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ESTADUAL DE LONDRINA

VANESSA DIAS ALVES

**PRODUÇÃO E CARACTERIZAÇÃO DE BIOMATERIAIS
A PARTIR DE FIBRAS NATURAIS OU AMIDOS COM
POLI(BUTILENO ADIPATO CO-TEREFTALATO) (PBAT)**

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Tese apresentada ao Programa de Pós-graduação em Ciência de Alimentos, do Departamento de Ciência e Tecnologia de Alimentos, da Universidade Estadual de Londrina como requisito à obtenção do título Doutor em Ciência de Alimentos.

Orientadora: Prof^a. PhD. Adelaide Del Pino Beléia

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RESUMO

Agropolímeros como amidos e fibras naturais são polímeros biodegradáveis de fonte renováveis que têm sido incorporados a matrizes poliméricas para melhorar a biodegradabilidade e reduzir custos. O objetivo desse trabalho foi produzir biomateriais baseados em amidos e fibras naturais com poli(butileno adipato co-tereftalato) por extrusão reativa. Biocompósitos foram produzidos incorporando fibras naturais (casca de aveia, pó de madeira e celulose) em matriz de PBAT modificado e não modificado. Blendas reativas de termoplástico amido-poliéster foram produzidas na razão de (50:50) e (60:40) MTPs-PBAT para aplicação em termoformados e TpS-PBAT ou MTpS-PBAT na razão de (30:70) para blendas de filmes. Os materiais produzidos foram caracterizados por propriedades mecânicas, de barreira e térmicas (DSC, TGA), infravermelho por transformada de Fourier (FTIR), espalhamento de luz dinâmico (DLS), viscosidade intrínseca (VI) e microestrutura (ESEM). A modificação do poliéster foi muito eficiente em promover forte adesão interfacial com as fibras naturais, aumentando as propriedades mecânicas (resistência à tração, módulo e alongação) e resistência ao impacto dos biocompósitos. Em geral, altas porcentagens de celulose resultaram em melhor interação entre as fibras e a matriz polimérica. A processabilidade do ATpM de amido de milho com alto teor de amilose foi muito melhor que a processabilidade de amido de milho regular e ceroso. As blendas ATpMPBAT formaram filmes, laminados e peças termoformadas mais transparentes e com superfícies mais homogêneas que as blendas de ATp. As propriedades mecânicas dos filmes de ATpM-PBAT foram superiores que dos filmes de ATp-PBAT. A modificação do ATP pela inserção de anidrido maléico (MA) teve um positivo efeito no equilíbrio de conteúdo de água dos filmes quando comparados com as amostras não modificadas.

Palavras-chave: Agropolímeros. Extrusão reativa. Biocompósitos. Blendas poliméricas e materiais de fonte renovável.

ALVES, Vanessa Dias. **Production and Characterization of Biomaterials Based in Natural Fibers and Starches with Poly(butylene adipate co-terephthalate) (PBAT)**. 183 f. Thesis (Doctorate in Food Science and Technology) – Universidade Estadual de Londrina, Londrina, 2007.

ABSTRACT

Agropolymers like starch and natural fibers are biodegradable polymers from renewable source which are often incorporated into materials to improve their environmental desirability and to reduce cost. The objective of this work was to produce biomaterials based starch and natural fibers with poly(butylene adipate coterephthalate) by reactive extrusion. Biocomposites were produced incorporating natural fibers (oat hulls, wood pulp and cellulose) into modified and non-modified PBAT. Biodegradable thermoplasticized starch-polyester reactive blends are produced in the ratio of TpS-PBAT or MTpS-PBAT(50:50) and (60:40) for thermoforming applications and TpS-PBAT or MTpS-PBAT (30:70) for films blends. The materials produced were characterized by mechanical, barrier and thermal (DSC, TGA) properties, fourier transform infrared spectroscopy analysis (FTIR), dynamic light scattering (DLS), intrinsic viscosity (IV) and microstructure analysis (ESEM). The maleation of the polyester proved to be very efficient in promoting strong interfacial adhesion with natural fibers, increasing the mechanical properties (stress at break, Young's modulus and elongation) and impact strength of the biocomposites. In general, higher percentages of cellulose resulted in better interaction between fiber and the polymeric matrix. The processability of high amylose corn starch MTpS was much better than the processability of regular and waxy corn starch MTpS. The MTpS-PBAT blends formed films, sheets and thermoformed pieces more transparent and had a more homogeneous surface than TpS-PBAT blends. The mechanical properties of MTpS-PBAT films are superior than TpS-PBAT films. The modification of the thermoplastic starch by grafting of maleic anhydride (MA), had an important positive effect on the equilibrium water content of the films as compared to the samples that were not maleated.

Keywords: Agropolymers. Reactive extrusion. Biocomposites. Polymeric blends. renewable raw materials.

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ABREVIações E SIGLAS

[η]	Viscosidade intrínseca.
ATp	Amido termoplástico.
ATpM	Amido termoplástico modificado.
DLS	Espalhamento de luz dinâmico.
DSC	Calorimetria diferencial de varredura.
ESEM	Microscopia eletrônica de varredura ambiental.
FTIR	Infravermelho com transformada de Fourier.
PBAT	Poli(butileno adipato co-tereftalato)
PVA	permeabilidade ao vapor de água.
TGA	Termogravimetria.
UR	Umidade relativa
€	Euro: moeda do mercado comum europeu.

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CAPÍTULO 1 – INTRODUÇÃO

Materiais poliméricos têm sido amplamente utilizados em diferentes aplicações devido a sua fácil processabilidade, custo-benefício e versatilidade de produtos que podem ser produzidos (KHARE & DESHMUKH, 2006). No entanto, são muitos estáveis e não se degradam facilmente, ocasionando sérios problemas ambientais (AVELLA *et al.*, 2005). No Brasil, do total de plásticos rígidos e flexíveis produzidos, apenas 16,5% são reciclados, o que equivale a 200 mil toneladas por ano. A maior limitação para a reciclagem é a diversidade das resinas, o que pode criar um problema na hora do reaproveitamento industrial (ABIEF, 2007).

O crescente acúmulo de lixo não biodegradável aliado à dificuldade de reciclagem da maioria das embalagens, tem estimulado o desenvolvimento de embalagens biodegradáveis de fontes renováveis. Dentre os polímeros naturais o amido tem se destacado, devido à combinação de preço atrativo, disponibilidade, biodegradabilidade e renovabilidade (AVÉROUS *et al.*, 2001).

Como material de embalagens, amido sozinho não forma filmes com propriedades mecânicas adequadas (TUIL *et al.*, 2000). Filmes de amido são quebradiços sem adição de plastificantes; higroscópicos e sensíveis às condições ambientais e apresentam baixa resistência em presença de plastificantes (KALAMBUR & RIZVI, 2006).

Blendas poliméricas, contendo quantidade variável de amido e poliésteres biodegradáveis, têm sido extensivamente estudadas, como alternativas para substituir plásticos tradicionais na área de embalagens (HUNEAULT & LI, 2007, PARANAWATI, 2006, SAKANAKA, 2007, AVEROUS, 2004). A associação de amido termoplástico (ATp) com poliésteres biodegradáveis tem a finalidade de melhorar propriedades

mecânicas e diminuir a sensibilidade a água dos ATp e por outro lado reduzir o custo (BOGOEVA-GACEVA *et al*, 2007)

Os polímeros biodegradáveis podem ser classificados de acordo com a sua origem, polímeros de fonte renováveis ou biológicos: a) extraídos de plantas (amidos, fibras, proteínas, etc.), b) obtidos por via microbiana (os polihidroxialcanoatos (PHA, PHB e PHB-VB) ou c) produzidos biotecnologicamente, ácido polilático (PLA) e derivados do petróleo: Policaprolactonas (PCL), Poli(butileno succinato co-adipato) (PBSA), e Poli(butileno adipato co-tereftalato) (PBAT). (VILPOUXL & AVÉROUS, 2004).

Nos últimos anos várias pesquisas têm investigado a sustentabilidade de fibras naturais reforçando compósitos para produção de materiais termoplásticos injetados em moldes. Esses materiais são utilizados devido a sua baixa densidade, custo, propriedades térmicas adequadas e biodegradabilidade (WOLLERDORFER & BADER, 1998 e KARMANI, DRISHANM & NARAYAN, 1997).

Agropolímeros, como amidos e fibras, são alternativas para reduzir o custo de produção de blendas e/ou compósitos, mesclando polímeros biodegradáveis de alto custo e comercialmente disponíveis com polímeros de baixo custo e de fontes renováveis (DUBOIS & NARAYAN, 2003).

O objetivo deste trabalho foi produzir e caracterizar plásticos rígidos e flexíveis biodegradáveis, incorporando o máximo possível de materiais de fontes renováveis.

Para os materiais rígidos, fibras naturais (casca de aveia, pó de madeira e celulose) foram utilizadas em extrusão reativa com polímero biodegradável o poli(butileno adipato co-tereftalato) (PBAT) para produção de biocompósitos. Na produção dos flexíveis foram produzidas blendas poliméricas a partir de amido termoplástico (ATp) e amido termoplástico modificado (ATpM) com o PBAT. Os processos utilizados foram: 1) extrusão reativa para modificação do PBAT e produção

do ATpM, 2) extrusão para produção de pellets de biocompósitos e blendas poliméricas, 3) Injeção em moldes, 4) produção de filmes planos e laminados e 5) obtenção de termoformados. Os biocompósitos, laminados e filmes foram caracterizados quanto às propriedades mecânicas, de barreira e térmica e microestrutura.

CONSIDERAÇÕES INICIAIS:

A escolha de escrever a tese em artigos e os artigos em inglês foi devido ao estágio de doutorado realizado no exterior. Deste modo, meu co-orientador Prof. Ramani Narayan, da Michigan State University – MI (USA), teve acesso ao texto com os dados obtidos no exterior antes da defesa e divulgação da tese.

Os processos de produção do amido termoplástico e blendas deste como o PBAT são dois métodos desenvolvidos e patenteados pelo grupo do Prof. Narayan, da Michigan State University. (Patente USA 7.153.354, 2006 e patente MSU 2006;0111511 A1) A contribuição desta tese aos trabalhos anteriores, foi otimização do processo de produção do amido termoplástico, utilização de diferentes fontes de amido (amido com alto teor de amilose e amido ceroso de milho) e o desenvolvimento do processo de termomoldagem para estes produtos.

As patentes referidas acima são licenciadas para a Corn Products Internacional Inc., que detem os direitos comerciais dessa tecnologia.

A parte dos termoformados constitui um processo inédito e está sendo patenteada pela Michigan State University, que já depositou a patente provisional (MSU 4.1-886 (ID08-026)) do dia 06 de dezembro de 2007.

CAPÍTULO 2 – REVISÃO BIBLIOGRÁFICA

Este capítulo apresenta os principais termos utilizados nos capítulos do trabalho e principais características relacionadas à produção e caracterização de plásticos biodegradáveis rígidos e flexíveis a base de amidos e fibras naturais com poliéster biodegradável.

2.1 MATÉRIAS-PRIMA PARA PRODUÇÃO DE PLÁSTICOS BIODEGRADÁVEIS

Atualmente, existem vários tipos de polímeros biodegradáveis comercialmente disponíveis, sejam de origem agrícola, sintetizados por processos fermentativos ou por síntese química tradicional. Segundo GUILBERT (2000) e AVEROUS (2002) os polímeros biodegradáveis podem ser divididos em quatro grupos (Figura 2.1):

- a) Polímeros agrícolas, usados sozinhos ou em misturas com polímeros sintéticos biodegradáveis;
- b) Polímeros microbianos, formados a partir de substratos de fontes renováveis ou sintéticos usados como substrato. Nesta classe incluem-se os polihidroxi-alcanoatos, com a sigla PHA, como o PHB (polihidroxibutirato) e o P(HB-V) (polihidroxibutirato co-valerato);
- c) mono ou oligômeros polimerizados por processos químicos convencionais e obtidos a partir de matérias primas renováveis usadas como substrato. O material mais conhecido dessa classe é o PLA (ácido poliláctico).

d) derivados por síntese, obtidos da indústria petroquímica por via sintética clássica. Esta última é representada por numerosos polímeros e subgrupos: a) os policaprolactonas (PCL), b) poliésteraminas (PEA), c) os copoliésteres alifáticos, como o polibutileno succinato adipato (PBSA) e d) os copoliésteres alifáticos aromáticos como o polibutileno adipato co-tereftalato (PBAT).

O PCL e o PLA são os polímeros que dominam o mercado, com exceção dos derivados de amido (AVEROUS, 2002). A desvantagem destes polímeros biodegradáveis para utilização em embalagens é o elevado preço quando comparados às embalagens de polímeros sintéticos tradicionais (Tabela 2.1).

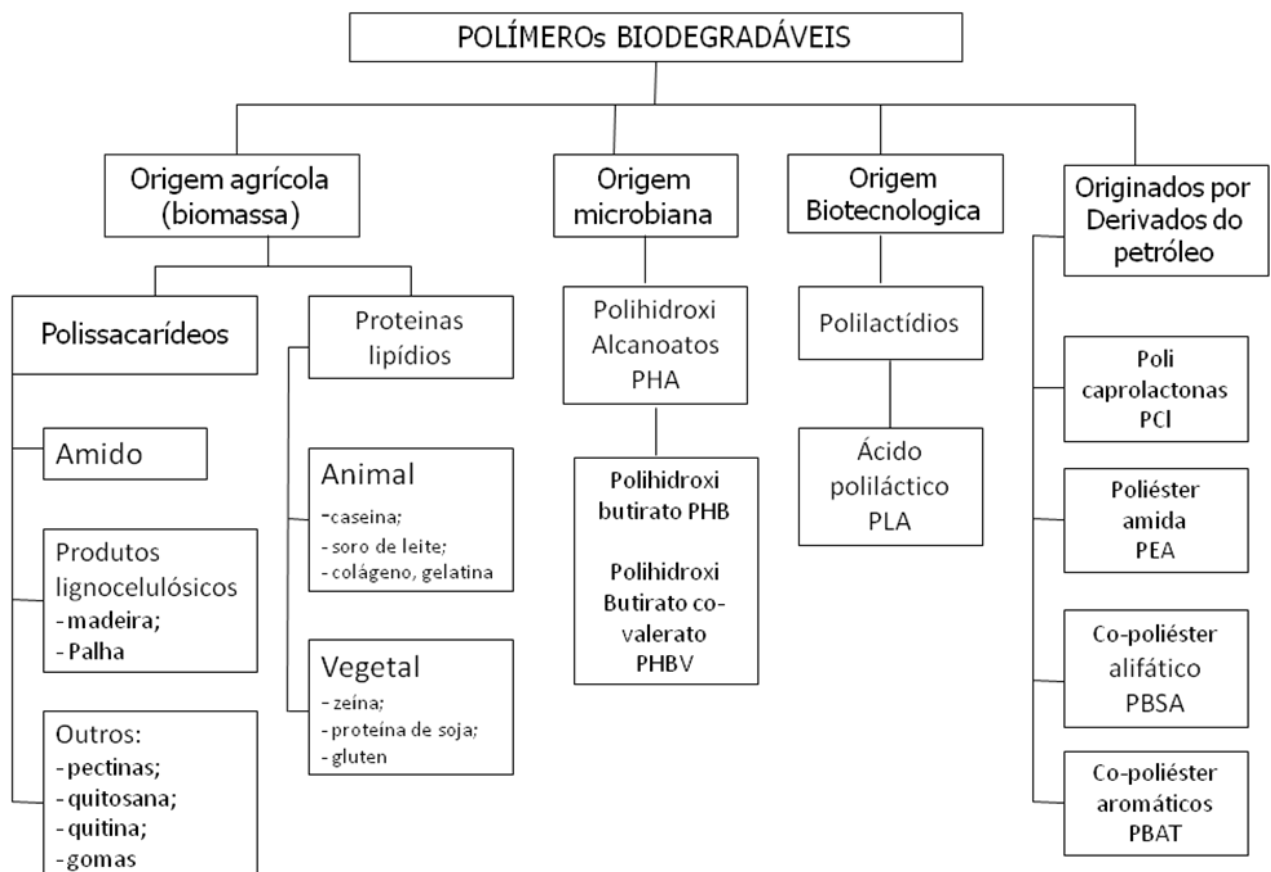


Figura 2.1 – Esquema dos polímeros biodegradáveis.
Fonte: VILPOUXL & AVEROUS (2004).

Blendas poliméricas contendo quantidade variável de amido e polímeros biodegradáveis têm sido extensivamente estudados como alternativas para substituir plásticos tradicionais na área de embalagens (HUNEAULT & LI, 2007, PARANAWATI, 2006, SAKANAKA, 2007, AVEROUS, 2004). Agropolímeros, como amidos e fibras, são alternativas para reduzir o custo de produção de blendas ou compósitos mesclando polímeros de custo elevado e comercialmente disponíveis com polímeros de custo reduzido e de fontes renováveis.

Tabela 2.1- Média de preços de polímeros biodegradáveis e alguns polímeros tradicionais.

Polímeros Tradicionais	Preço (€/kg)	Polímeros biodegradáveis	Preço (€/kg)
HDPE	0.92	PLA	3-4
LDPE	0.82	Amidos	2-4
PP	0.80	Poliésteres (PBAT, PBSA)	2.5-5
PS	1.08	PEA	5.58
PVC	0.78	PCI	8.3

HDPE = polietileno de alta densidade, LDPE = polietileno de baixa densidade, PP = polipropileno, PS = poliestireno, PVC = policloreto de vinila, PBAT = polibutileno adipato co-tereftalato, PBSA = Polibutileno succinato co-adipato, PEA = poliesteramidas e PCI= prolactonas.

Fonte: Adaptado de BOGOEVA-GACEVA *et al.*, 2007.

2.1.1 Agropolímeros

Agropolímeros são polímeros de origem agropecuária como polissacarídeos (ex. amido e celulose) e proteínas.

2.1.1.1 Amidos

O amido é constituído por uma mistura de dois polissacarídeos denominados amilose e amilopectina, em proporções que variam entre os amidos procedentes de diferentes espécies vegetais. Para amidos provenientes de mesma espécie o conteúdo de amilose e de amilopectina varia de acordo com o grau de maturação das plantas. As proporções destes dois polímeros influem na viscosidade e no poder de geleificação do amido. (BOBBIO e BOBBIO, 1995).

A amilose é formada por longas cadeias lineares, nas quais as unidades de D-glucopiranosose estão unidas por ligações glicosídicas $\alpha(1-4)$. Algumas moléculas de amilose possuem ramificações $\alpha(1-6)$, no entanto, essas ramificações correspondem apenas 0,3 -0,5% do total das ligações. Estas ramificações são ou muito longas ou muito curtas e os pontos de ramificação são separados por longas distâncias, que as propriedades físicas das moléculas de amilose são essencialmente de propriedades de moléculas lineares. Amilose tem massa molar relativamente baixo se comparada com moléculas de amilopectina, na ordem de 10^6 (BeMILLER & WHISTLER, 1996).

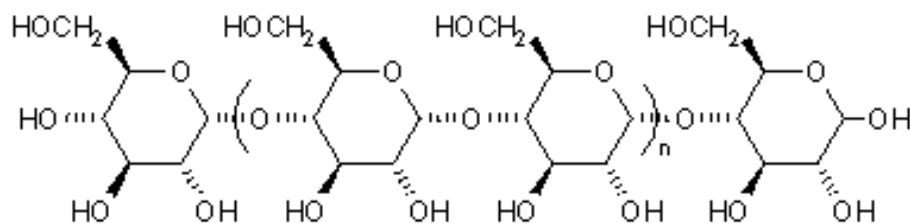


Figura 2.2 – Estrutura da amilose.
Fonte: BeMILLER & WHISTLER, 1996.

Em contraste à estrutura da amilose, a amilopectina tem uma estrutura altamente ramificada (Figura 2.3). As unidades de D-glucopiranosose em cada ramo linear são unidas por ligações $\alpha(1-4)$. Os pontos de ramificação são efetuados através de ligações $\alpha(1-6)$, na qual o carbono aldeídico 1 da glucose inicial é conectado ao carbono 6 da unidade de glucose, iniciando a ligação ramificada. Os pontos de ramificações constituindo 4 -5% do total de ligações. As ramificações da molécula de amilopectina são em forma de *cluster* e formam estruturas em dupla hélice. Possui massa molar de 10^7 a 5×10^8 , ficando classificadas entre as maiores macromoléculas existentes na natureza (BeMILLER & WHISTLER, 1996).

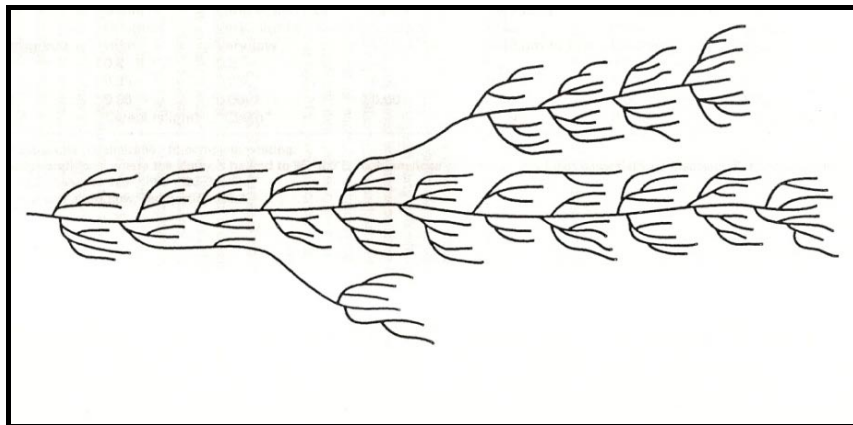


Figura 2.3 – Estrutura da amilopectina.
Fonte: BeMILLER & WHISTLER, 1996.

Os amidos de algumas espécies mutagênicas de milho, cevada, arroz e trigo, etc, contêm elevado teor de amilose (amidos com 50% ou mais de amilose) ou um aumento na porcentagem de amilopectina (amidos cerosos com 99-100% de amilopectina) (HUNG, MAEDA & MORITA, 2006). A diferente razão amilose/amilopectina destes amidos leva a uma diferença na estrutura granular, propriedades físico-química e qualidade dos produtos finais (Figura 2.4).

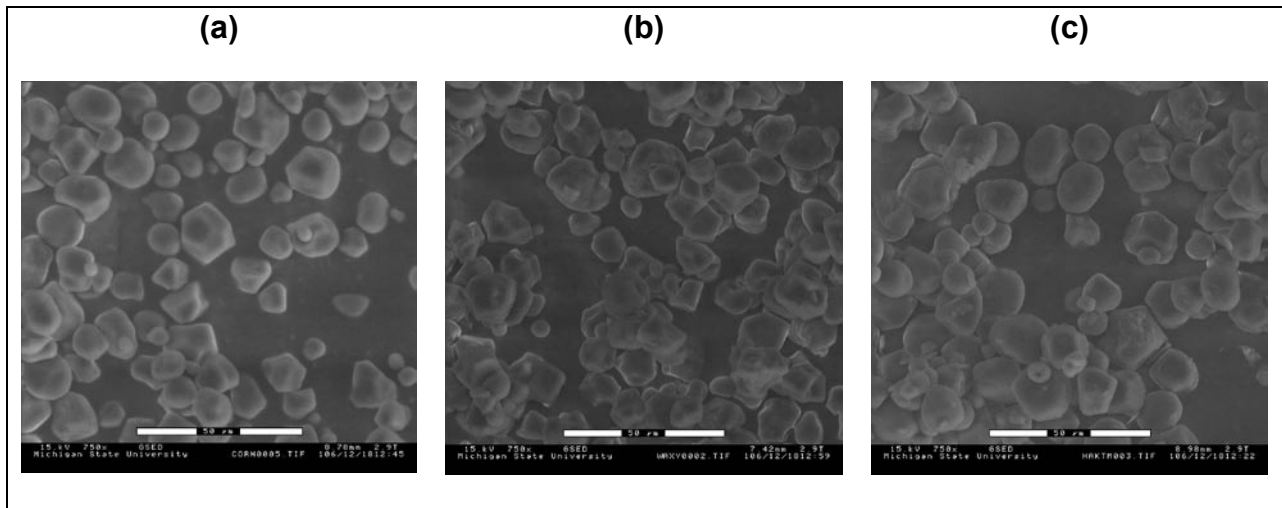


Figura 2.4 – Micrografias de amidos por microscopia eletrônica de varredura ambiental: a) amido de milho, b) amido de milho ceroso e c) amido com alto teor de amilose (70%).

Fonte: presente trabalho.

As principais fontes comerciais de amido são: milho, mandioca, batata, trigo e arroz (ELLIS, COCHRANE, DALE *et al.*, 1998) e tem sua utilização nas mais diversas indústrias, como nas indústrias alimentícias, farmacêuticas e de cosméticos, papéis, têxteis. Nos últimos 30 anos tem crescido o interesse de utilizar amidos na produção de biofilmes biodegradáveis.

Tabela 2.2 – Constituição dos principais amidos comerciais

Fontes de amido	Amilose (%)	Amilopectina (%)
Amido de milho com alto teor de amilose	50-85	15-50
Milho	26	74
Amido de milho ceroso	1	99
Trigo	25	75
Mandioca	17	83
Batata	21	79

Fonte: ZOBEL & STEPHEN 1995.

2.1.1.1.1 Amido termoplástico (ATp)

Amido sozinho, não forma filmes com adequadas propriedades mecânicas (alta percentagem de alongação e resistência mecânica) (TUILL et al, 2000). Materiais baseados em amido têm desvantagens como: a) natureza quebradiça sem adição de plastificantes; b) alta higroscopicidade; c) deterioração das propriedades mecânicas quando expostos a condições ambientais (umidade) e d) baixa resistência em presença de plastificantes (KALAMBUR & RIZVI, 2006).

Amidos têm sido usados por diferentes métodos na produção de plásticos compostáveis. O amido não é um verdadeiro termoplástico, mas na presença de plastificantes (água, glicerol, sorbitol, etc) e em altas temperaturas funde e flui, permitindo seu uso em equipamentos de injeção e/ou extrusão por calandragem ou sopro, utilizados para os plásticos sintéticos. (VILPOUXL & AVEROUS, 2004) (Figura 5).

Na obtenção de amido termoplástico (ATp) é necessário que o amido perca sua estrutura granular semicristalina e adquira comportamento similar ao de um termoplástico fundido, obtido por extrusão mono ou dupla-rosca, através de introdução de energia mecânica e térmica (LOURDIN *et al.*, 1999). O ATp tem desvantagens que limitam sua utilização em embalagens, principalmente para aplicação em materiais termoformados, especialmente devido à fina espessura destes objetos (AVEROUS, FRINGANT & MORO, 2001). As maiores desvantagens do ATp são sensibilidade à água (ZOBEL, 1988), mudanças nas propriedades mecânicas com o tempo (AVEROUS 2004 apud VAN SOEST, 1999), cristalização devido à plastificação, absorção de água e baixa resistência ao impacto. A figura 2.5 apresenta as micrografias de amido granular (a) e amido termoplástico (b).

No trabalho conduzido por Huneault (2007), em extrusora dupla rosca, para obtenção de amido termoplástico foi necessário usar temperaturas elevadas (acima de 130°C) e altos teores de glicerol (acima de 30%) para permitir a processabilidade.

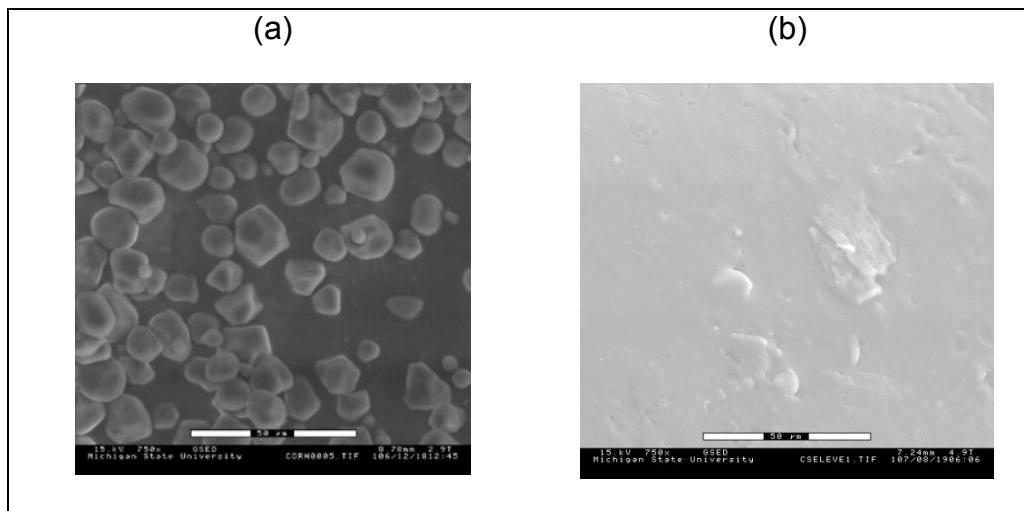


Figura 2.5 - Micrografias ESEM (Microscopia eletrônica de varredura ambiental): a) amido em forma granular e b) amido termoplástico modificado.

Fonte: presente trabalho.

2.1.1.1.2 Amido termoplástico modificado (ATpM)

Uma alternativa para melhorar a processabilidade do ATp e compatibilizar amidos e polímeros biodegradáveis é a modificação do ATp, reagindo amido com diácidos orgânicos ou anidridos em presença de plastificantes, usando iniciadores de reações por radical livre, produzindo amido termoplástico modificado (ATpM) (US patente 7153354, NARAYAN *et al*, 2006).

Essa patente relata a produção de amido termoplástico reativo e biodegradável (ATpM), que produz biomateriais com baixa viscosidade e boa processabilidade

comparados com ATp. Outro importante aspecto dessa invenção é que o processo não adiciona água e previne problemas como alta viscosidade, bloqueio da matriz da extrusora e formação de espumas no amido termoplástico fundido na saída da extrusora. Outra vantagem deste processo é que o ATpM resultante é altamente reativo com poliésteres. Desse modo, blendas de ATpM com poliésteres são facilmente processáveis em filmes, laminados ou peças por processos de injeção em moldes, resultando em produtos com balanço favorável em propriedades mecânicas, resistência a água, processabilidade e taxa de biodegradação.

O anidrido maléico (Figura 2.6), usado nesta modificação é um dos aditivos constituintes da lista positiva de polímeros e resinas para embalagens em contato com alimentos, sendo permitido seu uso desde que o limite de migração específica (LME) seja igual ou menor a 30 mg/kg (expressos como ácido maléico) (Resolução nº 105, de 19 de maio de 1999, ANVISA). O agente iniciador de radical livre, 2,5 dimetil, 2,5 di(terc-butilperoxi)hexano (Luperox 101) (Figure 2.7), também é um aditivo alimentar permitido pela FDA (órgão que regulamenta os medicamentos e alimentos nos Estados Unidos). Na legislação brasileira esse peróxido orgânico não é citado na lista de aditivos permitidos ou de não permitidos.

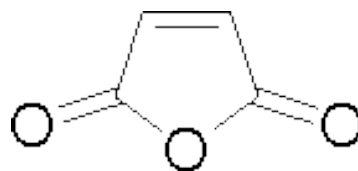


Figura 2.6 – Estrutura química do Anidrido Maléico.

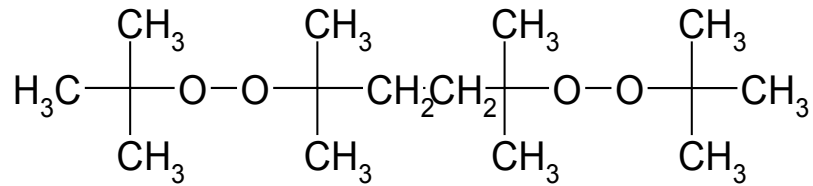


Figure 2.7 – Estrutura do Luperox (101) -2,5 dimetil, 2,5 di(terc-butilperoxi)hexano.

2.1.1.2 Resíduos agropecuários fibrosos

Com o aumento da produção agrícola brasileira, a produção dos resíduos agropecuários tem aumentado, demandando utilização máxima destes recursos naturais de forma sustentável. Uma tendência do agronegócio é o aproveitamento de resíduos com objetivo de agregar valor e/ou aproveitar toda a biomassa gerada nos processos industriais.

A maioria dos resíduos agropecuários são resíduos fibrosos como: cascas de frutas, vegetais e cereais, resíduos de fecularias e de indústrias moageiras de cereais como milho, trigo, aveia, arroz, etc. Esses resíduos são normalmente utilizados em rações animais. Mas em algumas indústrias o material não destinado a rações animais é utilizado como combustível, para queima em caldeiras, o que contribui para o aumento de emissão de CO₂ na atmosfera. Vários destes resíduos poderiam ser utilizados na produção de bioplásticos, como fonte de fibras, como casca de aveia, pó de madeira, sabugo de milho, bagaço de cana-de-açúcar, etc.

Resíduos agropecuários fibrosos, como as casca de aveia, são constituídos, basicamente, de carboidratos constituintes de parede celular como: celulose, hemicelulose, lignina e pectina (Figura 2.8). A adição de fibras a polímeros biodegradáveis tem o objetivo de aumentar a resistência dos materiais e diminuir custos.

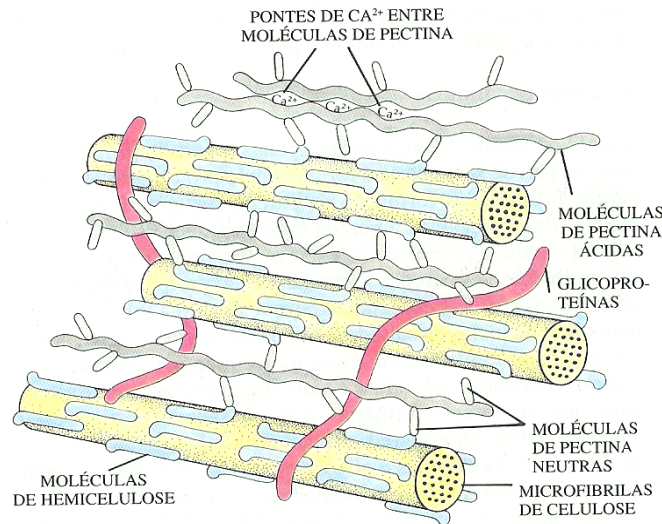


Figura 2.8 – Componentes da parede celular.
Fonte: RAVEN *et al.* 1996.

