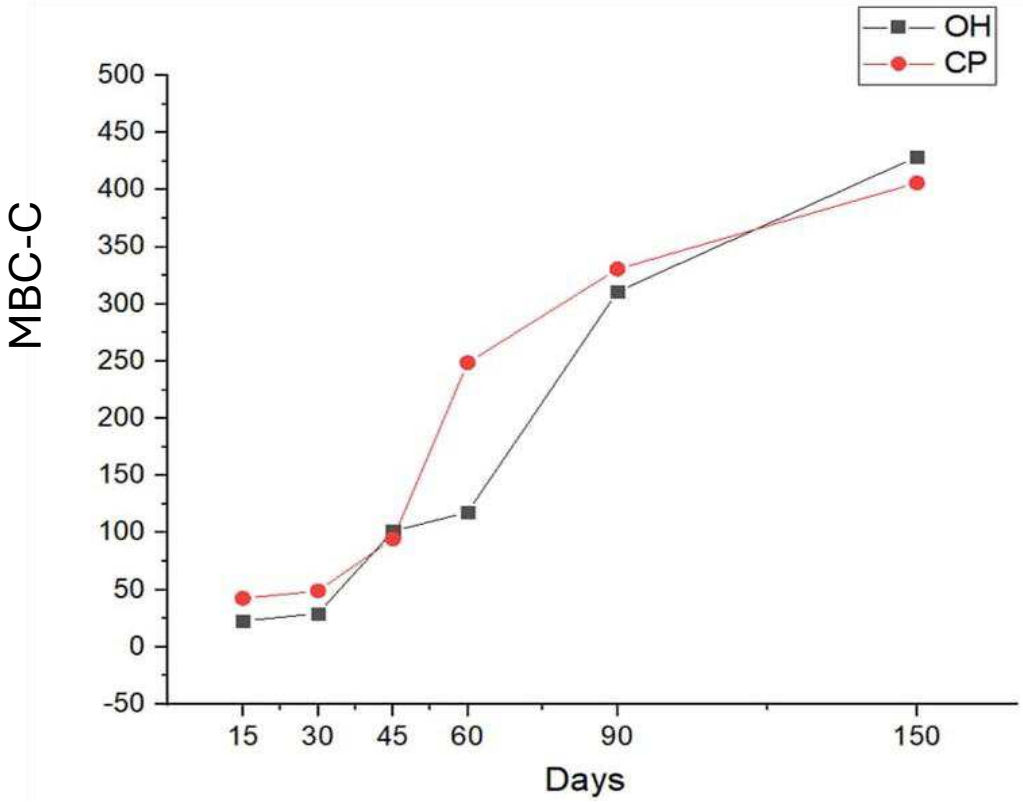
After 90 days, the formation of cavities or pores was evident on the surface of the injection-molded specimens, which may enhance moisture absorption and subsequently increase microbial activity (HUANG et al., 2018). Similar findings were reported by Moutlong et al. (2023), who observed cracks and cavities in PBS-based composites, including pure PBS, indicating structural breakdown. Blends containing chitin showed even more pronounced surface roughness and advanced degradation. Moreira et al. (2018) conducted SEM analysis of injection-molded materials composed of OH, polyvinyl alcohol (PVA), and glycerol, and observed severely degraded surfaces after just 7 days of soil burial. The modification of these structural components contributes to increased brittleness, which may explain the decline in mechanical performance and overall material integrity (Section 3.1) (AYU et al., 2020).

In the 150-day samples, a spherical structure was also observed, probably corresponding to a pollen grain, a common element in soil environments with no direct relation to the composite matrix.

### 3.4 Determination of microbial biomass carbon (MBC-C) in Fumigated and Non-Fumigated Samples

The results related to microbial respiration biomass analysis are shown in Figure 9. MBC-C is a technique used to quantify carbon dioxide ($CO_2$) or its consumption by soil microorganisms as an indicator of their metabolic activity; the greater the amount of $CO_2$ released, the higher the microbial activity.

**Figure 9 -** MBC-C of the biodegradable materials during the biodegradability test




$OH_{40\%}$ is the formulation containing oat hulls, starch, and PBS, while $CP_{40\%}$ is the formulation containing citrus pulp, starch, and PBS.

The MBC-C values increased along the biodegradation test because the soil contains microorganisms, such as bacteria and fungi, which, when in contact with the material under suitable conditions of moisture, pH, and nutrient availability, tend to metabolize the biopolymer. As the amount of available substrate increases, microbial metabolic activity also intensifies.

