MARIANNE AYUMI SHIRAI

DESENVOLVIMENTO DE MATERIAIS BIODEGRADÁVEIS A BASE DE AMIDO E POLI(ÁCIDO LÁTICO) PRODUZIDOS POR EXTRUSÃO TERMOPLÁSTICA

Londrina
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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 para a obtenção do título de Doutor em Ciência de Alimentos.

Orientador: Prof. Dr. Fabio Yamashita Co-orientadora: Profa. Dra. Carmen Maria Olivera Müller

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Londrina, 28 de novembro de 2013.

Aos meus pais Ricardo e Suzana, principais responsáveis pela formação do meu caráter e pelo amor incondicional; Ao meu irmão Alysson, meu laço eterno de amor e cumplicidade;
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Ontem um menino que brincava me falou Hoje é semente do amanhã Para não ter medo que este tempo vai passar Não se desespere e nem pare de sonhar Nunca se entregue, nasça sempre com as manhãs Deixe a luz do sol brilhar no céu do seu olhar Fé na vida, fé no homem, fé no que virá Nós podemos tudo, nós podemos mais Vamos lá fazer o que será"

(Gonzaguinha)

SHIRAI, Marianne Ayumi. **Desenvolvimento de materiais biodegradáveis a base de amido e poli(ácido lático) produzidos por extrusão termoplástica.** 151 f. Tese (Doutorado em Ciências de Alimentos) - Universidade Estadual de Londrina, Londrina, 2013.

RESUMO

Blendas de poli(ácido lático) (PLA) e amido estão sendo pesquisadas para a produção de filmes ou chapas planas pelo processo de extrusão por ser uma alternativa viável, pois além de serem biodegradáveis, são provenientes de fontes renováveis. Este trabalho teve como objetivo desenvolver filmes e chapas planas de amido de mandioca e PLA pelo processo de extrusão e avaliar o efeito da adição de ésteres de adipato e citrato como plastificantes, e ácidos adípico e cítrico como compatibilizantes. O trabalho foi dividido em cinco etapas, onde primeiramente foram produzidos filmes de amido termoplástico (ATP) por extrusão-sopro em balão e avaliou-se o efeito da adição de PLA plastificado com diferentes concentrações de ésteres de adipato e citrato. A plastificação do PLA e os processos de misturas feitos na extrusora foram essenciais para a obtenção dos materiais. Os ésteres de adipato proporcionaram filmes de menor espessura e maior elongação. Na segunda etapa foi pesquisado o efeito da adição de PLA e do tipo de extrusora (mono ou dupla rosca) empregado no preparo das blendas de ATP e poli(butileno adipato co-tereftalato (PBAT) destinadas à produção de filmes por extrusão-sopro em balão. O tipo de extrusora não mostrou diferença, entretanto a adição de PLA diminuiu a permeabilidade ao vapor de água (PVA) e elevou a rigidez dos filmes. Como a confecção de filmes por extrusão-sopro em balão não mostrou resultados favoráveis para produção em escala piloto, substituiu-se o tipo de PLA e passou-se a usar a extrusão plana. Assim, na terceira parte avaliou-se o efeito da adição de ésteres de adipato e citrato em chapas produzidos por extrusão plana. A incorporação de plastificantes reduziu a rigidez do material, a temperatura de transição vítrea (Tg) e a resistência à tração sem alterar a PVA. Os ésteres de adipato foram mais eficientes, pois também elevaram a elongação na ruptura dos materiais e as imagens de microscopia eletrônica de varredura revelaram que a blenda era imiscível. Como os ésteres de adipato proporcionaram resultados mais promissores, na quarta etapa os mesmos foram utilizados na fabricação de chapas com várias proporções de ATP e PLA. O aumento na proporção de amido não alterou a Tg, diminuiu a rigidez e a resistência à tração, aumentou o índice de cristalinidade e proporcionou um caráter hidrofílico, observado pelos resultados de isoterma de sorção de água e PVA. Dentre os ésteres de adipato, o adipato de diisodecila conferiu menores valores de PVA, manteve a resistência à tração e elevou a elongação na ruptura sendo, portanto selecionado para ser estudado como plastificante na etapa cinco. Blendas contendo 50/50 de ATP e PLA foram adicionados de ácido adípico e cítrico, individualmente e em mistura. Comparativamente, o ácido cítrico melhorou a adesão interfacial entre os polímeros e isso contribuiu nas propriedades mecânicas e de barreira. Com este trabalho concluiu-se que a produção de materiais de ATP e PLA por extrusão plana em escala piloto é viável, desde que ocorra a adição de plastificantes como éster de adipato, e o ácido cítrico mostrou-se eficiente como compatibilizante para o PLA e ATP.

Palavras-chave: Blenda. Polímero biodegradável. Ésteres de adipato. Ésteres de citrato. Compatibilizantes.

SHIRAI, Marianne Ayumi. **Development of biodegradable materials based of starch and poly(lactic acid) produced by thermoplastic extrusion.** 151 p. Doctoral thesis (Doctor Degree in Food Science) - Universidade Estadual de Londrina, Londrina, 2013.

ABSTRACT

Poly(lactic acid) (PLA) and starch blends is a promising option to produce films and sheets by extrusion because in addition to being biodegradable, these polymers are derived from renewable sources. The main objective of this work was develop cassava starch and PLA films and sheets by extrusion and evaluate the effect of addition of adipate and citrate esters as plasticizers, and adipic and citric acids as compatibilizers. This study was divided into five steps. In the first step, thermoplastic starch (TPS) films were produced by blown extrusion and the effect of adding PLA plasticized with adipate or citrate esters on the opacity, mechanical and microstructural properties was evaluated. The plasticization of PLA and mixture steps by twin-screw extruder were essential to obtain the materials by blown extrusion. Adipate esters conferred films with lower thickness and higher elongation at rupture. In the second step, the effect of the type of the extruder (single- or a twin-screw extruder) used in the preparation of the blends, and the addition of PLA on the functional properties of TPS and poly(butylene adipate-co-terephthalate) (PBAT) films produced by blown extrusion was studied. The type of extruder did not affect the properties of the films, but the addition of PLA decreased the water vapor permeability (WVP) and increased films rigidity. The production of the films by blown extrusion at pilot scale did not show promising results. For this reason, the type of PLA was substituted and calendaring-extrusion started to be used. Thus in the third step the effect of adipate and citrate ester on the properties of the sheets produced by calendaring-extrusion was evaluated. The incorporation of plasticizers decreased the rigidity, the glass trasition temperature (Tg), and tensile strength without changing the WVP. Adipate esters were more effective because the elongation at rupture was also improved, but the micrographs images revealed that the blends were immiscible. As adipate esters provided promising results, in the fourth step these plastcizers were used to produce sheets with various proportions of TPS and PLA. The increase in the concentration of TPS did not alter the Tg, decreased the rigidity and tensile strength, increased the crystallinity index and promoted hydrophilic characteristic as observed on the water sorption isotherm and WVP. Among the adipate esters, diisodecyl adipate conferred lower values of WVP, maintained the tensile strength and increased the elongation at rupture. Therefore the diisodecil adipate was selected as plasticizer to be studied in the fifth stage. Adipic and citric acids were added in the blends containing 50/50 of TPS and PLA plasticized with diisodecil adipate. Citric acid increased the interfacial adhesion between the polymers, improving mechanical and barrier properties. The production of TPS / PLA sheets at pilot scale using calendaring-extrusion was viable when adipate ester as plasticizer was employed, and citric acid was an effective compatibilizer.

Key-words: Blend. Biodegradable polymer. Adipate ester. Citrate ester. Compatibilisers.

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LISTA DE ABREVIATURAS E SIGLAS

ABNT	Associação Brasileira de Normas Técnicas
ASTM	American Standard for Testing and Methods
ATB	Citrato de acetil tributila
ATE	Citrato de acetil trietila
ATP ou TPS	Amido termoplástico
a_w	Atividade de água
BUR	Razão de estiramento
DEA	Adipato de dietila
DIA	Adipato de diisodecila
DMA	Análise dinâmico-mecânica
DSC	Calorimetria diferencial de varredura
FTIR	Espectroscopia no infravermelho com transformada de Fourier
GAB	Guggenhein, Anderson e de Boer
MM ou MW	Massa molar ou Molecular weight
PBAT	Poli(butileno adipato co-tereftalato)
PBSA	Poli(butileno succinato adipato)
PCL	Poli(s-caprolactona)
PEA	Poli(esteramina)
PEG	Polietilenoglicol
PET	Poli(tereftalato de etileno)
PHA	Poli(hidroxialcanoatos)
PHB	Poli(hidroxibutirato)
PHBV	Poli(hidroxibutirato-co-hidroxivalerato)
PLA	Poli(ácido lático)
Pph	Partes por cem ou parts per hundred
OS	Poliestireno
PVA ou WVP	Permeabilidade ao vapor de água
PVOH	Poli(álcool vinílico)
Rpm	Rotação por minuto ou Rotation per minute
Tanõ"	Fator de perda
TBC	Citrato de tributila
Tg	Temperatura de transição vítrea

TGA	Análise termogravimétrica
Tm	Temperatura de fusão
URE ou RH	Umidade relativa de equilíbrio
Xc	Índice de cristalinidade

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CAPÍTULO 1
INTRODUÇÃO

O impacto ambiental causado por resíduos plásticos não biodegradáveis tem se tornado uma preocupação mundial e métodos de eliminação destes materiais são limitados a algumas técnicas, como incineração, uso de aterros sanitários e reciclagem. Uma alternativa seria o uso de materiais plásticos que ao mesmo tempo são biodegradáveis e provenientes de fonte renovável, que diminuiria a dependência dos derivados de petróleo que não são renováveis (FRANCHETTI; MARCONATO, 2006; RHIM; PARK; HÁ, 2013; SCHWACH; SIX; AVÉROUS, 2008).

Globalmente, os biopolímeros compõem cerca de 300.000 toneladas do mercado de plásticos. Apesar de parecer muito, isto representa menos de 1% dos 181 milhões de toneladas de plásticos sintéticos que o mundo produz a cada ano. O mercado de bioplásticos tem crescido de 20 a 30% por ano, mas ainda não é suficiente para atender todas as necessidades (NAMPOOTHIRI; NAIR; JOHN, 2010). Os biopolímeros, provenientes de fonte renovável e biodegradável, tem atraído grande atenção podendo não só substituir os polímeros existentes em várias aplicações, mas também proporcionar novas combinações de propriedades para novas aplicações (BABU; O'CONNOR; SEERAM, 2013).

