Universidade
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JAQUELINE CAMISA

DESENVOLVIMENTO DE MATERIAIS BIODEGRADÁVEIS A BASE DE FARINHA DE AVEIA POR EXTRUSÃO COM MATRIZ PLANA E CALANDRAGEM

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Tese apresentada ao Programa de Pós-Graduação em Ciência de Alimentos, do Departamento de Ciência e Tecnologia de Alimentos, como requisito para obtenção do título de Doutor.

Orientador: Prof. Dr. Fábio Yamashita

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"... a história humana, embora velha de milênios,
quando comparada às enormes tarefas que
estão diante de nós, talvez esteja apenas começando”
Norberto Bobbio

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RESUMO

As embalagens biodegradáveis são uma alternativa para minimizar o impacto ambiental causado pelos materiais plásticos convencionais e a farinha de aveia é uma matéria-prima promissora para produção de materiais biodegradáveis. O objetivo do trabalho foi desenvolver materiais biodegradáveis por extrusão com matriz plana e calandragem utilizando blendas de farinha de aveia com poli (adipato co-tereftalato de butileno) (PBAT), com propriedades mecânicas e processabilidade adequada para produção em escala industrial. Na primeira etapa do trabalho foram produzidos laminados biodegradáveis a partir de blendas de farinha de aveia, amido, PBAT e glicerol e todas as formulações apresentaram processabilidade adequada. De acordo com resultados obtidos na primeira etapa, foram testadas formulações utilizando farinha de aveia, PBAT e glicerol, com adição de ácido cítrico e anidrido maleico como compatibilizantes. Os resultados não foram satisfatórios, pois as blendas apresentaram baixa processabilidade. Foram testadas novas formulações utilizando farinha de aveia modificada por peróxido de hidrogênio e/ou por extrusão e todos os laminados apresentaram processabilidade adequada no processo de extrusão plana. A resistência à tração, alongamento na ruptura e o módulo de Young variaram de 1,79 a 2,08 MPa, 40 a 53% e 10 a 19 MPa, respectivamente, e o tratamento com peróxido de hidrogênio teve influência sobre as propriedades mecânicas dos materiais. Numa outra etapa foram produzidos laminados de farinha de aveia modificada com peróxido de hidrogênio utilizando ácido cítrico e anidrido maleico como compatibilizantes. A resistência à tração, alongamento na ruptura o módulo de Young dos laminados variaram de 0,98 a 2,66 MPa, 34 a 48% e 4 a 34 MPa, respectivamente e todos os componentes da blenda tiveram influência sobre as propriedades mecânicas. Os materiais desenvolvidos no trabalho são uma alternativa para a substituição de materiais não biodegradáveis por causa do baixo custo, boa processabilidade e utilizar matérias-primas provenientes de fontes renováveis.

Palavras-chave: Ácido Cítrico. Anidrido Maleico. Biopolímero. Compatibilizador. Extrusão. Peróxido de Hidrogênio. Poli (adipato co-terefetalato de butileno) (PBAT).

CAMISA, Jaqueline. **Development of biodegradable materials based on oat flour by flat die extrusion-calendering process**. 2015. 88 f. Thesis (Doctor Degree in Food Science) – Universidade Estadual de Londrina, Londrina, 2015.

ABSTRACT

Biodegradable materials are an alternative to minimize the environmental impact caused by conventional plastics and oat flour is a promising raw material for the production of biodegradable materials. The objective of the work was to develop biodegradable materials by flat die extrusion-calendering process using blends of oat flour and poly (butylene adipate co-terephthalate) (PBAT), with mechanical properties and processability suitable for industrial scale production. Biodegradable sheets were produced from blends of oat flour, starch, glycerol and PBAT and all formulations had adequate processability. Based on these results, new formulations were tested using oat flour, PBAT and glycerol with addition of citric acid and maleic anhydride as compatibilizer. The results were not satisfactory because the blends showed poor processability. New formulations were tested using oat flour modified by hydrogen peroxide and / or by extrusion and all sheets showed adequate processability. The tensile strength, elongation at break and Young's modulus ranged from 1.79 to 2.08 MPa, 40 to 53%, and 10 to 19 MPa, respectively, and the treatment with hydrogen peroxide had influence on the mechanical properties of materials. In another step sheets were produced with oat flour modified by hydrogen peroxide using citric acid and maleic anhydride as compatibilizer. The tensile strength, elongation at break Young's modulus of the sheets ranged from 0.98 to 2.66 MPa, 34 to 48% and 4 to 34 MPa, respectively, and all components of the blend had an influence on the mechanical properties. The developed materials are an alternative to the replacement of non-biodegradable materials because of their low cost, good processability and using raw materials from renewable sources.

Key words: Citric Acid. Maleic anhydride. Biopolymer. Compatibilizer. Hydrogen peroxide. Poly (butylene adipate co-terephthalate)

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LISTA DE ABREVIATURAS E SIGLAS

AOAC	Association of Analytical Communities
ASTM	American Standard for Testing and Material
CA	Ácido Cítrico
EB	Alongamento na Ruptura
EP	Alongamento na Perfuração
FT-IR	Espectroscopia de infravermelho com transformada de Fourier
FP	Força de perfuração
Gly	Glicerol
MA	Anidrido maleico
PBAT	Poli (adipato co-tereftalato de butileno)
PVA	Poli (álcool vinílico)
SEM	Microscopia eletrônica de varredura
SRPR	Resistência à penetração em velocidade lenta
TS	Resistência à tração
WLW	Perda de massa em água
WOF	Farinha de aveia
WVP	Permeabilidade ao vapor de água

SUMÁRIO

INTRODUÇÃO

Segundo a Pesquisa Nacional de Saneamento Básico do Instituto Brasileiro de Geografia e Estatística (IBGE) realizada em 2008, são recolhidas no Brasil cerca de 180 mil toneladas diárias de resíduos sólidos, sendo que as embalagens são um dos maiores contribuintes. É notável a enorme quantidade de plásticos utilizada na produção de embalagens, sendo sua grande maioria formada de polímeros não biodegradáveis derivados de petróleo.

A maioria dos resíduos plásticos tem sido incinerada ou enterrada, entretanto, a incineração de resíduos plásticos, em particular, leva a uma poluição ambiental secundária devido à produção de gases tóxicos (KIM et al., 2000).

Os países da comunidade europeia vêm apoiando o desenvolvimento de materiais de embalagem provenientes de fontes renováveis, pois se encontram preocupados principalmente com a escassez de petróleo e o grande volume de lixo urbano, buscando contribuir desta forma com o desenvolvimento sustentável (DAVIS; SONG, 2006).

Uma opção é a blenda de polímeros biodegradáveis comerciais com farinha de aveia visando reduzir o custo da embalagem sem modificar de forma drástica as propriedades mecânicas e processabilidade dos materiais produzidos. Além disso, o processo de produção desses materiais mistos utilizaria os mesmos equipamentos empregados na produção de materiais plásticos convencionais.

Diante do exposto, este trabalho teve como objetivo principal desenvolver materiais biodegradáveis por extrusão com matriz plana e caladragem utilizando blendas de farinha de aveia com PBAT, com propriedades mecânicas e processabilidade adequada para produção em escala industrial. Concomitantemente, foi estudado o efeito da adição de compatibilizantes como ácido cítrico e anidrido maleico sobre as propriedades dos materiais.

O trabalho está apresentado na forma de capítulos e com exceção da revisão bibliográfica, os demais capítulos encontram-se na forma de artigo e em inglês. Desta forma, esta tese está dividida da seguinte forma:

Capítulo 1 - Revisão bibliográfica.

Apresenta um levantamento bibliográfico sobre farinha de aveia, PBAT, modificação com peróxido de hidrogênio, uso de compatibilizantes, produção de material biodegradáveis por extrusão e caracterização desses materiais.

Capítulo 2 – Desenvolvimento de materiais biodegradáveis com farinha de aveia por planejamento de mistura.

Com base em resultados prévios, foram selecionados o teor de farinha de aveia, amido, PBAT e glicerol nas formulações, portanto esse capítulo discorre sobre a desenvolvimento de laminados biodegradáveis a partir de misturas de farinha de aveia / amido / PBAT / glicerol, com capacidade de processamento adequada, utilizando planejamento de mistura.

Capítulo 3 – Blendas de farinha de aveia produzidas por extrusão reativa com ácido cítrico e anidrido maleico.

Com base nos resultados do capítulo 2 optou-se pela retirada do amido das formulações. Sendo assim, foram elaborados materiais biodegradáveis de farinha de aveia com adição de ácido cítrico e anidrido maleico com subsequente extrusão utilizando PBAT e glicerol.

Capítulo 4 – Laminados produzidos por extrusão de farinha de aveia modificada / PBAT.

As formulações do capítulo 3 não apresentaram boa processabilidade, portanto nesse capítulo foi estudado o efeito da modificação de farinha de aveia com peróxido de hidrogênio sobre as propriedades mecânicas e barreira ao vapor de água de laminados produzidos com farinha de aveia / PBAT / glicerol.

Capítulo 5 – Misturas de farinha de aveia modificada / PBAT compatibilizadas com ácido cítrico e anidrido maleico

Com base nos resultados do capítulo 4, produzir laminados biodegradáveis a partir de farinha de aveia modificada com peróxido de hidrogênio / PBAT / glicerol / utilizando anidrido maleico e ácido cítrico como compatibilizante.

CAPÍTULO 1

REVISÃO BIBLIOGRÁFICA

1 Materiais Biodegradáveis

A produção e utilização de plásticos em todo o mundo têm aumentado (THOMPSON et al., 2009) e a preocupação ambiental associada à grande disposição de materiais plásticos têm proporcionado a investigação de alternativas para substituição parcial dos plásticos convencionais por biodegradáveis.

De acordo com a Associação Brasileira da Indústria do Plástico (ABIPLAST, 2014), estima-se que são retirados do meio ambiente por ano, aproximadamente 805 mil toneladas de resíduos pós-consumo, que dão origem a mais de 725 mil toneladas de materiais plásticos reciclados.

Os materiais mais utilizados na fabricação de materiais para embalagens são mostrados na Tabela 1.

Tabela 1- Materiais utilizados na fabricação de materiais para embalagens.

Tipo de material	Unidade monomérica	Características
Polipropileno	Propeno	Boa resistência mecânica, boa barreira ao vapor de água e oxigênio.
Polietileno	Etileno	Boas propriedades mecânicas, termossoldável.
Polivinilideno	Vinilideno	Boa barreira ao vapor de água e oxigênio, não muito resistente, termossoldável.
Poliéster	Etilenoglicol + ácido tereftálico	Boas propriedades mecânicas, barreira pobre ao vapor de água e oxigênio.
Poliamida (Nylon)	Diamina + vários ácidos	Boa resistência, termossoldável, barreira pobre ao vapor de água e oxigênio.

Fonte: THARANATHAN (2003).

O setor de pesquisa e desenvolvimento possui como desafio a pesquisa e o planejamento de embalagens com componentes que favoreçam a sua degradação ambiental, pois envolvem itens que se contrapõem à função primordial da embalagem de proteção e manutenção da estabilidade de alimentos (FORLIN; FARIA, 2002). Com o intuito de aumentar o índice de biodegradação, a produção de polímeros biodegradáveis a partir de fontes renováveis torna-se a melhor alternativa frente ao problema da disposição dos resíduos plásticos (DAVIS; SONG, 2006).

Segundo estabelecido pela American Standard for Testing and Methods (ASTM-D-883), polímeros biodegradáveis são aqueles cuja degradação resulta primariamente da ação de microrganismos tais como bactérias, fungos e algas de ocorrência natural. Em geral, derivam desse processo CO_2, CH_4, componentes celulares microbianos e outros produtos (ASTM, 1999).

Os polímeros biodegradáveis podem ser divididos em quatro famílias: (1) polímeros agrícolas obtidos por fracionamento de biomassa; (2) polímeros microbianos, poliésteres obtidos a partir da fermentação de produtos agrícolas; (3) mono ou oligômeros polimerizados por processos químicos convencionais obtidos a partir do produto de fermentação de matérias-primas agrícolas e (4) derivados por síntese, obtidos da indústria petroquímica por via sintética clássica (VILPOUX; AVEROUS, 2003; AVEROUS; BOQUILLON, 2004).

Muitas pesquisas têm sido desenvolvidas com diferentes materiais, que contém em sua composição amido, celulose e lipídios, na tentativa de minimizar, diminuir ou solucionar o problema da poluição através da obtenção de plásticos biodegradáveis. O amido é mais utilizado nas pesquisas, pois possui baixo custo, abundância e vasta gama de aplicações (BENGTSSON; KOCK; GATENHOLM, 2003; PELISSARI; YAMASHITA; GROSSMANN, 2011).

O amido de mandioca tem sido empregado na elaboração e obtenção de materiais biodegradáveis (DEBIAGI et al., 2010; MALI et al., 2005; MELO et al., 2011; MULLER; YAMASHITA; LAURINDO, 2008; OLIVATO et al, 2012a; OLIVATO et al, 2012b). Já os amidos de batata e de milho são fontes que também têm sido pesquisadas na obtenção de materiais biodegradáveis (BENGTSSON; KOCK; GATENHOLM, 2003; FAKHOURI et al, 2010; JANSSON; THUVANDER, 2004; THIRÉ; SIMÃO; ANDRADE, 2003).

As propriedades dos materiais biodegradáveis dependem do biopolímero utilizado, das condições de fabricação e das condições ambientais que são importantes fatores por causa da natureza higroscópica dos biopolímeros (SOBRAL, 2000).

2 Aveia

A aveia é uma cultura de origem mediterrânea que está encontrando novos usos, pois agricultores e pesquisadores estão buscando novas maneiras de integrá-la em sistemas de produção onde considerem economicamente viáveis (SUTIE; REYNOLDS, 2004).

No Brasil, o cultivo de aveia vem crescendo continuamente, concentrando-se na região Sul, Mato Grosso do Sul, São Paulo e sul de Minas Gerais. O cultivo de aveia é destinado, basicamente, para a produção de forragem, mas com aumento crescente da área destinada à produção de grãos desse cereal para outros fins (CBPA, 2006).