The progressive increase in MBC-C (Figure 8) values over time suggests that the biopolymer served as an effective carbon source for microbial growth, indicating active biodegradation under the tested soil conditions. After 90 days of analysis, a statistically significant increase was observed for both OH and CP biodegradable materials (up to twice as high for OH). The initial colonization may have been slow; however, once adapted, the microbial populations multiplied rapidly between 60 and 90 days after colonization. CP showed a more pronounced increase throughout the cycles, possibly due to its higher content of soluble sugars.

Nevertheless, by the end of the assay, both samples reached similar levels, suggesting that OH released nutrients more slowly but continuously.

Moreira et al. (2018) produced thermoplastic injection-molded materials using various types of natural fibers, including OH, in blends containing polyvinyl alcohol (PVA), glycerol, cassava starch, rock phosphate, sugar, yeast, and powdered milk. The biodegradation assay also involved burying the samples in soil using containers filled with earth. The microbial biomass carbon (MBC-C) results were 277 µg C/g after 14 days and 348 µg C/g after 35 days, which are higher than those observed in the present study at approximately the same time points, 22 µg C/g and 29 µg C/g at 15 and 30 days, respectively, for the OH samples. The lower results can be attributed to differences in experimental conditions, sample formulations, soil composition, and other factors that influence the outcome.

Reis et al. (2013) produced films for Kraft paper coating using chitosan and palmitic acid to evaluate their biodegradation, and for the MBC-C analysis, only the sample containing both palmitic acid and chitosan showed a considerable increase in material biodegradation between 15 and 60 days (1.500 µg C/g for both); however, stabilization was observed after 60 days. For the formulations with chitosan alone or the uncoated Kraft paper, no increase in MBC-C levels was observed, indicating that there was no organic matter in the soil. Despite the higher values (1.500 µg C/g) observed between 15 and 60 days in the referenced study, the specimens in the present work continued to show a steady increase in MBC-C up to 150 days, indicating ongoing microbial activity in the soil. Additionally, the larger contact area of the films compared to the injected materials in the soil may have contributed to a higher initial level of microbial activity.

### 3.5 Moisture Sorption Isotherms

The results of the sorption isotherms of the biodegradable materials, fitted using the GAB model, are presented in Table 2. The parameter $m_0$ refers to the monomolecular moisture content, that is, the amount of water strongly bound to the surface of the material. The constant k is associated with the sorption heat of water in the multilayer region, while C represents an energetic constant related to the affinity of the first layer of water molecules with the material.

**Table 2 -** GAB model parameters of the biodegradable materials' moisture sorption.

| | $OH_{40\%}$ | | | $CP_{40\%}$ | | |
|---|---|---|---|---|---|---|
| **Formulation** | **m0 (g $100g^{-1}$)** | **k** | **C** | **m0 (g $100g^{-1}$)** | **k** | **C** |
| 30 | 2.18 | 0.76 | 2.18 | 0.8204 | 1.352 | 10.000 |
| 90 | 7.97 | 0.56 | 10.000 | 3.9807 | 0.7073 | 10.000 |
| 150 | 2.96 | 0.59 | 10.00 | 3.078 | 0.56880 | 10.000 |

In the first 30 days, the $m_0$ values observed for the samples containing OH and CP indicated a lower affinity for water compared to the 90-day cycle. This behavior may be related to the initial phase of microbial activity in the soil, with an adaptation period followed by an increase in degradation. After 90 days, both materials showed a significant increase in $m_0$, indicating structural degradation of the matrix and exposure of polar functional groups (such as –OH and –COOH), resulting from the breakdown of starch and natural fibers. Both OH and CP, in addition to the starch itself, composed of glucose units, contain fractions of hemicellulose and cellulose, all rich in hydrophilic groups capable of absorbing water and accelerating the degradation of the polymer matrix (AYU et al., 2020; LI et al., 2015; HORIUCHI et al., 2025).

By the end of the experiment, at 150 days, a reduction in $m_0$ was observed for both formulations. This result may be attributed to the depletion of active sites (hydrophilic groups) due to mineralization or microbial consumption of the more degradable fractions of the materials. Furthermore, as indicated by FTIR analyses (3.2 section), the preferential degradation of starch and natural fibers led to a higher proportion of PBS remaining in the matrix, a polymer that is more hydrophobic and structurally resistant to degradation (LI et al., 2013), which contributed to the lower water retention capacity observed at the end of the period. The reduction in the value of the parameter k over time may be associated with the degradation of the polymeric matrix in the soil, leading to the formation of cavities and increased porosity, as observed in the SEM analysis (Section 2.3). This structural disorganization

compromises the material's ability to retain water in multilayer formations, indicating material degradation (TAVARES et al., 2023; TAO et al., 2018).