Dentro da categoria de biopolímeros, o amido tem se destacado e sido aplicado na produção de filmes biodegradáveis. Esta macromolécula apresenta como vantagens a biodegradabilidade, abundância e o menor custo em relação aos polímeros sintéticos biodegradáveis. No entanto, o amido apresenta algumas limitações como natureza hidrofílica e perda das propriedades mecânicas quando exposto a condições ambientais de alta umidade relativa, diferente dos materiais não biodegradáveis geralmente utilizados na indústria de embalagens (AVELLA et al., 2005; KALAMBUR; RIZVI, 2006; LI; HUNEAULT, 2011).

Uma forma de suprir as necessidades do amido e manter a biodegradabilidade seria a obtenção de blendas com outros biopolímeros hidrofóbicos. Entre os mais estudados estão os poliésteres alifáticos e aromáticos como o poli(ácido lático) (PLA), policaprolactona (PCL), poli(butileno adipato co-tereftalato) (PBAT) e poli(hidroxibutirato) (PHB).

Dentre estes, o polímero mais promissor é o PLA, um poliéster alifático e biodegradável produzido a partir de fontes renováveis, com propriedades

comparáveis às do polipropileno (PP) e poli(tereftalato de etileno) (PET), tais como transparência, boa processabilidade e elevada resistência à tração (DRUMRIGHT; GRUBER; HENTON, 2000; GARLOTTA, 2001; MARTIN; AVEROUS, 2001; PILLIN; MONTRELAY; GROHENS, 2006). Por apresentar baixa elongação e alta resistência à tração a aplicação do PLA é limitada para produção de embalagens rígidas ou semirrígidas. Para a produção de filmes e chapas é necessário que o material apresente flexibilidade em temperatura ambiente, boa processabilidade e termossoldabilidade. As propriedades de barreira a gases também são relevantes para esta aplicação.

Somado aos fatores citados, o PLA por ser hidrofóbico é termodinamicamente imiscível com o amido e a mistura desses componentes resulta em incompatibilidade das fases e propriedades funcionais deficientes. Idealmente, o amido e o PLA deveriam se ligar covalentemente através de grupos funcionais já existentes ou a partir da introdução de novos grupos funcionais (KALAMBUR; RIZVI, 2005). Nesse sentido, diversos tipos de compatibilizantes e plastificantes estão sendo estudados para diminuir a tensão interfacial entre o amido e o PLA, aumentar a flexibilidade dos materiais e melhorar a processabilidade em extrusoras.

Em virtude de suas propriedades já apresentadas, muitos estudos estão sendo feitos sobre a produção de materiais a partir de blendas de amido e PLA utilizando processos de *casting,* moldagem por injeção e termoprensagem, tendo poucos trabalhos na literatura sobre produção por extrusão-sopro em balão e extrusão plana.

Diante do exposto, este trabalho teve como objetivo principal desenvolver materiais biodegradáveis a partir de blendas de PLA e amido de mandioca por extrusão-sopro em balão e por extrusão plana, e caracterizá-los quanto às suas propriedades ópticas, térmicas, mecânicas, estruturais, viscoelásticas e de barreira ao vapor de água. Concomitantemente, foi estudado o efeito da adição de plastificantes como ésteres de adipato e ésteres de citrato e de compatibilizantes como ácido cítrico e ácido adípico sobre as propriedades funcionais dos materiais.

Este trabalho será apresentado em capítulos e com exceção da revisão bibliográfica, os demais capítulos desta tese encontram-se na forma de artigo e em inglês, pois resultam dos artigos publicados ou enviados para publicação em revistas internacionais no decorrer do doutorado. Para manter a característica

original dos artigos, os mesmos foram mantidos em inglês quando inseridos na tese. Desta forma, esta tese está dividida da seguinte forma:

Capítulo 2 - Revisão Bibliográfica.

Apresenta uma revisão bibliográfica sobre amido, PLA, blendas de amido e PLA, plastificantes e compatibilizantes para o PLA, produção de materiais biodegradáveis por extrusão e caracterização de materiais biodegradáveis.

Capítulo 3 - Development of biodegradable flexible films of starch and poly(lactic acid) plasticized with adipate or citrate esters.

Este capítulo foi publicado na revista *Carbohydrate Polymers.* Discorre sobre a produção de filmes por extrusão sopro utilizando blendas com alto teor de amido termoplástico e PLA plastificado com ésteres de adipato e citrato.

Capítulo 4 - Thermoplastic starch/polyester films: Effects of extrusion process and poly(lactic acid) addition.

Este capítulo foi publicado na revista *Materials Science and Engineering: C.* Neste trabalho foram avaliados os efeitos da adição de PLA e do processo de extrusão (extrusora mono- e dupla-rosca) utilizado no preparo de blendas de amido e PBAT. A partir dessas blendas foram produzidos filmes por extrusão-sopro em balão e os materiais foram caracterizados quanto às propriedades mecânicas, viscoelásticas, microestruturais e de barreira ao vapor de água.

Capítulo 5 - Adipate and citrate esters as plasticizers for poly(lactic acid) / thermoplastic starch sheets.

Este capítulo marca a mudança no processo de extrusão-sopro em balão para extrusão plana e do tipo de PLA utilizado na produção das blendas. Assim, foi avaliado o efeito da adição de ésteres de adipato e citrato como plastificantes em chapas de amido termoplástico e PLA produzidos por extrusão plana. Os materiais foram caracterizados quanto às propriedades mecânicas, viscoelásticas, microestruturais e de barreira ao vapor de água.

Capítulo 6 - Production and characterization of poly(lactic acid) / thermoplastic starch sheets plasticized with adipate esters.

Com base nos resultados obtidos no Capítulo 5, foram selecionados os ésteres de adipato para serem utilizados como plastificante na produção por extrusão plana de chapas com diferentes proporções de amido termoplástico e PLA. Os materiais foram caracterizados quanto às propriedades mecânicas, térmicas, microestruturais e de barreira ao vapor de água.

Capítulo 7 - Adding carboxylic acids to poly(lactic acid) / thermoplastic starch sheets produced by calendaring-extrusion.

Neste capítulo foi avaliado o efeito da adição de ácidos carboxílicos como o ácido adípico e cítrico na produção de chapas de amido termoplástico e PLA plastificado com éster de adipato. Os materiais foram caracterizados quanto às propriedades mecânicas, térmicas, microestruturais e de barreira ao vapor de água.

Capítulo 8 - Conclusões gerais

Neste capítulo é apresentada uma conclusão geral da tese.

Os Anexos A, B e C correspondem às imagens das chapas planas produzidas nos capítulos 5, 6 e 7, respectivamente.

CAPÍTULO 2
REVISÃO BIBLIOGRÁFICA

2.1 POLÍMEROS BIODEGRADÁVEIS

Polímeros biodegradáveis são materiais sintéticos ou naturais em que a sua degradação resulta primariamente da ação de microrganismos, tais como fungos, bactérias e algas de ocorrência natural, gerando gás carbônico (CO_2), metano, componentes celulares e outros produtos, segundo estabelecido pela *American Standard for Testing and Methods* (ASTM-D-833).

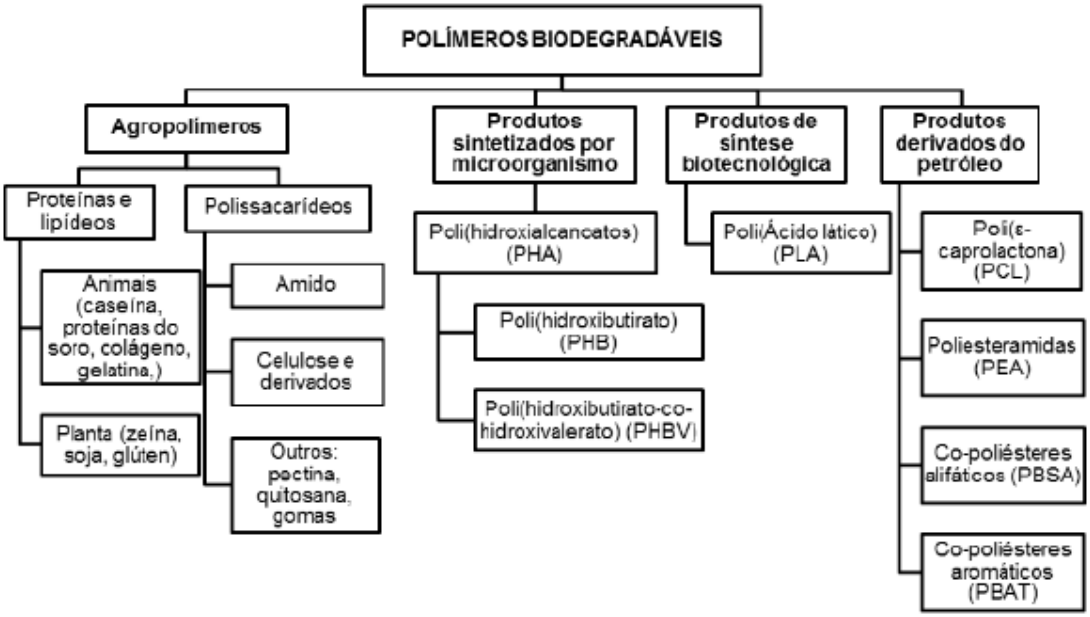
Vários são os institutos de normalização no campo de materiais biodegradáveis, alguns desses são: *American Society for Testing and Materials, Comité Européen de Normalisation, Deutsches Institut für Normung, International Organization for Standardization, Japanese Institute for Standardization* e *Organisation for Economic Cooperation and Development.*

No Brasil, em 2008 a Associação Brasileira de Normas Técnicas (ABNT) publicou a norma técnica sobre embalagens plásticas degradáveis e/ou renováveis, que é dividida em duas partes: NBR 15448-1 (Terminologia) e NBR 15448-2 (Biodegradação e Compostagem).