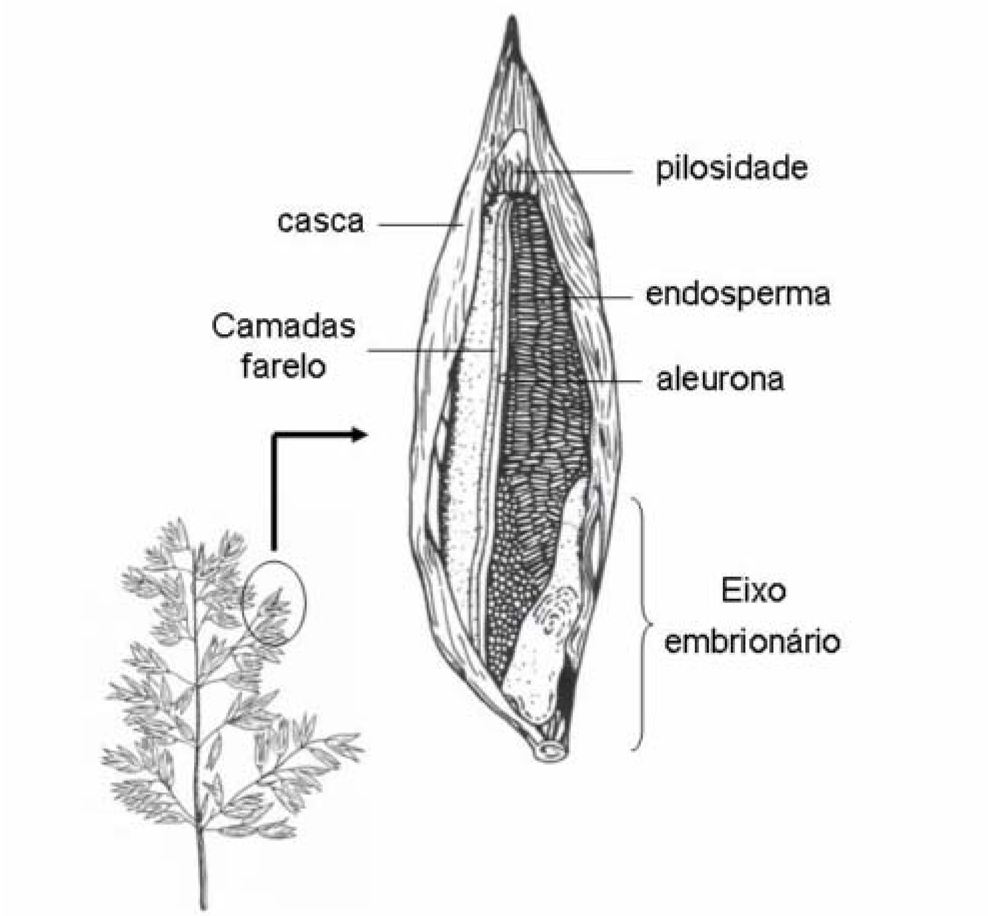
A estimativa de área plantada de aveia no Brasil em 2015 é de 186,5 mil hectares (CONAB, 2015). As principais regiões de cultivo deste cereal no Paraná concentram-se na área de influência da Cooperativa Agrária Mista Entre Rios Ltda. (Guarapuava, PR), da indústria SL Cereais e Alimentos (Mauá da Serra, PR) e na região de Ponta Grossa (CBPA, 2006).

Entre as espécies mais cultivadas estão a *Avena sativa*, *Avena strigosa* (com maior área de cultivo na América do Sul) e *Avena strigosa* subsp. nudibrevis (cultivada na Grã Bretenha). A aveia branca (*Avena sativa* L.) é uma espécia autógama pertencente à família Poaceae, tribo Aveneae (LOSKUTOV, 2008).

A espécie *Avena sativa* L. é considerada ideal para a produção de grãos, enquanto que as demais espécies apresentam uma aptidão mais forrageira, estimando-se que esta espécie ocupe cerca de 80% da área mundial de aveia destinada à produção de grãos (CBPA, 2006).

O grão de aveia (Figura 1) é uma cariopse semicilíndrica e afinada nas extremidades. A cariopse pode ser definida como um fruto-semente onde parte do fruto está fortemente aderido à semente, em que é constituída pelo germe e pelo endosperma, envolvidos pelas camadas de hialina, aleurona e testa. O endosperma, por sua vez é formado pela camada de aleurona e pelo endosperma amiláceo. A cariopse é desenvolvida em coberturas florais formando parte da palha envolvendo essas cariopses tão firmemente que permanecem aderidas mesmo após a colheita e se constituem na casca dos grãos de aveia (FLOSS, 2005).

Figura 1- Panícula da aveia e detalhe das seções longitudinal e transversal do grão de aveia.



Fonte: (DALMOLIN, 2011).

A preparação tradicional de aveia para consumo humano é mais trabalhosa do que a de trigo, pois os grãos devem ser secos, moídos e peneirados (SUTIE; REYNOLDS, 2004).

A composição química da aveia diferencia-se dos demais cereais pelos altos teores de proteínas, ácidos graxos insaturados e principalmente pela fração de fibras (LÀSZTITY, 1998; SÁ; DE FRANCISCO; SOARES, 1998).

A aveia apresenta de 9 a 11% de fibra alimentar total, que é responsável por muitos benefícios à saúde humana (PEDÓ; SGARBIERI, 1997). A concentração de fibra alimentar solúvel no grão de aveia é relativamente maior quando comparado aos demais cereais. No centeio, os valores variam de 1 a 3% e em arroz, sorgo, triticale e trigo estão em quantidade inferior a 1%. Os componentes mais importantes da fibra solúvel são as ß-glucanas, moléculas lineares compostas de ligações ß (1-3) e (1-4), entre as unidades D-glicopiranosil. As ß-glucanas são polissacarídeos não amiláceos encontrados nas paredes celulares do endosperma da aveia e da cevada (GUTKOSKI; TROMBETTA, 1999). A fibra alimentar solúvel da aveia é composta por pectinas, ß-glucanas, mucilagens, algumas hemiceluloses e amido resistente. Os principais componentes das fibras insolúveis são a celulose e as hemiceluloses (WEBER; GUTKOSKI; ELIAS, 2002).

Segundo Làsztity (1998), a aveia apresenta elevado teor proteico, variando entre 12,4 e 24,5% no grão descascado. Os carboidratos variam entre 75 e 80% da massa seca, com o amido em maior quantidade. Apresenta ainda elevada proporção de polissacarídeos não amiláceos que é o principal componente da fibra total.

Entre os açúcares normalmente determinados nas frações cariopse, casca, farelo e farinha de aveia estão a sacarose, rafinose, glicose, frutose, maltose, estaquiose e frutosanas. As concentrações de açucares são semelhantes as dos demais cereais, destacando-se a sacarose e rafinose (LÀSZTITY, 1998).

Pedó e Sgarbieri (1997) relatam que os lipídios da aveia apresentam predominância de ácidos graxos insaturados. A porcentagem de lipídios no grão de aveia varia entre 5,0 e 9,0%, valor superior, se comparados com outros grãos, como trigo (2,1-3,8%), arroz (1,83-2,5%), milho (3,9-5,8%), cevada (3,3-4,6%) e centeio (2,0-3,5%) (MORRISON, 1978). Este percentual é devido ao ácido palmítico e aos ácidos graxos insaturados, como o oleico e linoleico, representando em torno de 95% do total (GUTKOSKI; EL-DASH, 1999).

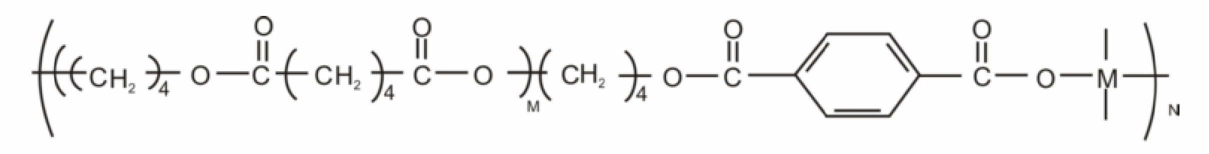
A quantidade de minerais na farinha pode variar de 8% a 47% (PETERSON; BRINEGAR, 1986). As frações cariopse, farelo e farinha de aveia apresentam concentração de tocóis (vitamina E) de 4,09%, 3,48% e 2,77%, respectivamente (RFN, 2010).

Dentre os produtos de aveia processados pelas indústrias encontramos o farelo que é obtido pela moagem da aveia e posterior separação da farinha por peneiramento e aspiração (WOOD et al., 1989). Durante o processamento do farelo de aveia, surge um produto secundário, que é a farinha de aveia, apresentando maior teor de amido e menores teores de proteínas, lipídios e fibra alimentar, em relação aos da farinha integral (PATON; LENZ, 1993).

3 Poli (adipato co-tereftalato de butileno) (PBAT)

O poli (adipato co-tereftalato de butileno) (PBAT) (Figura 2), é a combinação de um polímero sintético biodegradável (poliéster alifático) com um polímero sintético não biodegradável (poliéster aromático) formado a partir da reação entre 1,4 butanodiol, ácido adípico e ácido tereftálico. O PBAT supera as desvantagens de muitos materiais alifáticos, pois possui maior resistência à tensão, maior taxa de elongação e menor permeabilidade ao oxigênio, aliando estas boas propriedades materiais com a biodegradabilidade (COSTA, 2008).

Figura 2 - Estrutura molecular da unidade monomérica do PBAT.



Fonte: OLIVATO (2010).

O PBAT é biodegradável e compostável, se degrada em algumas semanas com a ajuda de enzimas naturais, por isso tem sido empregado na elaboração e obtenção de materiais biodegradáveis (BRANDELERO, YAMASHITA; GROSSMANN, 2010; GARCIA et al., 2011; HERRERA et al., 2002; JIANG; WOLCOTT; ZHANG, 2006; SCAPIM, 2009).

4 Plastificantes

Materiais de polímeros naturais, como p.ex., de amido, são quebradiços sendo muitas vezes necessária a adição de plastificantes na formulação para aumentar a flexibilidade e processabilidade. Estes aditivos reduzem as forças intermoleculares e aumentam a mobilidade das cadeias poliméricas. Também atuam diminuindo possíveis descontinuidades e zonas quebradiças (GONTARD; GUILBERT; CUQ, 1993). Garcia, Martino e Zaritzki (2000) relataram que filmes plastificados à base de amido mostram superfícies homogêneas, sem poros ou fissuras, o que não aconteceu nos filmes não plastificados.

Plastificantes são moléculas geralmente pequenas (baixa massa molar), pouco voláteis, que competem com as ligações de hidrogênio e interações eletrostáticas polímero-polímero (MANGAVEL et al., 2003).

Espera-se que um plastificante reduza o módulo de elasticidade, força de tensão, dureza, densidade, viscosidade do material fundido, temperatura de transição vítrea, enquanto que, ao mesmo tempo, aumente a flexibilidade, alongamento na ruptura e tenacidade. Um plastificante ideal deve ser compatível com o polímero, estável em altas e baixas temperaturas de ambiente, lubrificar suficientemente em uma ampla faixa de temperatura, ser insensível à radiação ultravioleta do sol, ter baixo custo e, acima de tudo, cumprir os regulamentos de saúde e segurança (RAHMAN; BRAZEL, 2004). O mercado atual oferece numerosas opções de plastificantes, contudo, sua escolha deve ser realizada de acordo com as características do polímero ao qual será adicionado.

O glicerol é um composto orgânico utilizado como plastificante em filmes biodegradáveis, pertencente à classe dos polióis. É líquido à temperatura ambiente, higroscópico, inodoro, viscoso e de sabor adocicado. Encontra-se presente em todos os óleos e gorduras de origem animal e vegetal, em sua forma combinada, ou seja, ligado a ácidos graxos tais como o ácido estereárico, oleico, palmítico e láurico para formar a molécula de triacilglicerol. O glicerol combinado também está presente em todas as células animais e vegetais, fazendo parte de sua membrana celular, na forma de fosfolipídios.

O glicerol vem sendo utilizado como plastificante por vários pesquisadores na produção de materiais biodegradáveis de amido de milho (FAKHOURI et al, 2010), amido de mandioca (ALVES et al., 2007; CHANG; KARIM; SEOW, 2006; MULLER; YAMASHITA; LAURINDO, 2008; SHIMAZU; MALI; GROSSMANN, 2007) e concentrado proteico de soro (SHAW et al., 2002).

5 Processos de produção de materiais biodegradáveis

Dentre os processos utilizados para a produção de materiais biodegradáveis estão a técnica denominada *casting* e a extrusão. A técnica de *casting* consiste na desidratação de um dado volume de solução filmogênica aplicada sobre um suporte de área conhecida, o que permite o controle da espessura dos materiais. A formação do material por *casting* depende da coesão entre as moléculas formadoras e o grau de coesão, que por sua vez, depende da estrutura química do biopolímero, dos procedimentos e parâmetros de fabricação (temperatura, tempo de secagem, técnica de evaporação do solvente, umidade relativa), da presença de plastificantes, bem como a espessura do material (GONTARD; GUILBERT, 1996).

Galdeano (2007) estudou o comportamento de filmes produzidos por *casting* e laminados de amido de aveia com diferentes plastificantes e observou que ambos podem ser empregados para fabricação de embalagens biodegradáveis de baixa solicitação mecânica e curto tempo de uso. Entretanto, comparados aos termoplásticos comuns, esses materiais ainda revelam algumas desvantagens, principalmente devido ao seu alto caráter hidrofílico.

Atualmente, a maior parte da produção de materiais sintéticos é feita por extrusão. Esta tecnologia oferece as vantagens associadas ao sistema contínuo de produção, incluindo versatilidade, baixo custo operacional e necessidade de menos espaço por unidade de operação (SOTHORNVIT et al., 2007). Para viabilizar a produção de materiais biodegradáveis em escala comercial, o ideal seria utilizar a mesma tecnologia disponível atualmente para os materiais sintéticos.

A extrusora é um equipamento constituído basicamente de um alimentador, uma rosca sem-fim, um cilindro encamisado, uma matriz de saída do material e um sistema de corte. O alimentador pode ser equipado com um agitador ou rosca, a fim de manter um fluxo contínuo de alimentação e permitir um bom funcionamento da extrusora, evitando flutuações no processo e nas características do produto extrusado. A rosca é a parte central e principal do equipamento e sua geometria influencia o processo.

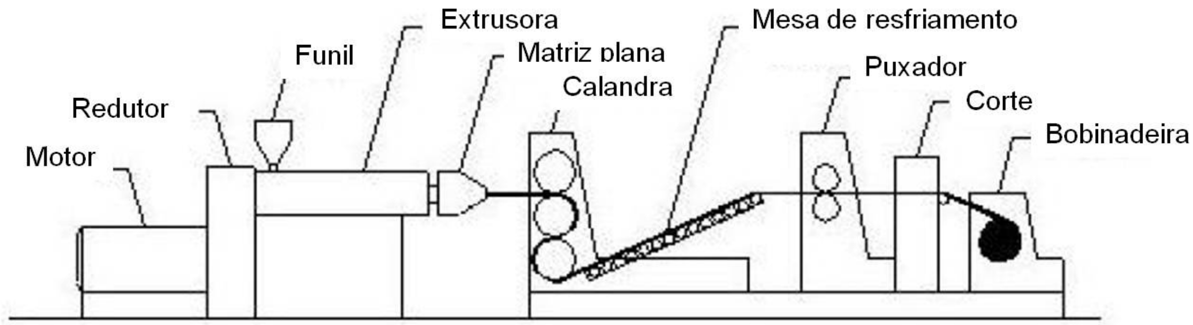
As extrusoras disponíveis comercialmente podem ser de rosca cônica simples, dupla rosca, ou rosca “supercônica”. Equipamentos com dupla rosca, amplamente empregados no preparo e na extrusão de formulações de resinas termoplásticas, atingem o máximo de sua capacidade quando o seu torque é plenamente utilizado. Devido as suas excelentes características de mistura e à sua estrutura flexível, as máquinas extrusoras com duas roscas, que giram com mesma velocidade, são mais viáveis econômica e tecnicamente no preparo de formulações de polímeros termoplásticos (CRIPPA, 2006).