### 3.6 Ready biodegradability Test (OECD 301B)

The Ready Biodegradability Test (OECD 301B) was designed to evaluate whether a material can be rapidly biodegraded by microorganisms under ideal environmental conditions, using an aerobic aqueous medium (sludge) (DOMÍNGUEZ-SOLERA, et al., 2025). The principle of the OECD 301B method was based on measuring the carbon dioxide ($CO_2$) generated during the aerobic degradation of an organic substance, with total organic carbon (TOC) determined according to the SMEWW Method 5310B. The method involves the catalytic thermal oxidation of organic carbon to $CO_2$, followed by its detection by infrared spectroscopy. According to OECD 301B, a substance is considered readily biodegradable if it reaches at least 60% conversion of TOC into $CO_2$ within a 10-day window (DOMÍNGUEZ-SOLERA, et al., 2025).

Based on the Ready Biodegradability Test (OECD 301B) (Table 3), both biodegradable materials (OH and CP) were classified as readily biodegradable. In 9 days of analysis, OH underwent 63% degradation, while CP reached 72 %. Therefore, both can be considered environmentally favorable materials for applications requiring biological degradation, and the values obtained are comparable to those reported in the literature for other biopolymers. Menzies et al. (2023) conducted a Ready Biodegradability Test using polyethylene glycol (PEG) and PVOH with varying molecular weights, observing that the lower molecular weight polymers exhibited the highest degradation levels (>70% in 28 days and >80% in 60 days, respectively).

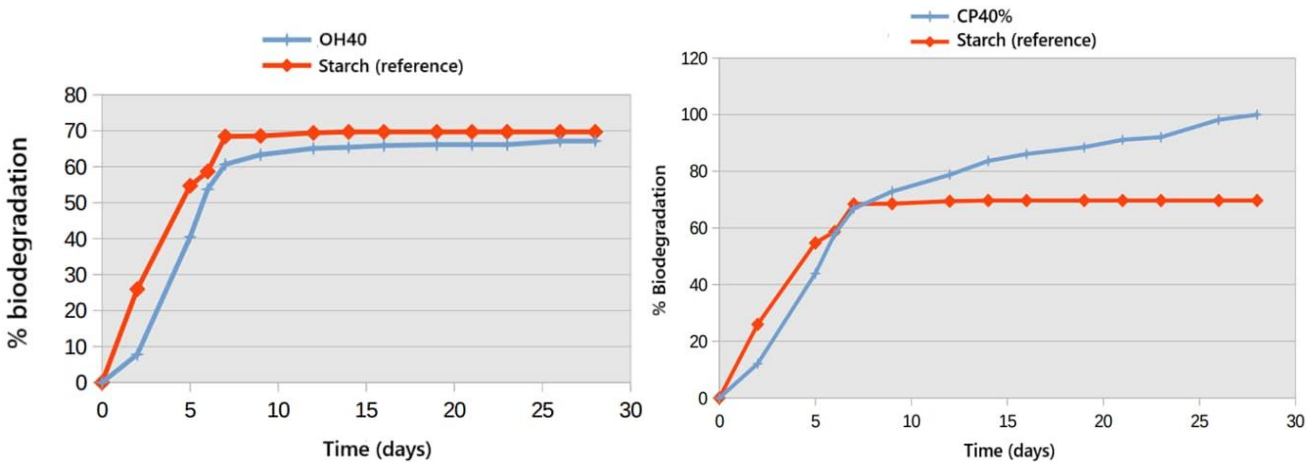
The CP sample exhibited excellent biodegradability, even outperforming the P.A. starch used as reference (Figure 10). Compared to OH, CP exhibited a significantly faster degradation rate, achieving 100% biodegradation after 28 days, whereas OH plateaued at approximately 66% and stabilized after day 16. As discussed in Section 3.1, after 150 days, OH also showed lower mass loss (50%) compared to CP (65%). This behavior is related to the higher pectin content in CP, a water-soluble polysaccharide, and the greater lignin content in OH, which may hinder enzymatic action and act as a barrier to microbial degradation.