Avérous e Boquillon (2004) propuseram a classificação dos polímeros biodegradáveis em quatro famílias: (i) os produtos obtidos a partir do fracionamento de biomassa, também conhecidos como agropolímeros; (ii) os produtos sintetizados por microrganismos; (iii) os produtos de síntese biotecnológica e (iv) os produtos derivados do petróleo (Figura 2.1).

Dentro da família dos agropolímeros encontram-se os polissacarídeos (amido, celulose e derivados, pectina, quitosana, gomas etc.), proteínas de origem vegetal e animal (caseína, colágeno, gelatina, proteínas do soro de leite, zeína, soja e glúten) e os lipídeos (ceras) que são obtidos através do fracionamento da biomassa. Os polissacarídeos e as proteínas são geralmente utilizados para a confecção de filmes, enquanto os lipídeos na forma de ácido graxos e emulsificantes são empregados para conferir caráter hidrofóbico e diminuir a permeabilidade ao vapor de água.

Figura 2.1 – Classificação dos polímeros biodegradáveis



Fonte: Adaptado de Avérous e Boquillon, (2004).

Os polímeros produzidos por microrganismos (PHA), por via biotecnológica (PLA) e os provenientes da indústria petroquímica (PCL, PEA, copoliésteres alifáticos e aromáticos) são também categorizados como poliésteres biodegradáveis. Alguns poliésteres podem ser empregados na produção de plásticos biodegradáveis devido à presença de ligações éster potencialmente hidrolisáveis. A família dos poliésteres é composta por dois grandes grupos, os alifáticos (linear) e os aromáticos (presença de anéis aromáticos na estrutura química). (NAMPOOTHIRI; NAIR; JOHN, 2010).

Dentre os polímeros citados, o PLA pode ser uma alternativa sustentável para produtos derivados de petroquímicos, pois os lactídeos podem ser produzidos em larga escala a partir da fermentação microbiana de produtos agrícolas, principalmente aquelas ricas em carboidratos (JOHN; NAMPOOTHIRI; PANDEY, 2006).

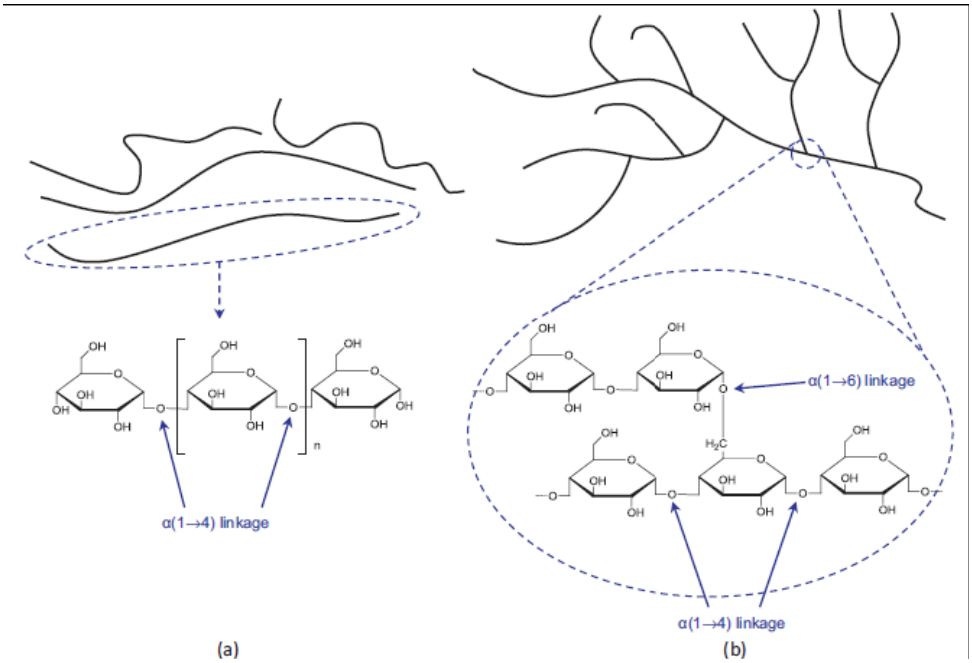
2.1.1 Amido

O amido pode ser obtido de diversas fontes vegetais, como cereais, raízes e tubérculos, e também de frutas e legumes, mas a extração em nível comercial se restringe aos cereais, raízes e tubérculos. O amido é o polissacarídeo

de reserva dos vegetais e está armazenado sob a forma de grânulos, que apresentam certo grau de organização molecular, conferindo aos mesmos um caráter parcialmente cristalino, ou semicristalino, com graus de cristalinidade que variam de 20 a 45%. A orientação regular das regiões amorfas e cristalinas é que dão ao grânulo sua característica de birrefringência, conhecida como Cruz de Malta (HERNÁNDEZ-URIBE, 2003).

O amido é formado por dois tipos de polímeros de glicose, a amilose e a amilopectina, com estruturas e funcionalidade diferentes (Figura 2.2). A amilose é um polímero linear composto por unidades de D-glicose ligadas por ligações a-(1—4), com grau de polimerização de 200 a 3000, dependendo da fonte do amido. A amilopectina é um polímero altamente ramificado, com unidades de D-glicose ligadas através de ligações a-(1—4) e ramificações em a-(1—6) (ELLIS et al., 1998). Variações nas proporções entre estes componentes e em suas estruturas e propriedades podem resultar em grânulos de amido com propriedades físico-químicas e funcionais muito diferentes, que podem afetar as suas aplicações industriais (MALI; GROSSMANN; YAMASHITA, 2010).

Figura 2.2 – Estrutura química da amilose (a) e amilopectina (b)



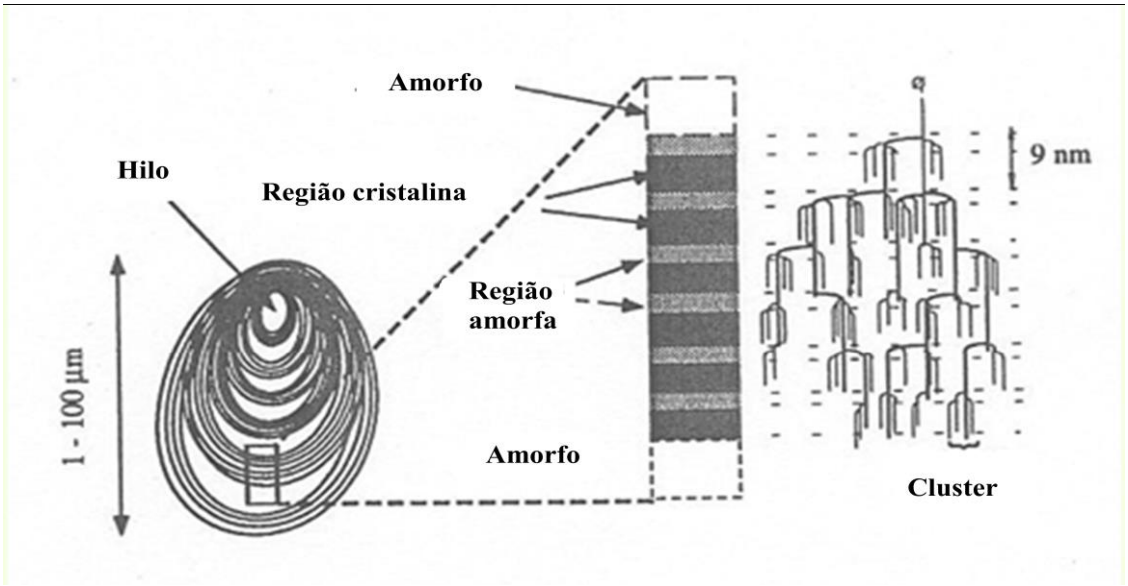
Fonte: XIE et al., (2013).

O amido nativo é parcialmente cristalino (semicristalino), com cristalinidade de 20-45%. A amilose e os pontos de ramificação da amilopectina

formam a região amorfa e a amilopectina é o principal componente cristalino dos grânulos de amido. As regiões cristalinas são constituídas pelas estruturas em dupla hélice formadas pelas cadeias lineares mais externas das moléculas de amilopectina, e apresentam domínios compostos por lamelas cristalinas e amorfas alternadas, de aproximadamente 9 a 10 nm de espessura (Figura 2.3). Essas lamelas representam as regiões cristalinas (cadeias laterais dos *clusters)* e regiões amorfas (regiões ramificadas) das moléculas de amilopectina (GALLANT; BOUCHET; BALDWIN, 1997; SOUZA; ANDRADE, 2002).

A quantidade relativa de estruturas cristalinas é influenciada pela proporção amilose / amilopectina, distribuição de massa molar, grau de ramificação, comprimento das cadeias externas da amilopectina, bem como da origem botânica (VAN SOEST; VLIEGENTHART, 1997). A amilose e os pontos de ramificação da amilopectina formam a região amorfa e a amilopectina é o principal componente cristalino dos grânulos de amido (GALLANT; BOUCHET; BALDWIN, 1997; SOUZA; ANDRADE, 2002).

Figura 2.3 – Estrutura do grânulo de amido indicando as regiões amorfas e cristalinas.

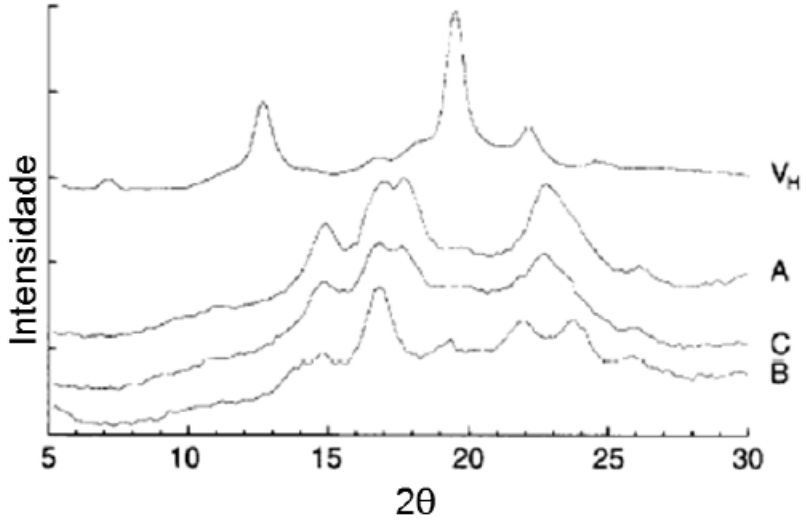


Fonte: JENKINS e DONALD, (1995).