A extrusora se comporta como um trocador de calor devido às trocas envolvendo as paredes do cilindro, a rosca e o material. Desempenha também a função de reator químico de processamento de biopolímero e de misturas de alimentos, pois é capaz de cozinhar, gelatinizar, desnaturar e esterilizar, usando altas temperaturas (até 250 °C), em um tempo de residência relativamente curto (de 1 a 2 minutos) e altas pressões (que podem atingir até 25 MPa).

A extrusão com matriz plana e calandragem (extrusão plana) é um processo bastante utilizado pelas indústrias, e nesse processo o polímero fundido, ao sair da extrusora é forçado através de uma matriz plana, que determina a espessura e a largura do filme ou laminado. O material ainda em estado fundido entra na calandra, que é formada por cilindros metálicos, tendo a função de resfriar e dar polimento ao material. Há ainda outros periféricos de extrusão como os puxadores e bobinadeiras. Uma representação esquemática de uma planta de extrusão plana é apresentada na Figura 3.

Galicia-García et al. (2011) caracterizaram as propriedades térmicas e microestruturais de filmes biodegradáveis produzidos com amidos nativos de milho, milho ceroso, batata e amido fosforilado de milho, adicionados de fibras celulósicas de bagaço de cana-de-açúcar e plastificados com glicerol. Os filmes foram produzidos pelo processo de extrusão plana. Segundo os autores os filmes obtidos apresentaram boas propriedades funcionais para seu uso como materiais de embalagem, concluindo que o processo de extrusão apresenta aplicabilidade para o uso em blendas de amido.

Figura 3 - Representação esquemática de uma extrusora com matriz plana e calandras.



Fonte: VIDAL (2011).

6 Modificações com peróxido de hidrogênio

O peróxido de hidrogênio apresenta participação importante no aumento das propriedades de hidratação das fibras, atuando na degradação da lignina, através de sua remoção por solubilização e/ou modificação estrutural, promovendo também um aumento no grau de hidratação da celulose e quebra da sua cristalinidade (NING; VILLOTA; ARTZ, 1991).

Durante o processamento, o peróxido de hidrogênio decompõe-se naturalmente em oxigênio e água, não deixando resíduo (McNEILLIE; BIESER, 1993). Inglett (1995) produziu uma modificação pronunciada em subprodutos lignocelulósicos, através de multiestágios de cisalhamento combinado com soluções de peróxido de hidrogênio alcalino em temperaturas elevadas, obtendo produtos capazes de reter grandes quantidades de água.

Galdeano e Grossmann (2005) avaliaram o efeito do tratamento com peróxido de hidrogênio alcalino a 7%, associado à extrusão, nas propriedades de hidratação de casca de aveia, e obtiveram um aumento de 70% na capacidade de retenção de água e de 55% no volume de intumescimento.

7 Compatibilizantes

O compatibilizante atua como agente de auxílio na superação da diferença de polaridade. Ele permanecerá na interface destes polímeros, melhorando a adesão entre as duas fases poliméricas, o que pode diminuir a tendência de separação destes polímeros, pela redução da tensão interfacial (SHI et al., 2008; OLIVATO, 2010).

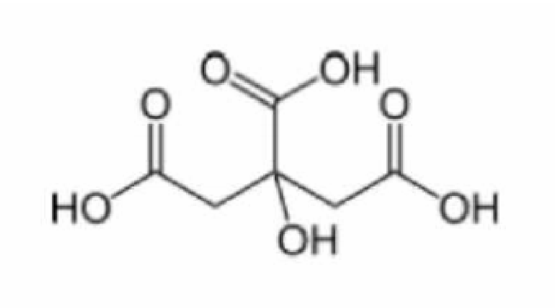
Vários estudos foram realizados com o objetivo de avaliar o uso de compatibilizantes em blendas biodegradáveis. O ácido cítrico mostrou um comportamento satisfatório, quando usado como compatibilizante (SHI et al., 2008; MA et al., 2009; GHANBARZADEH, ALMASI, ENTEZAMI, 2011; OLIVATO et al., 2012a; OLIVATO et al., 2012b; GARCIA et al., 2011), assim como o anidrido maleico (OLIVATO et al., 2012b).

8 Ácido cítrico

O ácido cítrico (Figura 4) é um ácido orgânico, apresentando em sua estrutura um grupo hidroxila e três grupos carboxílicos (GHANBARZADEH, ALMASI, ENTEZAMI, 2011).

Por conta de sua estrutura multicarboxílica ele pode ser utilizado como agente de compatibilização. O intuito é que este ácido promova reações, como a esterificação e a transesterificação (ligações cruzadas), entre os polímeros para uma melhora na compatibilidade dos mesmos (OLIVATO et al., 2012a; GARCIA et al., 2011).

Figura 4 Estrutura do Ácido Cítrico.

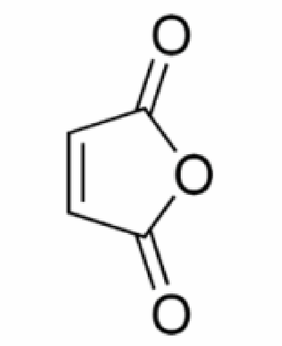


Estudos comprovam que a utilização de ácido cítrico como compatibilizante melhorou as propriedades mecânicas, térmicas e de barreira de filmes biodegradáveis à base de amido de mandioca e PBAT, produzidos através da extrusão-sopro em balão (OLIVATO et al., 2012a; OLIVATO et al., 2012b). Este efeito foi devido à estrutura desse ácido, que promoveu a esterificação aumentando a hidrofobicidade do amido, tornando-o mais compatível, ou ainda como agente de ligação cruzada (SHI et al., 2008; OLIVATO et al., 2013).

9 Anidrido Maleico

O anidrido maleico (anidrido cis-butenodióico) é um sólido incolor, amplamente utilizado na indústria de plásticos como compatibilizante entre polímeros com diferenças de hidrofilicidade (KALAMBUR; RIZVI, 2006).

Figura 5 - Estrutura do Anidrido Maleico



A principal razão para a utilização do anidrido maleico como compatibilizante é a facilidade com que ele pode ser enxertado nas cadeias poliméricas na temperatura de fusão destes materiais, e assim, a reação pode ser realizada durante o processo de extrusão reativa (KALAMBUR; RIZVI, 2006).

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CAPÍTULO 2

DEVELOPING BIODEGRADABLE MATERIALS WITH WHOLE OAT FLOUR BY EXPERIMENTAL MIXTURE DESIGN

ABSTRACT: Several studies have focused on the development of biodegradable material using biopolymers from renewable sources. The objective of this work was to develop biodegradable sheets by flat die extrusion-calendering process from blends of whole oat flour, starch, poly (butylene adipate-co-terephthalate) and glycerol as plasticizer using experimental mixture design. All formulations had adequate processability and the sheets showed homogenous surfaces, without cracks, insoluble particles or bubbles. The whole oat flour is a promising raw material to produce biodegradable sheets, the developed materials have adequate mechanical properties to be tested as biodegradable packaging, and their properties can be adjusted by changing the formulation.

Keywords: Biodegradable sheets. Poly (butylene adipate-co-terephthalate). Starch.

1 Introduction

The production and use of plastics throughout the world have increased (THOMPSON et al., 2009) and environmental concerns associated with the disposal of plastic material have provided the investigation of alternatives to partial replacement for conventional biodegradable plastics.

Several studies have focused on the development of biodegradable packaging using biopolymers from renewable sources, and among them starch has become one of the most promising candidates due to its high availability, renewability and low cost (TANG et al., 2012).

There are several studies that used cassava, potato and corn starches to produce biodegradable materials (DEBIAGI et al., 2010; MALI et al., 2005; MULLER; YAMASHITA; LAURINDO, 2008; OLIVATO et al., 2012; BENGTSSON; KOCH; GATENHOLM, 2003; FAKHOURI et al., 2010; JANSSON; THUVANDER, 2004;. THIRÉ; SIMÃO; ANDRADE, 2003), and according to the authors the challenges are to reduce their hydrophilic character, to improve their mechanical and permeability characteristics and to scale-up the production by increasing their processability.

In order to solve these limitations and due to the high cost of synthetic biodegradable polyesters, several studies have been conducted blending starch with biodegradable polymers by extrusion, as it is the usual method to produce plastic materials (BRANDELERO; YAMASHITA; GROSSMANN, 2010; SCAPIM, 2009).

Flour is another raw material used for the production of biodegradable materials. Pelissari et al., (2013) produced biodegradable films from banana starch and banana flour using casting technique. The films of flour were more resistant, more flexible and less soluble than starch films.

Elizondro, Sobral and Menegalli (2009) develop film based on blends of *Amaranthus cruentus* flour and poly (vinyl alcohol) (PVA). Amaranth flour/PVA blended films were made by casting. All the mechanical properties were enhanced when the PVA content was increased (up to 50%) in the blend. The water solubility of the blend decreased as the PVA content increased.

Dias et al., (2010) developed biodegradable films based on rice starch and rice flour with glycerol or sorbitol as plasticizer. SEM analysis of starch and flour films revealed compact structures. Rice flour films had similar mechanical properties to those of starch-based films. However, their water vapor permeabilities were two times higher than those of starch based films. Films with sorbitol were less permeable to water and more rigid, while films with glycerol were more plasticized and had poorer water vapor barrier properties.

Whole oat flour (WOF) has some interesting characteristics as a raw material to produce biodegradable materials such as low cost, high starch content, the presence of fibers that can act as a reinforcement of the polymer matrix and lipids that can reduce the hydrophilicity of the material. No studies on the production of biodegradable materials using WOF as raw material were found in consulted literature.

The objective of this work was to develop biodegradable sheets from blends of whole oat flour, starch, poly (butylene adipate-co-terephthalate) and glycerol as plasticizer with adequate processability, mechanical and barrier properties using an experimental mixture design.

2 Experimental

2.1 MATERIALS

The sheets were produced with whole oat flour (WOF) (SL Alimentos Ltda, Brazil) (moisture 8.74%, lipids 6.20%, ashes 2.00% and protein 17.42%), native cassava starch (Indemil, Brazil), glycerol (Dinâmica, Brazil) and poly (butylene adipate-co-terephthalate) (PBAT) (BASF, Germany) under the brand name Ecoflex®.

2.2 METHODS

2.2.1 PRODUCTION OF BIODEGRADABLE SHEETS

The PBAT, glycerol, WOF and starch were manually mixed, and extruded in a pilot single-screw extruder (model EL-25, BGM, Brazil) with a screw diameter (D) of 25 mm and a screw length of 28D to produce cylindrical strands. The barrel temperature profile was 90/120/120/120 °C from the feeding zone (zone 1) to the die zone (zone 4) at a screw speed of 30 rpm, using a die with six holes of 2 mm diameter. The strands was pelletized and extruded in a extrusion-calendering line consisting of a pilot co-rotating twin-screw extruder (model D-20, BGM, Brazil), with a screw speed of 100 rpm and temperature profile of 90/120/120/125/120 °C, feed speed of 33 rpm and equipped with a 0.8 mm flat die and a three-roll calender (AX Plasticos, Brazil).

An experimental mixture design with constrains (determined by preliminary tests) was used to assess the effect of the three components: WOF, starch and glycerol. All formulations contained the same concentration of PBAT (30 wt% of the total), with the remaining 70 wt% contributed by glycerol, WOF and starch (Table 1). Mixture models (Eq. 1) were determined using the Statistica software version 7.0 (STATSOFT, 1995), using the mixture design procedure.

$$y = \beta_1.x_1 + \beta_2.x_2 + \beta_3.x_3 + \beta_{12}.x_1.x_2 + \beta_{13}.x_1.x_3 + \beta_{23}.x_2.x_3 \qquad \text{(Eq. 1)}$$

where y is the dependent variable, β is the regression coefficient for each component, x_1 is the starch percentage, x_2 is the WOF percentage, and x_3 is the glycerol percentage.

Table 1 – Component and Pseudo-components of the biodegradable sheets according to the mixture design.

Formulation	Component* (wt%)			Pseudo-components**		
	Starch	WOF	Glycerol	x_1	x_2	x_3
1	0.750	0	0.250	1.0000	0	0
2	0	0.750	0.250	0	1.0000	0
3	0.700	0	0.300	0.9330	0	0.067
4	0	0.700	0.300	0	0.9330	0.067
5	0.725	0	0.275	0.9670	0	0.033
6	0	0.725	0.275	0	0.9670	0.033
7	0.375	0.375	0.250	0.5000	0.5000	0
8	0.35	0.350	0.300	0.4665	0.4665	0.067
9	0.363	0.363	0.275	0.4835	0.4835	0.033

* All formulations contained the same concentration of PBAT (30 wt% of the total)

**To calculate the pseudo-component values, the equation $xi = ci\text{-}ai / 1\text{-}\sum ai$ was used, where x_1=starch, x_2 = WOF and x_3=glycerol; *ci* is the actual concentration and *ai* is the lower limit of each component in the mixture design.

2.2.2 DENSITY

Five samples of each sheet were cut (20 x 20 mm), and were conditioned for 7 days in a desiccator containing anhydrous $CaCl_2$ (~ 0% RH). After this period, samples were weighed and measured (thickness, length and width) to calculate the density.

2.2.3 OPACITY

The opacity was determined using a colorimeter (BYK Gardner, USA), illuminant D65 (day light) and 10°, at 3 different spots in each sample, according to Hunterlab methods (Hunter Associates Laboratory, 1997). Sample opacity (Y) was calculated as the ratio between the opacity of the sample placed under a black pattern (Yb) and the opacity of the sample placed under a white pattern (Yw) (Eq. 2).

$$Y\ (\%) = (Yb/Yw).100 \qquad \text{(Eq. 2)}$$

The measurements were performed in triplicate.

2.2.4 MECHANICAL PROPERTIES

The tensile strength, elongation at break and Young's modulus of the sheets was determined based on the ASTM method D882-02 (2002) using a texture analyzer, model TA.XT2i (Stable Micro Systems, England) fitted with a 50 kg load cell. Ten samples of each formulation (70 mm x 20 mm) were conditioned at 53 ± 2% RH for 48 h before testing. The crosshead speed was set at 0.8 mm/s, and the initial distance between the grips was 30 mm.

The slow rate penetration resistance (SRPR) of the sheets was performed according to ASTM method F1306-90 (2002) using the same texturometer used for tensile testing, with a 3.2 mm diameter hemispherical probe. Ten samples for each formulation (30 mm diameter) were conditioned at 23 ± 2 °C and 53 ± 2% RH for 48 h before testing. The force to perforation (FP) and the elongation to perforation (EP) were determined at 25 mm/min.

2.2.5 WEIGHT LOSS IN WATER

Samples were previously dried for three days in a desiccators containing anhydrous $CaCl_2$ (~ 0% RH). After weighing, the sheets were immersed in distilled water, in a proportion of 30:1 (water / sample) for 48 h at 25 °C. The samples were dried at 105 °C for 4 h, and the weight of the conditioned specimen after treatment was used to determine the percentage (%) of weight loss in water.