2.1.1.3 Poliésteres biodegradáveis

Os poliésteres biodegradáveis podem ser classificados em dois grandes grupos de acordo com sua origem: os agrícolas (obtidos a partir de fontes renováveis) e os poliésteres oriundos de reações químicas de monômeros de origem petrolífera (Tabela 2.3) (AVEROUS, 2004).

Tabela 2.3 – Classificação dos principais poliésteres biodegradáveis disponíveis comercialmente.

Matéria-prima	Poliéster	Nome comercial	Empresa	
AGRÍCOLA	PLA	Natureworks	Cargill-Dow LLC (EUA)	
		Lacty	Shimadzu (Japao)	
		Lacea	Mitsui Chemicals (Japao)	
		Hepylon	Chronopol (EUA)	
		CPLA	Dainippon Ink Chem. (Japão)	
		PLA	Galactic (Bélgica)	
	PHB, PHBV	Biopol	Monsanto-Metabolix (EUA)	
		Biocycle	Copersucar (Brasil)	
	PHBHx, PHBO, PHBOd	Nodax	Procter & Gamble (EUA)	
PETRÓLEO	PCI	CAPA	Solvay (Bélgica)	
		Tone	Union Carbide (EUA)	
		Celgreen	Daicel (Japão)	
	PEA	BAK	Bayer (Alemanha) ¹	
		Poliésteres alifáticos (ex.	Bionolles	Showa Highpolymer (Japão)
			Enpol	Ire Chemical ltd (Korea)
	Skygreen		SK Chemicals (Korea)	
	Poliésteres aromáticos (ex. PBAT)	Lunare SE	Nippon Shokybari (Japão)	
		Eastar Bio	Eastman Chemical (EUA)	
Ecoflex		BASF (Alemanha)		
Biomax		Dupont (EUA)		
		PHEE	Dow Chemicals (EUA) ¹	

¹ A produção destes poliésteres foi interrompida.

Fonte: AVEROUS, 2004

2.1.1.3.1 Poli(butileno adipato co-tereftalato) (PBAT)

O poli(butileno adipato co-tereftalato) (PBAT) é um co-poliéster biodegradável, aromático obtido por síntese química, o qual possui nome comercial de *Ecoflex*. É produzido pela empresa BASF, pela condensação do 1,4 butenodiol com o ácido 1,4-benzenodicarboxílico (tereftálico) e ácido hexanodióico (adípico) (Figura 2.9). O PBAT

é um importante polímero biodegradável, que tem sido objeto de investigação de diversos pesquisadores em diferentes aplicações: em blendas com amido termoplástico (PARAMAWATI, 2006), blendas com polímeros de recursos naturais PLA (JIANG, MOLCOTT & ZHANG, 2006) e em compósitos baseados em fibras ligno-celulosicas (LE DIGABEL & AVEROUS, 2006 e AVEROUS & LE DIGABEL, 2006).

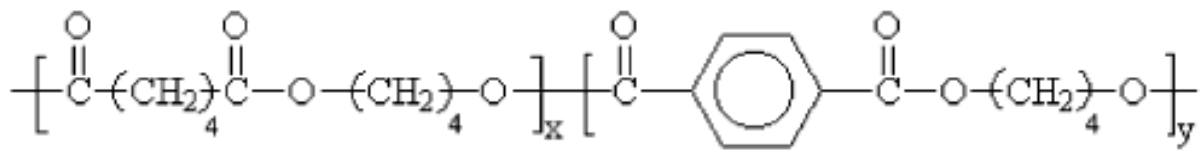


Figure 2.9 - Polibutileno adipato co-tereftalato (PBAT).

A BASF apresenta em seu portfólio de produtos duas linhas dedicadas a este co polímero: a) Ecovio®, combinação do Ecoflex® com 45% de ácido polilático (PLA) e b) Ecobrás®, plástico de fonte renovável e compostável desenvolvido em parceria com a afiliada brasileira da Corn Products International, Inc., que possuem em sua composição mais de 50% de matéria-prima renovável, Tabela 2.4.

Tabela 2.4 – Perfil de propriedades do Ecovio® e Ecobrás®

Propriedades	Unidade	Método	Ecovio®	Ecobrás®	PE-LD
Densidade	g/cm ³	ISO 1183	1,24 – 1,26	1,32	0,922- 0,925
Temperatura de fusão	°C	DSC	110-120 140-155	-	111
Modulo de elasticidade	MPa	ASTM D638	-	300	260
Resistência à tração	MPa	ASTMD13000	-	13	26

PE-LD = Polietileno de baixa densidade.

Fonte: Adaptado ficha técnica Ecovio® e Ecobrás®

2.2 BLENDA DE ATP E POLÍMEROS BIODEGRADÁVEIS

Materiais a base de amido ou de amido termoplástico (ATp) são hidrofílicos, o que reduz suas aplicações, principalmente em embalagens. A produção de blendas de amido ou ATp com polímeros hidrofóbicos resultam em materiais com propriedades menos hidrofílicas. Blendas de ATp com diferentes materiais biodegradáveis têm sido objeto de estudo de diversos pesquisadores, como blendas com PLA (HUNEAULT & LI, 2007), PHB (GODBOLE, *et al.*, 2003), PBSA (SAKANAKA, 2007) e PBAT (PARANAWATI, 2006).

Blendas de amido termoplástico com poliésteres biodegradáveis podem melhorar propriedades mecânicas (resistência a tração e alongação) e diminuir a sensibilidade à água dos ATp. Por outro lado, os biopoliésteres comerciais não são competitivos com plásticos provenientes do petróleo, devido ao seu alto custo (3.5 a 5.0 €/kg) (BOGOEVA-GACEVA *et al.*, 2007). Blendas de ATp com polímeros

biodegradáveis de alto custo é uma alternativa de redução de custo de produção de biomateriais (DUBOIS & NARAYAN, 2003).

Blendas de ATp e polímeros biodegradáveis têm sido estudadas extensivamente como alternativa para substituir materiais de embalagens como filmes ou plásticos por injeção em moldes. O desafio para desenvolver materiais baseados em amido termoplástico é a natureza quebradiça de blendas com alta concentração de amidos e o custo de blendas com baixos teores de amido ($\leq 30\%$) (TUILL *et al.*, 2000).

Uma das maneiras de melhorar as propriedades mecânicas, reduzir higroscopicidade e aumentar biodegradabilidade das blendas poliméricas é a compatibilização das blendas usando amido termoplástico modificado (ATpM) em extrusão reativa com poliéster biodegradável, patente número US 2006;0111511. (NARAYAN *et al.*, 2006)

2.3 BIOCAMPÓSITOS A BASE DE FIBRAS

Compósitos têm sido definidos como materiais produzidos a partir de dois ou mais componentes e consistindo em duas ou mais fases. Estes materiais devem ser heterogêneos, pelo menos em nível microscópico. Compósitos podem ser divididos em três classes gerais: a) particulados, matriz contínua e um preenchimento descontínuo de partículas discretas, b) estruturais ou rede de interpenetração compósita, consistindo em duas fases contínuas e c) fibras reforçando plásticos (NIELSON & LANDEL, 1994). Nesta última classe, o uso de fibras, sintéticas ou naturais, tem o objetivo de melhorar as propriedades mecânicas e a matriz polimérica promove a ligação com as fibras. Neste trabalho, o termo biocompósitos é usado significando compósitos biodegradáveis.

Nos últimos anos, várias pesquisas têm investigado a viabilidade do uso de fibras naturais reforçando compósitos para produção de materiais termoplásticos injetados em moldes (CURVELO *et al*, 2001). Esses materiais têm sido usados devido à sua baixa densidade e vantagens ecológicas (WOLLERDORFER & BADER, 1998). As vantagens das biofibras em relação a materiais tradicionais de reforço de termoplásticos são: reduzida irritação dérmica e respiratória, boas propriedades térmicas, fácil separação e biodegradabilidade (KARMANI, DRISHANM & NARAYAN, 1997).

2.3.1 Compatibilização entre Fibras e Poliésteres Biodegradáveis

Altas concentrações de fibra e sua pouca compatibilidade com poliésteres biodegradáveis resultam em propriedades mecânicas e físicas pobres nos produtos finais. Uma alternativa para melhorar as propriedades mecânicas é a funcionalização do poliéster.

A funcionalização de poliéster por extrusão reativa é uma maneira efetiva de compatibilizar fibras com a matriz polimérica, enxertando na matriz polimérica um grupo altamente reativo. Essas matrizes poliméricas modificadas podem reagir com grupamentos hidroxilas de celulose, para formar ligações covalentes, promovendo forte adesão interfacial.

Devido à sua alta reatividade, o anidrido maléico tem sido enchertado em diferentes polímeros, biodegradáveis ou não, para produzir polímeros funcionais (KALAMBUR & RIZVI, 2006; MALDAS & KOLTA, 1990; SATHE, RAO & DEVI, 1994).

Anidrido maléico foi primeiramente usado como para modificar polímeros não biodegradáveis, como polietileno, polipropileno e outros polímeros (SATHE, RAO & DEVI, 1994; VERMESCH & GROENINCKX, 1994). Estudos conduzidos por Bhattacharya e colaboradores (VAIDYA & BHATTACHARYA, 1994 e 1995, BHATTACHARYA, VAIDYA, ZHANG & NARAYAN, 1995, RAMKUMAR *et al.*, 1996, RAMKUMAR, BHATTACHARYA & VAIDYA, 1997, JOHN *et al.*, 1997, MANI & BHATTACHARYA, 1998, 1998^a, 2001, MANI *et al.*, 1998) utilizaram esse anidrido na modificação de polímeros biodegradáveis como PCL, PBSA, poli(butileno succinato adipato) (PBS) e Eastar Bio[®] co-poliéster; e por Narayan e colaboradores (CARLSON *et al* 1998 e 1999), na modificação de PLA. Estes estudos indicaram que a extrusão reativa dos polímeros modificados e amidos podem produzir blendas com boas propriedades finais.

O uso de polímeros modificados como compatibilizador entre fibras e matriz polimérica foi primeiro reportado com poliolefinas na preparação de compósitos com fibras de madeira (MALDAS & KOLTA, 1990). Vários autores utilizaram polipropileno modificado com anidrido maléico em compósitos com fibras naturais. (KARMANI, DRISHNAM & NARAYAN, 1997; JOSEPH, JOSEPH & THOMAS, 1999; VAN DE VELDE & KEIKENS, 2001, GAUTHIER *et al.*, 1998, JOSEPH *et al*, 2002, KAZAYAWOKO, BALATINECZ, & MATUANA, 1999, FUNG *et al*, 2003 e RANA *et al.*, 1998). Estes estudos relatam o aumento da adesão interfacial entre as fibras naturais e a matriz polimérica e conseqüente melhoria das propriedades mecânicas dos compósitos, após a modificação do polímero.

2.4 PROCESSAMENTO DE PLÁSTICOS BIODEGRADÁVEIS

Os plásticos biodegradáveis a base de amido e/ou fibras naturais podem ser processados nos mesmos equipamentos utilizados para plásticos tradicionais. A seguir serão relatados os principais processos utilizados: extrusão de filmes planos e laminados, injeção em moldes e termoformagem.

2.4.1 Extrusão

O processo de extrusão consiste basicamente em forçar a passagem do material por dentro de um cilindro aquecido de maneira controlada, por meio da ação bombeadora de uma ou duas roscas sem fim, que promovem o cisalhamento e homogeneização do material, bem como sua plastificação. Na saída do cilindro o material é comprimido contra uma matriz de perfil desejado, a qual dá formato ao produto, podendo o mesmo em seguida ser calibrado, resfriado, cortado ou enrolado. RODOLFO-JR *et al*, 2006.

2.4.1.1 Extrusoras

A extrusora é um equipamento constituído por um alimentador, uma rosca (ou duas para extrusoras dupla rosca), um cilindro encamisado, um sistema de aquecimento e resfriamento e uma matriz de saída de material (Figura 2.10).

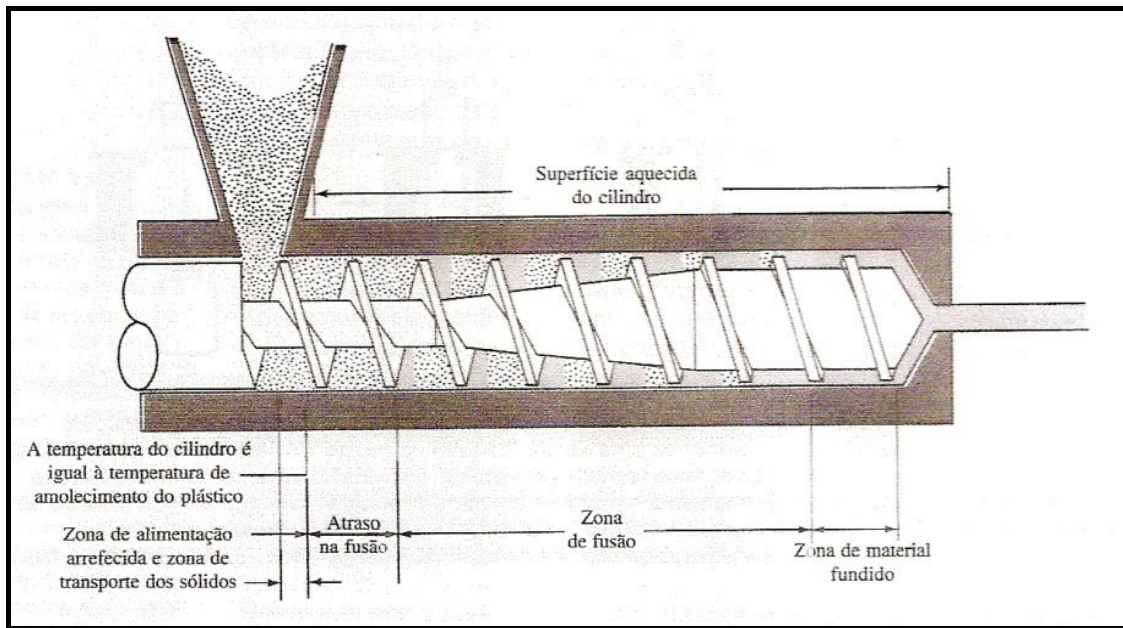


Figura 2.10 - Esquema de uma extrusora monorosca, mostrando as diversas zonas funcionais.

Fonte: SMITH, 1996.

O funil de alimentação tem a função de alimentar por igual a extrusora com o material a ser processado. Como geralmente os materiais não escoam por si só, os alimentadores são equipados com um agitador adicional.

O parafuso exerce várias funções como, por exemplo, puxar, transportar, fundir e homogeneizar o material e, por isso, é a principal parte de uma extrusora. Para extrusoras de parafuso único o mais difundido é o parafuso de três zonas (Figura 2.10), já que com ele é possível processar térmica e economicamente a maioria dos termoplásticos. Para extrusoras de dupla rosca (Figura 2.11) a configuração pode mudar de acordo com o material (Figura 2.12).

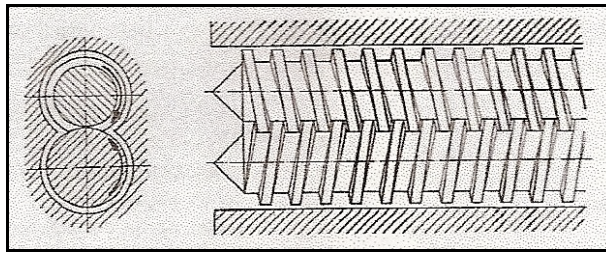


Figura 2.11 – Cilindro e parafusos de extrusora dupla rosca.
Fonte: MICHAELI *et al.*, 1995.

Dependendo de cada tipo de extrusora, a pressurização é obtida na zona de entrada ou na de saída. Como o processo de fusão não fornece sempre uma massa fundida completamente homogênea, para estes casos são construídas, no parafuso zonas de mistura (Figura 2.12).

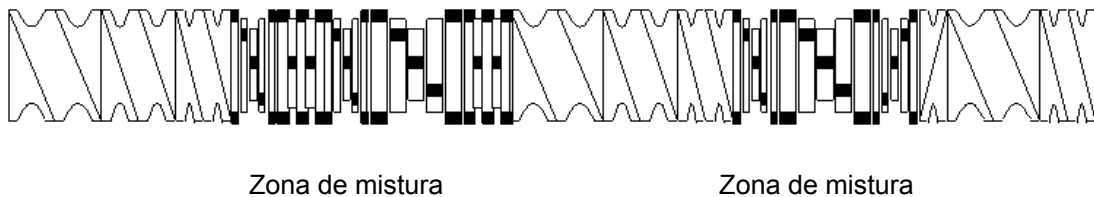


Figura 2.12 – Configuração de parafuso de extrusora dupla rosca ressaltando as zonas de misturas.
Fonte: NABAR, 2004

A fusão do material na extrusora não ocorre apenas devido ao atrito, mas também por introdução externa de calor. O sistema de aquecimento é dividido em zonas que podem ser aquecidas ou resfriadas isoladamente.

Dependendo da finalidade da extrusão vários acessórios podem ser adicionados ao processo, por exemplo: a) banho de água para resfriamento e um sistema de corte

para produção de *pellets*; b) unidade de sopro para formação de filmes tubulares ou c) sistema de calandragem para formação de filmes planos ou laminados.

2.4.2 Processamento de Filmes Planos e/ou Laminados

A produção industrial de filmes pode ser obtida por dois processos: por sopro, ou pelo processo denominado *cast* ou produção de filmes planos ou laminados

O processo de produção de filmes planos ou laminados consiste na extrusão de polímeros fundidos através de um molde chato para formar um filme ou chapa fina. Esse filme é seguidamente, conduzido na superfície de um rolo de resfriamento (revestido de cromo). O filme esfria imediatamente e suas bordas são aparadas antes da bobinagem. A Figura 2.13 apresenta foto do sistema de calandragem adaptado à extrusora para produção de filmes planos ou laminados, em escala laboratorial.



Figura 2.13 – Sistema de calandragem para formação de filmes planos ou laminados.

Fonte: foto do equipamento utilizado no presente trabalho.

Devido à capacidade de esfriamento rápido, o filme plano geralmente tem melhor aparência do que a do filme de sopro e pode ser produzido em linhas de velocidades mais alta, com pequena variação de espessura (CABRAL *et al.*, 1984). Contudo, tem a desvantagem de maior índice de resíduos por conta do aparo das bordas e pouca orientação do filme no sentido perpendicular.

2.4.3 Processamento de Plásticos por Injeção em Molde

A injeção é o principal processo de fabricação de peças de plásticos. Cerca de 60% de todas as máquinas de processamento de plásticos são injetoras. Com elas podem ser fabricadas peças desde miligramas até 90kg. A injeção classifica-se como um processo de moldagem. A figura 2.14 apresenta os principais componentes de uma injetora de parafuso móvel, e a figura 2.15 mostra um esquema do processo de injeção em moldes (MICHAELI *et al.*, 1995).

As vantagens desse processo consistem em:

- Passagem direta de material fundido para peça pronta;
- Não é necessário nenhum ou apenas pouco retrabalho da peça;
- Processo totalmente automatizável;
- Elevada produtividade;
- Excelente qualidade da peça acabada.

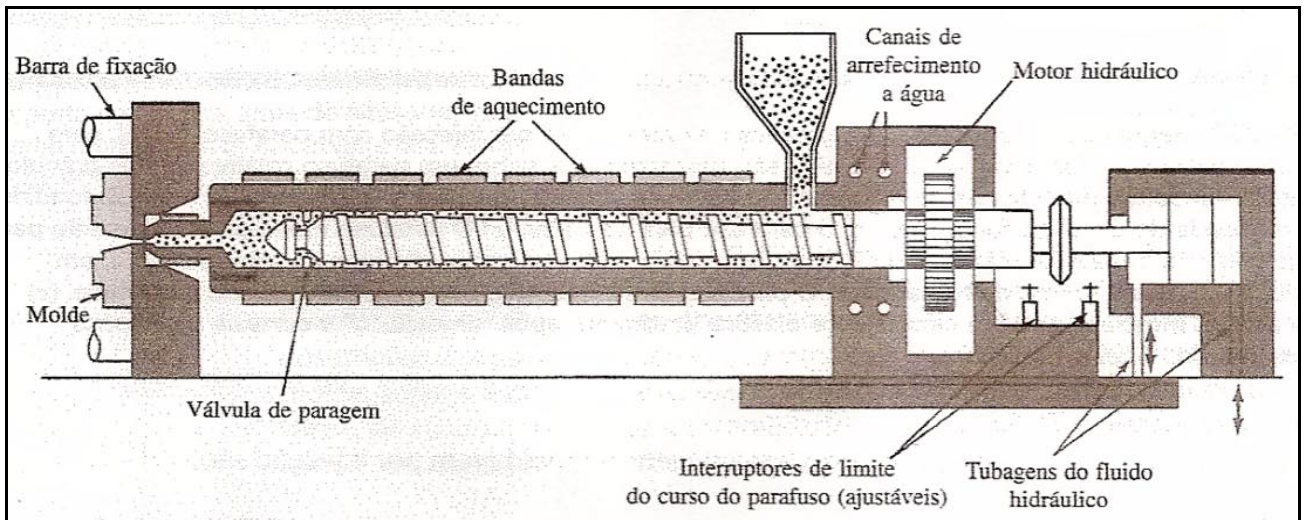


Figura 2.14 - Secção de uma máquina de moldagem por injeção, com parafuso móvel.
Fonte: SMITH, 1996.

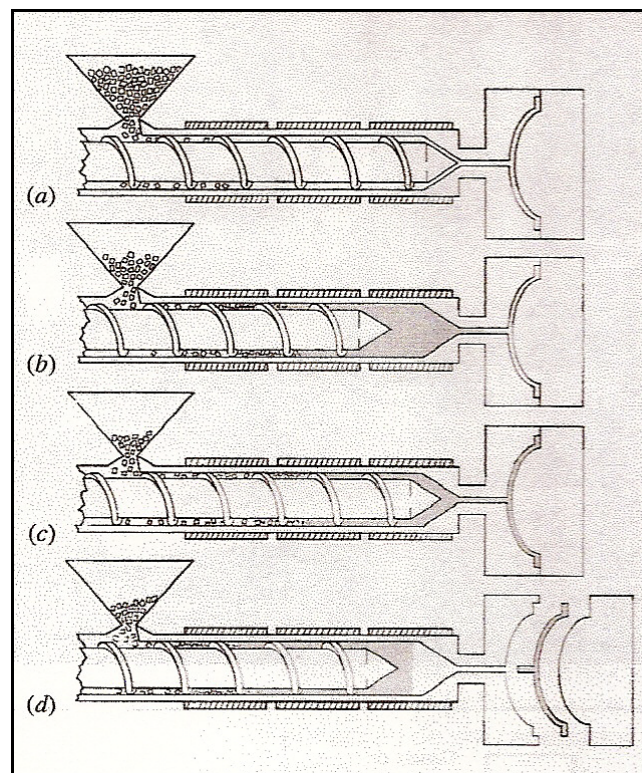


Figura 15 – Sequência de operações do processo de moldagem por injeção com parafuso móvel: a) Plastificação b) Injeção do termoplástico ao molde c) Resfriamento do molde e d) Desmoldagem e extração.

Fonte: SMITH, 1996.

2.4.4 Processamento de Bioplásticos por Termoformagem

A termoformagem é a transformação do plástico sob ação do calor e força. O processamento é feito em materiais semi-manufaturados, laminados ou placas com espessura entre 0,1 e 12 mm. Como só os termoplásticos podem ser levados, por aquecimento, do estado fixo até o elástico, somente estes materiais podem ser termoformados (Figura 2.16) (MICHAELI *et al.*, 1995).

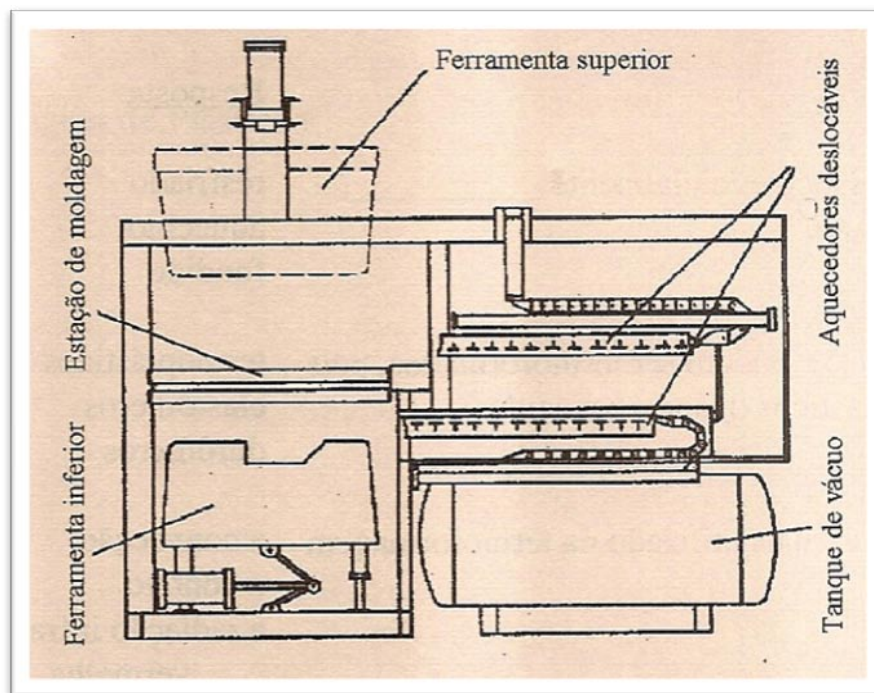


Figura 2.16 –Esquema da estação de termoformagem de escala laboratorial.
Fonte: MICHAELI *et al.*, 1995.

O processo ocorre em três etapas: aquecimento, moldagem e resfriamento. Na primeira etapa o material é preso no suporte e aquecido. O sistema de aquecimento pode ser por convecção, por contato ou por infra-vermelho. Na segunda etapa o

material aquecido é levado através do suporte sobre o molde. A última etapa inicia assim que o material encosta na superfície fria do molde (Figura 2.17) (MICHAELI *et al.*, 1995).

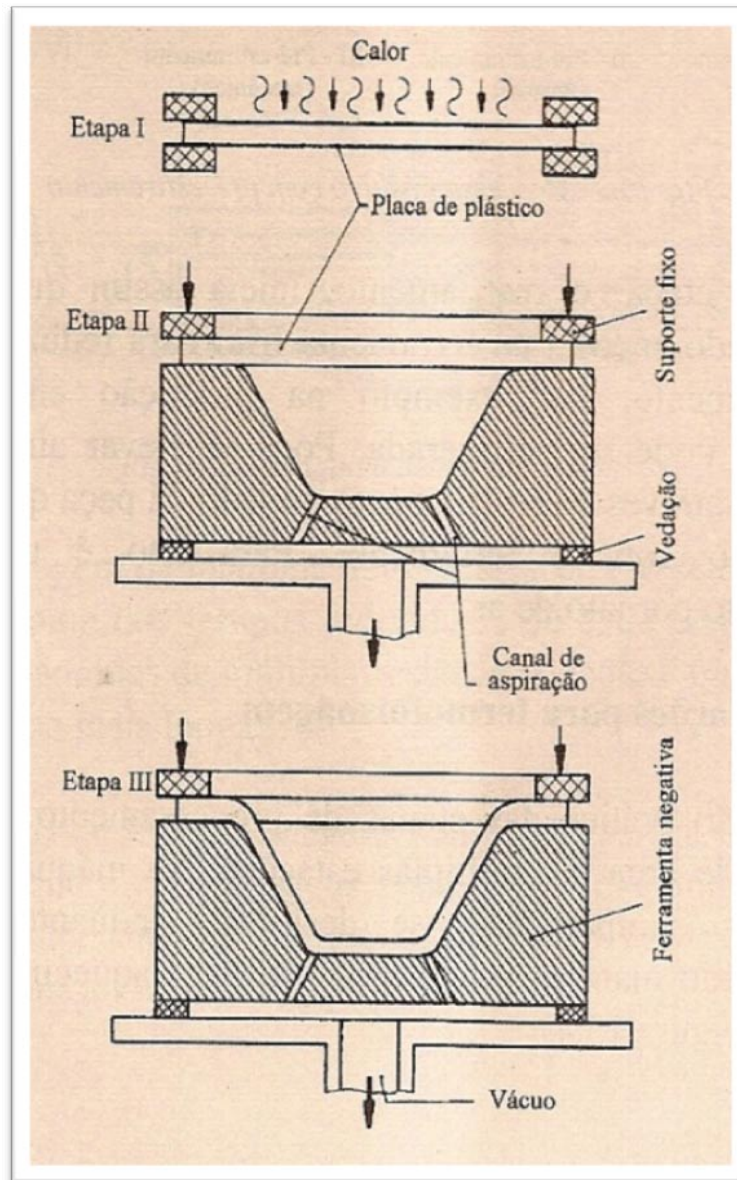


Figura 2.17 – Esquema do processo de formação do molde.
Fonte: MICHAELI *et al.*, 1995.

2.5 CARACTERIZAÇÃO DE BIOMATERIAIS

Na escolha dos materiais biodegradáveis para a produção de biofilmes deve-se levar em consideração as propriedades funcionais dos mesmos e as características do alimento no qual os filmes serão aplicados.

2.5.1 Propriedades Mecânicas

A maioria dos plásticos é utilizada devido às suas propriedades mecânicas e baixo custo. Por essa razão as propriedades mecânicas podem ser consideradas as mais importantes de todas as propriedades dos polímeros para a maioria das aplicações (NIELSON & LANDEL, 1994). As propriedades mecânicas de biomateriais são características importantes para sua utilização como embalagem para alimentos, devido ao manuseio a que estão sujeitos os produtos durante a distribuição e comercialização.

As propriedades mecânicas dos filmes dependem da natureza do material filmogênico e de sua estrutura de coesão, a qual está relacionada com a aptidão do polímero em formar ligações fortes e/ou numerosas em nível molecular. Em resumo, as propriedades mecânicas dos filmes dependem da formulação, do processo de obtenção, modo de aplicação e da espessura.

As propriedades de tração são úteis para identificação e caracterização de filmes flexíveis e materiais rígidos (injetados em moldes), com aplicação no desenvolvimento, na especificação e na avaliação da qualidade desses

materiais. Expressam a resistência do material à deformação por alongamento quando submetido à tração, solicitação característica das máquinas de acondicionamento, dos processos de conversão (impressão, laminação) e do manuseio de embalagens.

Valores de propriedades mecânicas, tais como resistência a tensão, módulo de elasticidade, alongação, entre outros, podem servir como base de comparação do desempenho mecânico dos diferentes polímeros, assim como para avaliação dos efeitos decorrentes da modificação do polímero-base (reforços, cargas, aditivos, plastificantes), para especificações, etc (CANEVAROLO, 2003). Estes valores de propriedades mecânicas são obtidos através de ensaios mecânicos padronizados, a partir de testes de perfuração, tração e testes de impacto. Os principais ensaios são de acordo com ASTM D-4332 e ASTM D-882-91. A figura 18 apresenta uma curva característica da relação resistência à tração versus deformação de filmes flexíveis.

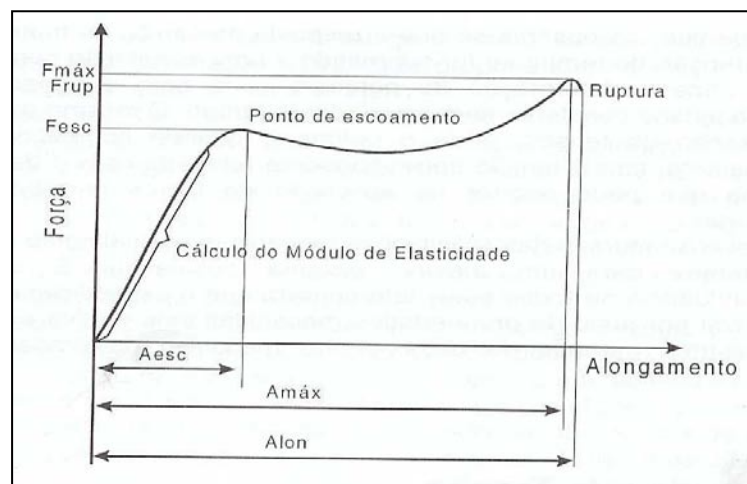


Figura 2.18- Curva característica da relação força de tração versus alongamento.

Fonte: SARANTÓPOULOS *et al.*, 2002.

Em função da resposta à deformação por tração, os materiais podem ser classificados em 3 tipos, como mostra a Figura 2.19: a) polímeros frágeis, b) plásticos e c) altamente elásticos (CALLISTER, 2002).

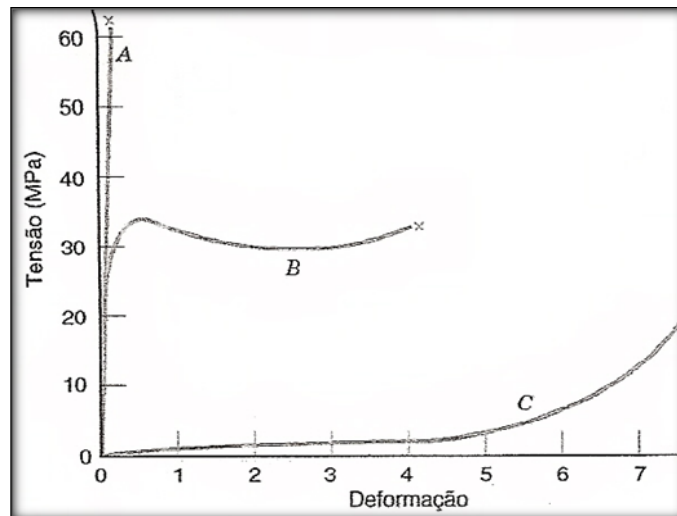


Figura 2.19 – Comportamento tensão-deformação para polímeros frágeis (curva A), plásticos (curva B) e altamente elásticos (curva C).
Fonte: CALLISTER, 2000.