Grânulos de amido apresentam estruturas cristalinas que proporcionam padrões específicos de difração de raios-X, e são classificadas como sendo dos tipos *A, B ou C,* conforme a fonte botânica. O padrão *A* é característico

de amidos de cereais, o padrão *B* do amido de tubérculos, de frutas, de milho com alto teor de amilose e dos amidos retrogradados. A forma polimórfica do tipo *C* é considerada uma mistura das formas *A* e *B* e é característica do amido de leguminosas. O tipo *C* ainda pode ser classificado como *Ca, Cb* e *Cc* de acordo com sua proximidade com as estruturas típicas do tipo *A* ou *B* (MA; YU, 2004; VAN SOEST et al., 1996). A Figura 2.4 apresenta o perfil dos difratogramas dos amidos de milho (tipo *A),* batata (tipo *B)* e ervilha (tipo *C)* e da amilose cristalizada (tipo *VH).*

Figura 2.4 – Difratogramas de amidos com cristalinidade dos tipos A, B, C e V_H



Fonte: VAN SOEST e VLIEGENTHART, (1997).

A diferença no padrão de cristalinidade está associada à densidade do empacotamento das duplas hélices, sendo que os amidos que possuem padrão *A* são mais densos. Além desta característica, estão associados com padrões de cristalinidade o conteúdo de água e o tamanho de cadeia de amilopectina. O amido tipo *B* apresenta conteúdo de água maior e as cadeias longas de amilopectina são mais numerosas quando se compara com amidos tipo *A* (HULLEMAN et al, 1999; VAN SOEST et al, 1996).

A aplicação do amido na produção de filmes se baseia nas propriedades químicas, físicas e funcionais da amilose para formar géis e na sua capacidade para formar filmes. As moléculas de amilose em solução, devido à sua linearidade, tendem a se orientar paralelamente, aproximando-se o suficiente para que se formem ligações de hidrogênio entre hidroxilas de polímeros adjacentes.

Como resultado, a afinidade do polímero por água é reduzida, favorecendo a formação de pastas opacas e filmes resistentes (WURZBURG, 1986). De acordo com Tharanathan (2003), a predominância de amilose no amido proporciona filmes mais resistentes. A estrutura ramificada da amilopectina gera filmes com diferentes propriedades mecânicas, como a diminuição da resistência a tração.

2.1.2 Amido Termoplástico

O amido tem sido estudado como matéria-prima na produção de materiais biodegradáveis por extrusão, pois é possível transformar o amido nativo em amido termoplástico (ATP). O amido não é um termoplástico verdadeiro, mas na presença de plastificante (água, glicerol, sorbitol, etc), altas temperaturas (90-180°C) e cisalhamento, ele funde e flui, permitindo seu uso em equipamentos de injeção e extrusão, assim como os plásticos sintéticos. Durante a obtenção do material termoplástico, a estrutura granular semicristalina do amido é destruída para dar origem a uma matriz polimérica homogênea e essencialmente amorfa (AVÉROUS et al., 2001; AVÉROUS; BOQUILLON, 2004; CURVELO; CARVALHO; AGNELLI, 2001; LIU et al., 2009; RÁQUEZ, et al., 2008; SOUZA; ANDRADE, 2002; VAN SOEST; VLIEGENTHART, 1997; VILPOUX; AVÉROUS, 2003; ZULLO; IANNACE, 2009).

Os fenômenos que possibilitam a destruição da organização dos grânulos de amido são a gelatinização e a fusão. A gelatinização é a transformação irreversível do amido granular em uma pasta viscoelástica, fenômeno que acontece na presença de excesso de água e leva à perda da cristalinidade e da ordem molecular do grânulo através do rompimento das ligações de hidrogênio que, inicialmente, mantinham a integridade deste. Por outro lado, quando o amido é aquecido na presença de pequenas quantidades de água, o fenômeno que indica o rompimento dos seus grânulos é conhecido como fusão, e exige temperaturas bem maiores para ocorrer a gelatinização (MALI; GROSSMANN; YAMASHITA, 2010).

O papel dos plastificantes é de desestruturar o amido granular a partir do rompimento das pontes de hidrogênio, acompanhado da solvatação parcial da cadeia do amido com o objetivo de reduzir as temperaturas de fusão e de transição vítrea (Tg) abaixo de sua temperatura de decomposição (230°C) (SOUZA; ANDRADE, 2002; STEPTO, 2003). Dentre os plastificantes mais utilizados estão os polióis como sorbitol e glicerol e devem ser compatíveis com o biopolímero

(GONTARD; GUILBERT; CUQ, 1993). O tipo e o teor de plastificante apresenta relação direta com as propriedades mecânicas e a Tg do material.

Assim como para os polímeros sintéticos, as propriedades mecânicas do ATP dependem da cristalinidade dos polímeros constituintes. Durante o resfriamento, após o processamento ou quando o amido termoplástico é armazenado, ocorre a formação de estruturas cristalinas devido à recristalização da amilopectina e cristalização da amilose, apesar de essa última não apresentar cristalinidade em seu estado nativo. A tendência do amido termoplástico à cristalização afeta diretamente suas propriedades (WIEDMANN; STROBEL, 1991).

Dois tipos de cristalinidade podem ser distinguidos em ATP imediatamente após o processo: (i) cristalinidade residual, onde é possível encontrar cristais do tipo *A*, *B* ou *C* devido à fusão incompleta do amido durante o processo; (ii) cristalinidade induzida pelo processo, verificada pela presença de cristais do tipo *VH, VA* ou *EH* que são formados durante o processamento, sendo formada pela cristalização da amilose e cristais do tipo *B* que é observada durante o armazenamento e é atribuída à cristalização lenta da amilopectina. A quantidade de cristalinidade residual está relacionada com as condições de processo como temperatura ou tensão de cisalhamento, da composição do amido e do plastificante (MA; YU, 2004; VAN SOEST et al., 1996).

O ATP apresenta alguns inconvenientes como caráter hidrofílico, propriedades mecânicas limitadas quando comparado com os polímeros sintéticos convencionais e variação em suas propriedades durante o armazenamento (AVELLA et al., 2005; AVÉROUS; BOQUILLON, 2004). Além da sensibilidade à umidade, o fato dos biopolímeros apresentarem propriedades mecânicas que se alteram com o tempo, a baixa resistência ao impacto e no caso dos produtos termoformados, a pequena espessura dos produtos formados, limitam o uso dos derivados de amido (AVÉROUS; FRINGANT; MORO, 2001).

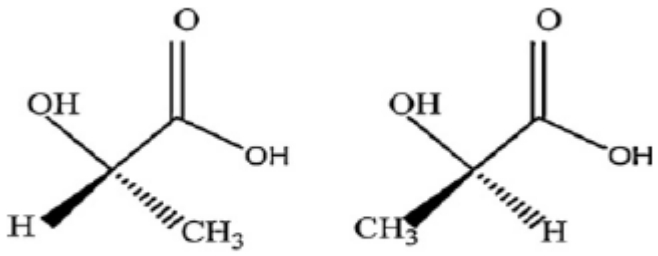
A sensibilidade à umidade e o envelhecimento crítico do ATP implicam na necessidade da realização de blendas com outros polímeros. Para manter a biodegradabilidade da blenda, poliésteres como PCL, PLA, PBAT podem ser utilizados. Algumas blendas a base de amido já estão sendo comercializados como o *Mater-Bi* (Novamont, Itália), *Ecobras* (BASF, Brasil) e *Bioplast* (Biotec, Alemanha).

2.1.3 Poli (Ácido Lático)

O ácido lático, unidade monomérica da cadeia de PLA, pode ser obtido industrialmente a partir de processo fermentativo com bactérias láticas ou por síntese química. O ácido lático possui um átomo de carbono assimétrico e se encontra em duas configurações opticamente ativa, sendo os isômeros L(+) e D(-) (Figura 2.5). O L-ácido lático desvia o plano de luz polarizada em sentido horário e o D-ácido lático rota em sentido anti-horário (AURAS; HARTE; SELKE, 2004; GUPTA; REVAGADE; HILBORN, 2007).

O interesse na produção do ácido lático pela via fermentativa tem se destacado, pois utiliza recursos de fontes renováveis em vez de produtos petroquímicos, além de produtos de alta especificidade, pois produz L(+) ou D(-) ácido lático opticamente puros. A produção biotecnológica oferece várias vantagens em comparação com a síntese química como baixo custo dos substratos, menor temperatura de produção e de consumo de energia (JOHN; NAMPOOTHIRI; PANDEY, 2006).

Figura 2.5 – Estruturas químicas dos L e D-Ácido lático.



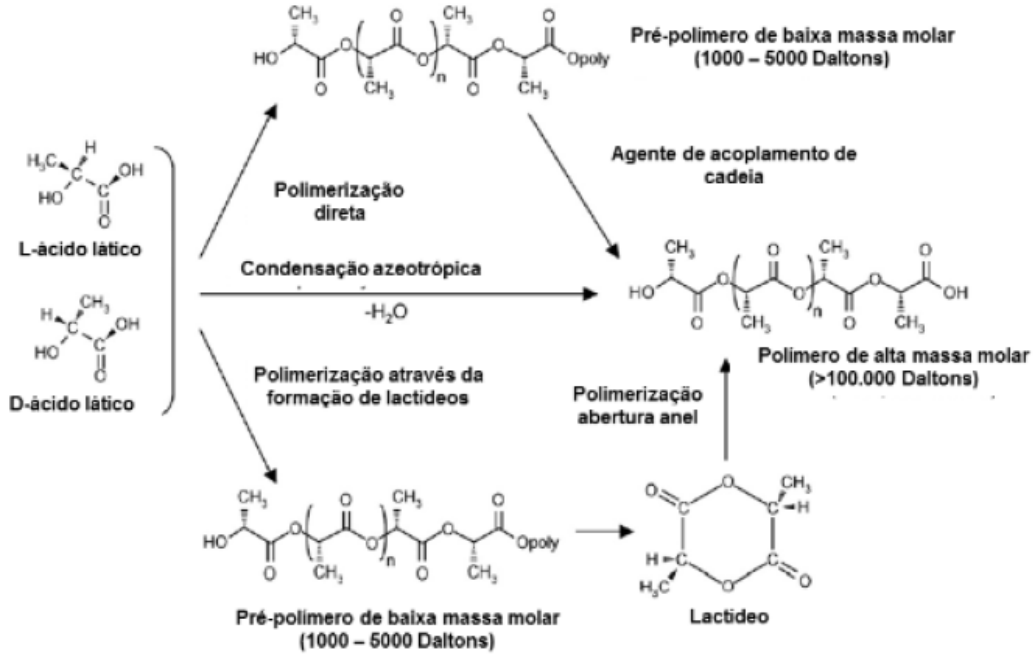
L-Ácido lático D-Ácido lático

Fonte: GUPTA, REVAGADE e HILBORN, (2007)

A existência de grupos hidroxila e carboxila na molécula de ácido lático permitem que este seja diretamente convertido em poliéster via reação de policondensação. Em geral, há três métodos que podem ser utilizados para a obtenção de polímeros de ácido lático de alta massa molar (> 100.000 Da): (i) policondensação direta; (ii) policondensação direta em solução azeotrópica e (iii) polimerização através da formação de lactídeos (AURAS; HARTE; SELKE, 2004) (Figura 2.6).