2.2.6 WATER VAPOUR PERMEABILITY (WVP)

The tests were conducted using the ASTM E-96-95 (1996) standard with some modifications. Before the analysis, the samples were conditioned at 25 °C and 53% RH for 48 h. Each sheet sample was fixed in a permeation cell with 60 mm internal diameter. The interior of the cell was filled with saturated $MgCl_2$ solution (32.8% RH), and the device was stored at 25 °C in a desiccator containing saturated sodium nitrate solution to provide 64% RH.

2.2.7 MOISTURE SORPTION ISOTHERMS

Samples with about 500 mg were previously dried for 20 days ($CaCl_2$, ~ 0% RH) and then placed at 25 ± 2 °C in separated desiccators containing saturated salt solutions, under desired relative humidity conditions (11, 32, 53, 75 and 90 % RH). Guggenheim-Anderson-de Boer (GAB) model (Eq. 3) was used to fit the experimental data.

$$M=m_0.C.K.a_w/(1-K.a_w).(1-K.a_w+C.K.a_w) \qquad \text{(Eq. 3)}$$

where M is the equilibrium moisture content, aw is the water activity, m_0 is the monolayer value (g water/ g solids) and C, K are the GAB constants. The GAB model parameters were determined by non-linear regression, using the Origin Software 8.0 (OriginLab, USA).

2.2.8 SCANNING ELECTRON MICROSCOPY (SEM)

A scanning electron microscope model Quanta 200 (FEI Company, Japan) was used to observe the fractured surface of the biodegradable sheets. The samples were submerged in liquid nitrogen and then broken (cryogenic fracture). Before coating with a gold layer, the samples were stored at 25 °C in a desiccator with $CaCl_2$ (~ 0% RH) for 3 days. The coating was produced with a sputter coater (BAL-TEC SCD 050, Leica Microsystems, Germany). Images were taken of the fractured surface at a magnification of 800×.

3 Results and Discussion

All formulations had adequate processability during extrusion-calendering process and the sheets showed homogenous surfaces, without cracks and / or insoluble particles or bubbles visible without magnification and the average thickness was 957 ± 50 μm.

3.1 DENSITY AND OPACITY OF THE SHEETS

The density and opacity of the biodegradable sheets are shown in Table 2 and the coefficients of the mixture design models are shown in Table 3. The coefficients of determination (R^2) were higher than 0.75 indicating the adequate fit of the mixture design model to the experimental data.

Table 2 – Density and opacity of the sheets.

Formulation	Density ($g.cm^{-3}$)	Opacity (%)
1	1.32±0.05	86.9±0.4
2	1.00±0.32	77.3±0.1
3	1.14±0.07	88.0±0.7
4	1.22±0.05	79.7±1.2
5	1.33±0.11	85.4±0.3
6	1.20±0.05	76.8±0.1
7	1.23±0.02	80.9±0.2
8	1.38±0.37	81.4±0.1
9	1.25±0.06	87.8±3.0

Table 3 – Mixture design model for density and opacity of the biodegradable sheets

Coefficient	Density ($g.cm^{-3}$)	Opacity (%)
β_1	1.34*	86.6*
β_2	1.01*	77.5*
β_3	0.70	101.6*
β_{12}	0.33	-
β_{13}	-	-
β_{23}	6.11*	-
R^2	0.80	0.77

β_1=Starch, β_2=Whole oat flour (WOF), β_3=Glycerol, β_{12}=interaction Starch x WOF, β_{13}=interaction Starch x Glycerol, β_{23}=interaction WOF x Glycerol.
* Significant effects ($p<0.05$).

According to the mixture model (Table 3), the higher the starch concentration the higher the density of the sheets, and the interaction WOF x glycerol was high and positive, i.e. higher WOF content tend to increase the material density only with high glycerol content. The PBAT compatibility with starch is higher than with WOF, consequently materials with higher starch content have a more cohesive and denser matrix. On the other hand the WOF needs more plasticizer than the starch to produce a cohesive and dense matrix, explaining the positive interaction between WOF x glycerol. The density values determined in this study are similar than those reported by Dias et al., (2010), for rice flour biodegradable films (~ 1.30 $g.cm^{-3}$).

According to the mixture model (Table 3), the higher the glycerol content the higher the opacity of the sheets, but all the components had similar effects, reflecting the low data variation, from 76.8 to 88.0%, and characterizing these material as highly opaque. Other results were found for films of banana flour that ranged between 35.8 and 70.0% (PELISSARI et al., 2013) and higher when compared with those of achira flour films (17.5 – 44.1%) (ANDRADE-MAHECHA; TAPIA-BLACIDO; MENEGALLI, 2012), amaranth flour films (6.5%) (TAPIA-BLÁCIDO; SOBRAL; MENEGALLI, 2005), and quinoa flour films (5.3%) (ARAÚJO-FARRO et al., 2010). These differences are mainly because the cited studies produced thin films by casting, and our materials were produced by extrusion as sheets (thicker than films).

3.2 MECHANICAL PROPERTIES

The tensile strength, elongation at break and Young's modulus of the biodegradable sheets are presented in Table 4.

Table 4 – Mechanical properties of the biodegradable sheets.

Formulation	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
1	4.69±0.53	499±181	21±10
2	1.49±0.08	72±9	19±3
3	2.74±0.54	355±91	13±5
4	1.00±0.05	71±7	11±2
5	3.51±0.67	423±252	18±3
6	1.51±0.07	106±12	16±4
7	1.77±0.15	102±21	17±4
8	1.64±0.08	96±17	14±2
9	1.44±0.26	76±11	14±3

The tensile strength, elongation at break and Young's modulus of the sheets varied widely depending on the formulation and ranged from 1.00 to 4.69 MPa; 71 to 499 % and 11 to 21 MPa, respectively (Table 4). Biodegradable films of amaranth flour produced by casting had tensile strength of 5.8 MPa and elongation at break of 13.8 % (ELIZONDO; SOBRAL; MENEGALLI, 2009). Dias (2008) had lower tensile strength in rice flour films than starch films and according to the authors, the proteins and lipids of the flour disrupted the starch matrix, decreasing the cohesive force. Biodegradable films of rice flour and PBAT (47 g/100 g of mixture) had tensile strength around 6.2-7.1 MPa, elongation at break around 290-300 %, and Young's modulus around 89-126 MPa (SOUSA; SOARES-JUNIOR; YAMASHITA, 2013), values higher than those obtained in this study.

According to the mixture model (Table 5), the higher the starch concentration the higher the tensile strength (TS), the elongation at break (EB) and the Young's modulus of the sheets, and the higher the glycerol concentration the lower these properties. The higher starch content leads to a denser matrix, because of the rich inter- and intramolecular interactions, yielding thus a more resistant materials (MALI, 2002; VICENTINI, 2003). The glycerol acts as a plasticizer, reducing the intermolecular forces between the polymer chains and increasing the elongation of the materials because of the higher molecular mobility as reported by other authors (PARRA et al., 2004; CUQ et al., 1997).

Table 5 - Mixture design model for mechanical properties of the biodegradable sheets.

Coefficient	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
β_1	4.15*	491*	20*
β_2	1.74*	75*	18*
β_3	-10.46	-1452*	-80*
β_{12}	-3.83*	-703*	-
β_{13}	-	-	-
β_{23}	-	1867*	-
R^2	0.93	0.99	0.81

β_1=Starch, β_2=Whole oat flour (WOF), β_3=Glycerol, β_{12}=interaction Starch x WOF, β_{13}=interaction Starch x Glycerol, β_{23}=interaction WOF x Glycerol.
* Significant effects ($p<0.05$).

The interaction starch x WOF was high and negative for both TS and EB properties, i.e. the mixture of starch and WOF weakens the matrix, and the higher the WOF content less resistant the material.

The interaction WOF x glycerol was high and positive for EB, i.e. sheets with high concentration of WOF and glycerol weakens the matrix, but raises the elongation because as discussed previously the WOF needs more plasticizer than the starch to produce a cohesive matrix.

The force to perforation (FP) and the elongation to perforation (EP) of the sheets varied widely depending on the formulation and ranged from 9 to 73 N, and 9 to 93 mm, respectively (Table 6). The FP is an important parameter for materials used as packaging of products with tips, edges and other protrusions (SARANTOPOULOS et al., 2002).

Oat starch films plasticized with glycerol and obtained by casting had FP of 17.32N (GALDEANO, 2007), amaranth films plasticized with glycerol and obtained by casting had FP of 2.3N (TAPIA-BLÁCIDO; SOBRAL; MENEGALLI, 2005). Some sheets obtained in this study were resistant to perforation. However, this difference may be related to the type of process applied and material thickness. In tensile testing, the thickness value is used to calculate the tension, however, for perforation this procedure is not performed, and probably the reason the films obtained in this study showed higher FP,by the presence of PBAT and the fact consist of sheets , which have thickness greater than films.

Table 6 – Slow Rate Penetration Resistance (SRPR) of the biodegradable sheets.

Formulation	FP (N)	EP (mm)
1	73±10	93±12
2	13±2	17±2
3	54±17	51±16
4	9±1	9±5
5	58±5	63±3
6	11±2	15±2
7	19±2	21±2
8	16±2	19±1
9	20±1	21±3

FP - force to perforation
EP - elongation to perforation

The mixture design model for force to perforation and elongation to perforation (Table 7) was similar to the others mechanical properties (Table 5), i.e., the higher the starch concentration the higher the FP, TS, EP and EB of the sheets, and the higher the glycerol concentration the lower these properties. The interaction starch x WOF was high and negative for FP, TS, EP and EB properties. The considerations made above for the TS and EB are valid for the SRPR properties.

Table 7 - Mixture design model for force to perforation and elongation to perforation of the biodegradable sheets.

Coefficient	Force to Perforation (N)	Elongation to Perforation (mm)
β_1	67*	80
β_2	15*	22*
β_3	-102	-227
β_{12}	-79*	-91*
β_{13}	-	-
β_{23}	-	-
R^2	0.98	0.94

β_1=Starch, β_2=Whole oat flour (WOF), β_3=Glycerol, β_{12}=interaction Starch x WOF, β_{13}=interaction Starch x Glycerol, β_{23}=interaction WOF x Glycerol.
* Significant effects ($p<0.05$).

3.3 WEIGHT LOSS IN WATER AND WATER VAPOR PERMEABILITY

The weight loss in water (WLW) of the sheets (Table 8) ranged from 2.7 to 7.5 %. Tapia-Blácido, Sobral and Menegalli (2005), studying amaranth films produced by casting and plasticized with glycerol and sorbitol, had values between 39 and 62%. Biodegradable films produced by casting and based on achira flour presented WLW around 38% (ANDRADE-MAHECHA; TAPIA-BLACIDO; MENEGALLI, 2012). Biodegradable sheets based in oat starch had WLW of about 23% (GALDEANO, 2007), greater than the values found in this work, probably due to the processing type and the PBAT in the formulations of the present study, since the PBAT is less hydrophilic than the others components.

Table 8 – Weight Loss in Water and Water Vapor Permeability of the biodegradable sheets.

Formulation	WLW (%)	WVP (x10^5) (g.day^{-1}.m^{-1}.Pa^{-1}).
1	3.5±1.1	2.4±0.3
2	5.8±0.5	1.5±0.1
3	2.7±1.0	2.0±0.1
4	7.5±0.2	1.4±0.1
5	5.7±0.6	2.0±0.1
6	4.2±0.9	1.3±0.1
7	4.7±0.1	1.9±0.1
8	7.0±1.4	1.7±0.2
9	3.4±0.1	1.8±0.2

WLW - weight loss in water
WVP - water vapor permeability

The water vapor permeability of the sheets ranged from 1.3 to 2.4 x 10^{-5} g.day^{1}.m^{-1}.Pa^{-1} (Table 8). According to Bilck, Grossmann and Yamashita (2010), cassava starch / PBAT films (30:70) had WVP of 4.22 × 10^{-6} g.m^{-1}.Pa^{-1}.day^{-1} at the same relative humidity gradient (33-64%), and this value is about 10 times lower than the WVP of the sheets, probably due to the higher concentration of PBAT of the films. According to Rodriguez et al., (2006), the starch polymer forms a continuous matrix cohesive and promotes good barrier to the transfer of oxygen and carbon dioxide, but a poor barrier to water vapor.

The mixture model for weight loss in water (WLW) (Table 9) showed a low coefficient of determination (R^2 < 0.30), so the mixture model cannot explain the WLW behavior.

According to the mixture model (Table 9), the higher the starch concentration the higher the water vapor permeability (WVP) of the sheets, and the interaction starch x glycerol was high and negative, i.e. higher glycerol content tend to decrease the WVP of the materials produced with high starch concentration. Several authors have reported that increasing the starch content increases the water vapor permeability, giving the increased number of hydrophilic groups derived from starch chains (MALI, 2002; ALVES et al., 2007; BERTUZZI; ARMADA; GOTTIFREDI, 2003).

Table 9 - Mixture design model for weight loss in water (WLW) and water vapor (WVP) of the biodegradable sheets.

Coefficient	Weight Loss in Water (%)	WVP (x10^{-5}) (g.day^{-1}.m^{-1}.Pa^{-1}).
β_1	3.5	2.3*
β_2	5.4*	1.5*
β_3	20.21	0.2
β_{12}	-	-
β_{13}	-	-3.8
β_{23}	-	-
R^2	0.30	0.95

β_1=Starch, β_2=Whole oat flour (WOF), β_3=Glycerol, β_{12}=interaction Starch x WOF, β_{13}=interaction Starch x Glycerol, β_{23}=interaction WOF x Glycerol.
* Significant effects ($p<0.05$).

3.4 MOISTURE SORPTION ISOTHERMS

The moisture sorption isotherms at 25 °C of the sheets are displayed in Figure 1 and GAB model adjusted parameters are shown in Table 10.

Figure 1 - Sorption isotherms of the biodegradable sheets.

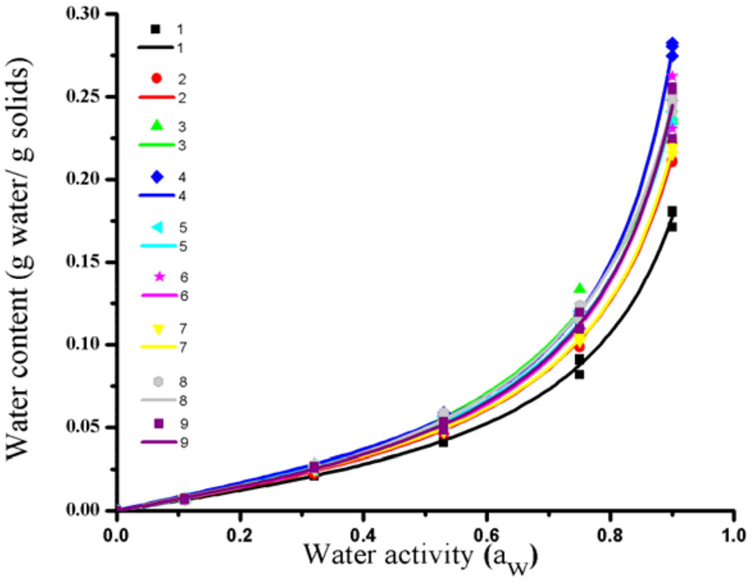


Table 10 – GAB model parameters for water sorption isotherms of the biodegradable sheets.