Os testes de tração são os mais freqüentemente relatados em literatura. A (Tabela 2.5) apresenta valores de tensão e deformação na ruptura de alguns filmes biodegradáveis e sintéticos obtidos em teste de tração.

Os testes de perfuração têm como objetivo determinar a resistência à perfuração de filmes, tornando possível a comparação entre materiais. A resistência à perfuração é um parâmetro de qualidade para materiais utilizados no acondicionamento de produtos com pontas e/ou sujeito à danificação externa que possam alterar a embalagem durante o acondicionamento e a distribuição.

A resistência ao impacto é uma das propriedades mais requisitadas para a especificação do comportamento mecânico de polímeros, principalmente para os plásticos rígidos. A habilidade de um material polimérico suportar choques acidentais pode decidir sobre o sucesso ou o fracasso de seu uso em uma determinada aplicação. Essa propriedade depende de um número significativo de variáveis: temperatura de

ensaio, velocidade de impacto durante o teste, sensibilidade a entalhes padronizados, força com que o corpo de prova sofre o impacto, a geometria do corpo de prova, condições de fabricação do corpo de prova e condições ambientais do ensaio (CANEVAROLO, 1995).

A norma mais utilizada para testes de impacto são as normas de ensaio de impacto Izod (ASTM D256). O corpo de prova utilizado neste tipo de ensaio de impacto deve ser entalhado. A razão do entalhe no corpo de prova é a necessidade de gerar concentração de tensões localizadas na extremidade do entalhe para promover fratura frágil ao invés de fratura dúctil. Os corpos de prova são preparados através de moldagem por injeção ou usinados a partir de placas planas. A espessura varia com a norma utilizada, para a norma ASTM D256 a espessura é de 3,2mm. Os entalhes são realizados por processos de usinagem do tipo fresa. As dimensões da profundidade, ângulo de abertura e raio da extremidade são devidamente padronizados pela norma referida (CANEVAROLO, 1995).

Tabela 2.5 – Propriedades mecânicas de filmes biodegradáveis e sintéticos obtidas em teste de tração.

Filmes	Processo utilizado	Espessura	UR %	Tensão (MPa)	Modulus (MPa)	Alongamento na ruptura (%)	Referências
ATp amido de batata com alto teor de amilose Amido/glicerol/água(57:31:12)	Extrusão Mono rosca laminados	-	-	4,9±0,3	36±6,6	80±10,8	THUWALL, BOLDIZAR & RIGDAHL, 2006
ATp:PBSA (30:70) ATp (25gglicerol/75g amido mandioca)	Extrusão dupla rosca/sopro		54	5,2±0,65	52±13,8	125±16,9	SAKANAKA, 2007
ATp:PBSA(70:30) ATp (25gglicerol/75g amido mandioca)	Extrusão dupla rosca/sopro		54	6,92±1,16	3,0±1,00	324,5±59,2	SAKANAKA, 2007
ATp:PLA (27:73) ATp(36%glicerol-amido de trigo)	Extrusão dupla rosca /Injeção	3,1mm		~40	2800	>20	HUNEAULT & LI, 2007
PBAT (Eastman) (Eastar bio14766/	Extrusão			9	52	>500	AVEROUS, 2004
PBAT (BASF)	Extrusão filmes	50µm	-	35-44	-	560-710	Ficha técnica Basf Brasil www.basf.com.br
PBAT-ATPM (70:30) ATpM – amido termoplástico de mandioca modificado	Extrusão e cast filmes	0,23		8,49±0,27	86,9±4,34	534±0,27	PARAMAWATI, 2006
Amido-PHB (30:70)	<i>casting</i>	-	-	19,23	949	9,4	GODBOLE et al, 2003
PEAD	—	—	—	25,90	—	300	BRISTON, 1988
PEBD	—	—	—	12,90	—	500	BRISTON, 1988

PEAD = polietileno de alta densidade; PEBD = polietileno de baixa densidade

2.5.2 Propriedades de Barreira

A permeabilidade é definida como uma propriedade do par filme/permeado (vapor de água, oxigênio e gás carbônico), em condições definidas de temperatura, umidade relativa, espessura e diferença de pressão parcial. A permeabilidade consiste num processo de solubilização e difusão, onde o vapor se dissolve em um lado do filme e se difunde até outro lado do mesmo (McHUGH & KROCHTA, 1994) (Figura 20).

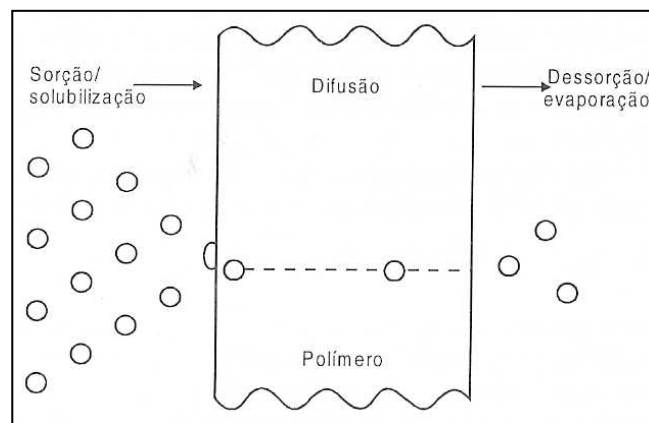


Figura 2.20 – Esquema de permeação de gases em materiais poliméricos.

Fonte: SARANTÓPOULOS *et al.*, 2002)

2.5.2.1 Permeabilidade ao vapor de água

A permeabilidade ao vapor de água (PVA) é considerada uma das propriedades de barreira de materiais e seu conhecimento imprescindível para

aplicações dos filmes em embalagens, porém não é uma propriedade restritiva. Um material muito permeável ao vapor de água poderá ser indicado para embalagens de vegetais frescos, enquanto um filme pouco permeável poderá ser indicado para produtos desidratados (SOBRAL & OCUNO, 2000).

Teoricamente, segundo a lei de difusão de Fick e a lei de sorção de Henry, a taxa de permeabilidade ao vapor de água (TPVA) deve variar com o inverso da espessura do filme e a permeabilidade ao vapor de água (PVA) deve ser constante (MARTIN-POLO *et al.*, 1992, CUQ *et al.*, 1996^a). CHEN (1995) afirma que a PVA varia exponencialmente com a espessura dos biofilmes e MALI (2002) observou que a PVA, diminuiu linearmente com o aumento da espessura dos filmes de amido de cará. Segundo PARK & CHINNAM (1995), a permeabilidade ao vapor de água pode variar com a espessura dos biofilmes devido às mudanças estruturais causadas pelo inchamento da matriz hidrofóbica, que afetam a estrutura dos biofilmes e provocam tensões internas que podem influenciar a permeação.

A PVA tende a aumentar com a adição de plastificantes hidrofílicos. Vários autores estudaram o efeito dos plastificantes sobre a PVA de biofilmes. MALI (2002); SOBRAL & OCUNO (2000) e GONTARD, GUILBERT & CUQ (1993) observaram aumento da PVA com o incremento do teor de glicerol. Em filmes hidrofílicos, a umidade relativa (UR) e a temperatura influenciam fortemente as propriedades de barreira. Ao aumentar a UR, produz-se um inchamento excessivo da matriz polimérica, que leva a um incremento na difusão das moléculas de água e, conseqüentemente, diminuem as propriedades de barreira destes materiais (BIQUET & LABUZA (1988) e KAMPER & FENNEMA (1984)). Com o aumento da temperatura, a permeabilidade ao vapor de água também aumenta, e estas variações são dependentes da umidade (DONHOWE & FENNEMA, 1993).

Na tabela 2.6 encontra-se valores de literatura para permeabilidade ao vapor de água de filmes e blendas a partir de amido.

Tabela 2.6 – Permeabilidade ao vapor de água de filmes biodegradáveis e sintéticos

Material	Espessura (mm)	Condições UR (%)	Método utilizado	Permeabilidade $\text{g}\cdot\text{m}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$	Referências
Amido de milho com alto teor de amilose/glicerol (100g/20g)	0,2		ASTM D-96	$\sim 4 \times 10^{-10}$	BERTUZZI et al, 2006
Amido de milho com alto teor de amilose/glicerol (100g/30g)	0,2		ASTM D-96	$\sim 4,7 \times 10^{-10}$	BERTUZZI et al, 2006
PBAT F BX 7011	50 μm	-	DIN 53122	170 ($\text{g}/\text{m}^2\cdot\text{d}$)	Ficha técnica Basf Brasil www.basf.com.br
Amido de mandioca	0,120	75-0	ASTM D-96	$5,9 \times 10^{-12}$	NAKAGAWA, 2003
Amido termoplástico de mandioca – PBAT (30:70)	0,23	-		$15,6 \pm 0,78 (\text{g}/\text{m}^2\cdot\text{d})$	PARAMAWATI, 2006
Celofane	-	90-0		$8,4 \times 10^{-11}$	SHELHAMMER & KROCHTA, 1997
PEBD ^a	0,025	95-0		$3,6 \times 10^{-13}$	SHELHAMMER & KROCHTA, 1997

^a PEBD = polietileno de baixa densidade.

2.5.3 Propriedades Térmicas

A análise térmica de materiais é definida como um grupo de técnicas nas quais uma propriedade física da substância e/ou de seus produtos de reação é medida em função da temperatura, enquanto essa substância é submetida a uma programação controlada de temperatura e sob uma atmosfera especificada (CANEVAROLO, 2003 apud IONASHIRO, 1980, WENDLANDT, 1986 HAINES, 1995).

As duas principais técnicas mais utilizadas na caracterização de materiais são a termogravimetria (TG) e a calorimetria diferencial de varredura (DSC).

2.5.3.1 Termogravimetria (TG)

A termogravimetria (TG) é uma técnica da análise térmica na qual a variação da massa da amostra (perda ou ganho) é determinada em função da temperatura e/ou tempo, enquanto a amostra é submetida a uma programação controlada de temperatura. Esta técnica possibilita conhecer as alterações que o aquecimento pode provocar na massa das substâncias, permitindo estabelecer a faixa de temperatura em que começam a se decompor, acompanhar o andamento da desidratação e de reações de oxidação, combustão, decomposição, etc. (CANEVAROLO, 2003).

No método termogravimétrico convencional ou dinâmico, são registradas curvas de massa da amostra em função da temperatura ou do tempo. Essas curvas são denominadas curvas termogravimétrica ou simplesmente, curvas TG. Na termogravimetria derivada (DTG), as curvas são registradas a partir das curvas TG e

correspondem as derivadas primeiras da variação de massa em relação ao tempo (Figura 2.21).

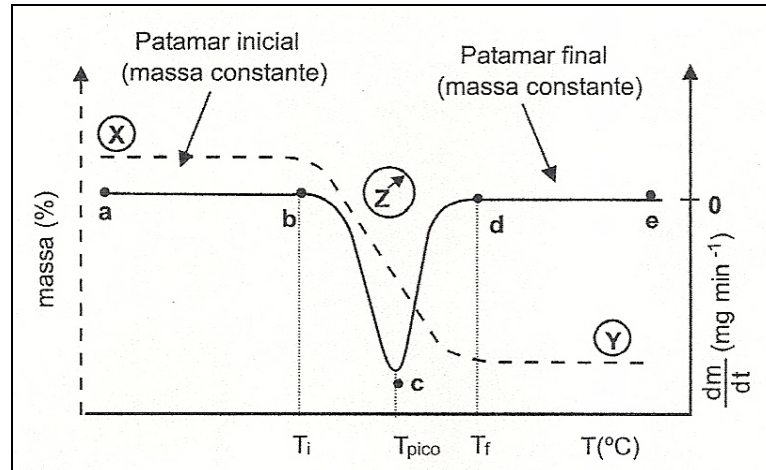


Figura 2.21- Curvas TG (linha tracejada) e DTG (linha sólida) de uma reação de decomposição térmica que ocorre em uma única etapa.

Fonte: CANEVAROLO, 2003.

Em materiais poliméricos, a TG tem sido largamente utilizada para avaliação da estabilidade térmica, determinação de conteúdo de umidade e de aditivos, estudos de cinética de degradação, análise de sistemas de copolímeros, estabilidade a oxidação e temperaturas de degradação.

2.5.3.2 Calorimetria diferencial de varredura (DSC)

A calorimetria diferencial de varredura (DSC) é usada para determinação das propriedades de biomateriais como temperatura de transição vítrea e temperatura de fusão (MALI, 2002, AVEROUS 2004) e em outros trabalhos na determinação da cristalinidade relativa a partir dos calores de fusão (SAKANAKA, 2007, ROSA, LOPES e CALIL, 2005 e MARTIN E AVEROUS, 2001).

Os eventos térmicos que geram modificações em curvas de DSC podem ser transições de primeira e de segunda ordem. As transições de primeira ordem apresentam variação de entalpia, endotérmicas (fusão, perda de massa, dessorção e reações de redução) ou exotérmicas (cristalização, reações de polimerização, oxidação, degradação oxidativa, adsorção entre outros) e originam a formação de picos. As transições de segunda ordem caracterizam-se pela variação de capacidade calorífica, porém sem variação de entalpia. Assim estas transições não geram picos, apresentando-se como um deslocamento da linha base em forma de S, tendo como exemplo característico e a transição vítrea (CANEVAROLO, 2003) (Figura 2.22).

A transição vítrea é uma transição de fase, que ocorre em materiais amorfos, ao serem submetidos a uma determinada temperatura, denominados de temperatura de transição vítrea (T_g) (PEREZ, 1994). Quando submetidos a temperaturas acima da T_g , os materiais se encontram no estado gomoso, abaixo da T_g , no estado vítreo. Com o aumento da temperatura, ao se ultrapassar a T_g , as cadeias da macromolécula têm a sua mobilidade aumentada e, neste ponto, as propriedades físicas e mecânicas sofrem uma forte mudança no comportamento.

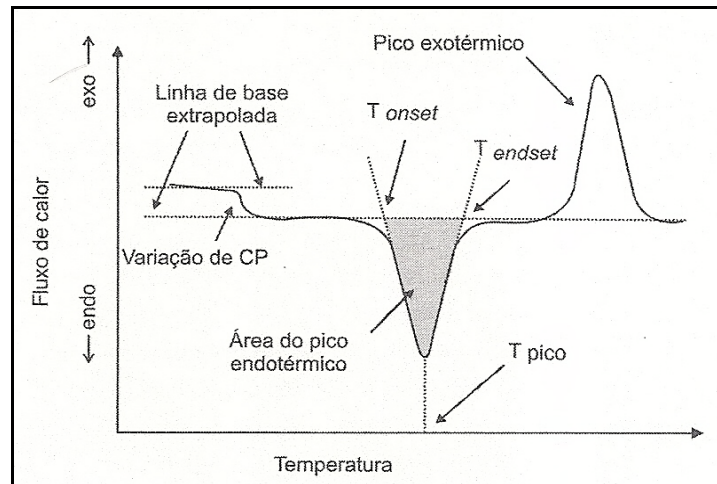


Figura 2.22 – Apresentação de uma curva DSC.
Fonte: CANEVAROLO, 2003.

2.5.4 Microestrutura

A estrutura e microestrutura dos plásticos estão intimamente ligadas com a composição e processo de formação dos materiais, sendo esta a principal determinante das propriedades dos mesmos.

A metodologia mais empregada na caracterização de materiais é a microscopia eletrônica de varredura (MEV) devido às várias características desta técnica: a) permite o estudo de estruturas superficiais ou internas; b) as imagens têm alta profundidade de foco, que significa obter diferentes relevos da superfície; c) são imagens tridimensionais e, portanto, mais fácil de interpretar que as imagens de projeção da microscopia de transmissão; d) produz imagens de alta resolução e e) métodos simples de preparação das amostras e obtenção de imagens (CANEVAROLO, 2003).

Neste trabalho foi utilizada a microscopia eletrônica de varredura ambiental (ESEM ou MEVA), a qual tem a vantagem em relação a MEV tradicional, de analisar a amostra diretamente sem nenhum recobrimento, devido à alta pressão utilizada, o que

impede a secagem drástica de materiais sensíveis à perda de água como a maioria de amostras biológicas.

2.5.5 Determinação da Redução de Massa Molar.

Vários métodos podem ser utilizados para avaliar a perda de massa molar nos processos de extrusão reativa e processos de produção de blendas e/ou compósitos poliméricos. A seguir serão descritos os dois métodos utilizados neste trabalho.

2.5.5.1 Viscosidade de soluções diluídas

Quando uma molécula pequena é dissolvida em um solvente, a viscosidade do sistema varia pouco. No caso de macromoléculas, as cadeias maiores assumem conformações variadas e cada segmento desta cadeia pode estar sob ação de velocidades de fluxo diferentes, acarretando um aumento significativo da viscosidade, mesmo em soluções diluídas (LUCAS, SOARES e MONTEIRO, 2001).

Para determinar a viscosidade intrínseca ou número de viscosidade limite, é necessário determinar a viscosidade reduzida ou inerente em diferentes concentrações e extrapolar a concentração zero. A tabela 2.7 apresenta definições dos tipos de viscosidade e suas relações.

Tabela 2.7- Definições de tipos de viscosidade e suas respectivas relações.

Nome	Definição	Equação que define	Unidade
Viscosidade relativa	Relação entre a viscosidade da solução e do solvente puro	$\eta_r = t/t_0$	adimensional
Viscosidade específica	Razão entre o tempo de escoamento da solução e do solvente puro.	$\eta_{sp} = \eta_r - 1 = t - t_0 / t_0$	adimensional
Viscosidade Reduzida	Relação entre a viscosidade específica e a concentração da solução.	$\eta_{red} = \eta_{sp} / C$	dL/g
Viscosidade inerente	Razão entre o logaritmo da viscosidade relativa e a concentração da solução	$\eta_{inh} = \ln \eta_r / C$	dL/g

Onde: η_r = Viscosidade relativa, η_{sp} = Viscosidade específica; η_{red} = Viscosidade reduzida; η_{inh} = viscosidade inerente; t = tempo de escoamento da solução e t_0 = tempo de escoamento do solvente puro; \ln = logaritmo neperiano e C = concentração da solução.

Fonte: Adaptado de LUCAS, SOARES E MONTEIRO, 2001.

Para se determinar a viscosidade intrínseca, viscosímetros capilares (Figura 2.23) devem ser selecionados de modo a apresentarem diâmetro capilar que permita tempo de escoamento na faixa de 100 a 150 segundos. A medição deve ser realizada em banho termostatizado com agitação.



Figura 2.23 – Viscosímetro capilar.

De acordo com a equação de Mark-Houwink (Equação 2.1), a viscosidade intrínseca de soluções diluídas é proporcional a massa molar de polímeros dissolvidos e depende de duas constantes K e a , que são dependentes da interação polímero/solvente.

$$[\eta] = KM^a$$

Equação 2.1

Sendo a viscosidade intrínseca proporcional a massa molar de polímeros, diminuição de massa molar de um polímero irá causar diminuição na viscosidade. Deste modo, estudos de mudança na massa molar durante processos de extrusão e reações podem ser acompanhados por essa técnica.

2.5.5.2 Espalhamento de luz dinâmico (DLS)

Espalhamento de luz dinâmico é descrito pela sigla DLS, a qual tem origem nas iniciais do nome em inglês “dynamic light scattering”. A técnica de DLS permite a rápida obtenção do coeficiente de difusão de macromoléculas em solução, a partir da análise da distribuição de frequência das flutuações na intensidade de luz espalhada em uma dada direção, isso é, detecção da intensidade da luz em um ângulo fixo. Estas flutuações originam-se das variações no índice de refração dentro do volume de espalhamento devido ao movimento browniano das partículas, sendo assim, as flutuações locais dentro do volume de espalhamento estão relacionadas com o coeficiente de difusão aparente e o vetor de onda do espalhamento. (LUCAS, SOARES e MONTEIRO, 2001).

O experimento de DLS consiste em obter flutuações do sinal de intensidade de luz espalhada com o tempo e realizar cálculos de correlações. Extrapolando-se os valores de coeficiente de difusão para concentração zero, obtêm-se o valor de D_0 e utilizando a equação de Stokes-Einstein (2.2) é possível determinar o raio hidrodinâmico (R_H), onde, K é a constante de Boltzmann, T é a temperatura absoluta e η é a viscosidade do solvente e D_0 é o coeficiente de difusão translacional puro.

$$R_H = KT/6\pi\eta D_0$$

Equação 2.2

O equipamento de espalhamento de luz dinâmico calcula o raio hidrodinâmico de cada amostra e a distribuição é calculada baseada na porcentagem de massa de

várias frações de acordo com o valor do raio hidrodinâmico. Deste modo, o raio hidrodinâmico pode ser diretamente relacionado à massa molar. Portanto, estudando o raio hidrodinâmico de diferentes amostras podemos correlacionar com a massa molar, considerando que maiores raios hidrodinâmicos correspondem a maiores moléculas e, portanto, maior massa molar.

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CAPÍTULO 3 – EFFECT OF MALEATED POLY(BUTYLENE ADIPATE CO-TEREPHTHALATE) (PBAT) AS A COMPATIBILIZER BETWEEN NATURAL FIBERS AND PBAT.

ABSTRACT

Composites of high cost biodegradable synthetic aromatic polyester with low cost biofibers are an alternative for the production of biodegradable plastics. The objective of this paper was to investigate the effect of maleated poly(butylene adipate-co-terephthalate) (PBAT) as a compatibilizer between PBAT and natural fibers (oat hulls, wood pulp and cellulose). A three-step process was used in the production of the composites: (a) maleation of PBAT using a free-radical initiator and characterization of maleated polyester (effect of MA percentage 2, 3 or 4%), grafting determination by titration, intrinsic viscosity (IV), thermal analysis (TGA) and FTIR; (b) blending PBAT and MA-*g*-PBAT/fibers (55:45); and (c) injection molding of the blends. The maximum MA grafted on the PBAT backbone was 1.5% by weight. This MA grafting yield was sufficient to successfully compatibilize the polyester and natural fibers. The maleation of the polyester proved to be very efficient in promoting strong interfacial adhesion with natural fibers by melt blending and injection molding processing. The maleated polyesters had lower intrinsic viscosity (IV) as compared to the original polyester. The maleation of PBAT increased the tensile mechanical properties (stress at break, Young's modulus and elongation) and impact strength of the biocomposites. The stress at break increased by 42.5%, 59.5% and 65.7% for the respective fibers: oat hulls, wood pulp and cellulose, in comparing the composites of fiber-MA-*g*-PBAT with those of fiber-PBAT. The mechanical properties of the different formulations showed the effect of cellulose content in the natural fiber (oat hulls (~31%), wood pulp (~73%) and cellulose (~93%)) composites. In general, higher percentages of cellulose resulted in better interaction between fiber and the polymeric matrix.

Key-words: Reactive extrusion, biodegradable, compatibilizer, maleic anhydride, biofibers.

3.1 INTRODUCTION

Conventional polymers such as polyethylene and polypropylene persist for many years after disposal. For this reason, these polymers seem inappropriate for application in plastics that are used for short time periods and then disposed of, such as food packaging. Furthermore, plastics are often soiled by food and other biological substances, making physical recycling of these materials impractical and generally undesirable. In contrast, biodegradable polymers disposed in bioactive environments are degraded by the enzymatic action of microorganisms.¹

Composite materials may be defined as materials made up of two or more components and consisting of two or more phases. Such materials must be heterogeneous at least on a microscopic scale. Composite materials may be divided into three general classes: (a) particulate filled materials consisting of a continuous matrix phase and a discontinuous filler phase made of discrete particles; (b) skeletal or interpenetration network composites consisting of two continuous phases and (c) fiber-filled composites.² In this last class, the use of fiber, synthetic or natural, has the role of improving mechanical properties while the matrix works to promote the fiber linkage. In this work, the term biocomposites is used meaning biodegradable composites.

During the last few years many efforts have been made to investigate the suitability of natural fibers as reinforcing components for thermoplastic and injection moldable materials because of their low density and ecological advantage. They open up further possibilities in waste management as they are biodegradable and therefore can lead to highly functional composite materials if used in combination with biodegradable thermoplastic polymers.³

Advantages of biofibers over traditional reinforcing materials such as glass fibers, talc and mica are ⁴: low cost, low density, high toughness, acceptable specific strength properties, reduced tool wear, reduced dermal and respiratory irritation, good thermal properties, ease of separation, enhanced energy recovery and biodegradability.

Cellulose is the most abundantly occurring natural polymer on earth and is an almost linear polymer of anhydroglucose. Because of its regular structure and array of hydroxyl groups, it tends to form strong hydrogen bonded crystalline microfibrils and fibers. Its most familiar use is associated with rigid materials: paper, cardboard or trays in packaging applications. Cellulose is normally the main component of the natural fibers.

The current biodegradable polymers may be divided into three categories, based on whether they are polymerized biologically or synthetically being: a) biosynthetic, b) semi-biosynthetic and (c) chemo-synthetic polymers.⁵ Poly(butylene adipate-co-terephthalate) (PBAT), a chemo-synthetic biodegradable aliphatic aromatic copolyester under the brand name Ecoflex[®], is made by condensing 1,4-butanediol with 1,4-benzenedicarboxylic acid (terephthalic acid) and hexanedioic acid (adipic acid). It is an important biodegradable polymer, which has been used in several applications, such as in film blended with thermoplastics starch⁶, blends with biobased polymers like Poly(lactide)⁷, and in lignocellulosic-based composites.^{8,9}

High levels of fibers and their incompatibility with biodegradable polyesters lead to poor physical and mechanical properties. An effective way to improve the compatibility between fibers and the polyester matrix is to functionalize the polyester matrix by grafting onto it highly reactive functions. These grafted reactive functions can react with the hydroxyl groups of the cellulose to form covalent bonds; and thus, they provide better control of the size of phase and strong interfacial adhesion. Anhydride functionality can be incorporated into a polymer chain by copolymerization or grafting of

anhydrides like maleic anhydride. The reactive extrusion technique has proved to be an effective way to introduce a variety of functional groups onto the surface of natural polymers.^{10,11}

Maleic anhydride was first used as a monomer to graft onto non-biodegradable polymers such as polyethylene, polypropylene and other polymers.^{11,12} Earlier results from research conducted by Bhattacharya and co-workers¹³⁻²³ on maleation of biodegradable polymers such as PCL, PBSA, poly(butylene succinate) (PBS) and Eastar Bio[®] co-polyester; and by Narayan and co-workers^{24,25} on maleation of PLA indicated that blends of anhydride functional polymers and starch could lead to products with useful end properties.

The use of maleated polymers to increase the fiber–matrix compatibility was first reported in traditional polymers polyolefins and such copolymers as styrene butadiene styrene butadienestyrene (SBS) and were employed in the preparation of wood fiber composites.^{10,26} Many other authors used maleated polypropylene composites.^{4, 27-34} It was reported that the fiber–matrix interfacial adhesion increased, and the mechanical properties of the composites improved after matrix modification.

The objective of this work was to investigate the effect of maleated PBAT as a compatibilizer between natural fibers (oat hulls, wood pulp and cellulose) and PBAT in terms of mechanical properties of the biocomposites.

3.2 MATERIAIS AND METHODS

3.2.1 Materials

Three different natural fibers were used: oat hulls, wood pulp and cellulose. Oat fiber was obtained from SL Alimentos (Mauá da Serra-PR, Brazil), wood fiber from Pinhopo Moagem de Madeira LTDA (Ponta Grossa-PR, Brazil) and cellulose fiber was obtained from Kayocell (USA). Poly(butylene adipate-co-terephthalate (PBAT)(film grade F BX 7011), an important biodegradable aliphatic-aromatic co-polyester, was purchased from BASF Corporation, under the trade name Ecoflex[®]. PBAT is made by condensing 1,4-butanediol with 1,4-benzenedicarboxylic acid (terephthalic acid) and hexanedioic acid (adipic acid) (Figure 3.1). 2,5-dimethyl-2,5-di-(*tert*-butylperoxy) hexane (Luperox 101) and maleic anhydride (MA) were purchased from Sigma-Aldrich Chemical Company (St. Louis, MO).

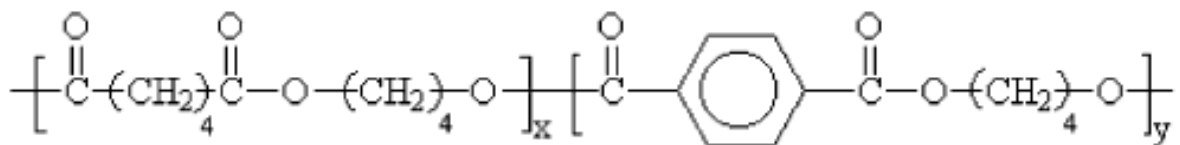


Figure 3.1 - Poly(butylene adipate-co-terephthalate) (PBAT).

3.2.2 Processing

The biocomposites production was carried in a three-step experimental process: (a) Maleation of biodegradable polyester (PBAT); (b) blending of PBAT and MA-g-PBAT with natural fibers and (c) molding injection of the composites. (Figure 3.2).

The details of the experimental protocols to prepare the maleated PBAT, PBAT-fibers and MA-g-PBAT-fibers composites are elucidated.

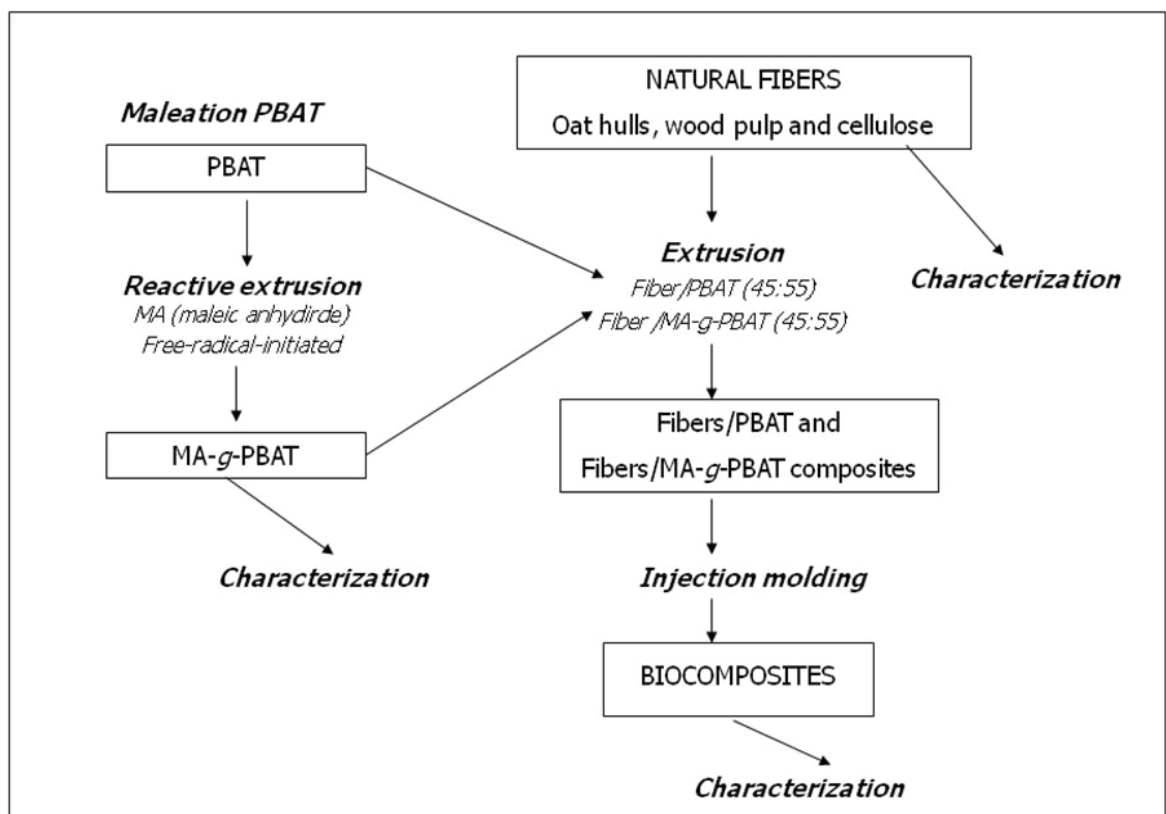


Figure 3.2 – Biocomposites production processing.

3.2.2.1 Maleation PBAT

The extruder used in the maleation of the polyester was a Century ZSK-30 twin-screw co-rotating extruder with a screw diameter of 30 mm, an L/D of 40. The temperature profile during extrusion was 20/125/145/165/185/185/185/185/185/180°C. The MA, free-radical-initiator (Luperox 101) and PBAT were mixed in a vented cabinet and put in a covered feeder set at a particular speed of 120 rpm. The screw speed was maintained at 100 rpm. Vacuum was applied at the vent port to remove the un-reacted maleic anhydride/water mixture. The effect of maleic anhydride concentration in the maleation processing of polyester was analyzed using three percentages of MA 2, 3 and 4%, keeping the concentration of free-radical initiator fixed at 0.5%.

3.2.2.2 Maleated PBAT Characterization

3.2.2.2.1 *Extent of maleation*

The extent of maleation for samples grafted with MA was determined by titration, which was a modification of the procedure developed by Li et al.³⁵ The un-reacted MA was removed by drying the samples at 85°C under vacuum. After dissolution of 1g of the dried sample in 100 mL of chloroform, 1 mL of hydrochloric solution in water (1 M) was added to hydrolyze anhydride functions into carboxylic acid functions. The solution was vigorously stirred for 30 minutes. Then, PBAT grafted with maleic acid moiety was

selectively recovered by precipitation into methanol, filtration and drying at 85°C in a vacuum oven overnight. The resulting dried and so-purified MA-*g*-PBAT was then dissolved in chloroform, and the solution was titrated to a phenolphthalein end point using potassium hydroxide in methanol. Under these conditions, the MA-*g*-PBAT was completely soluble, and did not precipitate during the titration. The MA content was calculated using a calibration curve. For determination of total MA present in the sample, the maleated polymer was dried, solubilized in chloroform and titrated to end point using potassium hydroxide in methanol using the same method utilized for the purified MA-*g*-PBAT.