A partir da polimerização direta somente polímeros de baixa massa molar (2 - 10 Da) são produzidos, principalmente devido à presença de água e impurezas (GUPTA; KUMAR, 2007). A adição de agentes de acoplamento de cadeia *(coupling agents)* permite a obtenção de polímeros de maior massa molar, mas isso adiciona custos e complexidade ao processo (GARLOTTA, 2001). Outra forma para obter PLA de alta massa molar é aliar à policondensação direta o uso de um solvente azeotrópico adequado. Trata-se de uma técnica de polimerização em solução que utiliza um catalisador com atividade catalítica elevada e solvente com alta temperatura de ebulição para remover a água. A principal desvantagem da policondensação com mistura azeotrópica é a toxicidade dos solventes e a dificuldade de obter polímeros com elevados graus de pureza (GUPTA; KUMAR, 2007).

Figura 2.6 – Métodos de síntese do PLA.

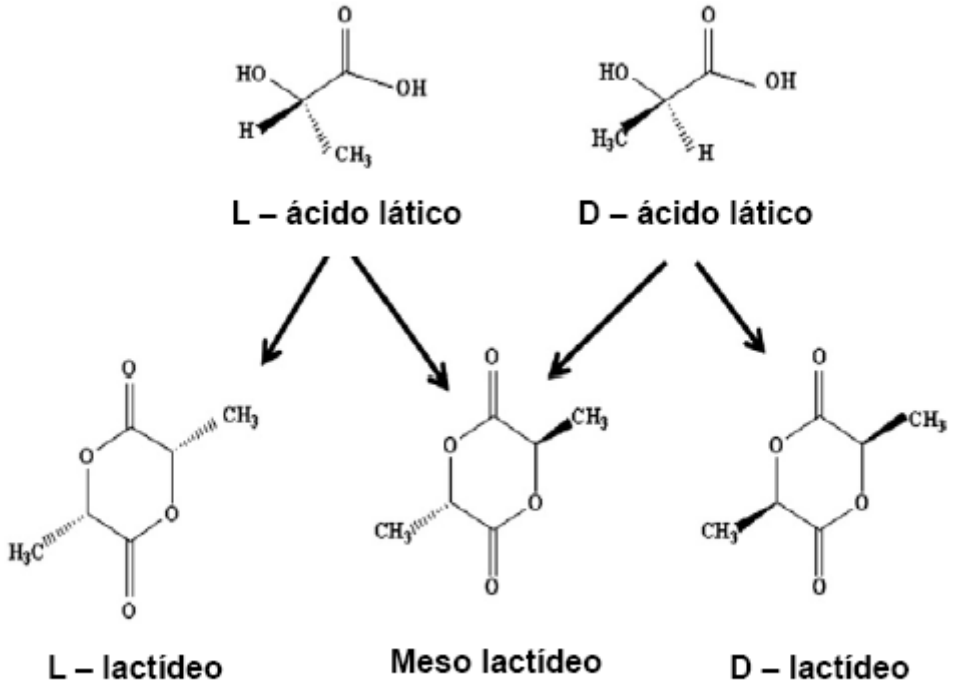


Fonte: Adaptado de AURAS, HARTE e SELKE, (2004); LIM, AURAS e RUBINO, (2008).

Em virtude das desvantagens da policondensação direta, a produção em escala comercial do PLA envolve a polimerização por abertura de anel *(ring opening polymerization)* do lactídeo que foi patenteado pela Cargill Dow em 1992 (VINK et al., 2003). O processo se inicia com uma reação de condensação do ácido lático para produzir o PLA de baixa massa molar, denominado de pré-polímero (1.000 a 5.000 Da). Em seguida este pré-polímero é convertido em uma mistura de

estereoisômeros de dímeros de lactídeos (Figura 2.7) através do uso de catalisadores, como octanoato de estanho, para melhorar a taxa e seletividade da reação de ciclização intramolecular. A mistura de lactídeos é purificada por destilação a vácuo e então o PLA de alta massa molar é produzido via polimerização por abertura do anel na presença de catalisadores adequados. Completada esta etapa, os eventuais monômeros residuais são removidos sob vácuo e reenviados para o início do processo.

Figura 2.7 – Estereoisômeros de lactídeos.



Fonte: Adaptado de NAMPOOTHIRI, NAIR e JOHN, 2010.

Em geral, o PLA comercial é um copolímero entre os ácidos L-polilático e D-polilático. A pureza óptica, definida como a porcentagem de isômeros L e D, afeta significativamente as propriedades do PLA, como o ponto de fusão, taxa e extensão da cristalização e propriedades mecânicas (GARLOTTA, 2001).

Polímeros com níveis elevados de L-lactídeos tendem a ser cristalinos enquanto materiais com conteúdos altos de D-lactídeos são amorfos (VINK et al., 2003). O poli-L-lactídeo (PLLA), produto resultante da polimerização do L-lactídeo, possui cristalinidade ao redor de 37%, temperatura de transição vítrea entre 50-80°C e temperatura de fusão entre 173-178°C. Já os polímeros com mais

de 15% de D-lactídeos em sua composição tendem a ser amorfos. As temperaturas de fusão e de transição vítrea e a cristalinidade tendem a diminuir com a redução do conteúdo de L-isômeros (DORGAN; JANSEN; CLAYTON, 2005; TSUJI; IKADA, 1996; URAYAMA; MOON; KIMURA, 2003).

O nível de cristalinidade do PLA irá modelar o seu desempenho mecânico, sua permeabilidade, seu comportamento frente ao processo térmico e sua biodegradação em ambiente de compostagem (AURAS; HARTE; SELKE, 2004; AURAS; SINGH; SINGH, 2006). Vale destacar que outros fatores como tamanho da partícula e forma do polímero, cristalinidade, porcentagem de isômeros D, concentração de ácido lático residual e impurezas metálicas advindas dos catalisadores também podem afetar a taxa de degradação do PLA (JAMSHIDIAN et al., 2010).

A Tabela 2.1 apresenta algumas características do PLA polimerizado com 96% de L-ácido lático e 4% de D-ácido lático.

Tabela 2.1 – Propriedades do PLA (96:4 - L:D)

Característica		Valor	Referência
Massa molar		66.000 g/mol	GARLOTTA (2001)
Densidade		1,27 (g/cm^3)	
Temperatura de transição vítrea		55°C	
Temperatura de fusão		165°C	
Calor específico	190°C	2.060 J/kg.°C	MEHTA et al., (2005)
	100°C	1.955 J/kg.°C	
	55°C	1.590 J/kg.°C	
Condutividade térmica	190°C	0,195 W/m.°C	
	109°C	0,197 W/m.°C	NATUREWORKS (2007)
	48°C	0,111 W/m.°C	
Resistência à tração		59 MPa	
Alongamento na ruptura		7,0%	
Resistência à flexão		106 MPa	
Resistência ao impacto Izod (sem entalhe)		195 J/m	NATUREWORKS (2007)
Resistência ao impacto Izod (com entalhe)		26 J/m	
Módulo de Young		1280 MPa	

2.2 BLENDAS DE POLI(ÁCIDO LÁTICO) E AMIDO

Do ponto de vista microscópico as blendas podem ser homogêneas ou heterogêneas, mas se apresentarem heterogeneidade macroscópica serão consideradas incompatíveis. As blendas podem ser consideradas sistemas miscíveis, quando apresentam interações favoráveis entre os segmentos das cadeias e não há ocorrência de separação de fases, ou imiscíveis e compatíveis quando apresentam boa processabilidade e propriedades mecânicas, sem apresentar interações especificas (MANRICH, 2005; MATZINOS et al., 2002).

A produção de blendas é o processo mais estudado com o intuito de melhorar as propriedades funcionais de materiais a base de PLA, através da mistura com diferentes plastificantes e polímeros (biodegradáveis e não-biodegradáveis). Apesar da existência da produção do PLA em escala comercial, o preço ainda continua relativamente alto quando comparado com outras resinas usualmente empregadas na indústria de embalagem (RASAL; JANORKAR; HIRT, 2010).

A blenda de PLA com amido é uma alternativa interessante, pois o amido é amplamente disponível e proveniente de fonte renovável, atua na redução de custos e aumenta a biodegradabilidade. Além disso, o amido possui estabilidade térmica adequada para ser fundido com plásticos sintéticos e isso possibilita a produção de novos plásticos biodegradáveis (KOZLOWSKI et al., 2007; LIM et al., 2008; MARTIN; AVÉROUS, 2001; WANG et al., 2007).

A concentração de amido em blendas com o PLA é o parâmetro chave que determina suas propriedades mecânicas. Geralmente, a resistência à tração e a elongação na ruptura diminuem com o aumento da concentração de amido. Deve-se considerar também que o amido é um polímero hidrofílico e as propriedades da blenda podem se alterar com o tempo, quando armazenados em condições de alta umidade relativa (NAMPOOTHIRI; NAIR; JOHN, 2010; KÓVACS; TÁBI, 2011).