Formulation	**C ***	**K ***	**m_0 *** (g water/ g solids)
1	1.92	0.92	0.033
2	1.82	0.93	0.032
3	1.36	0.90	0.044
4	2.28	0.97	0.032
5	1.81	0.94	0.035
6	1.79	0.95	0.033
7	2.14	0.94	0.030
8	1.36	0.92	0.042
9	1.77	0.94	0.034

* All the GAB models had $R^2 > 0.99$

The shape of the sorption curves was similar for all formulations (Figure 1). There was a sharp increase in the moisture content under water activities above 0.80 and all formulations could be considered highly hydrophilic. The GAB model was efficient to describe the moisture sorption isotherms of the sheets ($R^2 > 0.99$) (Table 10). The monolayer parameter (m_0) indicates the amount of water adsorbed in a single layer per mass of dry material being an estimative of sorption sites. The constant C is related to the monolayer sorption heat, the constant K is related to the multilayer heat of sorption, and it is independent of the composition of the material and determines the curvature of the isotherms at high water activities.

According to the mixture models (Table 11), the higher the glycerol concentration the higher the C and m_0, and the lower the K. Glycerol, a small and highly hydrophilic molecule, was the compound that had the greatest effect on the GAB model parameters, and also its interaction with starch and WOF. The starch and WOF had low and similar effects to the constants C, K and m_0, without interaction between them.

Table 11 - Mixture design model for GAB model parameters of the biodegradable sheets.

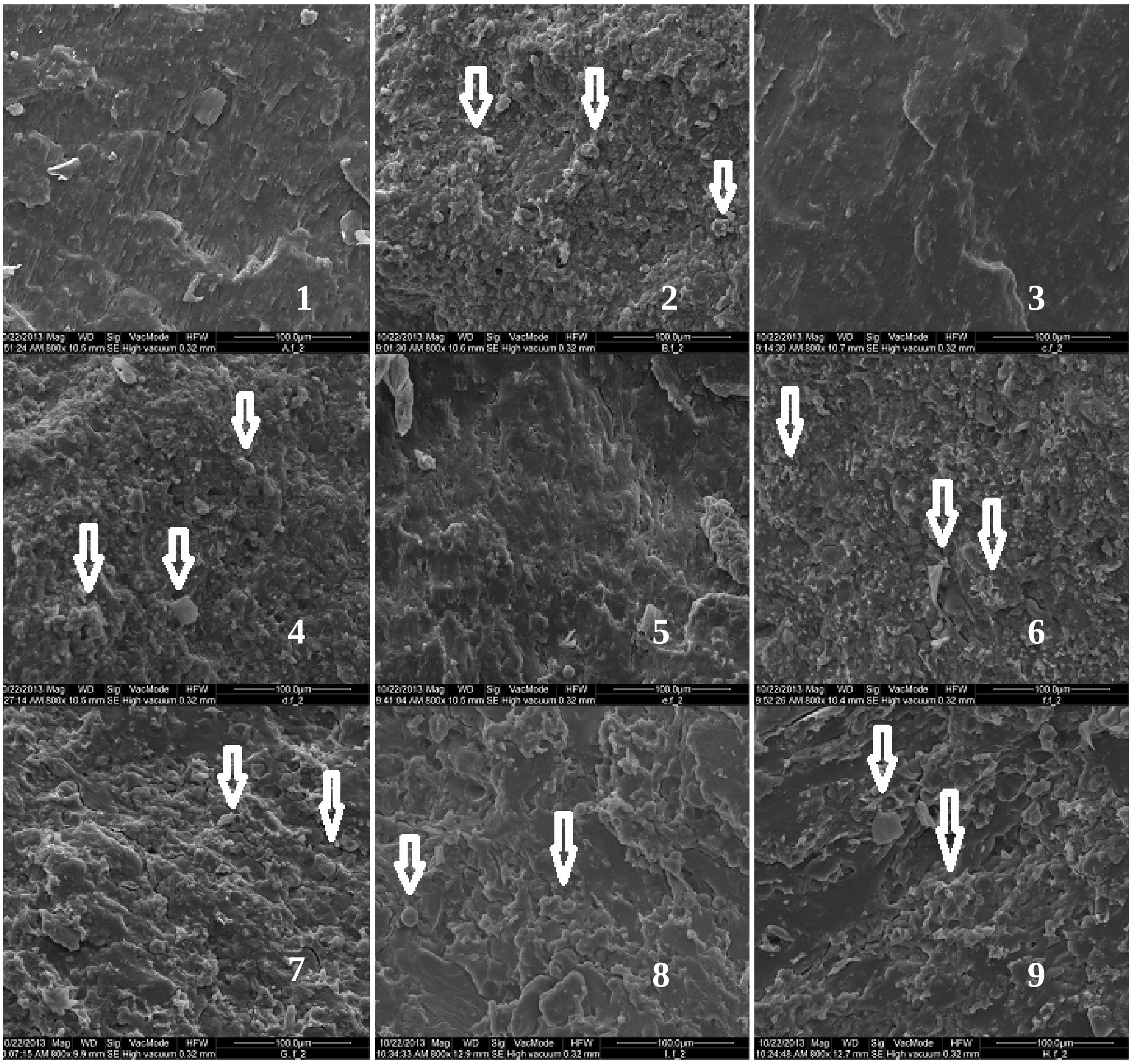
Coefficient	**C**	**K**	**m_0** (g water/ 100 g solids)
β_1	2.10*	0.93*	0.03*
β_2	1.86*	0.93*	0.03*
β_3	17.58	-10.35	1.64
β_{12}	-	-	-
β_{13}	-29.49	11.56	-1.51
β_{23}	-13.64	12.49	-1.68
R^2	0.66	0.80	0.88

β_1=Starch, β_2=Whole oat flour (WOF), β_3=Glycerol, β_{12}=interaction Starch x WOF, β_{13}=interaction Starch x Glycerol, β_{23}=interaction WOF x Glycerol.
* Significant effects ($p<0.05$).

3.5 SCANNING ELECTRON MICROSCOPY (SEM)

According to the SEM micrographs (Figure 2) the fracture of the sheets 1, 3 and 5 showed no phase separation because the PBAT has good compatibility with starch, and the sheets 2, 4, and 6 showed the presence of starch granules and oat hulls. In Figures 7, 8 and 9 it is possible to observe the continuous phase of the starch + PBAT and the presence of granules from WOF.

Figure 2 – SEM images of the sheets fractures. (Magnification 800x).



4 Conclusion

The presence of starch in the formulation has improved mechanical properties and increased PVA material. The Complexity of WOF matrix caused the loss of mechanical properties.

The whole oat flour is a promising raw material to produce biodegradable sheets by blending with starch, poly (butylene adipate-co-terephthalate) and glycerol, using extrusion-calendering process and their properties can be modified by controlling the formulation.

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CAPÍTULO 3

BLENDS OF WHOLE OAT FLOUR PRODUCED BY REACTIVE EXTRUSION WITH CITRIC ACID AND MALEIC ANHYDRIDE

Based on the results obtained in Chapter 2, it was proposed new blends and experimental conditions to produce biodegradable materials with better mechanical and barrier properties than those produced previously.

1 Experimental

1.1 MATERIALS

The sheets were produced with whole oat flour (WOF) (SL Alimentos Ltda., Brazil) (moisture 8.74%, lipids 6.20%, ashes 2.00% and protein 17.42%), citric acid (Dinamica, Brazil), maleic anhydride (Sigma–Aldrich, Germany), glycerol (Dinamica, Brazil) and poly (butylene adipate-co-terephthalate) (PBAT) (BASF, Germany) under the brand name Ecoflex®.

1.2 METHODS

1.2.1 PRODUCTION OF THE BIODEGRADABLE SHEETS

The formulations to produce biodegradable cylindrical strands based on blends of modified WOF, PBAT and glycerol are in Table 1.

Table 1 – Formulation of the biodegradable sheets.

Formulation	Ingredient (g/100 g)				
	PBAT	WOF	Glycerol	Citric Acid	Maleic Anhydride
F1	40	30	30	0	0
F2	40	30	28	2	0
F3	40	30	28	0	2
F4	40	30	26	2	2
F5	40	30	29	0	1
F6	40	30	29	1	0
F7	40	30	27	2	1
F8	40	30	27	1	2
F9	40	30	28	1	1

The whole oat flour (WOF) and citric acid and/or maleic anhydride were manually mixed and were extruded in a single screw extruder (AX Plasticos, Brazil), with D = 1.6 cm, L/D = 40, four heating zones and 8 mm diameter die. The temperature of all zones was maintained at 110 °C and the screw speed at 100 rpm.

The previously extruded WOF were manually mixed with PBAT and glycerol. The formulations were extruded in a pilot single-screw extruder (model EL-25, BGM, Brazil) with a screw diameter (D) of 25 mm and a screw length of 28D to produce cylindrical strands. The barrel temperature profile was 90/120/120/120 °C from the feeding zone (zone 1) to the die zone (zone 4) at a screw speed of 30 rpm, using a die with six holes of 2 mm diameter.

2 Results and Discussion

The blends could not be extruded because of the screw slippage, i.e., the screw was unable to develop enough tack to convey the material down the length of the barrel (GUYER, 2008). In another test, the materials were forced manually from the feeder to reduce the slippage but just the formulations F2 and F5 could be extruded, and the cylindrical strands can be observed in Figure 1.

Figure 1 - Biodegradable cylindrical strands

The blends had low processability and the cylindrical strands were dark, and fragile, making it impracticable to conduct mechanical tests.

3 Conclusion

The whole oat flour (WOF) modification by citric acid and / or maleic anhydride did not improve the mechanical characteristics of the WOF/PBAT/Glycerol blends. The blends proposed in this Chapter did not have adequate characteristics to produce biodegradable material by extrusion due to their poor processability.

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CAPÍTULO 4

MODIFIED WHOLE OAT FLOUR / POLY (BUTYLENE ADIPATE-CO-TEREPHTHALATE) SHEETS PRODUCED BY EXTRUSION

ABSTRACT: Biodegradable sheets was produced by flat die extrusion-calendering process using modified whole oat flour (WOF), poly (butylene adipate-co-terephthalate) (PBAT) and glycerol (GLY). The WOF was modified by hydrogen peroxide and / or by extrusion. All formulated sheets had adequate processability during extrusion-calendering process and the sheets showed homogenous surfaces. The tensile strength, elongation at break and Young's modulus of the sheets varied depending on the formulation and ranged from 1.79 to 2.08 MPa, 40 to 53% and 10 to 19 MPa. The force to perforation (FP) and the elongation to perforation (EP) of the sheets varied widely depending on the formulation and ranged from 21 to 27 N, and 21 to 26 mm, respectively. The WVP of the sheets ranged from 2.47 to 9.86 x 10^{-5} $g.day^{-1}.m^{-1}.Pa^{-1}$. The WOF modification enhanced some mechanical and water barrier properties of the sheets produced with WOF/PBAT/GLY by extrusion-calendering process but not enough to consider them satisfactory.

Keywords: Biodegradable. Calendering. Glycerol. Mechanical Properties

1 Introduction

Whole oat flour has desirable characteristics as raw material to produce biodegradable materials such as low cost, high fibers content, which may serve as reinforcing the polymeric matrix, and lipids that can reduce the hydrophilicity of the material.

Reactive extrusion is a low cost technique to modified biopolymers that combines heat, pressure, mechanical shear to promote chemical modifications using reagents like hydrogen peroxide (GALDEANO; GROSSMANN, 2005). Artz, Warren and Villota (1990) studied the effect of extrusion process in the functional properties of fibre and concluded that the effect was insignificant due to the short time inside the extruder. According to the authors, fibres are very resistant to modification; it would need to involve chemical treatments to promote modification by extrusion.

Hydrogen peroxide in alkaline media could serve as a mild agent for solubilizing the macromolecular hemicelluloses due to its dual role in de-lignifying and bleaching. Hydrogen peroxide is unstable in alkaline conditions and readily decomposes to more active radicals such as the hydroxyl radicals (HO•) and superoxide anion radicals (O2•-), which participate in the de-lignifying mechanism.

This dual role of hydrogen peroxide in de0lignifying and bleaching were investigated for rye straws and maize stems (SUN et al., 1999; SUN; FANG; TOMKINSON, 2000).

The objective of this work was to study the effect of the modification of whole oat flour (WOF) on the mechanical and water vapour barrier properties of WOF/poly (butylene adipate co-terephthalate)/glycerol blends to produce biodegradable sheets by flat die extrusion-calendering process.

2 Experimental

2.1 MATERIALS

The sheets were produced with whole oat flour (WOF) (SL Alimentos Ltda, Brazil) (moisture 8.74%, lipids 6.20%, ashes 2.00% and protein 17.42%), hydrogen peroxide (BIOTEC, Brazil), glycerol (Dinamica, Brazil) and poly (butylene adipate-co-terephthalate) (PBAT) (BASF, Germany) under the brand name Ecoflex®.

2.2 METHODS

2.2.1 WHOLE OAT FLOUR MODIFICATION AND CHARACTERIZATION

The whole oat flour (WOF) was conditioned up to 32% moisture, by adding NaOH solution sufficient to reach the desired moisture and pH of 11.5, and stored in polyethylene bags at 7-10 °C for 24 hours (GALDEANO; GROSSMANN, 2005).

The modifications performed on WOF were M1 (WOF without modification - control), M2 (WOF extruded), M3 (WOF with hydrogen peroxide), and M4 (WOF with hydrogen peroxide and extruded).

For the modifications M3 and M4, it was added 7 g hydrogen peroxide (200 V) / 100 g WOF, mixed manually and kept under refrigeration (7 to 10° C) for 24 hours (GALDEANO; GROSSMANN, 2005).

For the modifications M2 and M4, the WOF were extruded in a single screw extruder (AX Plasticos, Brazil), with screw diameter (D) of 16 mm and a screw length of 40D, four heating zones and 8 mm diameter die. The temperature of all zones was maintained at 110 °C and the screw speed at 100 rpm. After the extrusion, the samples were dried in an air-circulating oven at 50 °C up to 8% humidity, and grounded (IKA-A 11 Basic Mill, Brazil).

The WOF proximate composition (moisture, ash, protein, crude fibres) was determined according to AOAC (2005). For pH determination, 9 g of WOF was homogenized in 60 mL of distilled water, and rested for 30 minutes before the determination.

2.2.2 BIODEGRADABLE SHEETS PRODUCTION AND CHARACTERIZATION

The modified WOF were manually mixed with PBAT and glycerol and extruded in a pilot single-screw extruder (model EL-25, BGM, Brazil) with a screw diameter (D) of 25 mm and a screw length of 28D to produce cylindrical strands. The barrel temperature profile was 90/120/120/120 °C from the feeding zone (zone 1) to the die zone (zone 4) at a screw speed of 30 rpm, using a die with six holes of 2 mm diameter. The strands were pelletized, and extruded in a plastic sheet extrusion line consisting of a pilot co-rotating twin-screw extruder (model D-20, BGM, Brazil), with a screw speed of 100 rpm and temperature profile of 90/120/120/125/120 °C, feed speed of 33 rpm and equipped with a 0.8 mm flat die and a three-roll calender (AX Plastics, Brazil). For all blend formulations were used 40% (w/w) of PBAT, 30% (w/w) of glycerol and 30% (w/w) of modified WOF and the formulations were denominated F1, F2, F3 and F4, depending on the WOF modification (M1, M2, M3 and M4, respectively).