3.2.2.2.2 *Intrinsic viscosity (IV)*

The intrinsic viscosity measurements were carried out at 25°C in a constant temperature bath using Cannon Ubbelohde viscometer (size 1B). PBAT and MA-*g*-PBAT samples were dissolved in chloroform and diluted to required concentrations. Determination of the intrinsic viscosity of the samples was done by plotting a Huggins plot of reduced viscosity and inherent viscosity versus concentration of the sample.⁴⁰ The y-intercept of the reduced viscosity and inherent viscosity lines was taken as the intrinsic viscosity of the sample. As the y-intercept of both lines was not the same, the intrinsic viscosity was taken as the average of the two values.

3.2.2.2.3 *Thermogravimetric analysis (TGA)*

A high resolution Thermal Gravimetric Analyzer (TGA) 2950 from TA Instruments was used to determine the degradation temperature of the original PBAT and MA-g-PBAT. Nitrogen was used as the purge gas with the sample purge being 60 ml/min and the balance purge being 40 ml/min. The sample was heated to 700°C at the rate of 10 K per min.

3.2.2.2.4 *Fourier transform infrared spectroscopy (FTIR)*

The FTIR spectra of PBAT and MA-g-PBAT thin films were scanned from 400 cm^{-1} to 4000 cm^{-1} using a Perkin Elmer Model 2000 FTIR. Polymer samples were dissolved in dichloromethane and cast to obtain a thin film. They were then dried and scanned to obtain the spectra.

3.2.2.3 Chemical composition of natural fibers

Ash, protein fat and humidity were determined according to the standard AOAC (1995) methods.³⁶ The cell wall composition was determined in a six-step method: 1° Step – Extraction of soluble sugars (six extractions in ethanol 80%, during 20 min at 80°C); 2° Step – Starch removal with DMSO at 90% for 24h; 3° Step – Pectin extraction - in ammonium 0.5% (p/v), dialysis and liofilization.; 4° Step – Lignin, in NaClO and

acetic acid, dialysis, lyophilization; 5° Step – Hemicellulose: three extractions in NaOH (0.1M, 1M and 4M) in NaBH₄; dialysis and lyophilization. 6° Step – Cellulose updegraff reagent (5% nitric acid, 15% acetic acid at 100°C for 90 min), lyophilization. Three samples of each natural fiber (500mg) were analyzed in triplicate.

3.2.2.4 PBAT and MA-g-PBAT composites

Biodegradable graft copolymers of PBAT and natural fiber were blended by extrusion processing (Table 3.1). The matrix was neat PBAT in one case and maleated PBAT (MA-*g*-PBAT) in another. PBAT and MA-*g*-PBAT were separately blended with natural fibers in a twin-screw co-rotating extruder. The maximum grafting percentage of maleic anhydride on the polyester was determined, and that particular formulation was then blended with natural fibers in ratios of 55:45. These blends were used as injection molding processing aids in the production of biocomposites. Vacuum was applied at the vent port to remove any water (if present) or un-reacted maleic acid that was not removed during maleation processing.

Table 3.1 – Extrusion Temperature Settings

Temperature (°C)	Zone1	Zone2	Zone3	Zone4	Zone5	Zone6	Zone7	Zone8	Zone9	Die
	15	95	125	150	160	165	170	170	170	150
Motor speed	100 rpm									
Feeder speed	120 rpm									

3.2.2.5 Injection molding procedure

Tensile bars were injection molded using a Cincinnati Milacron VSX85 model equipped with a mold making ASTM type IV bars (16.51 X 1.19 x 0.32 cm). Processing temperatures during molding were different for each natural fiber source (Table 3.2).

Table 3.2 – Injection Molding Temperature Settings.

Samples	Temperature setting (°C)			
	Zone 1	Zone 2	Nozzle	Mold
PBAT	150	150	160	27
Oat hulls fiber blends	154	154	160	27
Wood fiber blends	165	165	171	27
Cellulose fiber blends	182	182	187	27

3.2.2.6 Mechanical testing

The tensile samples of PBAT and fiber blends with PBAT and MA-*g*-PBAT were conditioned as recommended by ASTM D-4332³⁷, in a constant environment room at $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ RH for at least 40 hours before testing. At least five samples were tested for each blend and property.

Tensile tests were performed on tensile bars using UTS Mechanical Testing Equipment Model SFM-20 fitted with a 100 lb load cell, following the ASTM D-638-90³⁸ and Izod impact tests were performed using the ASTM D-256-90 standard.³⁹ Each data point on the graph represents an average of five points.

3.2.2.7 Statistical analysis

One control sample, PBAT was tested to evaluate the effects of natural fibers and maleated PBAT on mechanical properties of the biocomposites. Analysis of variance (ANOVA), Tukey mean comparison test ($p \leq 0.05$) and regression analysis were performed employing Statistica software (Statsoft, Oklahoma – USA).

3.3 RESULTS AND DISCUSSION

The results of the various aspects of PBAT-fibers and MA-g-PBAT-fibers graft copolymers will be presented and discussed: chemical composition of natural fibers; maleation of PBAT with determination of MA grafting on the polyester along with intrinsic viscosity and thermal (TGA) analyses; and mechanical properties of biocomposites produced by injection molding processing.

3.3.1 Fiber Chemical Composition

The oat hulls and wood pulp fibers are two alternatives for use in biocomposite production due to their low price and abundance. These two fibers are residue from the oat processing and wood industries, respectively. The cellulose fibers are an industrial product obtained from wood pulp. The three raw materials used showed difference in chemical composition. The main difference among the fibers is the cellulose content; oat hulls have 31% of cellulose and 49% of hemicellulose, wood pulp has approximately 73% of cellulose and cellulose fiber has 93% of cellulose (Table 3.3).

Table 3.3 – Chemical Composition of Natural Fibers.

Composition	Oat hulls	Wood fiber	Cellulose fiber
Protein	0.1±0.01	0.12±0.01	0.15 ± 0.03
Lipids	0.2±0.03	0.10±0.02	0.13 ± 0.02
Total carbohydrates	96.1	98.7	98.7
Soluble sugar	0.1	0.1	0.1
Lignin	11.4	9.4	0.3
Pectin	4.6	5.4	2.3
Hemicellulose	49.2	12.2	4.4
Cellulose	30.8	71.7	91.6
Ash	3.7±0.03	1.4±0.03	1.1 ± 0.06

3.3.2 Maleated PBAT Characterization

The maleated and neat PBAT samples were characterized on the basis of extent of maleation, intrinsic viscosity (IV) and thermal analysis (TGA).

3.3.2.1 Extent of maleation

A calibration curve was constructed using the same maleic anhydride (MA) used in the maleation of PBAT, varying the percentage from 0 to 6.2%. A calibration graph displaying the percentage of maleic anhydride versus the volume of KOH (L) was used

to calculate the percentage of MA of the samples by utilization of the linear regression equation ($y=498.28X - 0.114$, $R^2=0.9989$). Three samples of each formulation were titrated in triplicate.

The maximum grafting percentage of maleic anhydride (MA) into the polyester was achieved with the formulation of 2% MA, the percentage of MA grafted on the PBAT backbone was 1.5% by weight. The results of titration are presented in Table 3.4. The samples with 3% and 4% MA loading did not show significant differences, each having inferior grafting compared with the sample loaded with 2% MA. Contrary to the trend observed in the literature for other biodegradable polymers like PLA²⁵, PBS and PBSA²³, the graft content decreased as the maleic anhydride concentration increased. This result could suggest that there is an optimum radical concentration (which is dependent on the [peroxide]/[maleic anhydride] ratio) to promote grafting efficiency.

Table 3.4 – Grafting Percentages of Maleic Anhydride Grafted PBAT Determined by Titration.

Samples	% MA grafted
2% MA/PBAT	1.5 ± 0.07 ^a
3% MA/PBAT	1.1 ± 0.21 ^b
4% MA/PBAT	1.1 ± 0.09 ^b

Means at same column with different letters are significantly different ($p \leq 0.05$).

3.3.2.2 Intrinsic viscosity measurements

Solution viscosity is a measure of the size or extension in space of polymer molecules. It is empirically related to molecular weight for linear polymers; the simplicity of the measurement and the usefulness of the viscosity-molecular weight correlation make this analysis a valuable tool for characterization of polymers. The figure 3.3 shows the typical graphs for calculate the intrinsic Viscosity.

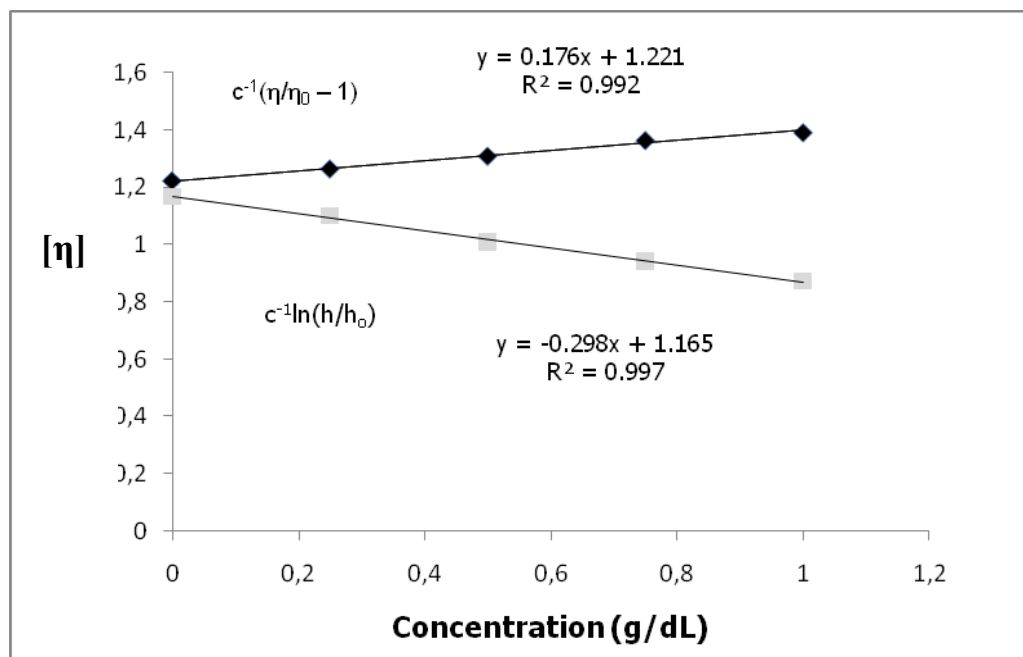


Figure 3.3 – Intrinsic Viscosity Graph of PBAT.

The intrinsic viscosity values are in Table 3.5. In general, the intrinsic viscosity decreases as the percentage of maleic anhydride increases. The samples 2% MA-g-PBAT and 3% MA-g-PBAT did not show differences ($p \leq 0.05$). The decrease in intrinsic viscosity with increasing percentage of maleic anhydride could be the result of chain

scission reactions occurring with an increase of maleic anhydride concentration. Several papers related the decrease of molecular weight in maleated process.^{23,25}

Table 3.5 – Intrinsic Viscosity Measurements.

Samples	Intrinsic Viscosity (dL/g)
Neat PBAT	1.21 ± 0.101^a
2% MA/PBAT	1.02 ± 0.021^b
3% MA/PBAT	0.95 ± 0.081^b
4% MA/PBAT	0.72 ± 0.078^c

Means at same column with different letters are significantly different ($p \leq 0.05$).

3.3.2.3 Thermal analysis (TGA)

The thermogravimetric analyses of the samples showed decomposition temperatures of 375.3, 381.4, 376.0 and 380.7 °C for PBAT, 2%MA-*g*-PBAT, 3%MA-*g*-PBAT, 4%MA-*g*-PBAT, respectively. The maleated samples and PBAT did not show significant differences ($p < 0.05$) in decomposition temperatures. These results could indicate that the maleation process did not change the thermal stability.

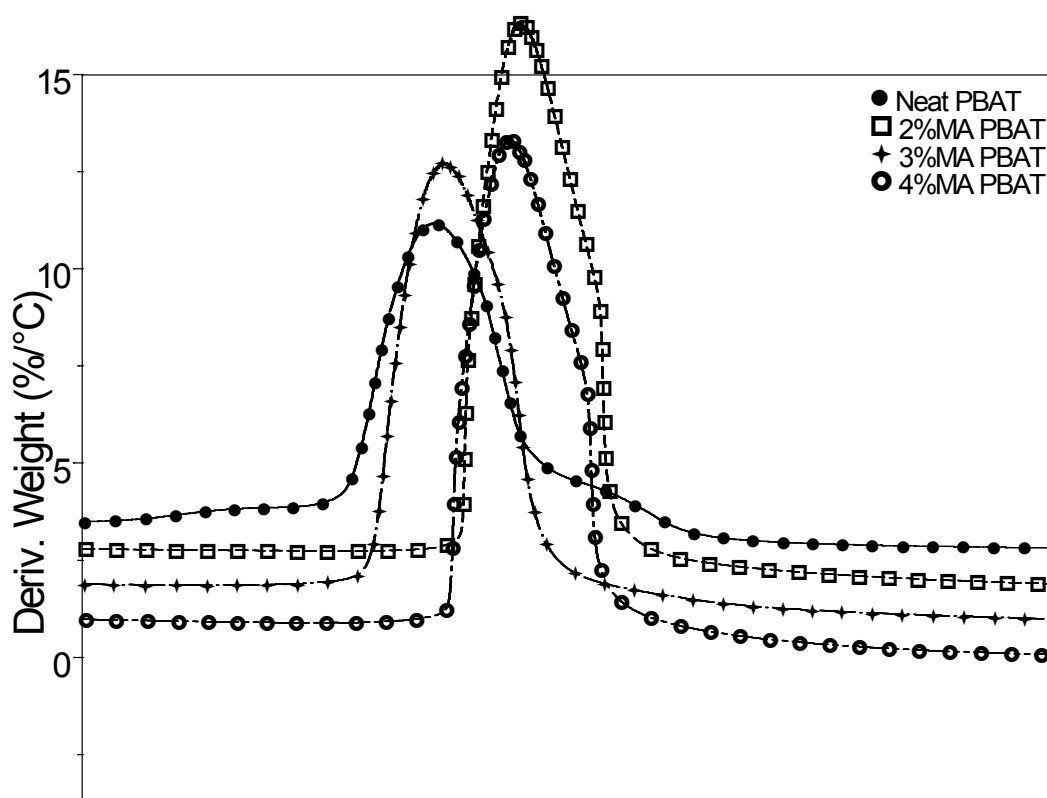


Figure 3.4 - TGA derivative weight graphs of the maleated samples: (□)2% MA-g-PBAT, (+)3% MA-g-PBAT (o)4% MA-g-PBAT and (●) PBAT.

3.3.2.4 FTIR analysis

The grafting of MA onto the aliphatic-aromatic copolyester has been attested by FTIR (Figure 3.5). By comparison to the FTIR spectrum of pure copolyester and focusing on the carbonyl absorption peaks, one extra absorption band at 1780 cm^{-1} was observed for the grafted polyester, assigned to the symmetric stretching for the carbonyl functions of MA.^{41,42}

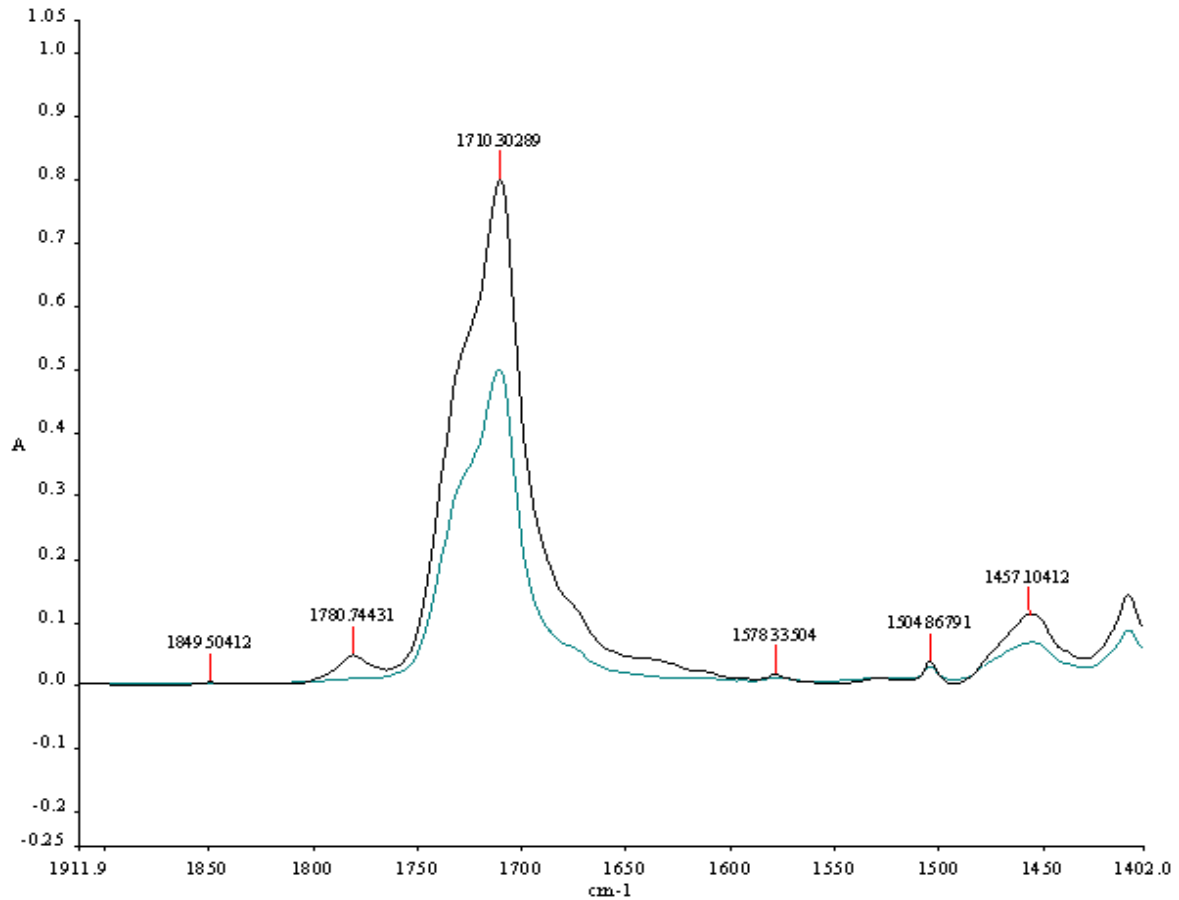


Figure 3.5 - FTIR of MA-g-PBAT and PBAT.

3.3.3 Effect of MA on the properties of MA-g-PBAT

The grafting of maleic anhydride (MA) onto poly(butylene adipate-co-terephthalate) (PBAT) was performed in an attempt to produce reactive functional groups, which would improve the interfacial adhesion between natural fibers and the polyester. The proposed free radical initiated maleation mechanism is depicted in Figure 3.6.⁴⁵ It is worth noting that some authors have proposed an end-chain grafting mechanism, involving the insertion through the aliphatic dicarboxylic acid units of the copolyesters.²³ The maleation of PBAT was carried out at only one temperature, i.e.

185°C, a temperature high enough to avoid the homopolymerization of maleic anhydride. It is important to note that the temperature did not significantly affect the grafting percentage of MA on the polyester backbone, as observed in earlier studies.^{24,25}

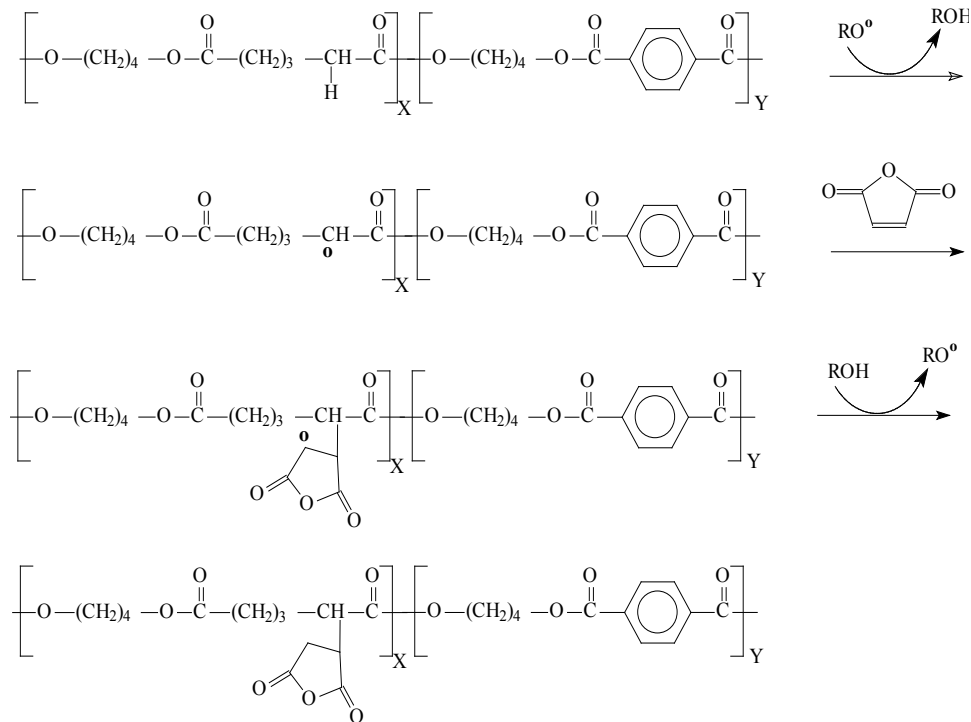


Figure 3.6- Proposed Free Radical Initiated Maleation Mechanism.⁴⁵

In comparing the maleated samples, the 4% MA-*g*-PBAT sample presented significantly different results from the others, showing a lower intrinsic viscosity and a lower thermal stability. The 2% MA-*g*-PBAT and 3% MA-*g*-PBAT samples did not show significant differences in intrinsic viscosity (IV) and thermal analysis (TGA) results, but the 2% MA-*g*-PBAT sample showed higher grafting percentage onto the biodegradable polyester backbone (1.5%). For this reason, the formulation 2%MA-*g*-PBAT was used in the production of natural fiber-PBAT composites.

3.3.4 Mechanical Properties of Natural Fibers with PBAT and MA-g-PBAT.

Most plastic materials are used because they have desirable mechanical properties at an economical cost. For this reason, the mechanical properties may be considered the most important of all the physical and chemical properties of high polymers for most applications.⁴³ Mechanical properties obtained from tensile and impact strength measurements on injection molded specimens are presented in Figure 3.7.

The effect of natural fiber reinforcement of PBAT showed different behaviors for different fiber sources. In the composites containing oat hulls, a decrease of stress at break was observed from that of the neat polymer (from ~14MPa (PBAT) to ~12MPa (oat – PBAT blend)). These results were in agreement with work by Le Digabel and Averous (2006)⁸ that found stress at break values similar or lower than to values of PBAT with the addition of 30% of lignocellulosic fillers. The wood flour addition did not change this tensile property (~14 MPa); however, the incorporation of cellulose fibers increased the stress at break to ~18 MPa. These values for wood and cellulose fibers are superior to the values reported in the study by Le Digabel and Averous (2006)⁸. Considering that wood fiber can be considered a lignocellulose fiber (9% lignin and 73% cellulose), the higher stress of this composite compared with the referenced work could be associate to higher content of natural fiber (45%). Similar behavior was observed for the cellulose fiber composites. In the literature, it was seen that an increase in natural fibers from 25% to 50% improved the mechanical properties of natural fibers polypropylene composites (Tajvid, Falk and Hermanson, 2006).⁴⁴.

Comparison of the Young's modulus of the control PBAT to those of natural fibers composites showed increases from 0.08 GPa to 0.46, 0.66 and 0.68 GPa,

respectively, for oat hulls, wood pulp and cellulose fiber. Le Digabel and Averous (2006)⁸ observed the same behavior. The elongation at break decreased drastically from approximately 400% to ~11% with the addition of each of the three different natural fibers. The same behavior was found in other work with PBAT-fiber (70:30)^{8,9}. It was reported in the literature that addition of natural fibers into a polymeric matrix improved the tensile strength and modulus and decreased the elongation.^{3,8, 44,46}

In the results of the impact tests, it was observed that fiber reinforcement decreased the impact energy values of neat PBAT from 215.5 J/m to 78.3, 91.0 and 122.2 J/m for oat, wood and cellulose fiber-reinforced composites, respectively. (Table 6) These results disagree with those reported in a study of kenaf fiber reinforced polypropylene³--that the addition of natural fibers increase the impact energy, but agree with results by Arzondo et al. (2004)⁴⁶, which indicated decreasing impact energy with sisal fiber addition. The neat PBAT and the biocomposites presented high impact energy compared with polypropylene (42.1 J/m).³

The mechanical properties differences among the oat hull-, wood pulp- and cellulose-reinforced composites are shown in Figure 3.7. The tensile strength and modulus of the cellulose-reinforced composites are superior to those of the wood pulp composites, which are higher than that of the oat hulls fiber composites. This behavior could be explained by differences in the origin of the fibers and consequently, the chemical composition. The content of cellulose is the greatest difference among the natural fibers utilized in this work: (oat hulls (~31%), wood pulp (~73%) and cellulose (~92%)). There was significant mechanical properties improvement when comparing the three biofibers, which showed the effect of cellulose content in natural fibers blends. In general, higher percentages of cellulose results in better interaction between fiber and the polymeric matrix.

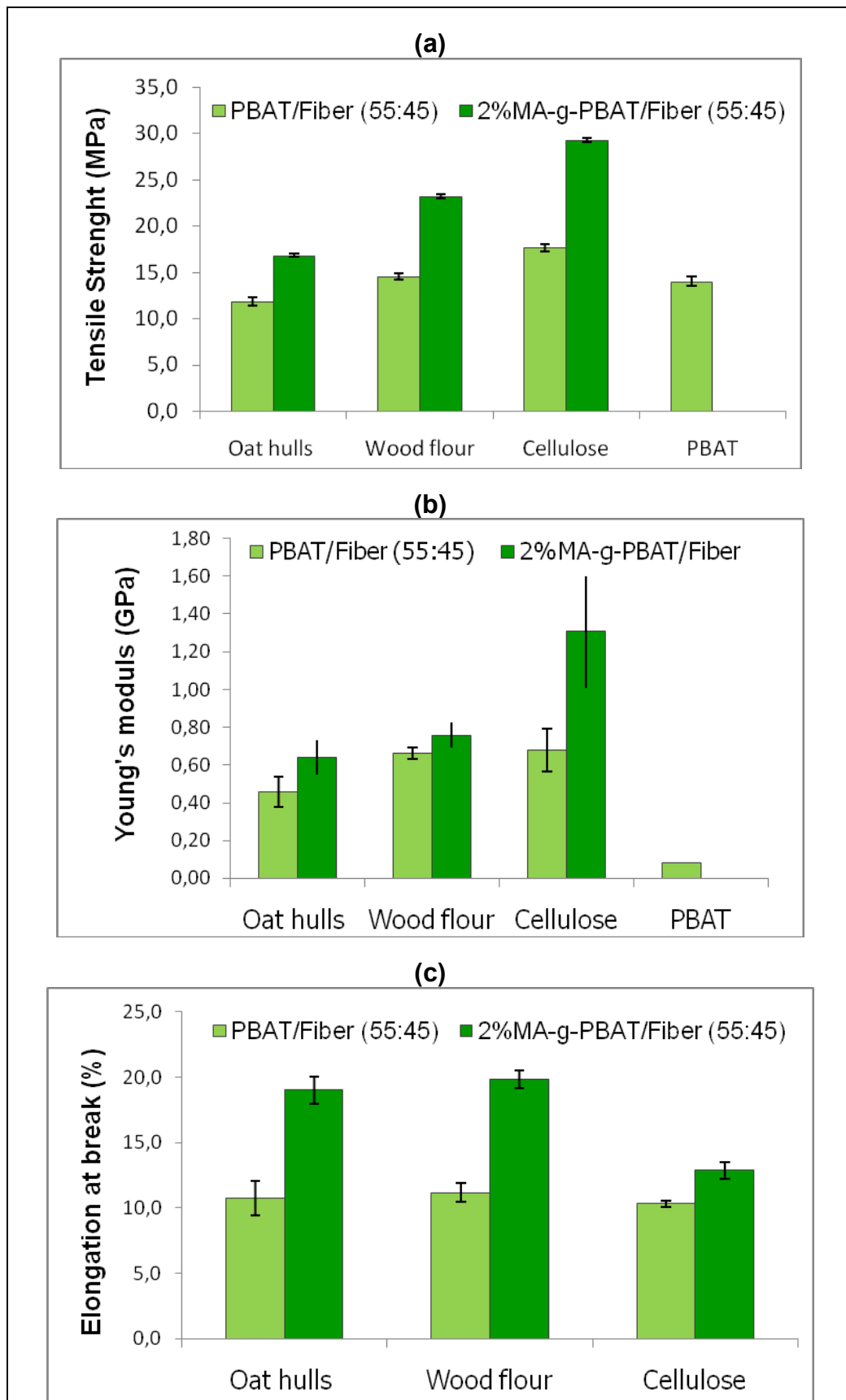


Figure 3.7 – Tensile properties: (a) stress (MPa), (b) elongation (%) and (c) Young's Modulus (%) of composites of PBAT and MA-g-PBAT with natural fibers.

The grafting of maleic anhydride (MA) onto poly(butylene adipate-co-terephthalate) (PBAT) was performed in an attempt to produce reactive functional groups, which would improve the interfacial adhesion between natural fibers and the polyester. The maleated PBAT as a compatibilizer between the natural fibers and the biodegradable polymer significantly affected the mechanical properties of the blends in comparison with neat PBAT matrix.

Composites based on the modified matrix have superior tensile mechanical properties (stress at break, Young's modulus and elongation) and impact energy compared to those containing the unmodified polyester, primarily as a result of improved adhesion and enhanced polar interaction at the fiber/matrix interface.

The maleation improved the tensile strength by 42.5%, 59.5% and 65.7% for the respective fibers: oat hulls, wood pulp and cellulose, when compared to the blends of fiber-PBAT (Table 5). The Young's moduli were 39.6%, 14.66% and 92.5% higher in the respective oat fiber, wood fiber and cellulose fiber reinforced MA-*g*-PBAT composites, compared to the neat PBAT-fiber blends. The elongation at break of the maleated PBAT with oat, wood and cellulose fibers improved by 76.9%, 77.5% and 24.7 % in relation to the non-modified biodegradable polymer. The improvement of tensile properties by using maleated polymers for compatibilization with fibers has been reported by many authors.²⁶⁻³² The effect of maleated PBAT in mechanical properties can be visualized in Figure 3.7.

Modification of PBAT improved the impact energy by 29.0%, 46.3% and 34.9%, respectively for oat-, wood- and cellulose-reinforced composites when compared with the fiber-reinforced neat polyester (Figure 3.8). This result is due to better interfacial adhesion in the modified biopolyester/fiber than in the non-modified PBAT/fiber.

The compatibilizing effect of modified PBAT in natural fiber composites could be attributed primarily to interfacial adhesion resulting from the presence of a matrix with

increased polarity that can react with the hydroxyl functionality on the cellulosic component of the natural fiber to form a linear graft copolymer, enabling it to function as a compatibilizer.

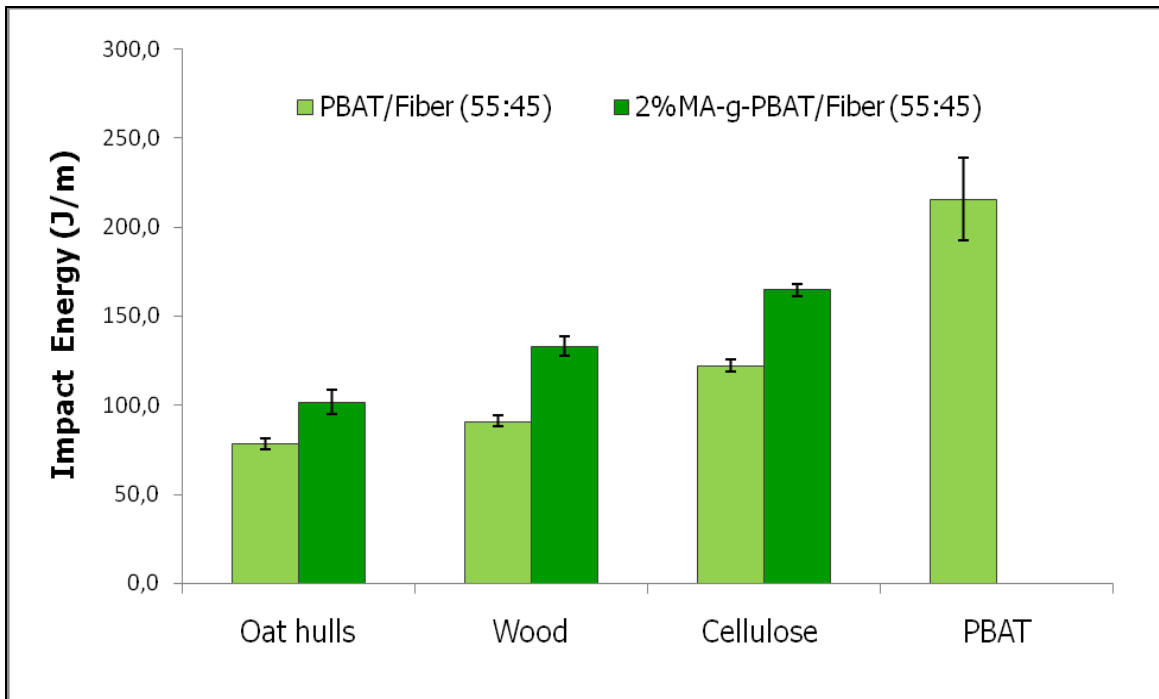


Figure 3.8 – Impact Energy (J/m) of composites of PBAT and MA-g-PBAT with natural fibers.