Ke e Sun (2001) caracterizaram blendas de PLA e amido com vários teores de umidade (0 a 50%), obtidos por processos de moldagem por injeção e termoprensagem. Foi observado que a umidade teve pouco efeito sobre as propriedades térmicas e de cristalização da blenda. A gelatinização do amido aumentou com a umidade e nas blendas com baixa umidade a microscopia mostrou que os grânulos de amido estavam intactos e incorporados na matriz do PLA. Com a

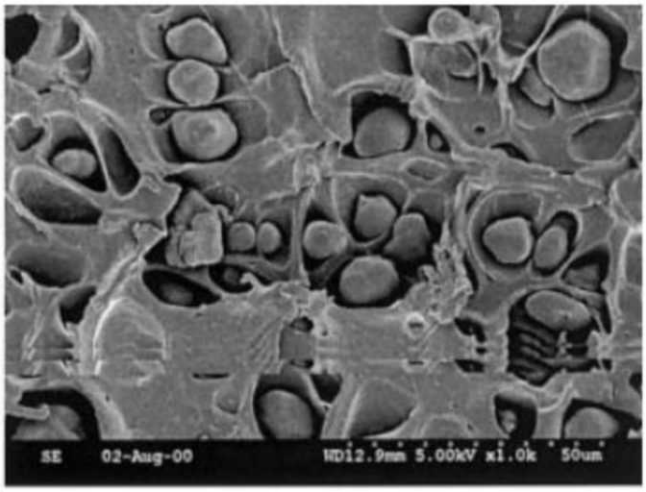
gelatinização do amido, as blendas ficaram mais uniformes, mas ainda assim foram encontradas pequenas quantidades de grânulos de amido, indicando imiscibilidade entre os dois polímeros.

Blendas de PLA e amido de milho com diferentes teores de amilose (0, 28, 50 e 70%) foram produzidos por extrusão no trabalho de Ke, Sun e Seib (2003). No geral, foi observado que a absorção de água diminuiu com o aumento de amilose, sem alterar as propriedades mecânicas da blenda. Entretanto, a blenda se tornou mais hidrofílica com o aumento da proporção de amido.

Li e Hunealult (2011) produziram blendas de amido e PLA por extrusão e compararam o efeito da adição de glicerol e sorbitol, individualmente ou misturados na concentração de 36% (m/m), como plastificantes para o amido. Os autores concluíram que nos materiais plastificados com sorbitol, o amido se dispersou de forma mais uniforme na matriz de PLA e apresentou maior resistência à tração e módulo de Young.

Na maioria dos estudos de produção de blendas de amido e PLA, as imagens de microscopia mostram uma estrutura incompatível, com espaços entre os grânulos de amido e a matriz de PLA, conforme ilustrado na Figura 2.8. Todos esses fatores influenciaram nas propriedades mecânicas, de permeabilidade ao vapor de água e cristalinidade dos materiais. Assim, é necessário incluir plastificantes para diminuir a rigidez do PLA e de compatibilizantes para aumentar a adesão interfacial e melhorar as propriedades funcionais da blenda.

Figura 2.8 – Imagem de microscopia eletrônica de fratura de blenda de amido:PLA (20:80).



Fonte: KE, SUN e SEIB, (2003).

2.3 PLASTIFICANTES PARA O PLA

Os plastificantes são amplamente utilizados para melhorar a processabilidade, flexibilidade e maleabilidade dos polímeros. No caso de polímeros semicristalinos e rígidos como o PLA, seu processamento por extrusão pode ser melhorado pela incorporação de plastificantes adequados que além de reduzir a Tg, devem diminuir a temperatura de fusão e a cristalinidade. Entre os principais plastificantes incorporados ao PLA estão: glicerol, polietileno glicol (PEG), polipropileno glicol, óxido de polipropileno, polioxietileno, oligômeros de ácido lático, ésteres de citrato, adipatos e óleo de soja epoxidado (KULINSKI; PIORKOWSKA, 2005; LJUNGBERG; ANDERSSON; WESSLÉN, 2003; PILLIN; MONTRELAY; GROHENS, 2006; THELLEN et al., 2005; ZENKIEWICZ; RICHERT; ROZANSKI, 2010).

A escolha do plastificante a ser utilizado para modificar as propriedades do PLA é limitada em virtude de sua aplicação. Quando a aplicação é em embalagens para alimentos, apenas substâncias não tóxicas aprovadas pela legislação vigente podem ser consideradas. Para plastificantes de baixo peso molecular, o que se deve considerar é a sua miscibilidade com o PLA para obter uma blenda homogênea. Além disso, os plastificantes não podem evaporar em temperaturas empregadas no processo de extrusão, e nem ter tendência à migração nas condições de utilização, pois pode servir como fonte de contaminação em alimentos que estiverem em contato com a embalagem. A migração também faz com que a blenda recupere as propriedades do PLA puro sendo que a taxa de migração depende da temperatura (LJUNGBERG; WESSLÉN, 2003).

Os plastificantes na quantidade de 10 a 20 % (m/m) são requeridos para provocar uma redução substancial na Tg do PLA e assim aumentar a mobilidade das cadeias poliméricas e melhorar a flexibilidade pela redução das forças intermoleculares. Dependendo do plastificante, a adição de quantidades maiores que 20 a 30 % (m/m) causa a separação de fases durante o envelhecimento e a cristalização do sistema, resultando em um aumento na rigidez do material (HASSOUNA et al., 2012; LJUNGBERG et al., 2003; ROMERO-BATISTA et al., 2005). Outro fator a se considerar é que o nível de plastificação do polímero depende fortemente da estrutura química do plastificante, incluindo sua composição química, massa molar e presença de grupos funcionais (VIEIRA et al., 2011).

Martin e Averous (2001) pesquisaram o efeito de diferentes plastificantes como glicerol, éster de citrato, polietileno glicol (PEG), polietileno glicol monolaurato e oligômeros de ácido lático em blendas de amido e PLA. Os autores concluíram que oligômeros de ácido lático e PEG (MM 400 Da) plastificaram melhor o PLA, enquanto o glicerol foi o menos eficiente. Outro estudo relatou que a adição de PEG (MM 400 Da) em PLA causou diminuição da Tg e houve aumento do alongamento e redução da fragilidade. Entretanto, a permeabilidade ao vapor de água aumentou devido à presença de grupos hidrofílicos do PEG na blenda (KULINSKI; PIORKOWSKA, 2005).

Ésteres de citrato são compostos obtidos a partir da esterificação do ácido cítrico com glicerol e tem sido reportado como um potencial plastificante para o PLA, pois apresentam miscibilidade com este e contribui na melhora da flexibilidade dos materiais produzidos. Entre os mais utilizados estão citrato de tributila, citrato de trietila, citrato de acetil tributila e citrato de acetil trietila (LABRECQUE et al., 1997; LJUNGBERG et al., 2003; LJUNGBERG; WESSLÉN, 2003).

Em blendas de PLA e ATP adicionadas de anidrido maleico e plastificado com citrato de acetil trietila a elongação aumentou quando concentrações acima de 8% foram empregadas (ZHANG; SUN, 2004). Entre as vantagens de utilizar os ésteres de citrato é que não são tóxicos, são biodegradáveis e são aprovados como aditivos em plásticos para aplicação médica, produtos de higiene pessoal e em contato com alimentos (RAHMAN; BRAZEL, 2004).

Ésteres de adipato, obtido a partir da esterificação do ácido adípico e glicerol, quando empregados na concentração 10 e 20% causam decréscimo na Tg e as propriedades mecânicas são melhoradas pela redução da resistência à tração e pelo aumento no alongamento na ruptura, sendo possível a produção de filmes flexíveis. Quando se considera a massa molar dos ésteres de adipato, os que contêm maior massa molar proporcionam materiais mais flexíveis, reduz a taxa de permeabilidade ao oxigênio e de migração quando comparado com outros plastificantes de menor massa molar nas mesmas concentrações (MARTINO; JIMÉNEZ; RUSECKAITE, 2009; MARTINO et al., 2010; MURARIU et al., 2008).

2.4 COMPATIBILIZANTES PARA BLENDAS DE AMIDO E PLA

Para aumentar a compatibilidade entre o PLA e o amido em blendas, têm sido empregados compatibilizantes como anidrido maleico (WANG; YU; MA, 2007; ZHANG; SUN, 2004), ácido acrílico (WU, 2005), diisocianato de difenil metileno (WANG; SUN; SEIB, 2002) e ácido cítrico (CHABRAT et al., 2012; TEIXEIRA et al., 2012; WANG et al., 2010). O compatibilizante reage com os componentes da blenda, reduz a diferença de polaridade e a tensão interfacial entre eles, permitindo uma aproximação entre as cadeias.

Os compatibilizantes geralmente exibem atividade interfacial em blendas de polímeros heterogêneos e seu efeito é atribuído a um aumento na adesão interfacial que conduz a uma melhora nas propriedades mecânicas. A formação de uma matriz polimérica mais compacta e homogênea diminui a permeabilidade ao vapor de água, pois dificulta a difusão da água através do material. Diferentes estratégias de compatibilização podem ser encontradas na literatura (IMRE; PUKÁNSZKY, 2013; RAQUÉZ et al., 2008; SCHWACH; SIX; AVÉROUS, 2008).

Dentre as técnicas de compatibilização pode-se citar a síntese de um componente, neste caso o compatibilizante, que pode ser obtido *in situ* (durante o processamento da blenda) ou *ex situ* (modificação prévia de pelo menos um polímero presente na blenda). A literatura apresenta diferentes rotas para compatibilização que são classificadas em três principais grupos (AVÉROUS, 2004; SCHWACH; SIX; AVÉROUS, 2008):

i. Funcionalização do amido ou poliéster. Esta funcionalização pode ocorrer por reação *in situ* entre o componente altamente reativo e o amido ou o poliéster, gerando um composto compatibilizante;
ii. Reticulação *in situ* do amido-poliéster com um agente de ligação (geralmente peróxido);
iii. Síntese *ex situ* de copolímeros (por exemplo, PLA enxertado com amilose).

Alguns trabalhos sobre compatibilização de PLA e ATP estão baseados, por exemplo, na acetilação do amido ou funcionalização do PLA com anidrido maleico ou com ácido acrílico. Diisocianatos e derivados do anidrido

maleico são usados para produzir grupos funcionais uretano e ligações éster, respectivamente (WANG; SUN; SEIB, 2002; ZHANG; SUN, 2004).