2.2.3 THICKNESS, DENSITY AND GRAMATURE

Five samples of each sheet were cut (20 x 20 mm), and were conditioned for 7 days in a desiccator containing anhydrous $CaCl_2$ (~ 0% RH). After this period, the samples were weighed and measured (thickness, length and width) to calculate the density and the gramature.

2.2.4 OPACITY

The opacity was determined using a colorimeter (BYK Gardner, Germany), illuminant D65 (day light) and 10°, at 3 different spots in each sample, according to Sobral et al., (2001). The measurements were performed in triplicate.

2.2.5 MECHANICAL PROPERTIES

The tensile strength, elongation at break and Young's modulus of the sheets was determined based on the ASTM D882-02 (2002) using a texture analyser, model TA.XT2i (Stable Micro Systems, England) fitted with a 5 N load cell. Ten samples of each formulation (70 mm x 20 mm) were conditioned at 53 ± 2% RH for 48 h before testing. The crosshead speed was set at 0.8 mm/s, and the initial distance between the grips was 30 mm.

The slow rate penetration resistance (SRPR) of the sheets was performed according to ASTM F1306-90 (2002) using the same texturometer used for tensile testing, with a 3.2 mm diameter hemispherical probe. Ten samples for each formulation (30 mm diameter) were conditioned at 23 ± 2 °C and 53 ± 2% RH for 48 h before testing. The force to perforation (FP) and the elongation to perforation (EP) were determined at 25 mm/min.

2.2.6 WEIGHT LOSS IN WATER

Sheet samples (1 x 2 mm) were previously dried for three days in desiccators containing anhydrous $CaCl_2$ (~ 0% RH). After weighing, the sheets were immersed in distilled water, in a proportion of 30:1 (water:sample) for 48 h at 25 °C. The samples were dried at 105 °C for 4 h, and the weight of the conditioned specimen after treatment was used to determine the percentage of weight loss (% wt) in water.

2.2.7 WATER VAPOUR PERMEABILITY (WVP)

The WVP was determined according to the ASTM E-96-95 (1996) with some modifications. Before the analysis, the sheet samples were conditioned at 25 °C and 53% RH for 48 h. The sample was fixed in a permeation cell with 60 mm internal diameter. The interior of the cell was filled with saturated $MgCl_2$ solution (32.8% RH), and the device was stored at 25 °C in a desiccator containing saturated sodium nitrate solution to provide 64% RH.

2.2.8 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

The sheet samples were conditioned in a desiccator containing anhydrous calcium chloride ($CaCl_2$) for 10 days before the analysis. The FT-IR analyses were performed in a spectrophotometer IR Prestige 21 (Shimadzu, Japan) from 4000 to 450 cm^{-1}, with a spectral resolution of 4 cm^{-1}, and 12 scans.

3 Results and Discussion

3.1 CHARACTERIZATION OF MODIFIED WHOLE OAT FLOUR.

The proximate composition of modified WOF (M1, M2, M3, and M4) are shown in Table 1.

The modifications performed on WOF were M1 (WOF without modification - control), M2 (WOF extruded), M3 (WOF with hydrogen peroxide), and M4 (WOF with hydrogen peroxide and extruded).

Table 1 – Proximate composition of modified whole oat flour.

Sample	Moisture content (%)	Ash (%)	pH	Protein (%)	Crude fibre (%)
M1	13.6^{a}±0.9	0.8^{a} ±0.1	6.5^{a} ±0.0	15.60^{a} ±0.61	0.59^{ab} ±0.24
M2	12.5^{a} ±0.7	0.8^{a} ±0.1	6.5^{a} ±0.0	15.32^{a} ±0.48	0.55^{ab} ±0.18
M3	14.2^{a} ±0.7	0.6^{a} ±0.1	6.3^{b} ±0.0	15.28^{a} ±0.35	0.13^{b} ±0.03
M4	12.3^{a} ±0.4	0.7^{a} ±0.1	6.0^{c} ±0.0	15.29^{a} ±0.40	0.76^{a} ±0.06

^{a,b} Different letters in the same column indicate significant differences according to Tukey test at 5% probability.

There was no change in the moisture, ash and protein contents of the samples after the modification processes. The sample modified with hydrogen peroxide and extruded (M4) had lower pH values than the samples without modification (M1) and extruded (M2).

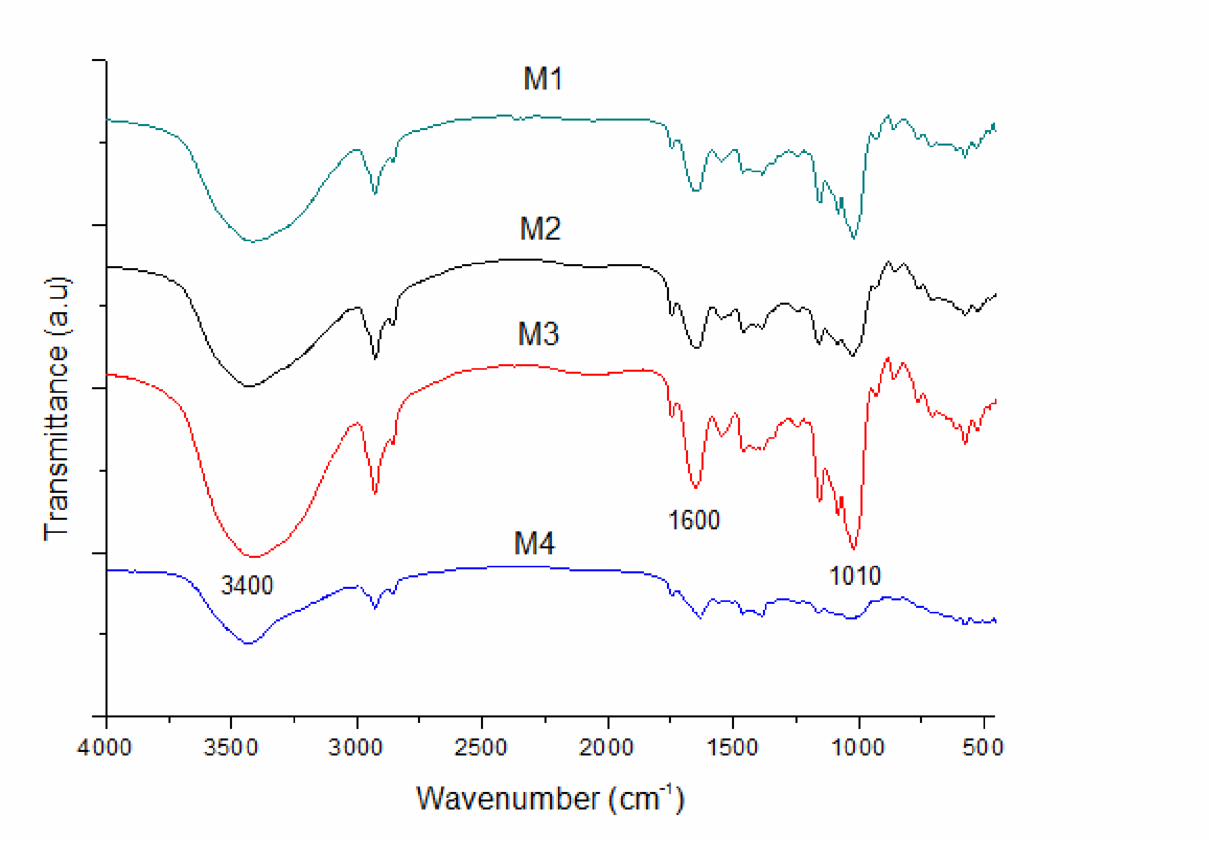
The extruded sample M2 had the higher fibre content, and the sample treated with hydrogen peroxide M3 had the lower content. Galdeano and Grossmann (2005) evaluated the effect of the treatment with alkaline hydrogen peroxide concomitant with extrusion on some properties of oat hulls, and observed an increase of protein and reduction of other components, mainly fibre. According to the authors, the extrusion and hydrogen peroxide degraded the fibre.

The Figure 1 shows the FT-IR spectra of the modified whole oat flour, all of them showed similar spectrum, and there was observed no new functional group due to the modification.

The bands in the region of 3400 cm^{-1} are related to C-H stretching due to the hydroxyl groups. The hydroxyl groups are present in large quantities in the starch and residual moisture of the samples (OLIVATO, 2010). The bands between 3400-2500 cm^{-1} are related to the carboxylic acid from fatty acids present in whole oat flour.

In the fingerprint region, around 900-1300 cm^{-1}, it was observed deformations C-O-C (1010), characteristics of starch.

Figure 1 – FT-IR spectra of the modified WOF.



The band at 1600 cm^{-1} corresponds to primary amine and it is related to the amide group of proteins, particularly to the C=O stretching. Others authors have also identified peaks in this region, for achira flour films (ANDRADE-MAHECHA, 2009).

3.2 CHARACTERIZATION OF THE BIODEGRADABLE SHEETS

All formulations had adequate processability during extrusion-calendering process and the sheets showed homogenous surfaces.

3.2.1 THICKNESS, DENSITY AND GRAMATURE OF THE SHEETS

The thickness, density and gramature of the biodegradable sheets are shown in Table 2.

Table 2 – Thickness, density and gramature of the biodegradable sheets.

Formulation	Thickness (μm)	Density ($g.cm^{-3}$)	Gramature ($g.cm^{-2}$)
F1	1015^{ab}±83	1.20^{b}±0.11	0.12^{b}±0.01
F2	1019^{ab}±40	1.21^{b}±0.05	0.13^{ab}±0.01
F3	1045^{a}±35	1.26^{ab}±0.07	0.13^{ab}±0.01
F4	974^{b}±51	1.41^{a}±0.14	0.14^{a}±0.01

^{a,b} Means with different letters at the same column indicate significant differences according to Tukey test at 5% probability.

The materials produced with formulation 4 (F4) showed the highest values of density and gramature, probably because the degradation of starch and other components of the WOF by the modification (M4), that compacted the polymer matrix. The density values were similar than those for rice flour biodegradable films (around 1.30 g/cm^3) (DIAS et al., 2010).

3.2.2 OPACITY

The opacity of the biodegradable sheets are shown in Table 3. The high opacities were due to the high sheets thickness (1013 ± 59 μm), and the composition of the material. Cereal products generally contain reducing sugars that promote non-enzymatic Maillard reaction, which promotes browning of extruded products (BERRIOS et al. 2004).

Table 3 – Opacity of the biodegradable sheets.

Formulation	Opacity (%)
F1	88^{a}±3
F2	85^{ab}±3
F3	78^{b}±5
F4	81^{ab}±4

^{a,b} Means with different letters indicate significant differences according to Tukey test at 5% probability.

The F3 sheets were less opaque than the F1 probably due to the hydrogen peroxide that acted as bleaching. Galdeano and Grossmann (2005) evaluated the effect of the treatment with alkaline hydrogen peroxide concomitant with extrusion on some properties of oat hulls and observed that lightness increased when reagent level was increased.

Depend on the use; it is desirable that the plastic packaging exhibit high transparency. On the other hand, for products sensitive to photo degradation the packaging need to be opaque.

3.2.3 MECHANICAL PROPERTIES

The tensile strength, elongation at break and Young's modulus of the biodegradable sheets are presented in Table 4.

The tensile strength, elongation at break and Young’s modulus of the sheets varied depending on the formulation and ranged from 1.79 to 2.08 MPa, 40 to 53 % and 10 to 19 MPa, respectively (Table 4).

Table 4 – Mechanical properties of the biodegradable sheets.

Formulation	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
F1	2.08^{a}±0.24	49^{a}±9	19^{a}±3
F2	1.79^{b}±0.10	50^{a}±6	14^{ab}±3
F3	1.97^{ab}±0.24	53^{a}±10	10^{b}±5
F4	2.05^{ab}±0.26	40^{b}±5	19^{a}±4

^{a,b} Means with different letters at the same column indicate significant differences according to Tukey test at 5% probability.

The extrusion treatment decreased the tensile strength (F2) and the peroxide and extrusion treatment (F4) decreased the elongation at break of the materials. These differences probably were due to the starch and fibre modification cause by the extrusion and the hydrogen peroxide, as discussed previously.

Biodegradable films of rice flour and PBAT (47 g/100 g of mixture) had tensile strength around 6.2-7.1 MPa, elongation at break around 290-300%, and Young's modulus around 89-126 MPa (SOUSA; SOARES-JUNIOR; YAMASHITA, 2013), higher values than those obtained in this work.

The force to perforation (FP) and the elongation to perforation (EP) of the sheets varied depending on the formulation and ranged from 21 to 27 N, and 21 to 26 mm, respectively (Table 5), and the F3 materials had the higher FP and EP values. These results agree with the elongation at break (Table 4) of the F3 material that had the higher value among all formulations.

Table 5 – Slow Rate Penetration Resistance (SRPR) of the biodegradable sheets.

Formulation	Force to perforation (FP) (N)	Elongation to perforation (EP) (mm)
F1	23^{b}±4	23^{ab}±4
F2	22^{b}±1	21^{b}±2
F3	27^{a}±3	26^{a}±3
F4	21^{b}±2	21^{b}±3

[a,b] Means with different letters at the same column indicate significant differences according to Tukey test at 5% probability.

Oat starch films plasticized with glycerol (17.32 N) (GALDEANO et al., 2014) and amaranth starch films plasticized with glycerol (2.3 N) (TAPIA-BLACIDO; SOBRAL; MENEGALLI, 2005) had lower perforation force than our sheets because the films are thinner than the sheets.

3.2.4 WEIGHT LOSS IN WATER AND WATER VAPOUR PERMEABILITY

The weight loss in water (WLW) of the sheets (Table 6) ranged from 20.44 to 27.68%.

Table 6 – Weight Loss in Water and Water Vapour Permeability of the biodegradable sheets.

Formulation	Weight Loss in Water (WLW) (%)	Water Vapour Permeability (WVP) ($x10^{-5}$) ($g.day^{-1}.m^{-1}.Pa^{-1}$)
F1	$27.68^a \pm 1.97$	$9.30^a \pm 0.72$
F2	$20.47^b \pm 0.20$	$9.86^a \pm 0.38$
F3	$20.44^b \pm 0.62$	$4.40^b \pm 0.05$
F4	$22.53^b \pm 0.19$	$2.47^c \pm 0.11$

^{a,b} Means with different letters at the same column indicate significant differences according to Tukey test at 5% probability.

The F1 sheets had higher WLW values when compared to other formulations. Galdeano et al., (2007) studied the effect of processing (casting and extrusion) on the properties of oat starch biodegradable sheets. According to the authors the extruded sheets, despite being thicker, they were more soluble than those sheets produced by casting because of the partial degradation of the polymer chains caused by the extrusion process.

Biodegradables films based on achira flour presented WLW around 38% (ANDRADE-MAHECHA; TAPIA-BLACIDO; MENEGALLI, 2012), values above found in this study because the author did not use PBAT in their formulations.