3.4 CONCLUSIONS

Free-radical initiated grafting of maleic anhydride (MA) onto a poly (butylene adipate-co-terephthalate) (PBAT) backbone was achieved by reactive extrusion. The maximum MA grafted on the PBAT backbone was 1.5% by weight. This degree of grafted MA was sufficient to successfully compatibilize the polyester and natural fibers. The maleated polyesters had lower intrinsic viscosity (IV) as compared to the original polyester.

Maleation of the polyester proved to be very efficient in promoting strong interfacial adhesion with natural fibers in biocomposites by melt blending and injection molding processing. Composites based on the modified matrix have superior tensile mechanical properties (stress at break, Young's modulus and elongation) and impact energy to those containing the unmodified biopolyester.

The mechanical properties of the different formulations showed the effect of cellulose content in natural fibers composites. In general, higher percentages of cellulose resulted in better interaction between fiber and the polymeric matrix.

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CAPÍTULO 4 – THERMOPLASTIC HIGH AMYLOSE STARCH MODIFIED BY TWIN SCREW REACTIVE EXTRUSION.

ABSTRACT

Modified thermoplastic high amylose starch (MTpS) was produced by reactive extrusion in a twin-screw extruder. The objective of this work is the preparation of reactive thermoplastic starch in the presence of glycerol and with different amounts of maleic anhydride (MA) and free-radical initiator, in order to improve processability and reactivity. The concentration of MA added varied from 2 to 6 wt% (of starch + glycerol), and the free-radical initiator, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, also called Luperox101, varied from 0.1 to 0.5 wt% (of starch + glycerol). Characterization of maleated thermoplastic starch was performed using dynamic light scattering, thermal analysis (DSC), and environmental scanning electron microscopy (ESEM). Further, proof of reactive extrusion was determined by fourier transform infrared spectroscopy (FTIR) and by soxlet extraction with acetone. Maleation improved processability due to reduced melt viscosity. The modified high amylose corn starch (20 or 30% glycerol) could be pelletized and gave pellets that were more transparent than thermoplastic starches not modified with maleic anhydride. The hydrodynamic radius increased as the percentage of maleic anhydride increased. However, as the percentage of Luperox 101 increased, the hydrodynamic radius decreased. It could be inferred that the molecular weight increased with increasing amounts of maleic anhydride and decreased as the percentage of free-radical initiator increased. Using the maximum temperature in the extrusion process of 165°C instead of 135°C caused a decrease in the hydrodynamic radius, due to the high influence of the temperature profile on the molecular weight of the thermoplastic starch. The MTpS samples presented higher melting temperatures compared to TpS samples. The soxlet studies indicated that using the maximum temperature of 165°C in the extrusion temperature profile resulted in more interaction between glycerol and starch than when the maximum temperature used was 135°C.

KEYWORDS: Biodegradable, thermoplastic starch, maleation, reactive extrusion.

4.1 INTRODUCTION

Plastic materials are widely used for many applications due to their processability and cost-effectiveness ¹. However, plastics are almost entirely petroleum-based and, therefore, made from non-renewable resources. Much research is being done to produce plastics from alternative, biobased, materials. The two requirements of such “eco-friendly” polymers are: (1) production of the polymer from a renewable resource, and (2) biodegradability ¹. Polymers made from starch can thus be considered “eco-friendly”, since they meet both criteria.

Starch may be sourced from many different agricultural products, for example, potato, corn, cassava, and wheat starch have all been used to produce thermoplastic starch ^{2, 3, 4, 5}. However, the starches of some mutant genotypes of maize, barley, rice and wheat, etc. contain either an increasing amylose content (i.e. high amylose or “amylostarch” with up to 70% amylose) or an increasing amylopectin content (i.e. “waxy starch” with 99-100% amylopectin). The different amylose/amylopectin ratios of these starches led to differences in granular structure, physiochemical properties and quality of end-use products ⁶.

Starch is not a thermoplastic material, but in the presence of a plasticizer (water, glycerol, sorbitol), high temperatures (90-180°C), and shear, it becomes thermoplastic ⁷. In the production of thermoplastic starch (TpS), the starch loses its semi crystalline granular structure and acquires thermoplastic behavior. This allows it to be used in injection molding, and cast and blown film processing in a similar manner to traditional plastics ⁸.

The production of thermoplastic starch by extrusion of starch and glycerol has been demonstrated ² and several researchers, including the Narayan group, have successfully manufactured starch that behaves like a pure thermoplastic material ^{9, 10}.

An alternative method to improve the processability and reactivity of thermoplastic starch is to modify the TpS by reacting starch with an organic dibasic acid or an anhydride in the presence of a plasticizer, using a free radical initiator, producing a chemically modified plasticized starch (MTpS) (US patent 7153354) ¹¹. This patent relates to biodegradable, reactive, chemically modified thermoplasticized starch (CMTpS) with low viscosity and good processability. An important aspect of this invention is that during the processing, no water is added. Chemically modifying the thermoplastic starch prevents problems such as high viscosity, clogging of the thermoplastic starch melt at the die, or foaming of the thermoplastic starch melt. Furthermore, the resulting chemically modified starch composition is highly reactive to yield graft copolymers with polyesters. These starch-polyester graft copolymers are readily processable into films and molded products using conventional plastics processing equipment, and the resultant product has the most preferred balance in mechanical properties, water resistance, processability, and rate of biodegradation ¹¹.

Since maleated thermoplastic starch can be used in blends with other biodegradable polymers for different applications such as films and sheets, or injection molded and thermoformed materials, it is necessary to understand the effect that maleation has on starch. The maleation of starch has been shown to decrease the molecular weight of starch when no initiator was used, however, the molecular weight increased when an initiator was used ¹¹. The decrease in molecular weight was attributed to the fact that starch is hydrolyzed in the presence of maleic acid. The increase in molecular weight was attributed to branching or cross-linking occurring with the addition of the initiator ¹².

The objective of this paper is the *in situ* preparation of reactive TpS from high amylose starch thermoplasticized in the presence of glycerol using different maleic anhydride and free-radical initiator contents in order to form maleated TpS (MTpS) having enhanced reactivity and reduced melt-viscosity.

4.2 MATERIAL AND METHODS

4.2.1 Materials

High amylose corn starch was used in this work. The corn starch was purchased from National Starch and Chemicals (Indianapolis, IN). Anhydrous glycerol, 99.9% assay, was purchased from J.T. Baker (Phillipsburg, NJ). Maleic anhydride was purchased from Sigma-Aldrich, Inc (St. Louis, MO). The initiator, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, also referred to as Luperox 101, was purchased from Sigma-Aldrich, Inc (St. Louis, MO). The solvent used in the studies was dimethyl sulfoxide, and was purchased from J.T. Baker (Phillipsburg, NJ).

4.2.2 Samples Preparation

Modified thermoplastic starch was produced in a co-rotating twin-screw extruder. The maximum temperature of the extruder was set to 165°C

(25/95/125/145/160/165/165/165/150/145°C), at this temperature profile, all samples had 80 wt% corn starch and 20 wt% glycerol. The amount of maleic anhydride (as weight percentage of starch and glycerol) varied while the amount of initiator was held constant at 0.25 wt% of starch and glycerol. The amount of maleic anhydride in the samples was 2, 4, or 6 wt%. Samples were extruded with varying amounts of initiator, while the amount of maleic anhydride was held constant at 2 wt% of starch and glycerol. These samples contain 0.1, 0.25, or 0.5 wt% of free-radical initiator. Table 1 shows the composition of the samples. To compare the effect of modification in some properties, TpS and MTpS containing 30% glycerol were produced in the twin-screw extruder, with a maximum temperature of 135°C (25/115/120/125/130/135/135/135/130/130°C), and characterized (samples 6 and 7).

Table 4.1 - Composition of the modified and non-modified thermoplastic starch (MTpS and TpS).

Sample	Max. Processing Temperature (°C)	Corn Starch (weight %)	Glycerol (weight %)	Maleic Anhydride (weight % of corn starch + glycerol)		Luperox 101
1 (MTpS)	165	80	20	2	0.1	
2 (MTpS)	165	80	20	2	0.25	
3 (MTpS)	165	80	20	2	0.5	
4 (MTpS)	165	80	20	4	0.25	
5 (MTpS)	165	80	20	6	0.25	
6 (MTpS)	135	70	30	2	0.1	
7 (TpS)	135	70	30	-	-	

4.2.3 Dynamic Light Scattering (DLS) Analysis

The samples were ground with a mortar and pestle into a powder. The powder was dissolved in dimethyl sulfoxide at a concentration of 10 mg/mL. Dynamic light scattering measurements were performed in a Dynapro dynamic light scattering apparatus by Protein Solutions. This equipment has a wavelength of 827.1 nm and scatters at an angle of 90 degrees, the temperature was held constant at 25°C and the laser intensity was set to 100% for all samples.

The dynamic light scattering equipment calculated the hydrodynamic radius of each sample using a regularization algorithm. A distribution is calculated based on the mass percentage of various fractions of varying hydrodynamic radius. Figure 4.1 shows a graph obtained for the DLS test.

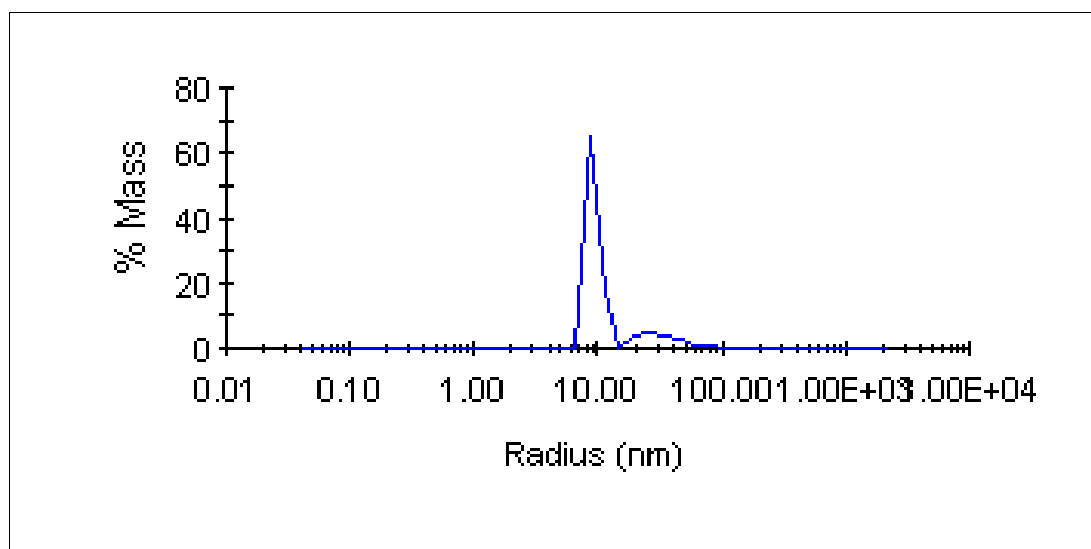


Figure 4.1 – Graph of dynamic light scattering measurements for sample 6 (MTpS high amylose starch, with 30% glycerol and 135°C).

4.2.4 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of TpS, MTpS and starch were scanned from 650 cm^{-1} to 4000 cm^{-1} using a Perkin Elmer Spectrum One FT-IR Spectrometer, to demonstrate the reactions that occurred in TpS in its reactive extrusion with MA, in the presence of a free-radical initiator.

4.2.5 Thermal Analysis (DSC)

Differential scanning calorimetry (DSC) was performed using a high resolution DSC 2920 from TA Instruments. The thermal transitions of the MTpS were determined. The purge gas, nitrogen, had a flow rate of 50 ml/min. Samples of the extruded pellets were cooled to -50°C and then heated to 200°C at a rate of $10^{\circ}\text{C}/\text{min}$, cooled to -50°C and then reheated to 200°C .

4.2.6 Environmental Scanning Electron Microscopy (ESEM) Analysis

An environmental scanning electron microscope (ESEM) (Phillips Electroscan 2020) was used to make observations of the fractured surface of the thermoplastic starch. Pieces of the extrudate samples were frozen in liquid nitrogen, and then broken.

The fractured surface was then viewed with the environmental scanning electron microscope.

4.2.7 Soxhlet Extraction Analysis

The unreacted glycerol was removed from the thermoplastic pellets by soxhlet extraction with acetone. The pellets were ground into a fine powder using a mortar and pestle. A piece of filter paper, measuring 10x10cm was cut, folded, and stapled at the bottom. Approximately 2 grams of the thermoplastic starch powder was accurately weighed into the folded filter paper and then the top was stapled shut. The packet was placed into an extraction thimble holder. Evaporated solvent condensed onto the packet containing the sample. The extraction was run for 72 hours. After extraction, the packet was removed and dried to constant weight. The top staple was then removed from the packet and the sample and filter paper (with bottom staple) were accurately weighed to determine the amount of material extracted during the soxhlet extraction [16].

4.2.8 Statistical Analysis

One control sample, non-modified thermoplastic starch TpS, was tested to evaluate the effect of free-radical initiator and percentage of maleic anhydride on the maleation process of high amylose corn starch. Tukey mean comparison tests ($p \leq 0.05$) were performed using Statistica software (Statsoft, Oklahoma – USA).

4.3 RESULTS AND DISCUSSION

The resultant MTpS had improved processability due to reduced melt viscosity. The proposed reaction of maleic anhydride with starch is shown in Figure 4.2¹⁶. The maleation process permitted formulations with less than 30% of glycerol to be extruded in the twin-screw extruder, resulting in pellets that were more transparent than thermoplastic starches not modified with MA (Figure 4.3).

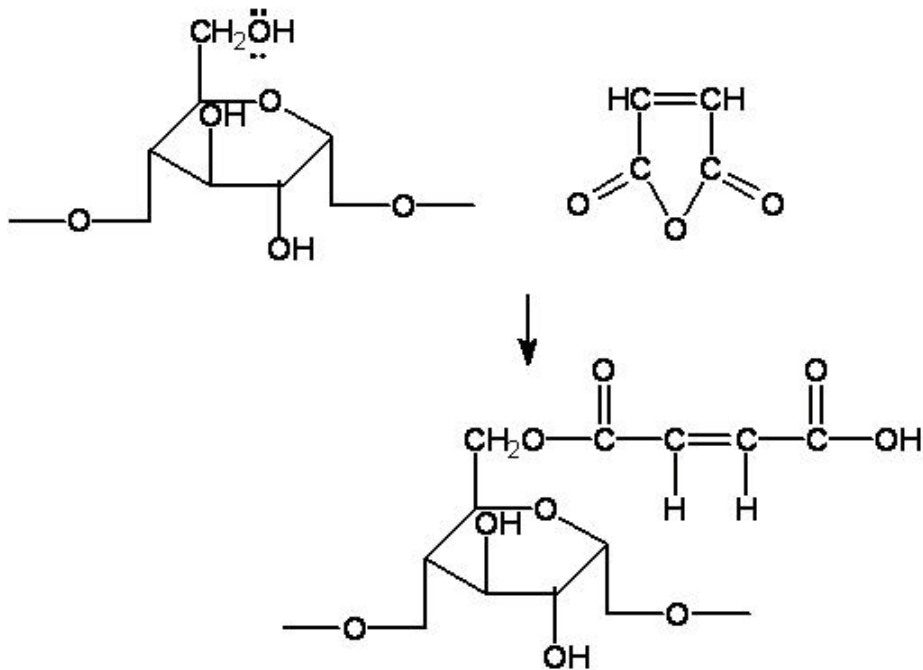


Figure 4.2 - Proposed reaction of starch with maleic anhydride¹⁶.

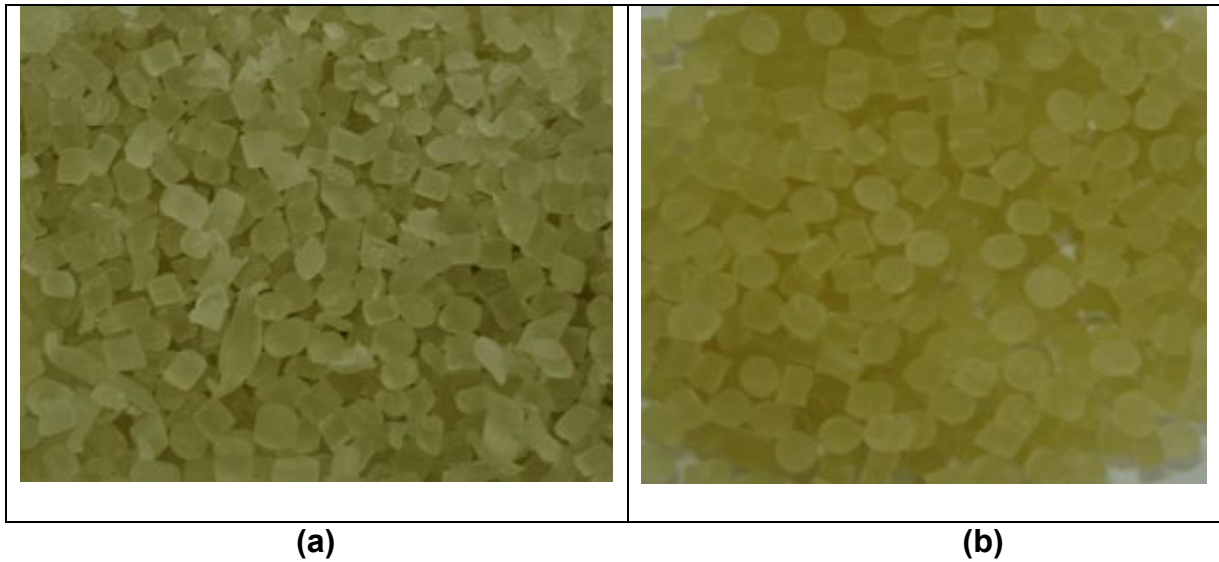


Figure 4.3 – Pictures of pellets of maleated thermoplastic starch (a) and pellets of thermoplastic starch (b) of high amylose corn starch.

4.3.1 Dynamic Light Scattering (DLS) Analysis

For each sample, the value of the hydrodynamic radius which has the largest mass percentage has been used for comparison purposes in this paper. In Figure 4.4, the effect of changes in Luperox 101 on the hydrodynamic radius of maleated thermoplastic starch is shown, while Figure 4.5 shows the effect of changes in maleic anhydride on the hydrodynamic radius of maleated thermoplastic starch.

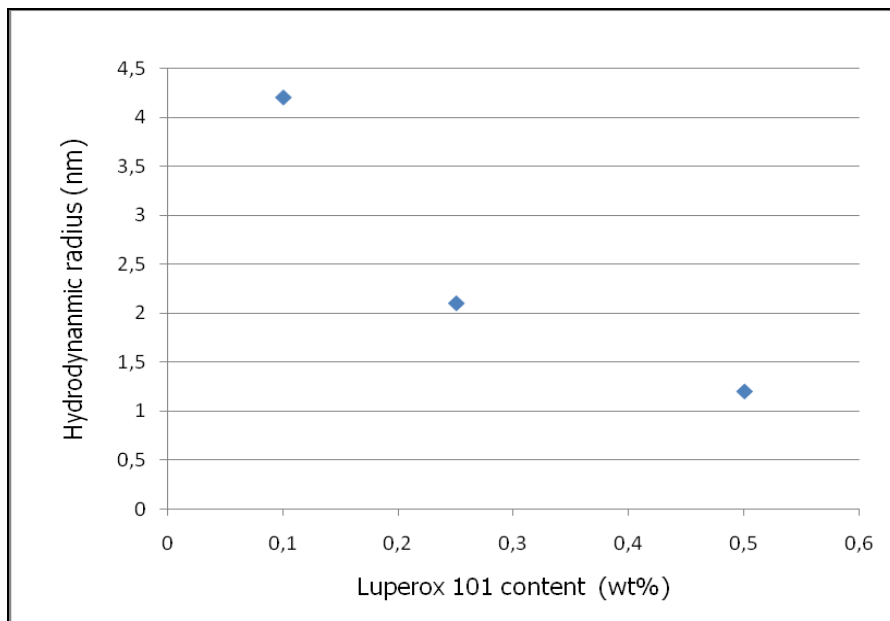


Figure 4.4 – Effect of changes in Luperox 101 content on the hydrodynamic radius of maleated thermoplastic starch (samples 1, 2 and 3).

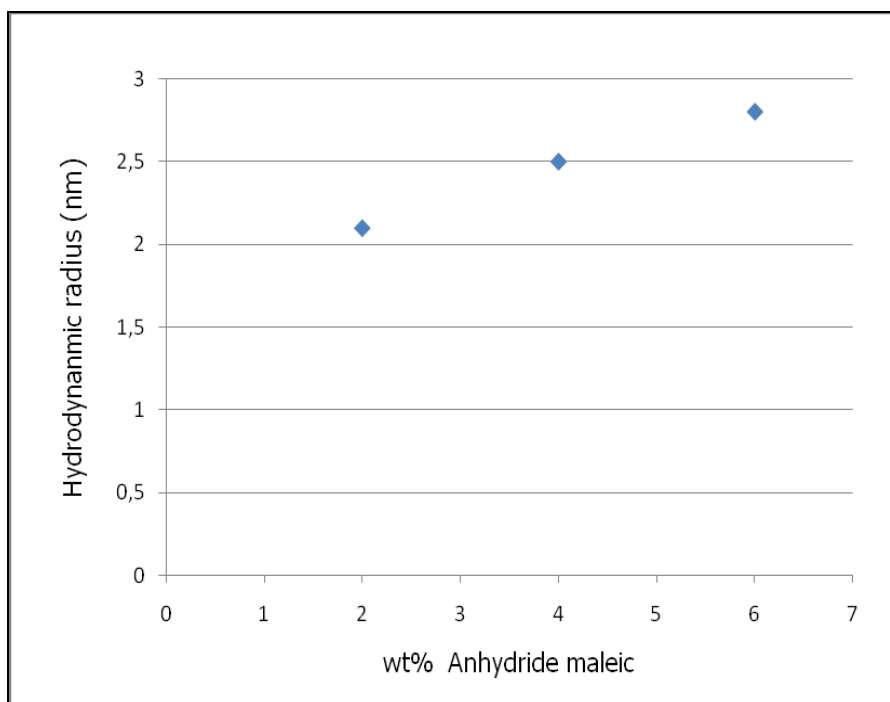


Figure 4.5 - Effect of Changes in Maleic Anhydride on the Hydrodynamic Radius of Maleated Thermoplastic Starch (samples 2, 4 and 6).

As the percentage of maleic anhydride increases, the hydrodynamic radius increases slightly, however, as the percentage of Luperox 101 increases, the hydrodynamic radius decreases. The increase in hydrodynamic radius with the increase in the percentage of maleic anhydride could be the result of grafting occurring between starch chains. Grafting would increase molecular weight and thus, increase the hydrodynamic radius of the samples. The decrease in hydrodynamic radius as the percentage of Luperox 101 increases could be the result of chain scission occurring. Chain scission would decrease molecular weight and thus decrease the hydrodynamic radius of the samples.

By comparing the granular high amylose starch with the thermoplastic and maleated thermoplastic starch (Figure 4.6), we can observe the effect of the maleation of starch. When 2% of anhydride maleic and 0.1% of Luperox 101 was used, the hydrodynamic radius decreased from 11.9 to 9.1nm. These results could indicate that the extrusion and maleation processing degrade the samples and could infer that there is a decrease in the molecular weight.

When comparing the maleated samples at 165°C and 135°C, we can observe the effect of temperature profile on the hydrodynamic radius. The values for the samples at 135°C are much larger than for the samples at 165°C. Using 165°C may degrade the samples and cause a drastic decrease in the hydrodynamic radius (9.1 to 4.2 nm). These results attest to the fact that the temperature has a high influence on the molecular weight of the maleated thermoplastic starch.

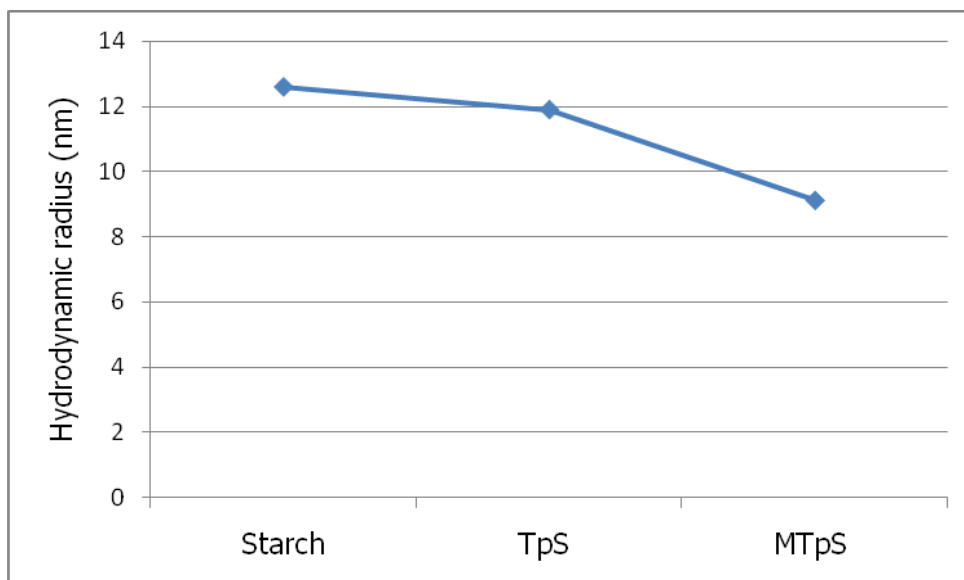


Figure 4.6 – Effect of starch modification on hydrodynamic radius. Starch (high amylose starch), MTpS (modified thermoplastic starch, 30% glycerol, 2% anhydride maleic, 0.1% luperox) (sample 6) and TpS (thermoplastic starch, 30% glycerol) (sample 7).

In comparison to other studies that have been performed to understand the effect of Luperox 101 on the molecular weight of biobased polymers, there is not a consistent trend. Carlson et al.¹³ showed that branching and chain scission depended not only on the amount of Luperox 101 in the process, but also on the temperature at which the extrusion occurred. Work done by Nabar et al.¹⁴ suggests that the effect of increasing the amount of maleic anhydride in maleated poly(butylene adipate-co-terephthalate) (PBAT), a biobased polyester, is to decrease the intrinsic viscosity of the samples (ie: decrease the molecular weight) and increasing the amount of initiator, Luperox 101, also decreases the intrinsic viscosity of the samples (ie: decrease the molecular weight). The results of Nabar et al. do not show the same trends as the data presented in this paper, however, the material that was maleated was PBAT, not high amylose corn starch. Other work by Nabar¹² shows that when using regular corn starch, the intrinsic viscosity of TpS is lower than the intrinsic viscosity of the starch, and that when

the starch is maleated, the intrinsic viscosity reduces even more. This is in agreement with our work.

However, using regular corn starch, without an initiator, the intrinsic viscosity decreased as the MA content increased. This trend is opposite to our findings, however, no initiator was used and the starch was regular corn starch, not high amylose corn starch¹⁶.

Other possible explanations for our results could be that the hydrodynamic radius increased as the percentage of MA increased due to more swelling of the molecules in DMSO when MA is grafted to the starch, or that aggregation of molecules occurred. This could be an area of further investigation.

Furthermore, as it was discussed by Roger et al¹⁵, measuring the hydrodynamic radius of starch in DMSO can lead to some uncertainties in measurements of pure amylose starch. This must be taken into consideration when viewing the hydrodynamic radius data from the DLS measurements. In this study all measurements were made under the same conditions so any errors due to the solvent/starch solution will be constant for all measurements. In this way, the DLS data gave us an understanding of how the hydrodynamic radius has changed due to the varying amounts of MA and Luperox 101, as well as different extrusion temperatures and glycerol contents.

4.3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra for TpS, MTpS, and high amylose corn starch are shown in Figure 4.7. The spectra for TpS and MTpS are quite similar, however, MTpS shows a band at 1700 cm^{-1} , which corresponds to the carbonyl group of maleic anhydride. This

is not present in either the high amylose corn starch or the TpS. Using glycerol as plasticizer, two additional peaks at 2928 and 2886cm^{-1} appeared due to the formation on inter and intramolecular bonding hydroxyl group bands between starch and glycerol. Moreover, the MTpS sample showed no peak at 1787 cm^{-1} corresponding to ring anhydride, suggesting the maleic anhydride ring was fully open.

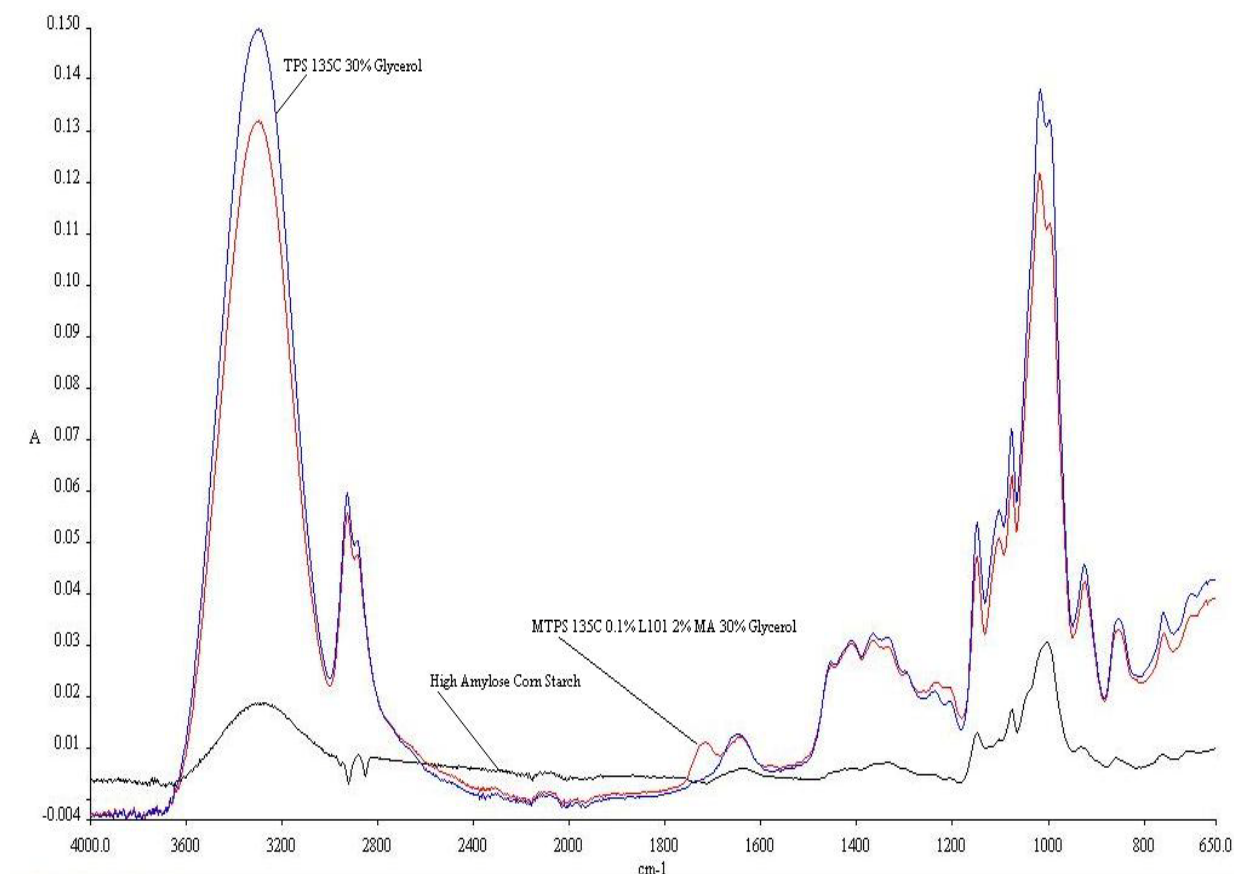


Figure 4.7 - FTIR Spectra for TpS 135°C 30% glycerol, MTpS 135°C 0.1% L101 2% MA 30% glycerol, and high amylose Corn Starch.

4.3.3 Thermal Analysis (DSC)

From the thermograms of the MTpS and TpS samples (Figure 4.8) we can observe a broad melting endotherm in TpS, while two melting endotherms are observed

in MTpS. This is attributed to the maleation of starch leading to segments having slightly different melting characteristics¹². The first endotherm relates to the melting process of the starch/water/glycerol/MA, while the second endotherm is much sharper due to the fact that grafting has occurred. MTpS samples presented melting temperature 10-40⁰C higher than TpS. The melting temperatures of MTpS varied from 123.58 to 157.3⁰C while the melting temperature of TpS was observed to be 112⁰C (Table 4.2). The higher melting temperature of maleated samples is one characteristic that will allow it to be blended with polymers, such as PLA, with higher melting temperature.