**Table 3 -** Ready Biodegradability Test of the biodegradable materials.

$OH_{40\%}$ is the formulation containing oat hulls, starch, and PBS, while $CP_{40\%}$ is the formulation containing citrus pulp, starch, and PBS.

| | $OH_{40\%}$ | | 2 $CP_{40\%}$ | |
|---|---|---|---|---|
| **Day** | **mg $CO_2$** | **Biodegradation ratio (%)** | **$MgCO_2$** | **Biodegradation ratio(%)** |
| 0 | 0 | 0 | 0 | 0 |
| 2 | 06.90 ± 0.70 | 7.81 | 10.60 ± 1.13 | 12.05 |
| 5 | 35.65 ± 2.19 | 40.48 | 38.7 ± 0.98 | 43.9 |
| 6 | 47.35 ± 0.77 | 53.73 | 50.8 ± 1.83 | 57.70 |
| 7 | 53.40 ± 1.83 | 60.66 | 58.85 ± 2.47 | 66.82 |
| 9 | 55.75 ± 1.48 | 63.35 | 64.2 ± 2.96 | 72.88 |
| 12 | 57.30 ± 1.69 | 65.10 | 69.35 ± 2.89 | 78.75 |
| 14 | 57.55 ± 1.62 | 65.91 | 73.75 ± 2.33 | 83.68 |
| 16 | 58.05 ± 1.90 | 66.16 | 74.05 ± 1.90 | 86.12 |
| 19 | 58.25 ± 2.05 | 66.16 | 77.90 ± 6.92 | 88.49 |
| 21 | 58.25 ± 2.05 | 66.16 | 80.25 ± 6.57 | 91.12 |
| 23 | 58.25 ± 2.05 | 66.16 | 81.10 ± 7.07 | 92.05 |
| 26 | 59.10 ± 2.12 | 66.16 | 86.45 ± 7.00 | 98.17 |
| 28 | 59.10 ± 2.12 | 66.16 | 90.00 ± 6.92 | 100 |

**Figure 10 -** Ready Biodegradability Test of the biodegradable materials compared to the P.A. starch reference




$OH_{40\%}$ is the formulation containing oat hulls, starch, and PBS, while $CP_{40\%}$ is the formulation containing citrus pulp, starch, and PBS.

## 4. Conclusion

The production and biodegradation assessment of biodegradable injection-molded materials containing OH and CP were successfully achieved.

Both materials exhibited degradation rates above 50% after 150 days in soil and were classified as readily biodegradable according to OECD 301B criteria. Formulations containing CP showed faster degradation over time, likely due to the presence of pectin and soluble polysaccharides that promote microbial activity by enhancing nutrient availability, compared to OH. The incorporation of NF proved to be a promising strategy for accelerating the degradation of pure biopolymers, such as PBS, contributing to the development of environmentally friendly materials with potential for specific applications.

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# CAPÍTULO VI – Conclusões e produção científica

## 1. CONCLUSÃO

Foi possível realizar a extrusão e a moldagem por injeção termoplástica de todas as formulações contendo polpa cítrica (PC) e casca de aveia (CA), demonstrando a viabilidade tecnológica do processamento desses materiais. Apesar da redução observada na resistência à tração e no alongamento na ruptura com o aumento da fração de fibras naturais, os injetados apresentaram propriedades mecânicas adequadas para aplicações específicas e de baixo esforço, como bandejas, utensílios de uso único e outros materiais descartáveis. A incorporação de PC e CA também mostrou-se eficiente na redução do custo do PBS e na melhoria da biodegradabilidade das blendas, também melhorando indicadores como a contração do material em processos comuns de injeção (índice de contração linear %).

Os ensaios de biodegradação em solo, aliados à análise pelo teor de carbono orgânico total (TOC), demonstraram que todas as formulações atenderam aos critérios da OECD 301B. Observou-se que as frações da blenda contendo amido e fibras naturais foram rapidamente consumidas pelos microrganismos, indicando que esses componentes promovem maior disponibilidade de nutrientes e aceleram a degradação do material.

Esses resultados evidenciam o potencial das fibras de polpa cítrica e casca de aveia como reforços naturais em blendas biodegradáveis de PBS e amido, contribuindo para o desenvolvimento de materiais sustentáveis com aplicação em produtos descartáveis, redução de custos e valorização de subprodutos agroindustriais, alinhando-se aos princípios da economia circular.

## 2. PRODUÇÃO CIENTÍFICA

Visando a divulgação dos resultados e promover a distribuição do conhecimento em relação à aplicação da casca da aveia, o capítulo III foi publicado como artigo científico (SILVA, Samuel Camilo da; CARVALHO, Fabiola Azanha de; YAMASHITA, Fabio. Potential biodegradable materials containing oat hulls, TPS, and PBS by thermoplastic injection. **Polímeros**, v. 34, p. e20240026, 2024).