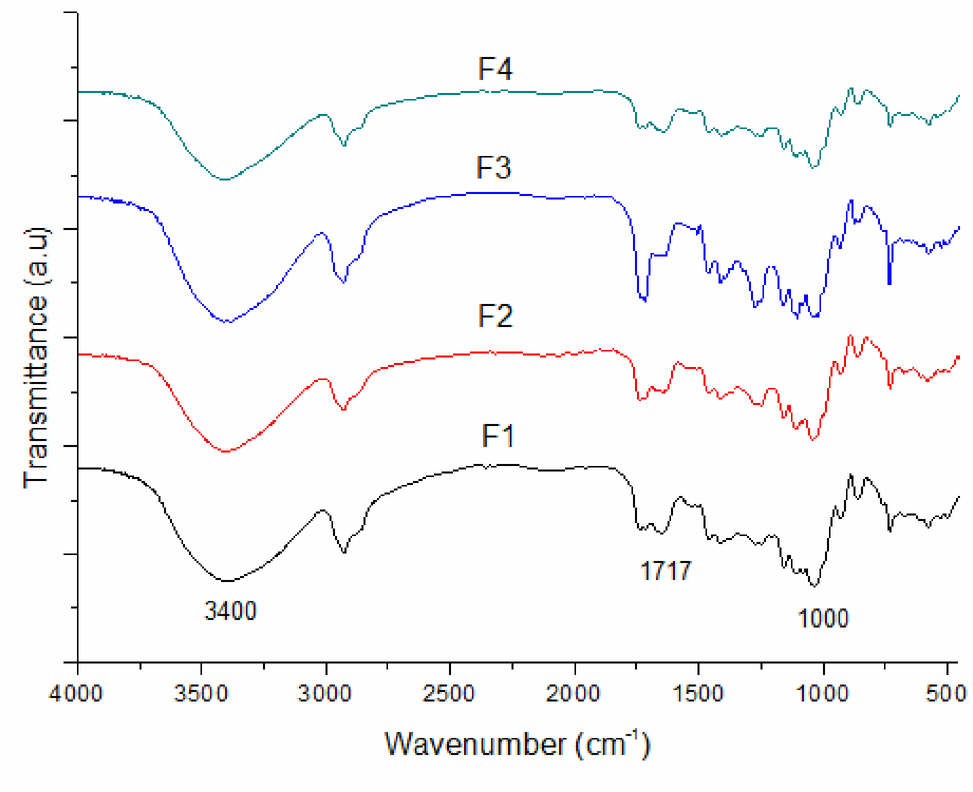
The water vapour permeability of the sheets ranged from 2.47 to 9.86 x 10^{-5} $g.day^{-1}.m^{-1}.Pa^{-1}$ (Table 6). The F4 sheets had the lower WVP, followed by the F3 ones, probably the WOF modification that enhanced the polymer matrix compacting, as discussed previously.

Flores et al., (2007; 2010) studied cassava starch films and the same films containing potassium sorbate and they obtained WVP values of 5.3 x 10^{-5} and 3.2 to 5.5 x 10^{-5} $g.day^{-1}.m^{-1}.Pa^{-1}$, respectively. Olivato et al., (2011) obtained WVP values of 5.45 x 10^{-6} $g.day^{-1}.m^{-1}.Pa^{-1}$ for extruded films of cassava starch, PBAT and glycerol (10% w/w).

3.2.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

The Figure 2 shows the FT-IR spectra of the modified WOF/Glycerol /PBAT sheets produced by extrusion-calendering process. The FT-IR spectra of all sheets were similar, and as discussed in Figure 1 (modified WOF spectra), there was observed no new functional group due to the WOF modification or the extrusion-calendering process.

Figure 2 – FT-IR spectra of the biodegradable sheets.



The bands in the 3400 cm^{-1} region are related to the O-H stretching due to the starch and moisture in the sheets (OLIVATO, 2010). The presence of carboxylic acid also results in broad band between 3400-2500 cm^{-1} related to the fatty acids present in the oat flour. The characteristic peak at 1717 cm^{-1}, in those sheets, characterizes the stretching of the carbonyl group (C = O), which is naturally present in the structure of PBAT (OLIVATO et al., 2012). The band observed around 1000 cm^{-1} is characteristic of the glycerol molecule (ELIZONDRO; SOBRAL; MENEGALLI, 2009).

4 Conclusion

The formulation 3 improved the PF parameter, while the formulations 3 and 4 showed a decrease of PVA. The whole oat flour (WOF) modification enhanced some mechanical and water barrier properties of the sheets produced with WOF/PBAT/Glycerol blends by extrusion-calendering process but not enough to consider them satisfactory.

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CAPÍTULO 5

BLENDS OF MODIFIED WHOLE OAT FLOUR / POLY (BUTYLENE ADIPATE-CO-TEREPHTHALATE) COMPATIBILIZED WITH CITRIC ACID AND MALEIC ANHYDRIDE

ABSTRACT: Biodegradable sheets were produced by flat die extrusion with whole oat flour modified with hydrogen peroxide, poly (butylene adipate-co-terephthalate) and glycerol, using citric acid and maleic anhydride as compatibilizers. The formulations were prepared according to an experimental mixture design and all sheets had adequate processability during extrusion, with homogenous surfaces and average thickness of 960±5 µm. The sheets presented high opacities, from 78 to 86%, due to the high thickness and the composition of the raw material (proteins, lipids, fibres). The tensile strength (TS), elongation at break (EB) and Young's modulus of the sheets varied widely depending on the formulation and ranged from 0.98 to 2.66 MPa, 34 to 48 % and 4 to 34 MPa, respectively. All components formulation leads to an increase in force to perforation (FP) and elongation to perforation (EP) and all interactions were positive, i.e. the increase of any of the components leads to increase in FP and EP. The maleic anhydride (MA) had a negative effect in WVP, i.e. higher MA content decreases the WVP of the materials. These materials represent an alternative to the use of non-biodegradable materials because of the low cost and the raw materials are from renewable sources.

Keywords: Extrusion-calendering process. Hydrogen peroxide. Mechanical properties. Sheets.

1 Introduction

Environmental awareness and the high cost of biodegradable petroleum-based materials have encouraged the development of biodegradable materials from renewable sources like starch (XIAOFEI et al., 2009).

Studies showed that to overcome the drawbacks of pure starch materials like poor mechanical properties, it is necessary to produce starch blends with biodegradable synthetic polymers, such as poly (butylene adipate-co-terephthalate) (PBAT) (COSTA, 2008; SCAPIM, 2009; BRANDELERO; YAMASHITA; GROSSMANN, 2010; FLORES et al., 2010; OLIVATO et al., 2012a; OLIVATO et al., 2012b), poly (lactic acid) (PLA) (YOKESAHACHART; YOKSAN, 2011; SHIRAI et al., 2013), among others.

Whole oat flour (WOF) has interesting characteristics as a raw material to produce biodegradable films such as low cost, high starch content, the presence of fibres that can act as a reinforcement of the polymer matrix and lipids that can reduce the hydrophilicity of the material.

PBAT- Starch blends have a low compatibility at the molecular level because starch has hydrophilic character, polyester has hydrophobic, and the compatibilizer acts as an auxiliary agent in overcoming the polarity difference. The compatibilizer remain at the interface of these polymers, improving the adhesion and reducing the tendency of separation (MA et al., 2009; SHI et al., 2008; OLIVATO, 2010).

Hydrogen peroxide has an important role in increasing the hydration properties of the fibers, acting in lignin through their removal by solubilization and / or structural modification, also promoting an increase in the degree of hydration of the cellulose and breaking its crystallinity (NING, VILLOTA, ARTZ, 1991).

Both citric acid and maleic anhydride have shown a satisfactory performance when used as compatibilizer (SHI et al., 2008; MA et al., 2009; GHANBARZADEH, ALMASI, ENTEZAMI, 2011; OLIVATO et al., 2012a; OLIVATO et al., 2012b; GARCIA et al., 2011). Some authors (SHI et al., 2007; WANG et al., 2009) have reported that citric acid could form an ester bond with starch. The esterification could take place between the carboxyl groups on citric acid and the hydroxyl groups in starch that could modify the characteristics of the material. Even if there is no formation of an ester bond between the citric acid and the starch, it was reported that citric acid form strong hydrogen bond interactions with the starch, stronger than glycerol (CHABRAT et al., 2012). Maleic anhydride can be grafted into the polymer chains at the melting temperature of PBAT and starch, and thus the reaction can be carried out during the reactive extrusion process (KALAMBUR; RIZVI, 2006).

The objective of this work was to produce biodegradable sheets by flat die extrusion of whole oat flour modified by hydrogen peroxide, PBAT, and glycerol, using maleic anhydride and citric acid as compatibilizer.

2 Experimental

2.1 MATERIALS

The sheets were produced with whole oat flour (WOF) (SL Alimentos Ltda, Brazil) (moisture 8.74%, lipids 6.20%, ashes 2.00% and protein 17.42%), hydrogen peroxide (BIOTEC, Brazil), citric acid (Dinamica, Brazil), maleic anhydride (Sigma–Aldrich, Germany), glycerol (Dinamica, Brazil) and poly (butylene adipate-co-terephthalate) (PBAT) (BASF, Germany) under the brand name Ecoflex®.

2.2 METHODS

2.2.1 PRODUCTION OF BIODEGRADABLE SHEETS

The whole oat flour (WOF) was conditioned up to 32% moisture, by adding NaOH solution sufficient to reach the desired moisture and pH of 11.5, and stored in polyethylene bags at 7-10 °C for 24 hours (GALDEANO; GROSSMANN, 2005). The whole oat flour (WOF) and hydrogen peroxide (200V) (7%) were manually mixed and the material was kept under refrigeration (7 to 10 °C) for 24 hours. After this period the WOF + hydrogen peroxide were manually mixed with PBAT, glycerol, citric acid and maleic anhydride, and extruded in a pilot single-screw extruder (model EL-25, BGM, Brazil) with a screw diameter (D) of 25 mm and a screw length of 28D to produce strands. The barrel temperature profile was 90/120/120/120 °C from the feeding zone (zone 1) to the die zone (zone 4) at a screw speed of 30 rpm, using a die with six holes of 2 mm diameter. The clyndrical strands were pelletized, and extruded in a pilot co-rotating twin-screw extruder (model D-20, BGM, Brazil), with a screw speed of 100 rpm and temperature profile of 90/120/120/125/120 °C, feed speed of 33 rpm and equipped with a 0.8 mm flat die and a three-roll calender (AX Plasticos, Brazil).

An experimental mixture design with constrains (determined by preliminary tests) was used to assess the effect of the three components over the biodegradable sheets: glycerol, citric acid, maleic anhydride (Table 1). Mixture models (Eq. 1) were determined using the Statistica software version 7.0 (STATSOFT, 1995), using the mixture design procedure.

$$y = \beta_1.x_1 + \beta_2.x_2 + \beta_3.x_3 + \beta_{12}.x_1.x_2 + \beta_{13}.x_1.x_3 + \beta_{23}.x_2.x_3 \qquad \text{(Eq. 1)}$$

where y is the dependent variable, β is the regression coefficient for each component, x_1 is the glycerol percentage, x_2 is the CA percentage, and x_3 is the MA percentage.

Table 1 – Formulation of the biodegradable sheets according to the mixture design.

Formulation	Component [a] (%)			Pseudo-component		
	Glycerol	CA	MA	x_1 (Glycerol)	x_2 (CA)	x_3 (MA)
1	12	0	0	1	0	0
2	10	2	0	0.934	0.066	0
3	10	0	2	0.934	0	0.066
4	8	2	2	0.868	0.066	0.066
5	11	0	1	0.967	0	0.033
6	11	1	0	0.967	0.033	0
7	9	2	1	0.901	0.066	0.033
8	9	1	2	0.901	0.033	0.066
9	10	1	1	0.934	0.033	0033

[a] In relation to the total weight of the mixture, the other 88 wt% corresponding to PBAT + WOF at 45:55 wt ratio of PBAT:WOF.

CA – Citric Acid

MA- maleic anhydride

2.2.2 DENSITY AND GRAMATURE OF THE SHEETS

Five samples of each sheet were cut (20 x 20 mm), and were conditioned for 7 days in a desiccator containing anhydrous $CaCl_2$ (~ 0% RH). After this period, samples were weighed and measured (thickness, length and width) to calculate the density and the gramature.

2.2.3 OPACITY

The opacity was determined using a colorimeter (BYK Gardner, USA), illuminant D65 (day light) and 10°, at 3 different spots in each sample, according to Hunterlab methods (Hunter Associates Laboratory, 1997). Sample opacity (Y) was calculated as the ratio between the opacity of the sample placed under a black pattern (Yb) and the opacity of the sample placed under a white pattern (Yw) (Eq. 2).

$$Y (\%) = (Yb/Yw).100 \qquad \text{(Eq. 2)}$$

The determination were performed in triplicate.

2.2.4 MECHANICAL PROPERTIES

The tensile strength, elongation at break and Young's modulus of the sheets was determined based on the ASTM D882-02 (2002) using a texture analyser, model TA.XT2i (Stable Micro Systems, England) fitted with a 5 N load cell. Ten samples of each formulation (70 mm x 20 mm) were conditioned at 53 ± 2% RH for 48 h before testing. The crosshead speed was set at 0.8 mm/s, and the initial distance between the grips was 30 mm.

The slow rate penetration resistance (SRPR) of the sheets was performed according to ASTM F1306-90 (2002) using the same texturometer used for tensile testing, with a 3.2 mm diameter hemispherical probe. Ten samples for each formulation (30 mm diameter) were conditioned at 23 ± 2 °C and 53 ± 2% RH for 48 h before testing. The force to perforation (FP) and the elongation to perforation (EP) were determined at 25 mm/min.

2.2.5 WEIGHT LOSS IN WATER

Samples were previously dried for three days in desiccators containing anhydrous $CaCl_2$ (~ 0% RH). After weighing, the sheets were immersed in distilled water, in a proportion of 30:1 (water:sample) for 48 h at 25 °C. The samples were dried at 105 °C for 4 h, and the weight of the conditioned specimen after treatment was used to determine the percentage of weight loss (%wt.) in water.

2.2.6 WATER VAPOUR PERMEABILITY (WVP)

The tests were conducted using the ASTM E-96-95 (1996) with some modifications. Before the analysis, the samples were conditioned at 25 °C and 53% RH for 48 h. Each sheet sample was fixed in a permeation cell with 60 mm internal diameter. The interior of the cell was filled with saturated $MgCl_2$ solution (32.8% RH), and the device was stored at 25 °C in a desiccator containing saturated sodium nitrate solution to provide 64% RH.

2.2.7 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

FT-IR analyses were conducted on the samples from 4000 to 450 cm^{-1} with a spectral resolution of 4 cm^{-1} with 12 scans. A spectrophotometer IR Prestige 21 (Shimadzu, Japan) was used. The samples were conditioned in a desiccator containing anhydrous calcium chloride ($CaCl_2$) for 10 days before the analysis.

3 Results and Discussion

All formulations had adequate processability during extrusion and the sheets showed homogenous surfaces and the average thickness was 960 ± 5 μm.

3.1 DENSITY AND GRAMATURE OF THE SHEETS

The density and gramature of the biodegradable sheets are shown in Table 2 and the coefficients of the mixture design model are shown in Table 3. The sheets density were similar than those reported by Dias et al., (2010) for rice flour biodegradable films (~ 1.30 g/cm^3).