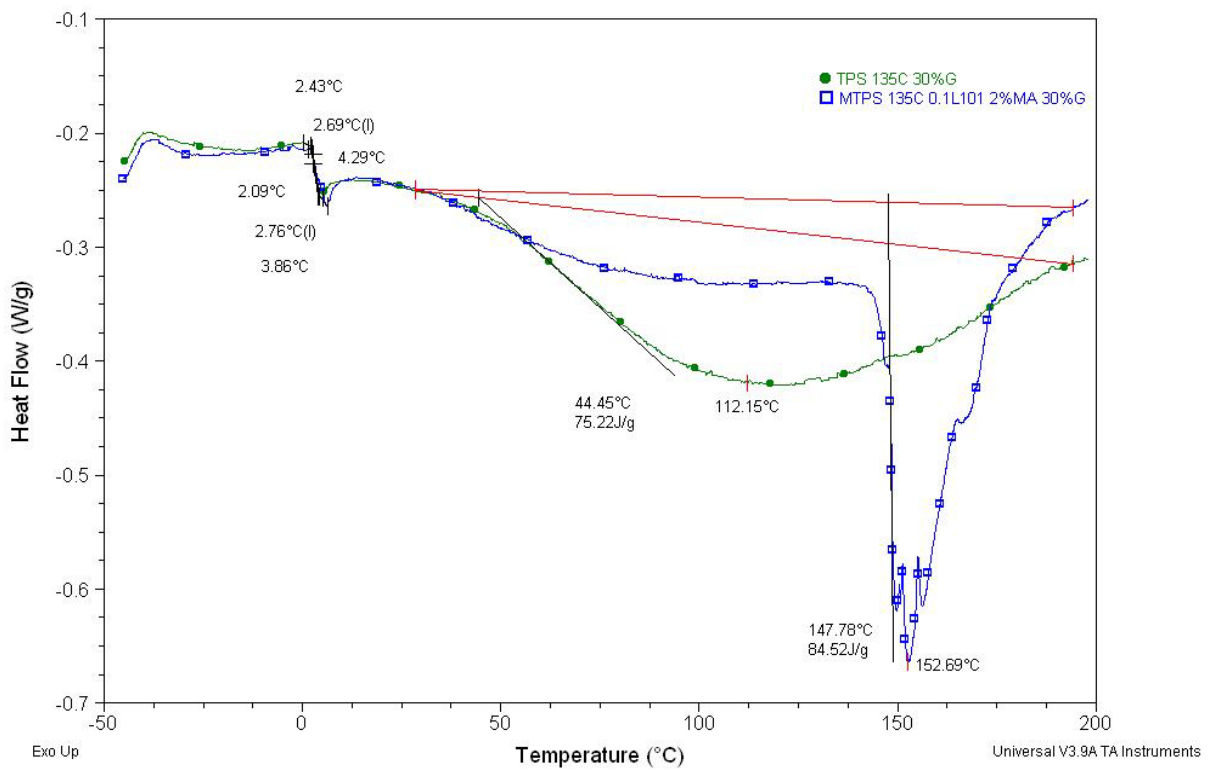


Figure 4.8 – DSC thermogram of the samples with 30%glycerol and extruded at the maximum temperature of 135⁰C: (a) MTpS and (b) TpS.

Table 4.2 – Melting temperature (T_m) in the first heating of the MTpS and TpS samples.

Samples	T_m (°C)
1 (MTpS)	157.3
2 (MTpS)	141.17
3 (MTpS)	132.6
4 (MTpS)	123.58
5 (MTpS)	145.22
6 (MTpS)	152.69
7 (TpS)	112.15

Another endotherm transition was observed for all the MTpS and TpS samples close to 0°C with positive values (from 0.27 to 5.43°C) in the first heating and close to 0°C with negative numbers (from -4.41 to -0.28°C) in the second heating. This transition looks like a small endotherm peak, that could be related to fusion of the water that could be still present in the pellets.

4.3.4 Environmental Scanning Electron Microscopy (ESEM) Analysis

Images of the samples taken with the environmental scanning electron microscope (ESEM) are shown in Figure 4.8. The samples that were processed at 165°C (a,b,c and d) appear to be smoother than the MTpS and TpS (samples 6 and 7) that were processed at 135°C (e and f). This could imply that there was better plasticization of the starch at higher temperatures and lower glycerol content.

Comparing the samples extruded at 165°C, the effect of MA content is not evident. In contrast the effect of the content of free-radical initiator content is evident. The sample with 0.5% Luperox (c) presented a more homogeneous and a smoother surface compared to the samples with 0.1 and 0.25% Luperox (a and b), due to the higher degradation. These observations are in agreement with the DLS data.

Also, since the DLS data indicates that the molecular weight of the starch is higher when the starch is extruded at 135°C, the higher molecular weight could make it more difficult for the starch to fully plasticize and regions of unplasticized starch may be present in the MTpS or TpS. The TpS sample appears to have the roughest surface. Observations of the material as it was extruded showed that MTpS flowed better than TpS. This could also indicate that there was less plasticization occurring during the extrusion of TpS compared with MTpS.

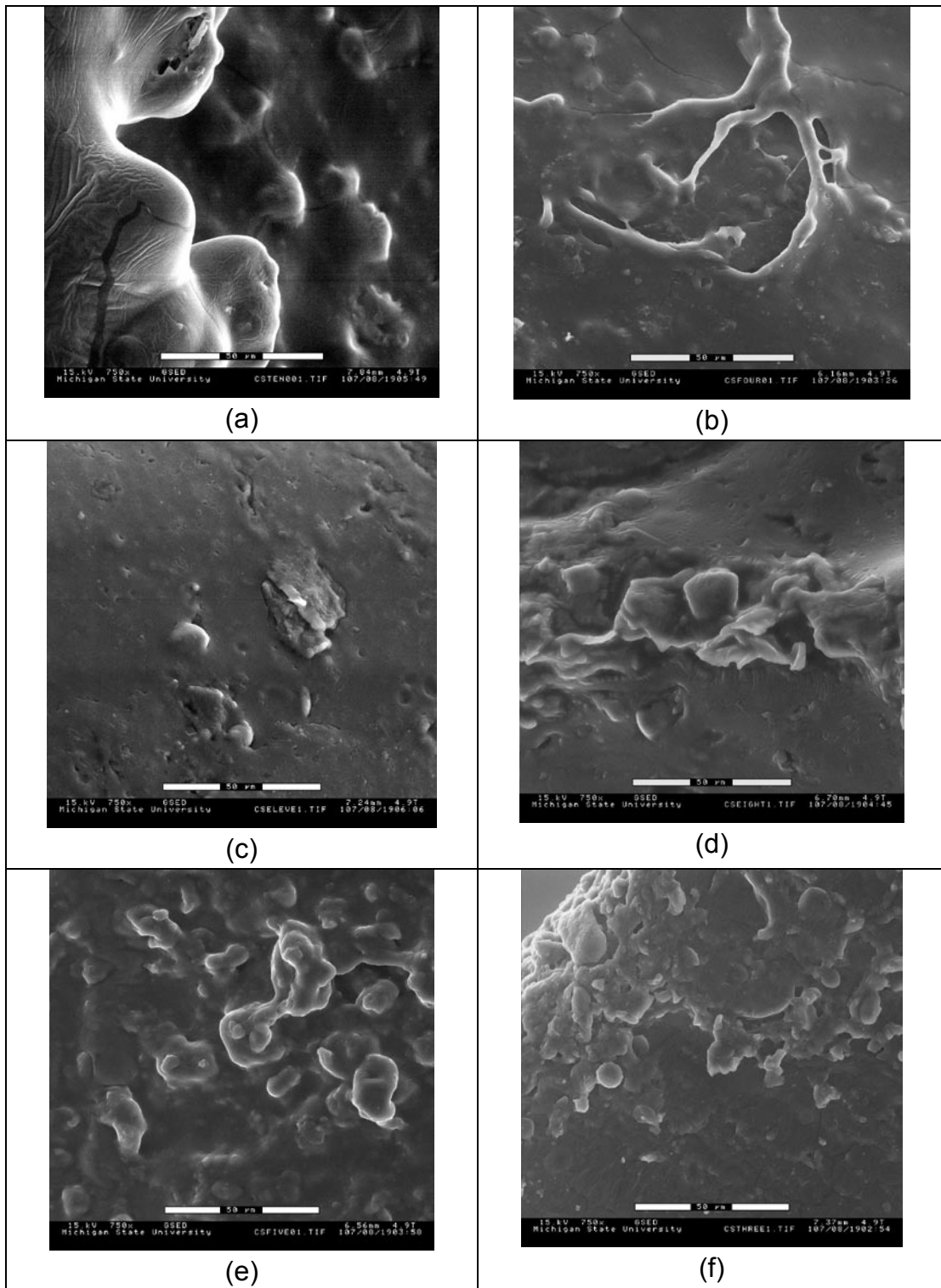


Figure 4.9 – Environmental scanning electron microscope images of extrudate samples. Images shown at 750x magnification. a) MTpS, at 165°C, 0.1% L101, 2% MA, 20% glycerol, b) MTpS, at 165°C, 0.25% L101, 2% MA, 20% glycerol, c) MTpS, at 165°C, 0.50% L101, 2% MA, 20% glycerol, d) MTpS, at 165°C, 0.25% L101, 6% MA, 20% glycerol, e) MTpS, at 135°C, 0.1% L101, 2% MA, 30% glycerol and f) TpS, at 135°C, 70% starch and 30% glycerol.

4.3.5 Soxlet Extraction Analysis

The results of the soxlet extraction with acetone of the MTpS and TpS are shown in Table 4.3. The calculated percentage of material extracted is tabulated for each sample. The values are an average of three soxlet extractions.

Table 4.3 – Percentage of Material Extracted After Soxlet Extraction of Maleated Thermoplastic Starch in Acetone for 72 Hours.

Sample	Composition	Glycerol Extracted (%)
1	ATpM, 165°C, 20% glicerol, 2%AM e 0,1%L101	71.8±7.05 ^a
2	ATpM 165°C, 20% glicerol, 2%AM e 0,25%L101	58.5±9.7 ^{a,b}
3	ATpM, 165°C, 20% glicerol, 2%AM e 0,5%L101	48.4±4.16 ^b
4	ATpM, 165°C, 20% glicerol, 4%AM e 0,25%L101	62.8±0.46 ^a
5	ATpM, 165°C, 20% glicerol, 6%AM e 0,25%L101	64.1±1.20 ^a
6	ATpM, 135°C, 30% glicerol, 2%AM e 0,25%L101	88.0±2.06 ^c
7	ATp, 135°C	97.7±2.69 ^d

Means at same column with different letters are significantly different ($p \leq 0,05$).

For the maleated thermoplastic starch extruded at 165°C, the soxlet extraction removed 49 to 72% of the original glycerol of the samples. These results demonstrate that a certain amount of glycerol could not be removed after 3 days due to the fact that the glycerol has been linked to the starch backbone and indicates that reactive extrusion has occurred. At this temperature, it was observed that the Luperox 101 content has more of an effect on the amount of glycerol extracted. When the Luperox 101 content changed from 0.1 to 0.5%, the amount of glycerol extracted changed from

72 to 59%. However, when the MA content changed from 2 to 6%, the glycerol extraction was not significantly different.

For the maleated thermoplastic starch extruded at 135⁰C, the soxlet extraction removed 88% of the glycerol added to the sample, while the TpS at the same temperature profile extracted almost all of original glycerol of the samples (98%). This result indicates that in maleated samples, chemical interactions occurred between starch and glycerol that hinder the extraction of the glycerol, while in the TpS these interactions were not present.

Comparing the MTpS extruded at 165⁰C and 135⁰C, the samples extruded at higher temperature had less glycerol extracted (from 49 to 72%) than samples at 135⁰C (88%). These results indicate that the interactions between plasticizer and starch that are promoted by reactive extrusion using MA, are more efficient at the higher temperature profile. Another difference observed is the color of the extruded samples. Samples extruded at 165⁰C were green in color while the MTpS sample extruded at 135⁰C had a yellow color. This is similar to the color of the TpS sample.

The maleation processing of the thermoplastic starch is a complex system, while the maleation of biodegradable polymers like PLA, PBAT is simple because only the polymer, MA and free-radical initiator are present. In the modification of thermoplastic starch during reactive extrusion the process becomes more complex due to water association with starch and the use of a plasticizer such as glycerol. Firstly, the presence of the plasticizer could interfere with the maleation reaction of starch, and MA could react preferably with the hydroxyl groups of the glycerol. Secondly, the residual humidity in the system may cause the opening of the MA ring and thus reduce its reactivity.

An important aspect of this process is that it permitted formulations with less than 30% of glycerol to be extruded in the twin-screw extruder and prevented problems

such as high viscosity, clogging of the thermoplastic starch melt at the die, or foaming of the thermoplastic starch melt. Furthermore, the resulting modified thermoplastic starch is highly reactive to yield graft copolymers with polyesters. These starch-polyester graft copolymers are readily processable into films, and molded products using conventional plastics processing equipment, and the resultant product has the most preferred balance in mechanical properties, water resistance, processability, and rate of biodegradation¹¹.

4.4 CONCLUSION

The resultant MTpS had improved processability due to reduced melt viscosity. The maleation process permitted formulations with less than 30% of glycerol to be extruded in the twin-screw extruder, resulting in pellets that were more transparent than thermoplastic starches not modified with maleic anhydride. The hydrodynamic radius increased as the percentage of maleic anhydride increased, however, as the percentage of Luperox 101 increased, the hydrodynamic radius decreased. It could be inferred that the molecular weight increased with increasing amounts of maleic anhydride and decreased as the percentage of free-radical initiator increased. Using the maximum temperature during the extrusion process of 165°C instead of 135°C caused a drastic decrease in the hydrodynamic radius, due to the high influence of the temperature profile on the molecular weight of the thermoplastic starch. The MTpS samples presented higher melting temperatures compared to the TpS sample. The soxlet studies indicated that using the maximum temperature of 165°C in the extrusion temperature profile resulted in more interaction between glycerol and starch than when the maximum temperature used was 135°C.

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CAPÍTULO 5 – BIODEGRADABLE THERMOPLASTICIZED STARCH-POLYESTER REACTIVE BLENDS FOR THERMOFORMING APPLICATIONS.

ABSTRACT

Maleated thermoplastic starch (MTpS) or thermoplastic starch (TpS) were synthesized and reactively blended with a biodegradable polyester, poly(butylene adipate-co-terephthalate) (PBAT). The blends were extruded to produce thermoformable sheets of material. The materials were characterized by mechanical properties (tensile and puncture tests), thermal analysis (DSC), Fourier transform infrared spectroscopy analysis (FTIR) and microstructure analysis (ESEM). The processability of high amylose corn starch MTpS is much better than the processability of regular corn starch MTpS. Even though the tensile properties for TpS and MTpS samples are similar, the maleated thermoplastic starch samples formed sheets and thermoformed pieces that were more transparent and had a more homogeneous surface. The effect of the amylose content of the different starches used did not present significant differences when the glycerol content of the plasticized starch was 30% and the ratio of thermoplastic starch/PBAT used was 50:50. When 20% of glycerol was used in the MTpS, the samples made from high amylose corn starch had better tensile properties than samples made from regular corn starch. Increasing the MTpS content of the blend to 60% decreased the tensile strength and elongation of the sheets. The sheet material was readily thermoformed into desired articles.

Key-words: Thermoplastic starch, biodegradable, thermoforming, reactive extrusion

5.1 INTRODUCTION

Starch, the storage polysaccharide of cereals, legumes and tubers, is a renewable and widely available raw material suitable for a variety of industrial uses. Corn is the primary source of starch, although considerable amounts of starch are produced from cassava, potato, wheat and rice. Starch has been considered for many years as a polymer with a high potential for packaging applications because of its low cost, renewability, and biodegradability.

As a packaging material, starch alone does not form films with adequate mechanical properties (high percentage of elongation, tensile, and flexural strength)¹. Starch by itself is unsuitable because of various disadvantages. These include: a) brittleness in the absence of plasticizers; b) hydrophilic nature of starch and poor water resistance; c) deterioration of mechanical properties upon exposure to environmental conditions like humidity and d) soft and weak nature of starch in the presence of plasticizers.²

Starch is not a thermoplastic material, but in the presence of a plasticizer (water, glycerol, sorbitol), high temperatures (90-180°C), and shear, the starch loses its semi-crystalline granular structure and acquires thermoplastic behavior⁴, allowing its use in injection molding, and in cast and blown films resin compositions.³

Thermoplastic starch has weaknesses that limit utilization of thermoplasticized starch in packaging applications, and particularly for thermoforming applications. These weaknesses are especially problematic due to the low wall thickness of the produced objects.⁵ Major drawbacks are water sensitivity⁶, change of mechanical properties with time⁷, crystallization due to aging, water adsorption, and low impact strength resistance.

Blends of thermoplastic starch (TpS) with biodegradable polyester can improve mechanical properties and decrease the water sensitivity of TpS. Commercial biodegradable polyesters have high cost (3.5 to 5.0 euro/kg)⁸, so blending starch with biodegradable polyesters is a price reduction strategy. Polymer blends containing varying amounts of starch have been studied extensively as possible replacements for plastics, mainly in the area of packaging as films or injection molded materials.

High levels of starch and its poor compatibility with biodegradable polyesters lead to poor physical and mechanical properties. An effective way to improve the compatibility between starch and the polyester matrix is to functionalize the polyester matrix by grafting highly reactive functional groups. Synthetic polymers that have been reactively blended with starch have the following functional groups, carbonyl, anhydride, epoxy, urethane, or oxazoline that can react with the hydroxyl or carbonyl groups in native and modified starches.²

Maleic anhydride (MA) has been grafted onto many different hydrophobic polymers, both biodegradable⁹⁻¹⁶ and non-biodegradable¹⁷⁻¹⁸, to produce functional polymers that are then blended with thermoplastic starch (TpS). Thus, the maleated polymers can act as compatibilizers between the non-functional polymer and the starch.

Another option for compatibilization of starch and polymers (biodegradable or non-biodegradable) is to modify the TPS by reacting starch with an organic dibasic acid or an anhydride in the presence of plasticizer, using a free radical initiator, producing a chemically modified plasticized starch (CMPS) (US patent 7153354).¹⁹ This invention relates to biodegradable, reactive, chemically modified, plasticized starch (CMPS) compositions with low viscosity and good processability. An important aspect of this invention is that the process uses no added water, and prevents problems such as high viscosity, clogging of the thermoplastic starch melt at the die, and foaming of the thermoplastic starch melt. Furthermore, the resulting chemically modified starch

composition is highly reactive to yield graft copolymers with polyesters. These starch-polyester graft copolymers are readily processable into films, and molded products using conventional plastics processing equipment, and the resultant product has the most preferred balance in mechanical properties, water resistance, processability, and rate of biodegradation.¹⁹

Current biodegradable polymers may be divided into three categories, based on whether they polymerize biologically or synthetically: a) biosynthetic (starch, cellulose, PHB, PHBV), b) semi-biosynthetic (PLA) and (c) chemo-synthetic polymers (PCI, PBSA, PBS, PBAT).⁸ Poly(butylene adipate-co-terephthalate) (PBAT), a chemo-synthetic biodegradable aliphatic aromatic co-polyester under the brand name EcoflexTM, is made by condensing 1,4-butanediol with 1,4-benzenedicarboxylic acid (terephthalic acid) and hexanedioic acid(adipic acid). It is an important biodegradable polymer, which has been used in several applications, like films, in blends with thermoplastics starch²⁰, blends with biobased polymers such as Poly(lactide)²¹, and lignincellulosic-based composites.²²⁻²⁴

This paper reports on reactive blending of thermoplasticized starch – in the form of maleated thermoplastic starch (MTpS) or thermoplastic starch (TpS) – with a biodegradable polyester, poly(butylene adipate-co-terephthalate), produced under the tradename Ecoflex, to produce sheets of material that can be thermoformed. Single-use disposable items are typically thermoformed. Making these biodegradable would be environmentally responsible. This is, to the best of our knowledge, the first report of a truly biodegradable thermoformed article.

5.2 MATERIALS AND METHODS

5.2.1 Materials

High amylose corn starch was purchased from National Starch and Chemicals (Indianapolis, IN). Regular corn starch was obtained from Cargill Inc. (Minneapolis, MN). Poly(butylene adipate-co-terephthalate) (PBAT) was purchased from BASF Chemicals (Ludwigshafen, Germany), under the trade name Ecoflex. Anhydrous glycerol, 99.9% assay, was purchased from J.T. Baker (Phillipsburg, NJ). Maleic anhydride was purchased from Sigma-Aldrich, Inc (St. Louis, MO). The initiator, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, also referred to as Luperox 101, was purchased from Sigma-Aldrich, Inc (St. Louis, MO).

5.2.1.1 Equipment

A Century CX-30 co-rotating twin-screw extruder, having a length/diameter ratio (L/D) of 42 and a screw diameter of 30 mm was used to prepare the thermoplastic starch and maleated thermoplastic starch, and to blend these materials with Ecoflex. A pelletizer was used to cut the extrudate strands into small pellets.

The blended material was then extruded through a Killion single-screw extruder, having a length/diameter ratio of 24 and a screw diameter of 1 inch. The extrudate exited the extruder in the form of a sheet of material and was collected on a roller.

Thermoforming of the sheets of blended material was done using a Labform thermoformer by Hydro-Trim Corporation.

5.2.2 Procedure

5.2.2.1 Production of thermoplastic starch (TpS) and modified thermoplastic starch (MTpS)

Thermoplastic starch (TpS) was produced in a co-rotating twin-screw CX-30 extruder. The corn starch (high amylose or regular) was fed into the feed port of the extruder using an external feeder. Glycerol, which was warmed in a water bath, was pumped into the extruder using a peristaltic pump. The feed rates of the external feeder and the peristaltic pump were set so as to accomplish a composition of 70 wt% starch and 30 wt% glycerol, and a total flow of approximately 11 kg/h of material through the extruder. The temperature profile of the extruder was 25/115/120/125/130/135/135/135/130/130°C from the feed throat to the die. The screw speed was set to 125 rpm. The vent port was kept open to remove any moisture. The extruded strand was air cooled and pelletized in line. The pellets were dried for two days in an oven at 65°C before being blended with Ecoflex.

Maleated thermoplastic starch (MTpS) was produced in a co-rotating twin-screw CX-30 extruder. Maleic anhydride was ground into a fine powder using a mortar and pestle and pre-blended with the corn starch (high amylose or regular) before being fed into the feed port of the extruder. The concentration of maleic anhydride used was 2 wt% with respect to the total mass. Luperox 101 was pumped into the feed throat of the extruder using a peristaltic pump. The concentration of Luperox 101 used was 0.1 wt% with respect to the total mass. Glycerol, which was warmed in a water bath, was pumped into the extruder using a peristaltic pump. The feed rates of the external feeder and the peristaltic pump for the glycerol were set so as to accomplish a composition of

80 wt% starch and 20 wt% glycerol. The total flow of all material through the extruder was approximately 11 kg/h. The temperature profile of the extruder for producing maleated thermoplastic starch was 25/95/125/145/160/165/165/165/150/145°C from the feed throat to the die. The screw speed was set to 125 rpm. A vacuum was pulled on the vent port of the extruder in order to remove unreacted maleic anhydride and moisture. The extruded strand was air cooled and pelletized in line. The pellets were dried for two days in an oven at 65°C before being blended with PBAT.

The temperature profile used with the maximum temperature of 165°C was defined in preliminary tests as the best temperature for production of MTPS of high amylose corn starch with 20% glycerol, as it was not possible to make TPS with 20% glycerol in twin-screw extruder due to its high viscosity. For comparison purposes, TpS and MTpS were also produced under the same conditions; with a temperature profile of 25/95/115/125/130/135/135/135/130/130°C and 30% glycerol. This was done to compare the modified and non-modified thermoplastic starch of the high amylose corn starch and regular corn starch.

5.2.2.2 Blend production of TpS and MTpS with PBAT

Blends of thermoplastic starch/PBAT or maleated thermoplastic starch/PBAT were produced in a co-rotating twin-screw CX-30 extruder. Pellets of TpS or MTpS were pre-mixed with PBAT in various weight of TpS (or MTpS) to weight of PBAT ratios (60:40 and 50:50) and fed into the feed port of the extruder using an external feeder (Table 5.1). The temperature profile of the extruder was 25/125/135/140/145/150/150/150/145/135°C from the feed throat to the die. The screw

speed was set to 100 rpm. The vent port was kept open to remove any moisture. The extruded strand was air cooled and pelletized in line. The pellets were dried for one day in an oven at 65°C before being extruded into sheets.

Table 5.1 – Composition of the blends of TpS and MTpS with PBAT.

Samples	Maximum temperature (°C)	Glycerol (%)	Luperox (%)	Blends composition	
				TpS/MTpS (%)	PBAT (%)
1	165	20	0.1	60	40
2	165	20	0.1	50	50
3	165	20	0.1	50	50
4	135	30	0.1	50	50
5	135	30	0.1	50	50
6	135	30	-	50	50
7	135	30	-	50	50
8	-	-	-	-	100

5.2.2.3 Thermoforming processing

Extruded sheets of the blended material were produced in a single-screw extruder. The pellets were gravity-fed into the extruder at the feed throat. The temperature profile of the extruder was 160/160/160/160/154°C for zone 1, zone 2, zone 3, clamp ring, and die, respectively. The screw speed was set to 65 rpm. The extruded sheet was cooled on a chill roller set at 21°C and then collected on an auxiliary roller. The speed of the chill roller was adjusted so as to produce a sheet with a thickness of 500µm.

Pieces of the sheets were cut with scissors and placed in the Labform thermoformer. The upper and lower heaters of the thermoformer were both set to 154°C. The thermoformer held the sheet of material between the upper and lower

heaters for varying lengths of time (from 24 to 40 seconds), depending on the composition of the material. The length of time was determined so as to ensure that the material was adequately heated, but did not sag too much. The material was then placed over the forming die and a vacuum of approximately 25 mmHg was pulled and held for 20 seconds. The thermoformed object could then be removed from the thermoformer and the excess material around the object was trimmed away with scissors. The shape of the object that was formed is shown in Figure 5.1, below.



Figure 5. 1. Picture of the object formed in the Labform thermoformer.

5.2.3 Fourier Transform Infrared Spectroscopy Analysis (FTIR)

The FTIR spectra of TpS, MTpS, starch, and blends of TpS or MTpS/PBAT pellets were scanned from 650 cm^{-1} to 4000 cm^{-1} using a Perkin Elmer Spectrum One FT-IR Spectrometer.

To prove that grafting had occurred between the MTpS and the PBAT, soxlet extraction in dichloromethane was performed on the pellets of the MTpS/PBAT blends. In this analysis, the PBAT is soluble in dichloromethane but starch is not, therefore, the

soxlet extraction removes the PBAT, glycerol and starch that is grafted on the PBAT backbone. FTIR spectra of the pellets before soxlet extraction and after soxlet extraction were obtained. Also, the solvent was collected after the extraction and evaporated, leaving a film whose FTIR spectrum was recorded.

5.2.4 Characterization of the Sheets and Thermoforming

5.2.4.1 Mechanical tests

Tensile samples of the blends of TpS and MTpS/PBAT blends were conditioned as recommended in standard method ASTM D-4332³⁷, in a constant environment room at $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ RH for at least 40 hours before testing. The tensile tests were measured in accordance with ASTM D-882-91 method (1996). Specimens (100mmx 25mm) of the extruded sheets of each formulation were clamped between the grips. Force-extension curves were recorded. The parameters determined were: tensile strength, modulus, and elongation. Seven samples were tested for each blend and property.

Puncture tests were performed on the sheets and thermoforming samples to determine puncture strength (N) and deformation (mm) using a TA.TX2i Stable Micro Systems texture analyzer (Surrey, England). Samples of diameters of 40mm were fixed on the plate of the equipment with a hole of 20mm diameter with help of tape (3M Scotch, Brazil). A Cylindrical probe of 5mm diameter was moved perpendicularly to the sheets surface at a constant speed of 1mm/s until the probe passed through the film.

Force-deformation curves were recorded. At rupture point force and deformation were determined. Each data point on the graph represents an average of four points.

5.2.4.2 Thermal analysis (DSC)

Differential scanning calorimetry (DSC) was performed using a high resolution DSC 2920 from TA Instruments. The thermal transitions of the blends and of PBAT were determined. The purge gas, nitrogen, had a flow rate of 50 ml/min. Pellets of the extruded samples were cooled to -50°C and then heated to 200°C at a rate of $10^{\circ}\text{C}/\text{min}$, cooled to -50°C and then reheated to 200°C .

5.2.5 Statistical Analysis

One control sample, PBAT, was tested to evaluate the effect of blends of TPS and MTPS with PBAT on mechanical properties of sheets and thermoforming pieces. Analysis of variance (ANOVA), Tukey mean comparison test ($p \leq 0.05$) and regression analysis were performed employing Statistica software (Statsoft, Oklahoma – USA).

5.3 RESULTS AND DISCUSSION

The chemistry, processing, and performance properties of TpS and MTpS/PBAT blends, sheets and thermoformed materials are presented and discussed, specifically, Fourier transform Infrared spectroscopy (FTIR), mechanical properties (tensile and puncture tests), thermal properties (DSC) and microstructure analysis of the materials is discussed.

5.3.1 Fourier Transform Infrared Spectroscopy Analysis (FTIR)

In figure 5.2, the FTIR spectra for high amylose (HA) starch, PBAT, and a blend of MTPS-PBAT is shown. Both the PBAT and the blend show a carbonyl stretch peak at 1710 cm^{-1} . They also show the ester C-O stretch at 1265 cm^{-1} . This is not observed in the HA starch sample. The HA starch and the blend samples exhibit a peak between $3200\text{-}3400\text{ cm}^{-1}$. This corresponds to -OH stretch, from starch and glycerol.

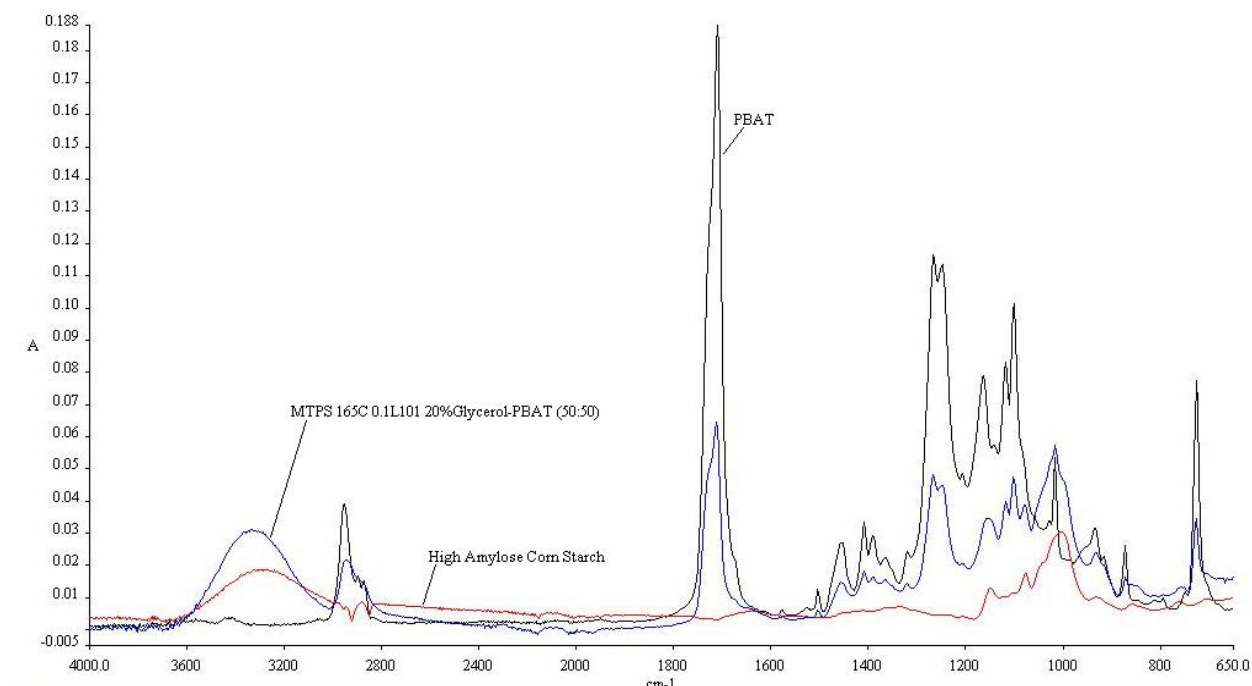


Figure 5.2: FTIR Spectra for HA Starch, PBAT, and MTpS 165 2%MA 0.1%L101 20%G-PBAT(50:50)

Figure 5.3 shows the FTIR spectra for as-extruded pellets of the sample “MTpS 165 60”, the pellets after soxlet extraction in dichloromethane, and the film produced when the solvent was evaporated. It is observed that the blend and the solvent film show a carbonyl stretch peak at 1710 cm^{-1} . This is similar to what is observed for pure PBAT. Also, the ester C-O stretch at 1265 cm^{-1} is exhibited in these two samples.

The grafting of MTpS and PBAT is difficult to prove by FTIR analysis, due to the fact that PBAT has an expressive peak close to the peak from carbonyl stretch at 1710 cm^{-1} and almost all of the starch peaks are underneath the PBAT curve, except the peak corresponding to -OH stretch. It can be observed that the solvent film after soxlet extraction presented one difference in relation of the curve for PBAT (Figure 5.2); the peak between $3200\text{-}3400\text{ cm}^{-1}$, that corresponds to -OH stretch from starch and glycerol. This indicates that the starch, glycerol, or both were extracted in dichloromethane with the PBAT.

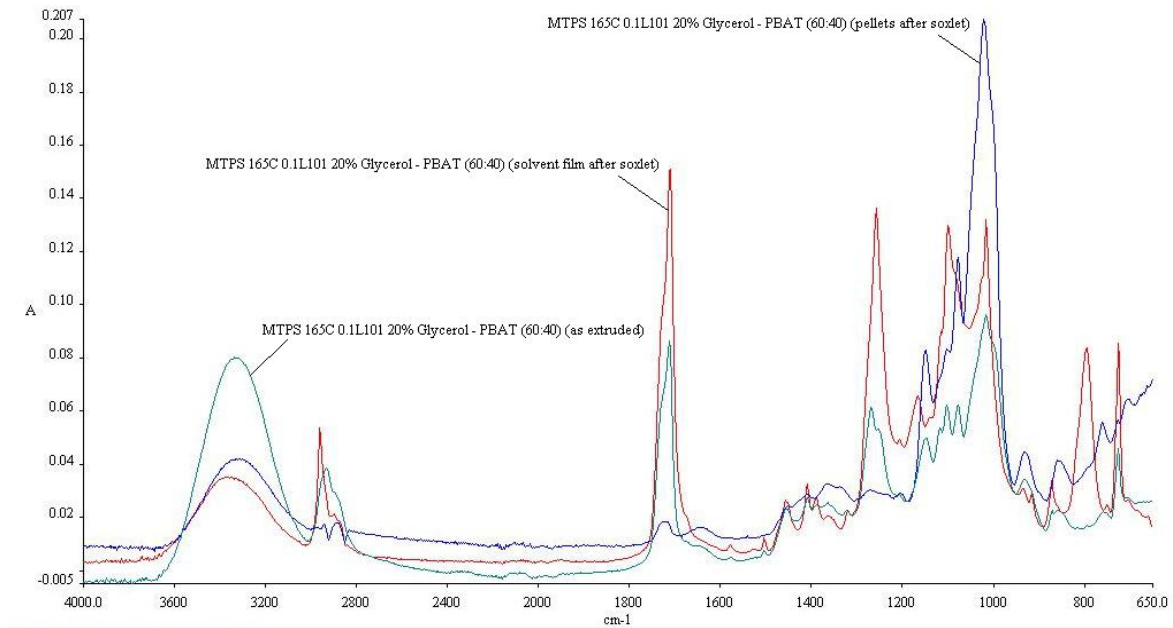


Figure 5.3: Red line-Film made after soxlet of MTpS 165 0.1L101 2%MA 20%G-PBAT(60:40), Blue line-Pellets left in thimble after soxlet of MTpS 165 0.1L101 2%MA 20%G-PBAT (60:40), Green line-As extruded pellets of MTpS 165 0.1L101 2%MA 20%G-PBAT (60:40)

5.3.2 Mechanical Properties

The mechanical properties of polymeric materials are the most important analysis due to the prerequisites that the polymers have for their applications.