A reticulação com peróxido ocorre quando este é aquecido e se decompõe em radicais que reagem com o amido e PLA. Com isso, macro radicais são produzidos e aleatoriamente reagem aumentando a compatibilidade entre o amido e o PLA. No trabalho de Schwach, Six e Averous (2008), verificou-se que ao adicionar 2% de peróxido de benzoila à blenda de amido de trigo e PLA (90/10) houve incremento do alongamento na ruptura de 20% para 30% devido ao efeito compatibilizante do peróxido. No entanto, ao empregar 4% de peróxido de benzoila as propriedades mecânicas pioraram devido ao excesso de compatibilizante que causaram degradação das macromoléculas.

A cadeia de PLA pode ser funcionalizada a partir da reação com anidrido maleico com o intuito de aumentar a reatividade ao longo da cadeia do poliéster e permitir a interação com os grupos hidroxilas das cadeias dos polissacarídeos. A reação de enxertia do anidrido maleico, na cadeia de PLA, pode ser feita por extrusão reativa utilizando-se peróxido como iniciador (geralmente 2,5-dimetil-2,5-di-t-butil-peroxi-hexano, comercializado com o nome Luperox® 101). Este procedimento proporciona melhora significativa das propriedades mecânicas e na compatibilização da blenda ATP e PLA, acompanhada de diminuição da Tg e das temperaturas de cristalização e de fusão. Além disso, o anidrido maleico melhora a plastificação do amido e a fluidez da blenda durante o processo de extrusão (DUBOIS; NARAYAN, 2003; HUNEAULT; LI, 2007; OROZCO et al., 2009; REN et al., 2009; WANG; YU; MA, 2007; ZHANG; SUN, 2004).

Os ácidos carboxílicos tais como cítrico, adípico, málico, tartárico, têm chamado atenção para serem utilizados como compatibilizantes, pois estão naturalmente presentes em frutas e são sintetizados por microrganismos durante processos fermentativos. Estes ácidos foram efetivos em filmes de amido e PBAT produzidos por extrusão sopro (OLIVATO et al., 2012a, 2012b; SILVA et al., 2013).

A influência do ácido cítrico em blendas de PLA/ATP (TEIXEIRA et al., 2012; WANG et al., 2010) e PLA/farinha de trigo (CHABRAT et al., 2012) foram pesquisadas. As explicações para a melhoria das propriedades funcionais destes materiais é que o ácido cítrico despolimeriza parcialmente o amido, melhorando a sua distribuição na matriz de PLA. Além do seu papel como compatibilizante, o ácido cítrico atua como plastificante, que auxilia na processabilidade do ATP, acelerando a

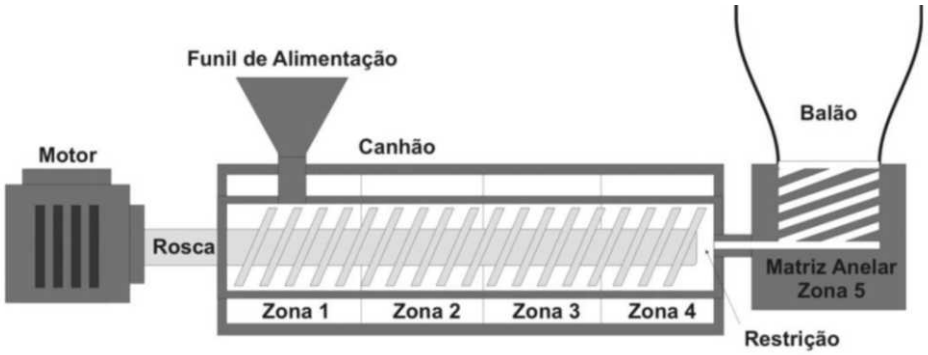
fragmentação e dissolução dos grânulos de amido (SHI et al., 2007). Pode-se considerar também que durante o processo de extrusão, ocorre a modificação do amido pela introdução de novos grupos carboxilas e éster que são pontos potencialmente reativos para ocorrência de reação intercruzada (OLIVATO et al., 2012b).

2.5 PRODUÇÃO DE MATERIAIS DE AMIDO E PLA

A maior parte da produção de filmes e chapas em escala industrial é feita por extrusão. Esta tecnologia oferece as vantagens associadas ao sistema contínuo de produção, incluindo versatilidade, baixo custo operacional e necessidade de menor espaço por unidade de operação (SOTHORNVIT et al., 2007).

A extrusão é um processo onde o material é arrastado sob altas pressões por uma rosca-sem-fim através de um canhão, circundado por resistências elétricas para manter as altas temperaturas necessárias, onde sofre um cisalhamento intenso e é expelido através de um orifício ou matriz (Figura 2.9).

Figura 2.9 – Esquema de uma extrusora.



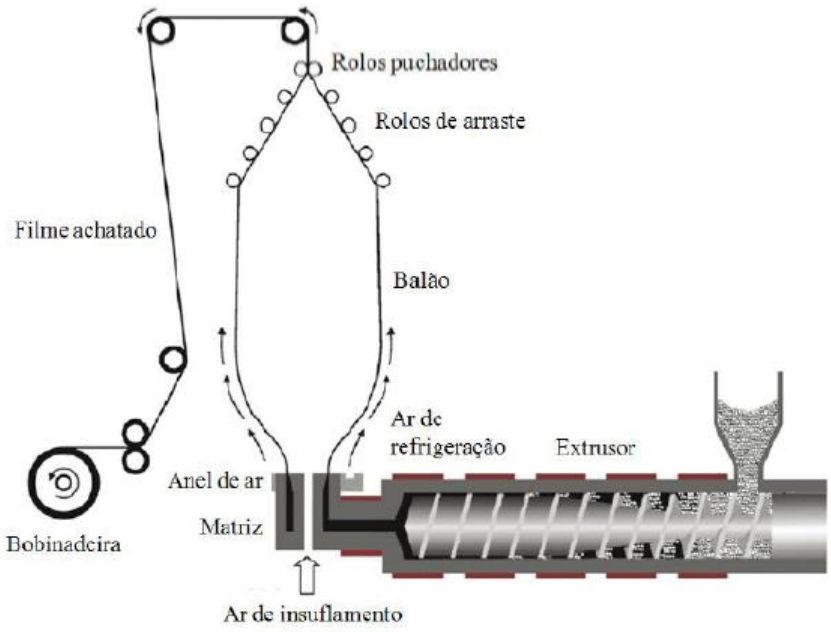
No mercado há extrusoras mono- e dupla-rosca, sendo as extrusoras dupla-rosca as mais utilizadas no preparo e na extrusão de formulações de blendas termoplásticas, devido a sua característica de mistura e flexibilidade de operação. Já as extrusoras mono-rosca são mais empregadas na obtenção do produto final, por serem mais simples e de menor custo (CRIPPA, 2006).

No processo de extrusão, a rosca é o componente mais importante para transportar, fundir, homogeneizar e plastificar o polímero, e é devido ao seu

movimento, e consequente cisalhamento, que ela gera cerca de 80% da energia térmica necessária para transformar o polímero, enquanto o restante da energia vem das resistências elétricas externas. Após a rosca da extrusora existe uma folga, para evitar o atrito e desgaste do parafuso, e em seguida vem o cabeçote que é um conjunto de peças onde fica a matriz, canal responsável pelo perfil do extrudado (MANRICH, 2005).

Uma das formas de se obter filmes por extrusão é pela técnica de sopro em balão, que são confeccionados a partir da extrusão do polímero fundido, na forma de um tubo, através de uma matriz anelar, no centro da qual ar é injetado, inflando o tubo até este atingir um diâmetro maior. Uma bolha é então formada, cujas paredes são estiradas na circunferência (pelo ar injetado) e na vertical, por rolos puxadores, ao mesmo tempo em que são resfriadas, e isto confere ao filme soprado uma orientação biaxial (Figura 2.10). Existem três tipos de fluxos durante o sopro: na matriz anelar, onde o fluxo é predominantemente de cisalhamento; entre a saída da matriz e o início da bolha, onde o fluxo é uma mistura de cisalhamento com fluxo elongacional; e até a linha de congelamento, em que o fluxo é predominantemente elongacional (GUERRINI et al., 2004).

Figura 2.10 – Representação de uma extrusora a sopro.



Fonte: LIM, AURAS e RUBINO, (2008).

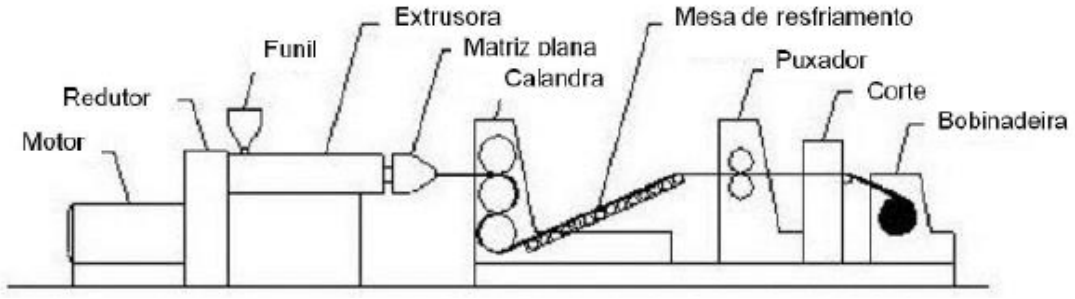
O PLA é mais rígido e alonga menos do que os polímeros usualmente utilizados para produção de filmes soprados, como o polietileno, cloreto de polivinila e polipropileno. Em virtude disso, a maioria dos trabalhos disponíveis trata sobre a produção de filmes de blenda de amido e PLA a partir do processo de moldagem por injeção ou termoprensagem. Lim, Auras e Rubino (2008) destacam que para melhorar a processabilidade do PLA por extrusão-sopro em balão, plastificantes, em conjunto com aditivos para aumentar a compatibilidade entre o amido e o PLA, devem ser pesquisados.

Thellen et al. (2005) produziram filmes de PLA plastificado com 10% éster de citrato e 5% de montmorilonita organicamente modificada por extrusão sopro e avaliaram as propriedades térmicas, mecânicas, de barreira e a biodegradação. A incorporação de montmorilonita, considerada uma nanoargila, diminuiu em 48% a permeabilidade ao oxigênio e em 50% a permeabilidade ao vapor de água, além de elevar a temperatura de degradação térmica e a rigidez do filme. Além disso, os filmes contendo montmorilonita apresentaram uma taxa de biodegradação superior aos dos filmes sem a nanoargila.