Table 2 – Density and gramature of the biodegradable sheets.

Formulation	Density ($g.cm^{-3}$)	Gramature ($g.cm^{-2}$)
1	1.34±0.19	0.14±0.02
2	1.45±0.13	0.14±0.01
3	1.14±0.11	0.11±0.01
4	1.34±0.16	0.12±0.01
5	1.49±0.12	0.13±0.01
6	1.46±0.08	0.14±0.01
7	1.25±0.10	0.12±0.01
8	1.25±0.11	0.11±0.01
9	1.30±007	0.13±0.01

Table 3 – Mixture design model for density and gramature of the biodegradable sheets.

Coefficient	Density ($g.cm^{-3}$)	Gramature ($g.cm^{-2}$)
β_1	1.40	0.13
β_2	1.49	0.47
β_3	1.36	0.41
β_{12}	-	-0.66
β_{13}	-	-0.43
β_{23}	-1.24	-1.30
R^2	0.82	0.94

β_1=Glycerol, β_2=CA β_3=MA, β_{12}=interaction Glycerol x CA, β_{13}=interaction Glycerol x MA, β_{23}=interaction CA x MA.
R^2 = coefficient of determination

According to the mixture design models (Table 3), increasing glycerol, CA, and MA content increase the density and gramature. The interaction between CA x MA was negative, i.e. higher CA and MA content decrease the density and gramature of the materials, which may be related to reduced availability of compatibilizers for performing cross-linking when they are used together (OLIVATO, 2010).

3.2 OPACITY

The opacity of the biodegradable sheets is shown in Table 4 and the coefficients of the mixture design model are shown in Table 5. The high opacities were due to the high sheets thickness (960 ± 5 μm), and the composition of the raw material (proteins, lipids, and fibres).

Table 4 – Opacity of the biodegradable sheets.

Formulation	Opacity (%)
1	86±3
2	82±3
3	83±3
4	82±7
5	80±1
6	83±5
7	86±4
8	78±1
9	83±1

Table 5 – Mixture design model for opacity of the biodegradable sheets.

Coefficient	Opacity (%)
β_1	84.99
β_2	96.10
β_3	71.13
β_{12}	-27.79
β_{13}	8.84
β_{23}	-
R^2	0.49

β_1=Glycerol, β_2=CA β_3=MA, β_{12}=interaction Glycerol x CA, β_{13}=interaction Glycerol x MA, β_{23}=interaction CA x MA.
R^2 = coefficient of determination

The coefficient of determination (R^2) of the mixture model was 0.49 and thus this model could not explain the opacity behaviour. The opacity ranged from 78 to 86 %, characterizing these materials as highly opaque. The opacity values found by Dias (2014) evaluating oat flour materials with addition of citric acid and magnesium stearate were 75-85%.

3.3 MECHANICAL PROPERTIES

The tensile strength, elongation at break and Young's modulus of the biodegradable sheets are presented in Table 6.

Table 6 – Mechanical properties of the biodegradable sheets.

Formulation	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
1	0.98±0.44	45±13	4±6
2	1.83±0.10	40±11	21±3
3	2.66±0.18	35±6	21±5
4	1.74±0.16	36±9	15±9
5	1.95±0.13	48±7	21±6
6	2.33±0.34	44±12	34±4
7	1.71±0.13	40±5	15±4
8	1.90±0.08	34±4	21±2
9	2.07±0.12	42±6	16±6

The tensile strength, elongation at break and Young’s modulus of the sheets varied widely depending on the formulation, and ranged from 0.98 to 2.66 MPa, 34 to 48 % and 4 to 34 MPa, respectively (Table 6).

According to the R^2 of the mixture models (Table 7), only the elongation at break behaviour could be explained by the model (R^2=0.94). Both glycerol and CA concentration had positive effect, and the MA had negative effect, and the interactions glycerol x CA, and CA x MA were positive for elongation at break.

The glycerol had the higher and positive effect on elongation at break, indicating that higher concentrations of this component causes an increase in the elasticity of the material, as proposed by many authors (MALI et al., 2006; MANGAVEL et al., 2003; SHI et al., 2007; BONA, 2007; LUO et al., 2009).

Table 7 - Mixture design model for mechanical properties of the biodegradable sheets.

Coefficient	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
β_1	1.38	46.49	11.48
β_2	0.04	33.02	-25.72
β_3	2.08	-10.42	39.23
β_{12}	4.57	-	119.72
β_{13}	4.86	72.06	-34.78
β_{23}	-	89.00	39.43
R_2	0.46	0.94	0.39

β_1=Glycerol, β_2=CA β_3=MA, β_{12}=interaction Glycerol x CA, β_{13}=interaction Glycerol x MA, β_{23}=interaction CA x MA.

Garcia (2010) analysed the mechanical properties of cassava starch/PBAT films produced by thermoplastic extrusion, and using citric acid as compatibilizer. The tensile strength and elongation at break of the films ranged from 1.81 to 7.15 MPa and 8.61 to 23.63%, respectively.

Olivato et al., (2012b) reported that increasing the proportion of CA in blends of starch/PBAT/glycerol there was an increase in the tensile strength, resulting in stronger films due to the crosslinking reactions (transesterification) between the polymeric molecules.

Chabrat et al., (2012) produced films with poly (acid lactic), glycerol and wheat flour with addition of citric acid, and reported that with increasing concentration of citric acid the elongation at break of the films decreased, due to the competition between glycerol and citric acid for the plasticization of films.

The force to perforation (FP) and the elongation to perforation (EP) of the sheets varied widely depending on the formulation and ranged from 14.20 to 29.90 N, and 14.19 to 30.52 mm, respectively (Table 8).

According to the mixture model (Table 9), all components of the formulation led to an increase in FP and EP. All interactions were positive, i.e. the increase of any of the components led to increase in FP and EP.

Table 8 – Slow Rate Penetration Resistance (SRPR) of the biodegradable sheets.

Formulation	FP (N)	EP (mm)
1	14±3	14±3
2	22±1	23±2
3	30±5	31±6
4	24±2	26±3
5	22±2	24±2
6	24±2	25±2
7	25±2	26±2
8	23±1	26±2
9	26±2	24±2

FP - force to perforation
EP - elongation to perforation

Table 9 - Mixture design model for Slow Rate Penetration Resistance (SRPR) of the biodegradable sheets.

Coefficient	Force to Perforation (N)	Elongation to Perforation (mm)
β_1	16.32	16.94
β_2	18.29	21.49
β_3	19.53	34.34
β_{12}	23.55	21.41
β_{13}	19.61	-
β_{23}	34.54	3.51
R^2	0.73	0.76

β_1=Glycerol, β_2=CA β_3=MA, β_{12}=interaction Glycerol x CA, β_{13}=interaction Glycerol x MA, β_{23}=interaction CA x MA.
R^2 = coefficient of determination

Resistance to perforation is an important parameter of materials used for packaging products with sharp edges. The FP and EP values found by Dias (2014) for oat flour materials with addition of citric acid and magnesium stearate were 12-22 N and 4.8-6.9 mm, respectively.

Oat starch films without plasticizer and plasticized with glycerol were more resistant (28.13 N and 17.32N, respectively) (GALDEANO, 2007) than cassava starch films without plasticizer (11.6 N) (VICENTINI, 2003) and amaranth starch films plasticized with glycerol (2.3 N) (TAPIA-BLACIDO; SOBRAL; MENEGALLI, 2005), stored at 57% RH.

Olivato et al., (2013) evaluate the effect of tartaric acid on the properties of starch/ PBAT blown films plasticised with glycerol. The inclusion of tartaric acid exerted a negative effect on puncture force, i.e., when the concentration of tartaric acid increases, the tensile strength and puncture force of the films were reduced.

3.4 WEIGHT LOSS IN WATER AND WATER VAPOUR PERMEABILITY

The sheets presented small weight loss in water (WLW) variation, wich ranged from 15.24 to 17.95 % (Table 10). The mixture model for weight loss in water (WLW) (Table 11) showed a low coefficient of determination ($R^2 < 0.18$), so the mixture model cannot explain the WLW behaviour.

Table 10 – Weight Loss in Water and Water Vapour Permeability of the biodegradable sheets.

Formulation	WLW (% wt.)	WVP ($\times10^{-5}$) ($g.day^{-1}.m^{-1}.Pa^{-1}$).
1	17.72±0.39	4.97±0.21
2	16.19±0.13	4.65±0.65
3	16.77±0.61	1.85±0.28
4	16.99±013	4.41±0.32
5	15.24±0.21	8.31±0.44
6	16.40±0.31	2.70±0.43
7	18.09±0.03	4.51±0.55
8	17.95±0.02	2.39±0.13
9	16.66±0.02	1.74±0.34

WLW - weight loss in water
WVP - water vapour permeability

Table 11 - Mixture design model for weight loss in water (WLW) and water vapour permeability (WVP) of the biodegradable sheets.

Coefficient	Weight Loss in Water (%)	WVP ($\times 10^{-5}$) ($g.day^{-1}.m^{-1}.Pa^{-1}$).
β_1	16.86	5.6
β_2	14.96	10.7
β_3	19.22	-12.8
β_{12}	2.65	-28.7
β_{13}	-5.48	33.2
β_{23}	2.39	12.7
R^2	0.18	0.80

β_1=Glycerol, β_2=CA β_3=MA, β_{12}=interaction Glycerol x CA, β_{13}=interaction Glycerol x MA, β_{23}=interaction CA x MA.
R^2 = coefficient of determination

Biodegradables films based on achira flour presented WLW around 38% (ANDRADE-MAHECHA; TAPIA-BLACIDO; MENEGALLI, 2012). Biodegradable sheets based in oat starch had WLW of about 23% (GALDEANO, 2007), higher than the values found in this study. The lipid and fibre content present in whole oat flour probably reduced the WLW, because both components interfere with the starch solubilization, and the blend composition did not affect it.

The water vapour permeability of the sheets ranged from 1.74 to 8.31 x 10^{-5} $g.day^{-1}.m^{-1}.Pa^{-1}$ (Table 10), and according to the mixture model (Table 11), the higher the glycerol and CA concentration the higher the water vapour permeability (WVP) of the sheets, and the interaction glycerol x CA was negative, i.e. higher glycerol content decreases the WVP of the materials produced with high CA concentration. MA had a negative effect, i.e. higher MA content decreases the WVP of the materials.

The use of plasticizers such as glycerol, increases the affinity of the films with water can impair their barrier properties (MALI et al., 2004; MÜLLER; YAMASHITA; LAURINDO, 2008). Glycerol was used as a plasticizer in biodegradable films of banana flour (PELISSARI et al., 2013), achira (ANDRADE-MAHECHA; TAPIA-BLÁCIDO; MENEGALLI, 2012) and rice (DIAS et al., 2010; SOUSA; SOARES-JUNIOR; YAMASHITA, 2013).

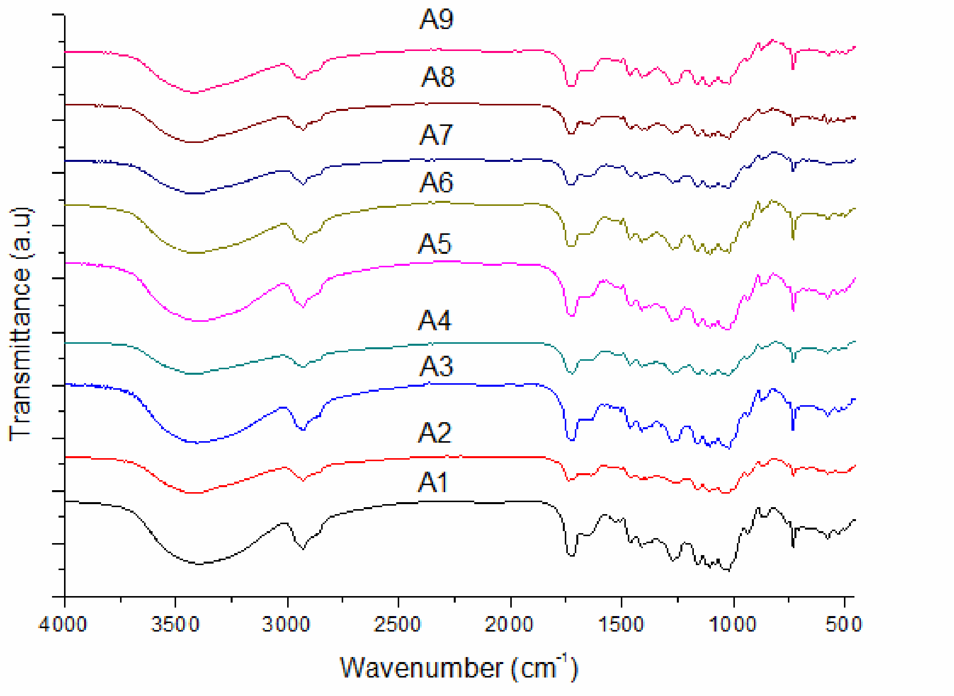
3.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FT-IR)

Figure 1 shows the FT-IR spectra (wavenumbers between 4000-500 cm^{-1}) of the biodegradable sheets produced by extrusion-calendering process.

The peaks at 2921 cm^{-1} and 2850 cm^{-1} indicates the presence of CH_2 groups, and some authors reported that the different intensities of the bands located between 2800-3000 are related to the amounts of amylose and amylopectin (KIZIL; IRUDAYARAJ; SEETHARAMAN, 2002).

The peak at 1707 cm^{-1} is due the PBAT, since peaks around 1715 cm^{-1} characterize the ester carbonyl stretch (C=O) present in the PBAT structure (OLIVATO et al., 2012b).

Figure 1 – FT-IR spectra of the biodegradable sheets.



Bands around 1785 cm^{-1}, related to the stretching of the carbonyl group present in maleic anhydride, was not detected because anhydrides are unstable and they are converted to acids when in contact with polar substances like starch, as well as by the high temperatures involved at the extrusion process (CARVALHO et al., 2007).

4 Conclusion

Biodegradable materials produced with modified whole oat flour, PBAT and glycerol, using citric acid and maleic anhydride as compatibilizers by flat die extrusion had adequate processability and mechanical properties, and the compatibilizers had an important role to improve these properties. These materials represent an alternative to the use of non-biodegradable materials because of the low cost and the raw materials are from renewable sources.

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CONCLUSÕES GERAIS

Foi possível produzir por extrusão com matriz plana e caladragem materiais biodegradáveis elaborados com amido, farinha de aveia integral, poli (adipato co-tereftalato de butileno) e glicerol. Os materiais apresentaram características adequadas de processabilidade e propriedades mecânicas.

A adição de ácido cítrico e anidrido maleico como compatibilizante melhoraram as propriedades mecânicas e permeabilidade ao vapor de água dos materiais biodegradáveis à base de farinha de aveia modificada com peróxido de hidrogênio, além de melhorar a processabilidade, manuseabilidade e as características visuais dos materiais.

A farinha de aveia pode ser considerada uma alternativa para produção de materiais biodegradáveis. Porém são necessários mais estudos, como a utilização de outros compatibilizantes, utilização de outros polimeros, ou modificação nas condições de processamento.