5.3.2.1 Tensile tests

The mechanical properties of the different samples provides performance metrics for these materials. The effect of: a) the temperature profile used in the extrusion of MTpS, b) the effect of the ratio of MTpS/PBAT of the blends, and c) the effect of the

starch source impacts the performance properties, and is discussed. Table 5.2 presents the tensile measurements of the sheets of TpS and MTpS/PBAT blends.

Table 5.2 – Thickness and statistical analysis of mechanical properties (determined by tensile tests) of sheets blends of TpS and MTpS with PBAT.

Samples	Code	Thickness (μm)	Tensile Strength (MPa)	Modulus (MPa)	Elongation (%)
MTPS HA 165 60	A	518.9 \pm 21.64 ^a	6.1 \pm 0.31 ^a	86.0 \pm 6.69 ^a	697.0 \pm 50.60 ^a
MTPS HA 165 50	B	515.8 \pm 6.15 ^a	9.0 \pm 0.82 ^b	95.0 \pm 11.71 ^a	881.0 \pm 139.13 ^{b,c,d}
MTPS corn 165 50	C	498.6 \pm 27.50 ^a	6.2 \pm 0.93 ^a	47.6 \pm 10.79 ^{b,c}	673.2 \pm 131.84 ^{a,d}
PBAT	D	510.2 \pm 24.60 ^a	15.3 \pm 2.90 ^c	83.1 \pm 10.12 ^a	824.1 \pm 153.45 ^{a,b,c,d}
MTPS HA 135 50	E	508.4 \pm 24.56 ^a	8.4 \pm 1.46 ^b	40.7 \pm 3.87 ^{b,e}	946.8 \pm 151.35 ^{b,c,d}
MTPS corn 135 50	F	506.5 \pm 9.82 ^a	9.2 \pm 0.62 ^b	52.1 \pm 5.10 ^c	938.6 \pm 52.27 ^b
TPS HA 135 50	G	524.7 \pm 20.26 ^a	8.6 \pm 0.57 ^b	67.1 \pm 10.64 ^d	852.5 \pm 33.27 ^c
TPS corn 135 50	H	508.7 \pm 9.81 ^a	8.0 \pm 0.99 ^b	36.6 \pm 4.21 ^e	807.2 \pm 111.20 ^{c,d}

Means at same column with different letters are significantly different ($p \leq 0,05$).

In examining the tensile strength of MTpS/PBAT sheets at 165°C and 20% glycerol, the increase of MTpS content to 60% decreased the tensile strength from 9.0 to 6.1MPa. Comparing the MTpS samples of high amylose corn starch and of regular corn starch, one can observe the effect of composition of starch on tensile properties. The blend using MTpS of high amylose corn starch (70% amylose) presented higher tensile strength (9.0 MPa) than the blend using MTpS of regular corn starch (25 - 28% amylose) (6.2MPa). This could be attributed to the linear structure of amylose chains at lower glycerol content. According to Rindlav-Westling, Stading, Hermansson & Gatenholm (1998), the amylose network structure is very stable, with strong molecular

orientation, forming films denser than amylopectin films. Higher amounts of amylose in starches give stronger films, while the branched structure of amylopectin generally leads to films with decreased tensile stress (Tharanathan, 2003, Lourdin et al, 1995, Alves et al 2007).

For all of the samples of sheets of TpS and MTpS/PBAT at 135°C and 30% glycerol, the tensile strength did not show a significant difference ($p \leq 0,05$)(Figure 5.4), probably due mainly to the effect of glycerol. For blends of MTpS/TpS with 30% glycerol, the effect of glycerol on tensile properties is more effective than the effect of the amylose/amylopectin ratio, and the effect of the different thermoplastic starch used (modified and non-modified).

These values of the tensile strength for TpS and MTpS blends were higher than blends of cassava TpS with the biodegradable polymer, PBSA (polybutylene succinate adipate), reported in literature; 5.2MPa for TpS/PBAT (30:70) and 7.0 MPa for TpS/PBAT (70:30) (Sakanaka, 2007²⁶). However, the values of tensile strength for TpS and MTpS blends were lower than those of synthetic films, such as HDPE (high density polyethylene) or LDPE (low density polyethylene), which present stress at break of 16 and 26 MPa, respectively (Salame, 1986; Bader & Goritz, 1994).

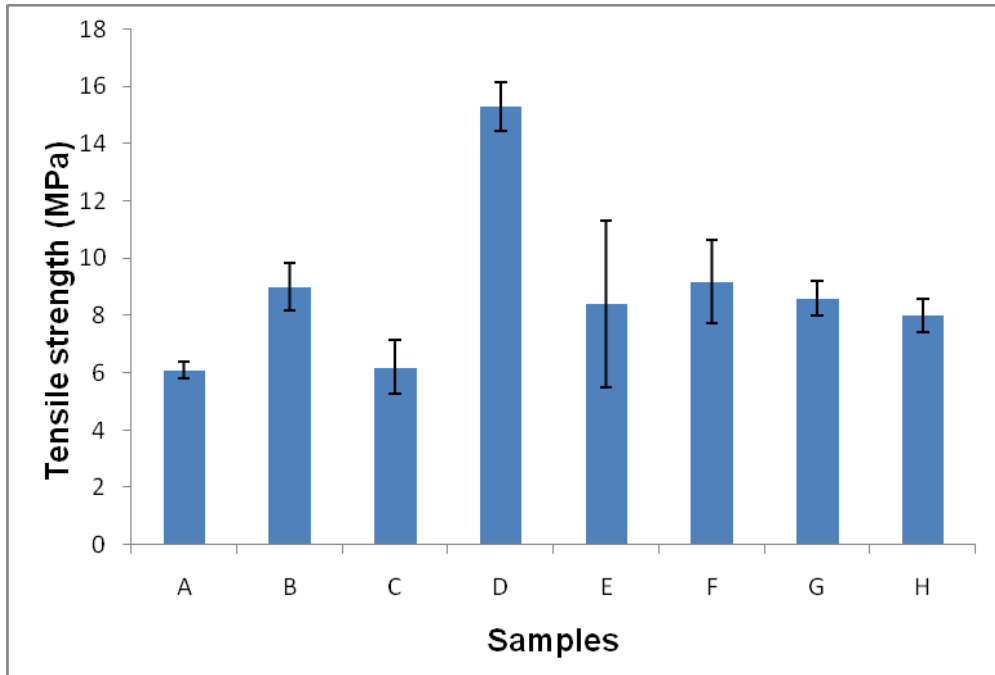


Figure 5.4- Tensile strength (MPa) of the samples: MTpS blends at 165°C and 20%glycerol; : (a) MTpS High amylose-PBAT (60:40), (b) MTpS High amylose-PBAT (50:50); (d) PBAT; (c) MTpS corn starch-PBAT (50:50); and (d) PBAT. Blends of TpS and MTpS blends at 135°C and 30% glycerol: (e) MTpS High amylose-PBAT (50:50); (f) MTpS corn starch-PBAT (50:50); (g) TpS High amylose-PBAT (50:50) and (h) MTpS corn starch-PBAT (50:50).

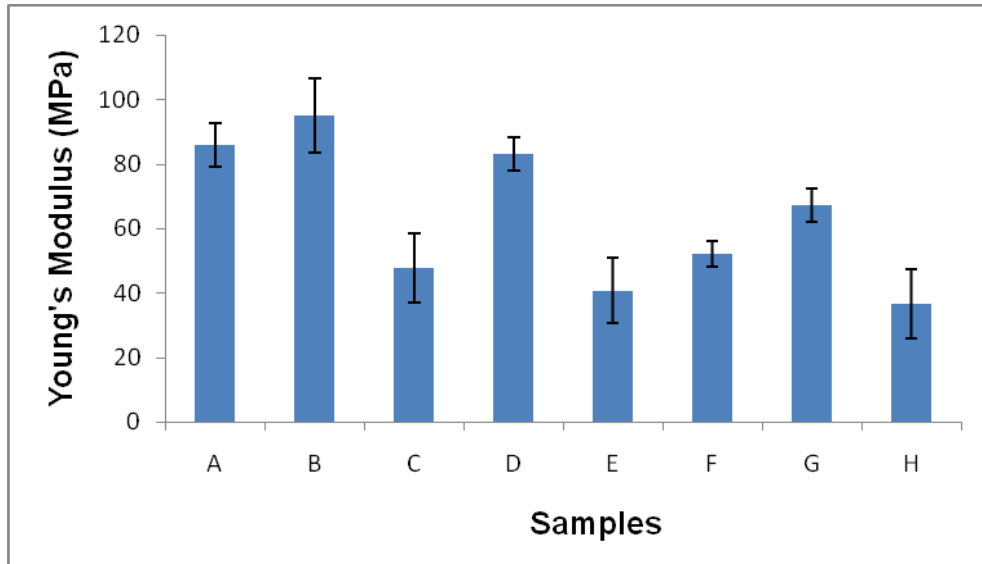


Figure 5.5- Young's Modulus (MPa) of samples: MTpS blends at 165°C and 20%glycerol; : (a) MTpS High amylose-PBAT (60:40), (b) MTpS High amylose-PBAT (50:50); (d) PBAT; (c) MTpS corn starch-PBAT (50:50); and (d) PBAT. Blends of TpS and MTpS blends at 135°C and 30% glycerol: (e) MTpS High amylose-PBAT (50:50); (f) MTpS corn starch-PBAT (50:50); (g) TpS High amylose-PBAT (50:50) and (h) MTpS corn starch-PBAT (50:50)

The samples of blends of MTpS made with high amylose corn starch (60% and 50% of MTpS) and PBAT at 165°C did not show differences in Young's modulus values among the samples, however, the MTpS of regular corn starch in the same conditions presented a lower Young's modulus (47.6MPa) than the other samples at 165°C and a lower Young's modulus than PBAT (83MPa).

Comparing the samples of MTpS and TpS at 135°C, the Young's modulus values are lower than for PBAT, except for the sample of TpS of high amylose corn starch (Figure 5.6).

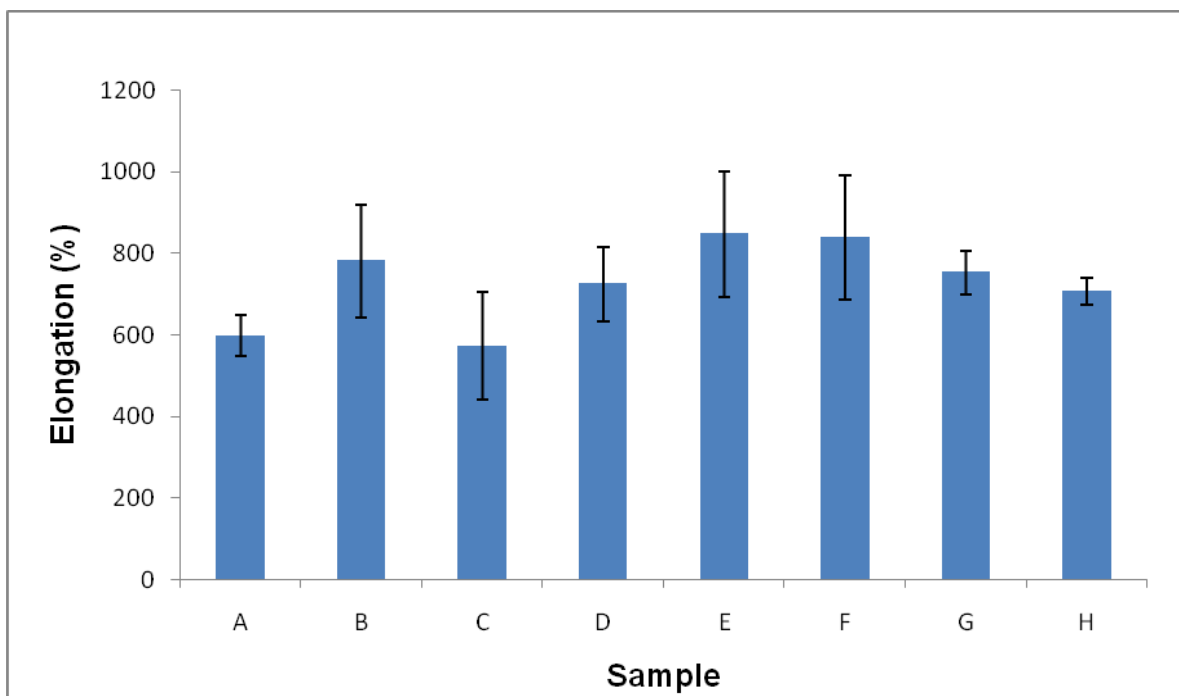


Figure 5.6 - Elongation (%) of samples: MTpS blends at 165°C and 20%glycerol; : (a) MTpS High amylose-PBAT (60:40), (b) MTpS High amylose-PBAT (50:50); (d) PBAT; (c) MTpS corn starch-PBAT (50:50); and (d) PBAT. Blends of TpS and MTpS blends at 135°C and 30% glycerol: (e) MTpS High amylose-PBAT (50:50); (f) MTpS corn starch-PBAT (50:50); (g) TpS High amylose-PBAT (50:50) and (h) MTpS corn starch-PBAT (50:50).

Comparing all samples of sheets of TpS/PBAT and MTpS/PBAT with sheets of PBAT, the elongation of the samples did not show significant differences ($p \leq 0,05$).

These results are due to high elongation of pure PBAT. In general, these results for elongation indicate that blends of MTpS and TpS with higher glycerol content (30%) and PBAT, in the ratio of 50:50, exhibited elongation comparable to that of pure PBAT.

The elongation depends of the interactions among the blend components and natural elongation of the polymers used. One of the characteristics of PBAT is its high elongation (~800%). In this work the addition of 50% of TpS or MTpS and 60% of MTpS made from high amylose starch, did not change the original elongation from that of the pure PBAT. These values were higher than those of other blends of TpS with biodegradable polymers reported in literature; PBSA (elongation of 233%), (Sakanaka, 2007²⁶), and PLA blends with TpS that showed elongation at the break varying from 5 to 20% (Huneault & Li, 2007¹⁶), and higher than those of synthetic films, such as HDPE (high density polyethylene) or LDPE (low density polyethylene), which present strain at break of 300 and 500%, respectively (Salame, 1986; Bader & Goritz, 1994).

According to Myllarinen, Partanen, Sepalla & Forsell (2002), glycerol and starch polymers are strongly interacted, and at low glycerol contents (< 20%), this interaction results in more brittle and stronger networks. In this paper, the samples of 20% glycerol did not show improvement in tensile strength due to the effect of the temperature. The samples of 20 and 30% of glycerol were extruded at different temperature profiles (maximum temperature of 165⁰C and 135⁰C, respectively). In this way, the lower glycerol content positively affected the tensile strength while the high temperature profile used negatively affected the tensile strength, due to the higher degradation of maleated samples at this temperature.

5.3.2.2 Puncture tests

The resistance of a material to puncture is a quality control parameter for materials used to contain products with sharp extremities or products that could be damaged from external forces during storage or distribution. Due to the shape and size of the thermoformed samples, it was not possible to perform tensile tests on the thermoformed pieces, however, puncture tests of the blends after thermoforming were performed. Table 5.3 shows the thickness (μm), puncture strength (N) and puncture deformation (mm) for the samples.

It should be noted that the sample “MTpS corn 165 50” was not able to be thermoformed properly, it produced a thermoformed object that was irregular in shape and thickness. Puncture tests of the thermoformed pieces were not run for this sample and for neat PBAT, due to its extreme flexibility

Table 5.3 – Mechanical properties determined by puncture tests of the thermoformed pieces of the blends of TpS and MTpS with PBAT.

Samples	THERMOFORMED PIECES		
	T ^a (μm)	PS ^b (N)	PD ^c (mm)
MTpS high amilose 165 60	283±9.6 ^a	26.0±0.80 ^a	10.3±0.44 ^a
MTpS high amilose 165 50	323±15 ^b	47.7±2.29 ^b	15.9±0.51 ^b
MTpS corn 165 50	-	-	-
MTpS high amilose 135 50	333±70 ^{a,b,c}	40.4±6.91 ^b	19.5±2.44 ^{c,d}
MTpS corn 135 50	380±78 ^{b,c}	27.7±5.56 ^a	20.0±0.72 ^c
TpS high amilose 135 50	333±16 ^b	52.3±2.35 ^c	16.6±1.37 ^b
TpS corn 135 50	363±23 ^c	48.4±2.41 ^b	18.6±0.84 ^d
PBAT	-	-	-

^a Thickness (μm) ^b puncture strength (N) and ^c puncture deformation (mm).

The thickness of thermoforming pieces varied more than 5%, this could interfere with the mechanical properties. The puncture test results showed similar behavior to the tensile test results. Comparing the samples extruded at 165⁰C, the samples that have more MTpS (60%) presented lower puncture strength and deformation than samples with 50% MTpS in the sheets and thermoformed pieces.

For the samples extruded at 135⁰C, blends of maleated thermoplastic starch presented higher puncture strength and lower puncture deformation than non-modified TpS. Comparing the thermoformed blends produced, high amylose corn starch (modified or not) presented higher puncture strength (N) than samples of regular corn starch.

Even though the tensile properties of TpS and MTpS blends presented similar numbers, the visual characteristics were very different. The MTpS blends have a more homogeneous surface and formed more transparent sheets than the TpS sheets. Another advantage is that MTpS could be blended with other biopolymers with higher melt temperatures, like PLA, without burning. The processability of MTpS of high amylose is much better than the processability of regular corn starch. MTpS of high amylose corn starch (20, 25 or 30% glycerol) can be pelleted while the MTpS of regular corn starch at the same condition cannot be pelletized. In this case, the materials were collected and ground into a powder before being blended with PBAT.

5.3.3 Thermal Analysis (DSC)

From the thermograms of the MTpS/PBAT and TpS/PBAT samples (Table 5.4) we can observe a melting temperature for PBAT of 113⁰C. MTpS and TpS blends

presented similar melting temperatures; varying from 115.6 to 123.1⁰C, measured at the second heating. The crystallization temperatures were similar for all the MTpS/TpS blends (from 72.4 to 79.5⁰C), while the PBAT presented a crystallization temperature of 33.0⁰C

Table 5.4 – DSC parameters: melting temperature (T_m), crystallization temperature (T_c) of the blends of MTpS and TpS with PBAT.

Sample	Cooling		Second Heating	
	T _c (°C)	ΔH _c (J/g)	T _m (°C)	ΔH _m (J/g)
MTPS HA 165 60	78.9	6.2	123.1	6.4
MTPS HA 165 50	79.5	7.7	123.1	6.0
MTPS corn 165 50	72.4	8.4	115.7	6.4
MTPS HA 135 50	75.8	6.9	117.8	6.2
MTPS corn 135 50	74.5	9.3	116.8	7.4
TPS HA 135 50	79.2	7.8	121.5	6.2
TPS corn 135 50	72.6	8.5	121.5	6.5
PBAT	33.0	20.1	113.6	16.2

5.3.4 Environmental Scanning Electron Microscopy (ESEM) Images

ESEM observations show the surface of the sheets of blends of MTpS and TpS samples. Figure 5.7 shows the samples containing MTpS that were extruded at 165⁰C and Figure 5.8 shows the samples containing MTpS and TpS that were extruded with a maximum temperature of 135⁰C. In general, the samples that were blended with the

thermoplastic starch extruded at 165°C are more homogeneous and smoother than the samples that were blended with MTpS and TpS samples that were processed at 135°C. This could imply that there was better plasticization of the starch with higher temperatures. According to Mali et al (2002)²⁷, a homogeneous matrix of films is a good indicator of their structural integrity and consequently good mechanical properties would be expected. However, better mechanical properties of the samples at 165°C were not observed. These results could be attributed to the thermoplasticization process. Although the MTpS presented better plasticization, there is also more degradation of starch in reactive extrusion to produce the MTpS.

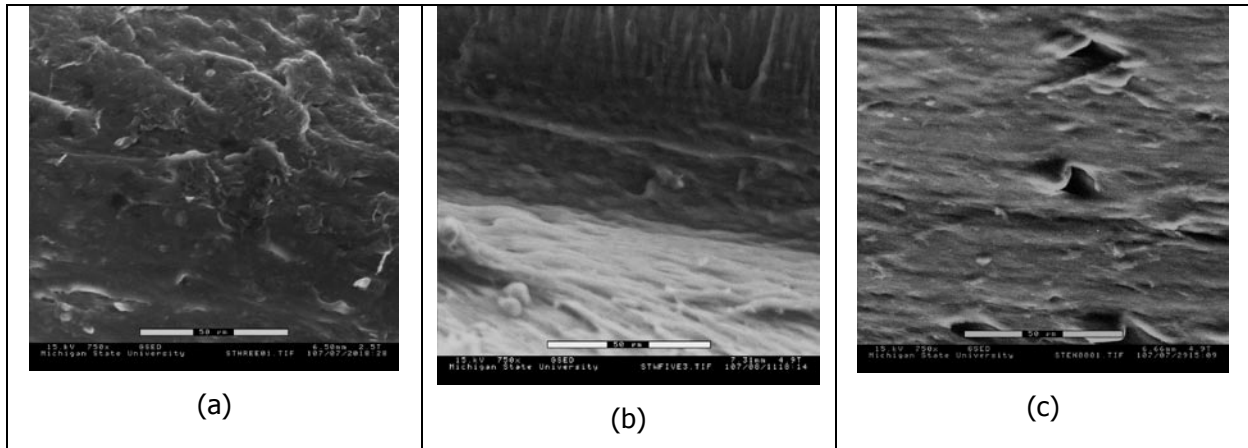


Figure 5.7 – ESEM images of the samples extruded at 165°C and 20% glycerol: MTpS high amylose 0.1L101/PBAT (60:40) (a). MTpS high amylose 0.1L101/PBAT (50:50) (b) and MTpS corn starch 0.1L101/PBAT (50:50) (c).

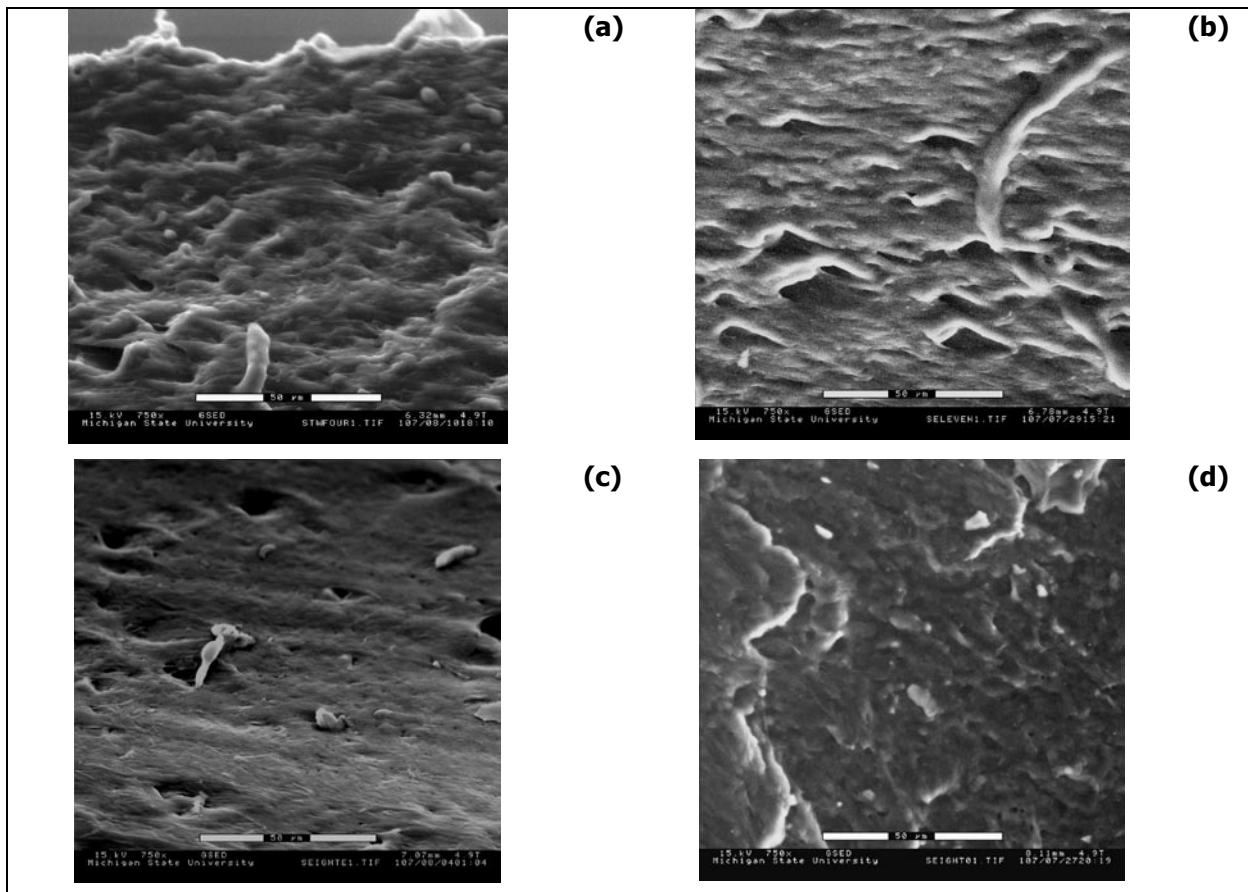


Figure 5.8 – ESEM images of the samples extruded at 135°C and 30% glycerol: TpS high amylose 0.1L101/PBAT (50:50) (a). MTpS high amylose 0.1L101/PBAT (50:50) (b). TpS corn starch 0.1L101/PBAT (50:50) (c) and MTpS corn starch 0.1L101/PBAT (50:50) (d).

5.4 CONCLUSION

Blends of plasticized starch, with or without maleation, with PBAT can form sheets which can be thermoformed. The processability of high amylose corn starch MTpS is much better than the processability of regular corn starch MTpS. The tensile properties are similar for blends of PBAT with TpS and MTpS that have been extruded at a maximum temperature of 135⁰C. However, the maleated thermoplastic samples formed sheets and thermoformed pieces that were more transparent and had a more homogeneous surface. The effect of amylose content of the different starches used did not present significant differences when the glycerol content was 30% and the ratio of thermoplastic starch/PBAT used was 50:50. When the MTpS contained 20% glycerol and the maximum processing temperature was 165⁰C, the blend containing MTpS of high amylose corn starch showed better tensile properties than the blend containing MTpS of regular corn starch, when the ratio of thermoplastic starch/PBAT used was 50:50. Increasing the MTpS (high amylose corn starch) content to 60% decreased the tensile strength and elongation of the sheets. The addition of 50% of TpS or MTpS decreased the tensile strength, but did not cause a significant difference in the elongation, compared to the elongation of PBAT.

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CAPÍTULO 6 – MECHANICAL AND BARRIER PROPERTIES OF FILMS OF THERMOPLASTIC STARCHES AND POLY(BUTYLENE ADIPATE CO-TEREPHTHALATE) (PBAT).

ABSTRACT

Blends of thermoplastic starches (modified and non-modified) with poly(butylenes adipate co-terephthalate) were produced in a twin-screw extruder using different sources of starch (high amylose, regular and waxy corn starch). The objective of this work was to observe the effect of different starch source and modification of the thermoplastics starches on mechanical properties, water vapor permeability (WVP) and water sorption isotherms of films of blends of thermoplastic starch with poly(butylenes adipate co-terephthalate). The films were characterized by mechanical and barrier properties, water sorption isotherms (WSI) and environmental scanning electron microscopy (ESEM). In general, the modification of the thermoplastic starch improved the mechanical and barrier properties, water resistance and microstructure of the blends with PBAT when compared with TpS-PBAT blend. All the MTpS and TpS blends films were more hygroscopic than PBAT films, but were less hygroscopic than films of thermoplastic starch. The modification of the thermoplastic starch by grafting of maleic anhydride (MA) in general had an important positive effect on the equilibrium water content as it was compared with the samples without maleation. The blends of modified and non-modified thermoplastic films had lower water vapor permeability than permeability of traditional polymers like LPDE and other biodegradable films.

Key-words: biodegradable, water permeability, maleation, biofilms

6.1 INTRODUCTION

Plastics have become a major factor in modern life and the massive volume of plastics in use has a significant effect on the environment. Major efforts are underway to reduce the impact of plastics on the environment and to make it more eco-friendly (Khare & Deshmukh, 2006)¹. Research and development is being carried out to synthesize polymers – such as lactic acid, caprolactone and starch from a renewable resource, especially from agricultural crops with the expectation that such bio-based polymers will be easy to fully degrade (Kalambur & Rizvi, 2006)².

Starch has been considered for many years as a polymer with a high potential for packaging applications because of low cost, renewability and biodegradability. Several studies have been done to analyze the properties of starch-based films (Lourdin, Della Valle & Colonna, 1995³; Arvanitoyannis, Billiaderis, Ogawa & Kawasaki, 1998⁴; García, Martino & Zaritzky, 1999⁵; 2000; Mali, Grossmann, García, Martino & Zaritzky, 2002⁶, 2004, 2005; Mali & Grossmann, 2003⁷; Sakanaka⁸ Huneault & Li⁹). Edible and/or biodegradable films are not able to replace synthetic packaging films; however they do have potential to replace the conventional packaging in some applications.

Starch consists primarily of branched and linear chains of glucose molecules, named as amylopectin and amylose, respectively. Amylose is essentially a linear molecule with a few branches, whereas amylopectin is a highly branched molecule. Preponderance of amylose in starches gives stronger films. (Tharanathan, 2003)¹⁰. The commercial starches come from many different agricultural products: potato, corn, cassava, and wheat starch, that have the amylose content between 17 and 28%. However, the starches of some mutant genotypes of maize, barley, rice and wheat, etc. contain either an increasing amylose content (i.e. high amylose or amylostarch with up

to 70% amylose) or an increasing amylopectin content (i.e. waxy starch with 99-100% amylopectin). The different amylose/amylopectin ratios of these starches led to differences in granular structure, physiochemical properties and quality of end-use products (Hung, Maeda & Morita, 2006)¹¹.

The functional properties of amylose films are in general slight better than those of amylopectin films regarding both films strength and barrier properties. The permeability of water vapor of films was higher for amylopectin than for amylose films, and the amylose films were independent of both crystallinity and microstructure (Rindlav-Westling et al, 1998)¹².

The hydrophilic nature of starchy polymers makes them sensitive to the environmental humidity and the presence of high level of glycerol strengthens this behavior. (Myllarinem et al, 2002)¹³. Blending thermoplastic starch with biodegradable polymers that are less hydrophilic it is one of alternative to produce materials more water resistant.

The objectives of the present work were to develop biodegradable films of blends of starches from different sources (high amylose corn starch, regular corn starch and waxy corn starch) with poly(butylenes adipate co-terephthalate), comparing the modified and non-modified thermoplastic starch by mechanical and barrier properties, water sorption isotherms, Water vapor permeability and microstructure.

6.2 MATERIALS AND METHODS

6.2.1 Materials

High amylose corn starch was purchased from National Starch and Chemicals (Indianapolis, IN). Regular corn starch was obtained from Cargill Inc. (Minneapolis, MN). Waxy (high amylopectin) corn starch was purchased from Corn Products (Sao Paulo, Brazil). Poly(butylene adipate-co-terephthalate) (PBAT) was purchased from BASF Chemicals (Ludwigshafen, Germany), under the trade name Ecoflex. Anhydrous glycerol, 99.9% assay, was purchased from J.T. Baker (Phillipsburg, NJ). Maleic anhydride was purchased from Sigma-Aldrich, Inc (St. Louis, MO). The initiator, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, also referred to as Luperox 101, was purchased from Sigma-Aldrich, Inc (St. Louis, MO).

6.2.1.1 Equipment

A Century CX-30 co-rotating twin-screw extruder, having a length/diameter ratio (L/D) of 42 and a screw diameter of 30 mm was used to prepare the thermoplastic starch and maleated thermoplastic starch, and to blend these materials with Ecoflex. A pelletizer was used to cut the extrudate strands into small pellets. The blended material was then extruded through a Killion single-screw extruder, having a length/diameter ratio of 24 and a screw diameter of 1 inch. The extrudate exited the extruder in the form of a film of material and was collected on a roller.

6.2.2 Procedure

6.2.2.1 Production of thermoplastic starch (TpS) and modified thermoplastic starch (MTpS)

Thermoplastic starch (TpS) was produced in a co-rotating twin-screw CX-30 extruder. The corn starch (high amylose, regular, or waxy) was fed into the feed port of the extruder using an external feeder. Glycerol, which was warmed in a water bath, was pumped into the extruder using a peristaltic pump. The feed rates of the external feeder and the peristaltic pump were set so as to accomplish a composition of 70 wt% starch and 30 wt% glycerol, and a total flow of approximately 11 kg/h of material through the extruder. The temperature profile of the extruder was 25/115/120/125/130/135/135/135/130/130°C from the feed throat to the die. The screw speed was set to 125 rpm. The vent port was kept open to remove any moisture. The extruded strand was air cooled and pelletized in line. The pellets were dried for two days in an oven at 65°C before being blended with Ecoflex.

Maleated thermoplastic starch (MTpS) was produced in a co-rotating twin-screw CX-30 extruder. Maleic anhydride was ground into a fine powder using a mortar and pestle and pre-blended with the corn starch (high amylose, regular, or waxy) before being fed into the feed port of the extruder. The concentration of maleic anhydride used was 2 wt% with respect to the total mass. Luperox 101 was pumped into the feed throat of the extruder using a peristaltic pump. The concentration of Luperox 101 used was 0.1 wt% with respect to the total mass. Glycerol, which was warmed in a water bath, was pumped into the extruder using a peristaltic pump. The MTpS was produced under the

same conditions used in production of the TpS samples, with a temperature profile of 25/95/115/125/130/135/135/135/130/130°C and 30% glycerol. This was done to compare the modified and non-modified thermoplastic starch of the high amylose corn starch, regular corn starch, and waxy corn starch.

6.2.2.2 Blend production of TpS and MTpS with PBAT

Blends of thermoplastic starch/PBAT or maleated thermoplastic starch/PBAT were produced in a co-rotating twin-screw CX-30 extruder. Pellets of TpS or MTpS were pre-mixed with PBAT in various weight of TpS/MTpS: weight of PBAT ratios (Table 6.1) and fed into the feed port of the extruder using an external feeder. The temperature profile of the extruder was 25/125/135/140/145/150/150/150/145/135°C from the feed throat to the die. The screw speed was set to 100 rpm. The vent port was kept open to remove any moisture. The extruded strand was air cooled and pelletized in line. The pellets were dried for one day in an oven at 65°C before being extruded into sheets.

Table 6.1 – Composition of the blends of TpS and MTpS with PBAT.

Samples	Maximum Temperature (°C)	Glycerol (%)	Luperox (%)	Blends composition	
				TpS/MTpS (%)	PBAT (%)
MTpS high amylose	135	30	0.1	30	70
MTpS corn	135	30	0.1	30	70
MTpS waxy	135	30	0.1	30	70
TpS high amylose	135	30	-	30	70
TpS corn	135	30	-	30	70
TpS waxy	135	30	-	30	70
PBAT					100

6.2.2.3 Film production

Extruded films of the blended material were produced in a single-screw extruder. The pellets were gravity-fed into the extruder at the feed throat. The temperature profile of the extruder was 160/160/160/160/154°C for zone 1, zone 2, zone 3, clamp ring, and die, respectively. The screw speed was set to 65 rpm. The extruded sheet was cooled on a chill roller set at 21°C and then collected on an auxiliary roller. The speed of the chill roller was adjusted so as to produce a sheet with a thickness of 150µm.

6.2.3 Films Characterization

6.2.3.1 Mechanical properties

Tensile samples of the blends of TpS and MTpS/PBAT blends were conditioned as recommended in standard method ASTM D-4332¹⁴, in a constant environment room at $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ RH for at least 40 hours before testing. The tensile tests were measured in accordance with ASTM D-882 method (1995)¹⁵ using a TA.TX2i Stable Micro Systems texture analyzer (Surrey, England). Specimens (30mmx 6mm) of the extruded sheets of each formulation were clamped between the grips. Force-extension curves were recorded. The parameters determined were: tensile strength, modulus, and elongation. Seven samples were tested for each blend and property.

6.2.3.2 Water vapor permeability (WVP)

WVP tests were conducted using ASTM method E96 (1995)¹⁶ with some modifications. Each film sample was sealed over a circular opening of 0.00181 m² of a permeation cell that was stored at 25°C in a desiccator to maintain a 75% RH gradient across the film, anhydrous calcium chloride (0% RH) was placed inside the cell and a sodium chloride saturated solution (75% RH) was used in the desiccator. The RH inside the cell was always lower than outside, and water vapor transport was determined from the weight gain of the permeation cell. After steady state conditions were reached (about 2 h), eight weight measurements were made over 3 days. Changes in the weight of the cell were recorded to the nearest 0.0001 g and plotted as a function of time. The slope of each line was calculated by linear regression ($r^2 > 0.99$) and the water vapor transmission rate (WVTR) was calculated from the slope of the straight line (g/s) divided by the cell area (m²). After the permeation tests, film thickness was measured and WVP (g.m⁻¹.s⁻¹.Pa⁻¹) was calculated as $WVP = [WVTR / S(R_1 - R_2)]d$; where S is the saturation vapor pressure of water (Pa) at the test temperature (25°C), R₁, the RH in the desiccator, R₂, the RH in the permeation cell and d is the film thickness (μm).

6.2.3.3 Water sorption isotherms

Sorption isotherms of native high amylose corn starch, regular corn starch and waxy corn starch, and films of blends of thermoplastic starch modified and non-modified were determined. Films samples with dimensions of 20X20mm² were dried in

desiccators with CaCl_2 (0% relative humidity), during 4 weeks. The dried samples were weighed to the nearest 0.0001 into hermetic bottle containers with different saturated salt solutions of known equilibrium relative humidity ranging from 11.3 to 90.2% or 0.11 to 0.90 aw (water activity) (Table 2), at 25°C, during 4 weeks. Equilibrium moisture content (%db) was calculated from the gain in weight (AOAC, 1996)¹⁷. Measurements were made in triplicate.

6.2.3.4 Environmental scanning electron microscopy (ESEM)

An environmental scanning electron microscope (ESEM) (Phillips Electroscan 2020) was used to make observations of the surface of the films. Pieces of the films samples were cut and then viewed with the environmental scanning electron microscope.

6.2.4 Statistical Analysis

One control sample, PBAT, was tested to evaluate the effect of blends of TpS and MTpS with PBAT on mechanical and barrier properties of the films. Analysis of variance (ANOVA), Tukey mean comparison test ($p \leq 0.05$) and regression analysis were performed employing Statistica software (Statsoft, Oklahoma – USA).

6.3 RESULTS AND DISCUSSION

In general, the modification of the thermoplastic starch (MTpS) improved the mechanical and barrier properties, water resistance and microstructure of the blends with PBAT when compared with TpS-PBAT blend.

6.3.1 Mechanical Properties

A food packaging generally requires high stress for deformation depending on the intended application. In general, a food packaging must be an undeformable material to provide structural integrity or reinforce food structure, or a deformable film for other applications (Gontard, Guilbert & Cuq, 1992)¹⁸.

Table 6.2 – Mechanical properties of TpS and MTpS blends films.

Samples	Thickness (m)	TS^a (MPa)	Elongation (%)	Modulus (MPa)
MTpS HA /PBAT	151±1.2 ^a	17.3±0.88 ^a	700.0±0,01 ^a	0.47±0.044 ^a
MTpS corn/PBAT	150 ±0.8 ^a	16,9±1,30 ^a	700.0±0,01 ^a	0,48±0,065 ^a
MTpS waxy/PBAT	145±4.5 ^a	11,7±1,84 ^b	700.0±0,01 ^a	0,41±0,016 ^b
TpS HA/PBAT	152±17,0 ^a	14,3±0,95 ^c	693,1±13,66 ^a	0,49±0,038 ^a
TpS corn/PBAT	141±0,8 ^a	10,5±1,30 ^b	660,4±45,60 ^a	0,48±0,040 ^a
TpS waxy/PBAT	148±4,1 ^a	14,5±1,17 ^{a,c}	686,2±23,16 ^a	0,51±0,063 ^a
PBAT	146±3,6 ^a	21,7±1,46 ^d	700.0±0,01 ^a	0,45±0,09 ^c

^aTS = tensile strength (MPa).

All the films blends had lower tensile strength (TS) than neat PBAT films. Maleated high amylose and corn starch films had superior tensile strength than non-modified starch blends. This result indicated that the maleic anhydride has had an effect on compatibility of the grafting reaction between thermoplastic starch and PBAT. Comparing the samples of waxy starch (modified and non-modified), the TpS-PBAT blend showed higher TS than modified blend. This result is contradictory to the results for high amylose and corn starch samples. This behavior could be related of the non-homogeneous surface of this TpS sample. Apparently when the PBAT and TpS are not totally blended, it seems that the TpS acts as reinforcement of the PBAT matrix and not like a blended material. This could explain the higher TS compared with the MTpS-PBAT waxy starch blend.

Comparing all films of TpS/PBAT and MTpS/PBAT with PBAT film, the elongation of the samples did not show significant differences ($p \leq 0,05$). These results are due to high elongation of pure PBAT. In general, these results for elongation indicate that blends of MTpS and TpS with higher glycerol content (30%) and PBAT, in the ratio of 30:70, exhibited elongation comparable to that of pure PBAT. These values were higher than those of other blends of TpS with biodegradable polymers reported in literature; PBSA (elongation of 233%), (Sakanaka, 2007⁸), and PLA blends with TpS that showed elongation at the break varying from 5 to 20% (Huneault & Li, 2007)⁹.

The addition of TpS or MTpS had a positive effect on increasing the modulus of the polymeric matrix. The blend of MTpS of waxy starch presented a lower Young's modulus than the others blends. Tensile strength break of films ranged from 10.5 to 21.7 MPa and elongation from 603 to 700% (Table 6.2). These values were higher than those of other starch films reported in literature (Mali *et al.*, 2004; 2005, Alves *et al.*, 2007), but depending of film formulation, not quite as high as those of synthetic films, such as HDPE (high density polyethylene) or LDPE (low density polyethylene), which

have stress at break of 16 and 26, respectively, and strain at break of 300 and 500%, respectively (Salame, 1986¹⁹; Bader & Goritz, 1994²⁰).

6.3.2 Water Sorption Isotherms (WSI)

The water sorption isotherms of films prepared with blend of PBAT with modified and non-modified thermoplastic starch are shown in Figure 3.1. For all the formulations, the MTpS-PBAT and TpS-PBAT blends films were more hygroscopic than films prepared only with PBAT, but were less hygroscopic than films prepared only with thermoplastic starch (Mali et al⁶, 2005, Muller, Yamashita & Laurindo, 2007²¹).

The samples of modified and non-modified thermoplastic starch had high glycerol content (30%) that had an effect on keeping the water content between 2.6 to 4.8% in the films after 30 days in desiccators at 0% RH (CaCl₂) (Table 6.3). This residual water present in the films plus the higher glycerol content resulted in more hygroscopic films when compared with the control film (PBAT). The plasticizers affect the water sorption of the films, since they have a great affinity for water.

The modification of the thermoplastic starch by grafting of maleic anhydride (MA) in general had an important positive effect on the equilibrium water content compared to the samples without maleation. The samples of high amylose and regular corn starch TpS-PBAT films had at 90%RH (relative humidity) approximately 25% moisture content while the modified thermoplastic blends of high amylose and regular corn starch had 15% of water in the same condition. These results indicated the effect of maleation of starch in decreasing the water sorption of the blends.

The TpS-PBAT and MTpS-PBAT films of waxy starch were not different ($p < 0.05$) in water sorption, showing similar isotherms curves. This behavior could be attributed to non-homogeneous surface of the films of TpS waxy starch blend. This surface could hinder water permeation and make this formulation less hygroscopic when compared with the high amylose and regular corn starch TpS-PBAT films.

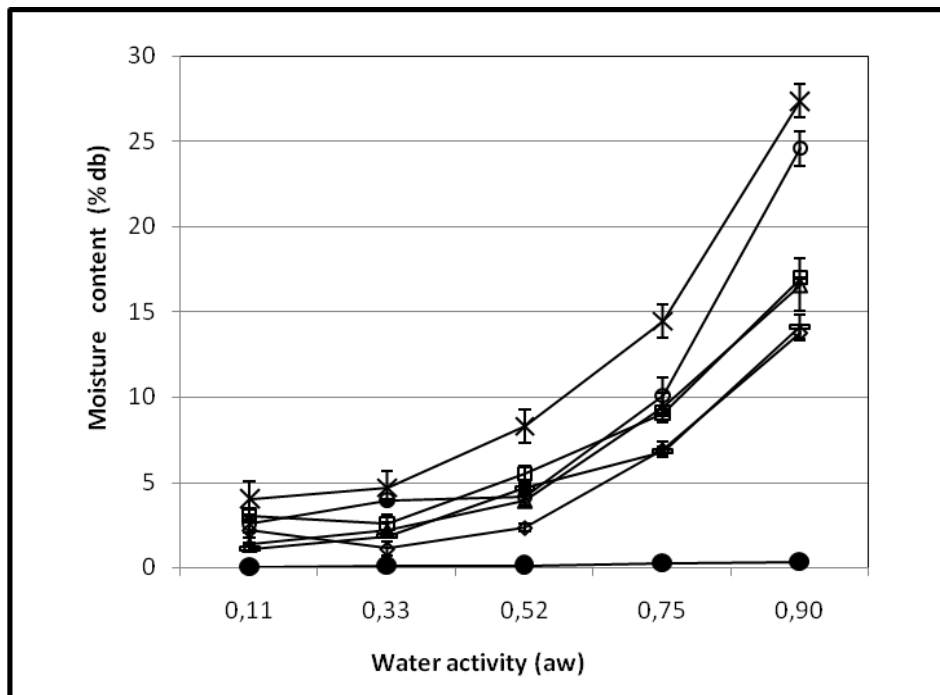


Figure 6.1 – Water sorption isotherms of blends of modified and non-modified thermoplastic starch and PBAT at 25°C. (-) MTpS high amylose, (Δ) MTpS corn, (□) MTpS waxy, (o)TpS high amylose, (x) TpS corn, (◇)TpS waxy and (●) PBAT.

Table 6.3 – Moisture content of the blends films after 30 days in 0% RH (CaCl₂).

Samples	Moisture content (%db)
MTpS high amylose /PBAT (30:70)	4.8
MTpS corn/PBAT (30:70)	4.4
MTpS waxy/PBAT (30:70)	3.2
TpS high amylose/PBAT (30:70)	3.7
TpS corn/PBAT (30:70)	5.1
TpS waxy/PBAT (30:70)	2.6
PBAT	0.1

6.3.3 Water Vapor Permeability (WVP)

Since a main function of a food packaging is often to avoid or at least to decrease moisture transfer between the food and the surrounding atmosphere, or between two components of a heterogeneous food product, water vapor permeability should be as low as possible (Gontard et al, 199²², Alves et al 2007²³).

The water vapor permeability of the films blend of TpS-PBAT and MTpS-PBAT are shown in table 5.4.

Comparing to the control (PBAT film) the TpS-PBAT samples (high amylose, corn and waxy) and the MTpS of waxy corn starch had no difference ($p \leq 0.05$) and the MTpS samples of high amylose and regular corn starch were significantly different, presenting higher water vapor permeability.

Table 6.4 – Water vapor permeability of the blends of MTpS-PBAT and TpS-PBAT of high amylose, corn and waxy corn starches.

Samples	Water Vapor Permeability ($g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$) $\times 10^{11}$
MTpS high amylose /PBAT (30:70)	8,5±0,44 ^a
MTpS corn/PBAT (30:70)	10,8±0,75 ^b
MTpS waxy/PBAT (30:70)	7,3±0,41 ^c
TpS high amylose/PBAT (30:70)	6,3±0,10 ^d
TpS corn/PBAT (30:70)	7,6±0,62 ^c
TpS waxy/PBAT (30:70)	5,3±0,96 ^d
PBAT	6,7±0,70 ^{c,d}

^a - Means at same column with different letters are significantly different (Tukey test, $p \leq 0.05$).

The water vapor permeability (WVP) values for the samples of PBAT and blends of TpS-PBAT and MTpS-PBAT varied between 5.3 to 10.8 $\times 10^{-11}$ $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$, depending of the formulation. With regard to synthetic polymers, the films obtained in this work had WVP values higher than these of low-density polyethylene (3.6×10^{-13} $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$) studied by Shellhammer & Krochta (1997)²⁴ and lower than those of other biodegradable films such as wheat gluten plasticized with glycerol (7.00×10^{-10} $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$), amylose (3.80×10^{-10} $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$), hydroxypropyl- methylcellulose with plasticizer and oil (1.90×10^{-10} $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$) (Gennadios, Weller, & Gooding, 1994)²⁵, and similar than those of cellophane (8.4×10^{-11} $g \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1}$), (Shellhammer & Krochta, 1997)²⁴.

6.3.4 Environmental Scanning Electron Microscopy (ESEM)

Images of the samples taken with the environmental scanning electron microscope (ESEM) are shown in Figure 6.2. The modified thermoplastic starch MTpS-PBAT films samples (a,c and e) appear to be smoother than the TpS-PBAT films samples (b,d and f). This could imply that there was better plasticization of the starch when using maleic anhydride and free-radical initiator in reactive extrusion to modify the thermoplastic starch; this also could indicate that there was less plasticization occurring during the extrusion of TpS compared with MTpS.

Comparing the three different sources of starches used in this work, in general the samples of regular and waxy corn starch (c,d,e and f) had a more homogeneous and a smoother surface when compared to the samples of high amylose corn starch (a and b). The samples of high amylose (TpS and MTpS) presented granules or part of starch granules, indicating that the starches were not completely plasticized. This result could indicate that the temperature profile used (temperature maximum of 135°C) was not enough to plasticize the high amylose corn starch.

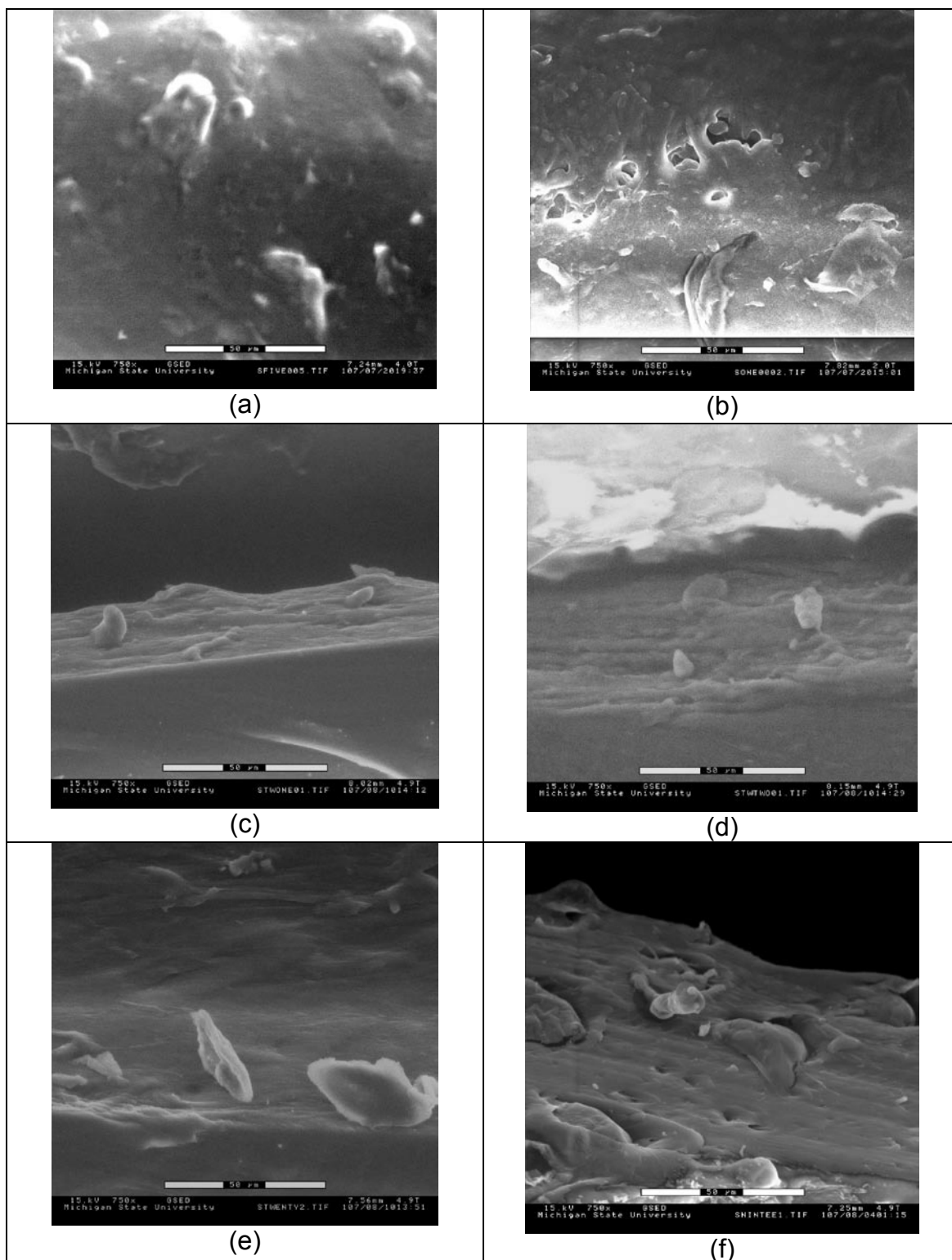


Figure 6.2 – Environmental scanning electron microscope (ESEM) images of films samples at 750x magnification: a) MTpS high amylose corn starch, b) TpS high amylose corn starch, c) MTpS regular corn starch, d) TpS regular corn starch, e) MTpS waxy corn starch and f) TpS waxy corn starch.

6.4. CONCLUSIONS

The maleation of the thermoplastic starch (MTpS) improved the mechanical and barrier properties, water resistance and microstructure of the blends with PBAT when compared with TpS-PBAT blend. The modification of the thermoplastic starch by grafting of maleic anhydride (MA) had an important positive effect on the equilibrium water content as it was used compared with the samples without maleation. The blends of thermoplastic films presented lower water vapor permeability than LPDE (low-density polyethylene) and other biodegradable films.

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CAPÍTULO 7 - CONCLUSÕES FINAIS

De uma maneira geral, a extrusão reativa foi uma metodologia eficiente na compatibilização entre fibras naturais e amidos com o poli(butileno adipato co-tereftalato) (PBAT).

A modificação do poliéster promoveu forte adesão interfacial com as fibras naturais, aumentando as propriedades mecânicas (resistência à tração, módulo de Young e alongação) e resistência ao impacto dos biocompósitos. Em geral, altas porcentagens de celulose resultaram em melhor interação entre as fibras e a matriz polimérica.

A processabilidade do ATpM de amido de milho com alto teor de amilose foi muito melhor que a processabilidade de amido de milho regular e ceroso. As blendas ATpM-PBAT formaram filmes, laminados e peças termoformadas mais transparentes e com superfícies mais homogêneas que as blendas de ATp.

As propriedades mecânicas dos filmes de ATpM-PBAT foram superiores que dos filmes de ATp-PBAT. A modificação do ATp pela inserção de anidrido maléico (MA) teve um positivo efeito no equilíbrio de conteúdo de água dos filmes quando comparados com as amostras não modificadas.

ANEXO A

Fotos dos Equipamentos Utilizados

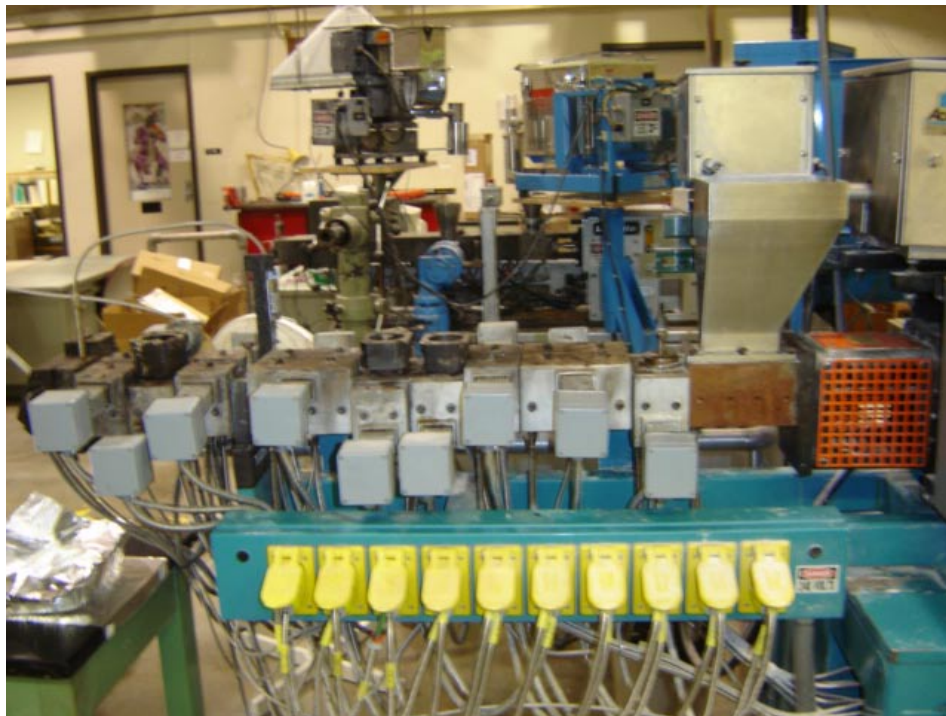
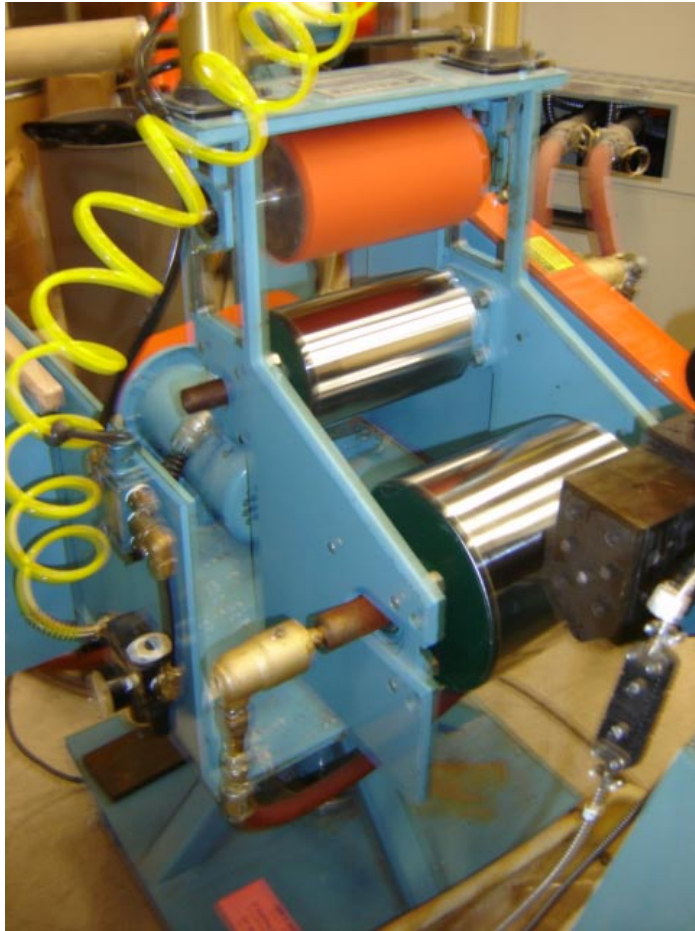


Figura A.1 – Foto da extrusora duplas rosca, Century ZSK 30.



(a)



(b)

Figura A.2 – Foto da extrusora monorosca (b)

ma de calandragem (a) para fabricação de filmes e laminados.



Unidade fixadora.



Unidade injetora.

Figura A.3 – Injetora em moldes.

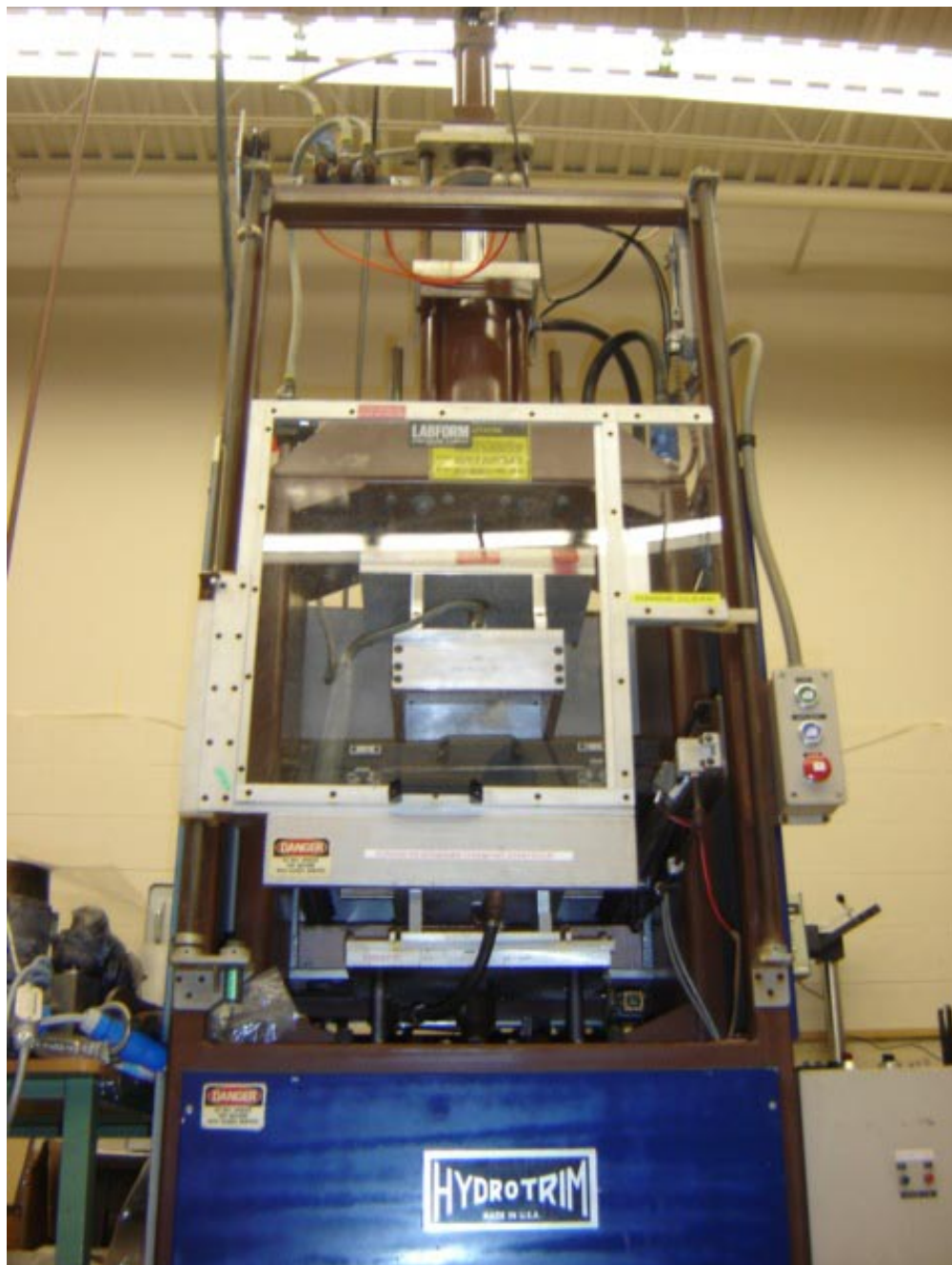
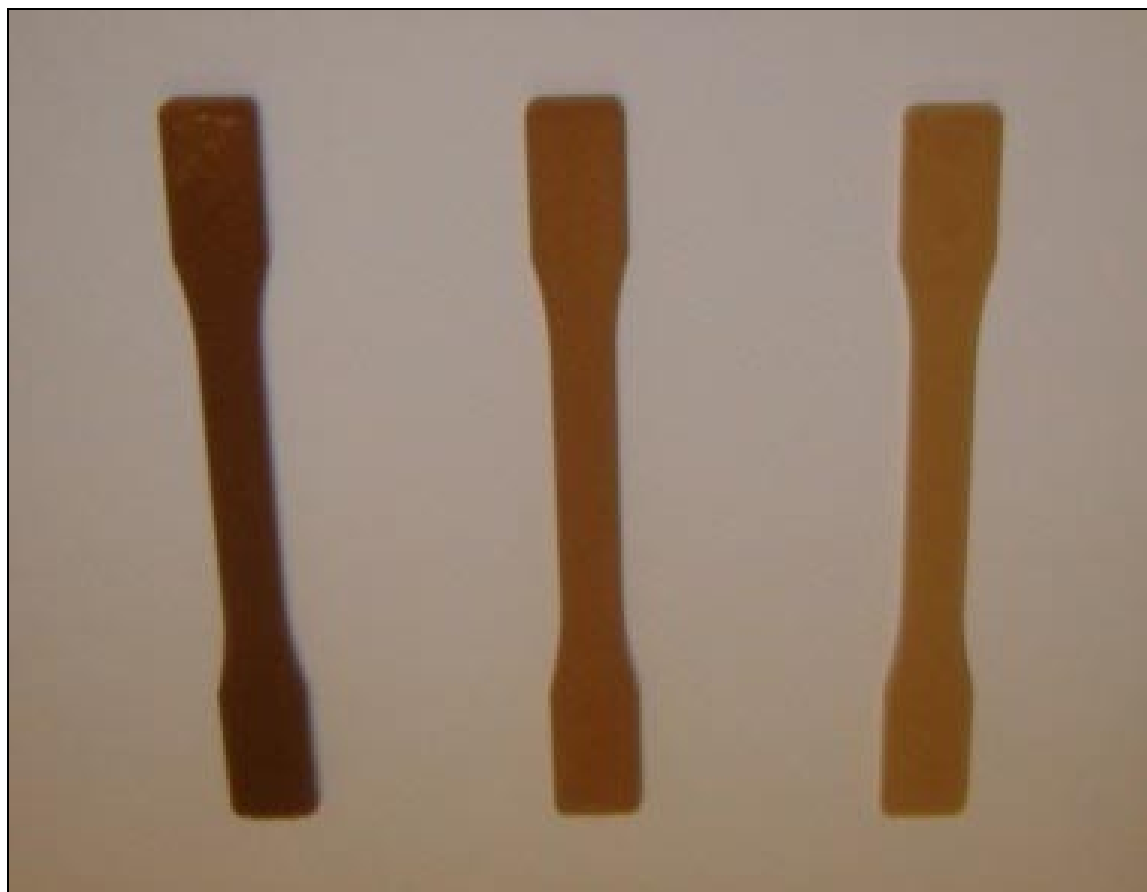


Figura A.4– Foto da termoformadora utilizada.

ANEXO B

Fotos dos Biocompósitos Produzidos.



(a)

(b)

(c)

Figura B.1 – Peças injetadas dos biocompósitos: (a) casca de aveia, (b) pó de madeira e (c) celulose.