Outra forma conhecida de produção comercial de filmes e chapas é o processo de extrusão plana (Figura 2.11). Este processo é utilizado para a confecção de filmes planos e chapas, passando o material fundido entre dois ou mais cilindros refrigerados com água, que giram a velocidades ligeiramente diferentes para solidificar e formar os materiais. O processo possibilita a obtenção de materiais planos com espessura constante. A espessura do filme é controlada pela abertura dos rolos finais da calandra, e seu acabamento superficial é determinado pelo acabamento da superfície do último cilindro de passagem (RODOLFO-JR et al., 2002).

Apesar de o processo parecer simples, o controle da espessura e da largura do produto final pode ser difícil dependo das condições de operação. A velocidade dos cilindros da calandra é superior à velocidade de saída do polímero da matriz da extrusora, portanto o polímero sofre uma força elongacional, podendo apresentar alguns defeitos. Geralmente os defeitos aparecem entre a saída da matriz e a entrada na calandra e são causados pela redução da largura do filme ou pela redução não homogênea da seção do filme durante o alongamento, aumentando a espessura nas bordas do filme (SAKAKI et al., 1996; SOLLOGOOG; DEMAY; AGASSANT, 2006).

Figura 2.11 – Esquema de uma extrusora plana.



Fonte: Vidal, (2011).

O processo de extrusão plana foi empregado na produção de filmes biodegradáveis de amido nativos de milho, milho ceroso, batata e amido fosforilado de milho, adicionados de fibras de bagaço de cana-de-açúcar e plastificados com glicerol. Os filmes obtidos apresentaram boas propriedades funcionais para seu uso como materiais de embalagem, sendo esse um processo de extrusão que apresenta aplicabilidade para o uso em blendas de amido (GALICIA-GARCÍA et al., 2011).

2.6 CARACTERIZAÇÃO DE MATERIAIS BIODEGRADÁVEIS

O emprego de materiais biodegradáveis em embalagens para alimentos vai depender, além de parâmetros como custo e disponibilidade, de suas propriedades funcionais, tais como: mecânicas (resistência e flexibilidade), ópticas (cor e opacidade), de barreira (permeabilidades ao vapor de água, ao O2 e ao CO2) e sensoriais. Essas propriedades dependem do biopolímero usado (conformação, massa molar, distribuição de cargas, polaridade), das condições de fabricação e das condições ambientais (temperatura e umidade relativa). Outro parâmetro que influencia as propriedades dos filmes é a espessura (CUQ et al., 1996; MAHMOUD; SAVELLO, 1992;). A seguir serão apresentadas as técnicas mais comumente empregadas na caracterização de materiais biodegradáveis.

2.6.1 Propriedades Mecânicas

A análise das propriedades mecânicas de blendas poliméricas é fundamental para prever o comportamento do material quanto à flexibilidade, resistência à ruptura, abrasão e demais reações que poderão ocorrer na embalagem

que afetarão a sua eficiência (MATZINOS et al., 2002). As propriedades mecânicas de embalagens biodegradáveis dependem da composição química de polímeros biodegradáveis, compatibilidade entre os polímeros e aditivos e parâmetros de processamento do material (GONTARD; GUILBERT, 1996).

As propriedades mecânicas de filmes podem ser medidas através de testes de perfuração, tração e relaxação. Nos testes de perfuração, uma sonda cilíndrica desce perpendicularmente à superfície do filme, que está fixado sobre um suporte de medida, até que ocorra o rompimento da amostra; são medidas a força e deformação na ruptura através dos gráficos de força *versus* deslocamento. As propriedades de tração são as mais relatadas e expressam a resistência do material ao alongamento e ao rompimento, quando submetido à tração.

As metodologias de análise das propriedades mecânicas se baseiam principalmente nas normas da ASTM D-882-91 (1996), que se aplica à determinação das propriedades de tração de filmes com espessura inferior a 1 mm e na ASTM D-638-93 (1993), para filmes com espessura igual ou superior a 1 mm. Dentre as propriedades de tração mais estudadas estão a resistência máxima à tração, o alongamento na ruptura e o módulo de elasticidade ou de Young.

2.6.2 Propriedades Térmicas

A análise térmica pode ser definida como um grupo de técnicas por meio da qual as propriedades físico-químicas de uma 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 específica controlada.

Algumas temperaturas, tanto de transição quanto de interesse técnico, podem muitas vezes ser obtidas de um único ensaio ou equipamento. A calorimetria diferencial de varredura (DSC), a análise dinâmico-mecânica (DMA) e a análise termogravimétrica (TGA) permitem obter informações relevantes sobre as propriedades térmicas dos polímeros como as temperaturas de transição vítrea (Tg), cristalização, fusão e de decomposição térmica.

Os eventos térmicos que geram modificações em curvas de DSC podem ser, basicamente, transições de primeira e segunda ordem. As transições de primeira ordem apresentam variações de entalpia (endotérmica ou exotérmica) e

dão origem à formação de picos. Como exemplo de eventos endotérmicos que podem ocorrer em amostras de polímeros pode-se citar: fusão, perda de massa da amostra (vaporização de água, aditivos ou produtos voláteis de reação ou decomposição), dessorção e reações de redução. Eventos exotérmicos observados em polímeros podem ser: cristalização, reações de polimerização, oxidação, degradação oxidativa, absorção e outros. As transições de segunda ordem caracterizam-se pela variação de capacidade calorífica, porém sem variações de entalpia. Assim, estas transições não geram picos nas curvas de DSC, apresentando-se como um deslocamento da linha base em forma de S. Um exemplo característico é a transição vítrea (Tg), na qual a entalpia não sofre variação, mas o calor específico sofre uma mudança repentina (CANEVAROLO, 2003).

A determinação das temperaturas de transição vítrea dos filmes ajuda na escolha das melhores condições de armazenamento e aplicação dos mesmos, uma vez que as propriedades mecânicas e de barreira dos polímeros sofrem grande influência da Tg. A permeação aos gases e ao vapor de água é maior acima da Tg, onde as cadeias de polímeros apresentam maior mobilidade, como também os filmes apresentam maior flexibilidade.

A determinação da temperatura de degradação térmica é importante para verificar se nas temperaturas de extrusão não está ocorrendo a degradação dos componentes da blenda, bem como se não houve volatilização dos plastificantes. Além disso, é possível determinar a estabilidade térmica dos materiais produzidos quando há incorporação de amido na blenda. De acordo com Wang et al. (2009), a temperatura de degradação do amido é em torno de 320°C e a do PLA é superior, ao redor de 390°C.

2.6.3 Propriedades Viscoelásticas

Os ensaios mecânicos de tensão-deformação em filmes levam em consideração apenas o caráter elástico que estes materiais apresentam e não fornecem informações sobre as características viscoelásticas dos mesmos. A caracterização da viscoelasticidade de filmes em geral é importante porque fornece informações relativas à conformação das macromoléculas do polímero e determinam o comportamento destes materiais em processos industriais como bobinagem.

As propriedades viscoelásticas de sólidos são demonstradas pelas curvas de relaxação, com testes que podem ser dinâmicos ou estáticos. Nos testes estáticos, uma deformação, ou uma tensão, é imposta e mantida constante durante o ensaio, sendo que a variação da tensão, ou da deformação, é observada, respectivamente, como resposta durante a evolução do tempo. O primeiro teste é chamado relaxamento de tensão, e o segundo, de teste de fluência. Nesses casos, o modelo utilizado no tratamento dos dados estabelece as propriedades viscoelásticas, que podem ser: módulo de elasticidade e módulo de viscosidade, nos testes de relaxamento de tensão, e módulo de fluência, no segundo teste (CHANDRA; SOBRAL, 2000; MENDIETA-TABOADA; CARVALHO; SOBRAL, 2008).

Vários modelos foram aplicados para descrever as propriedades viscoelásticas de filmes biodegradáveis, obtendo-se um bom ajuste. Cuq et al. (1996) desenvolveram um modelo viscoelástico independente da espessura para determinar as propriedades viscoelásticas de filmes de proteína miofibrilar de sardinha. Chandra e Sobral (2000) aplicaram os modelos de Maxwell, Maxwell generalizado e Burges em filmes de proteínas miofibrilares de tilápia do Nilo. Müller, Laurindo e Yamashita (2009) aplicaram o modelo de Peleg em filmes de amido incorporados com fibras, sendo o mesmo modelo pesquisado nos trabalhos de Nobrega et al. (2012a, 2012b) para descrever o comportamento viscoelástico de filmes de amido e PBAT produzidos por extrusão sopro.

Nos métodos dinâmicos, conhecido como análise dinâmico-mecânica (DMA), uma variação senoidal da deformação, ou da tensão, é imposta ao material, e uma variação da tensão necessária à imposição da deformação, ou no segundo caso, a deformação consequente da tensão aplicada, é observada como resposta, que também variará, porém defasada da deformação, com certo ângulo õ. Assim, a tensão pode ser resolvida em duas componentes: a componente em fase com a deformação, que representa a energia mecânica que o material é capaz de armazenar, sendo expressas pelo módulo de armazenamento (G') e a componente defasada 90° com a deformação e está relacionada com a energia mecânica dissipada, expressa pelo módulo de perda (G") (MENDIETA-TABOADA et al., 2008; HATAKEYAMA e QUINN, 1999).

Outra propriedade, o ângulo de fase, também conhecida como tan õ, fator de perda, fricção interna, ou amortecimento, pode ser calculado como a razão entre os valores de G" e de G'. O ângulo de fase expressa a capacidade de um

material em converter energia mecânica em calor, e é considerado muito útil na caracterização de sistemas poliméricos (CANEVAROLO, 2003).

Assim como no caso das curvas de DSC, também é possível se determinar o valor da Tg nas curvas de DMA. Normalmente, a transição vítrea é associada a uma inflexão na curva do módulo de armazenamento e/ou a um pico na curva de tan õ. O DMA ainda determina transições secundárias, que estão relacionadas à relaxação de grupos, ou parte de grupos, laterais da cadeia polimérica e, também, da temperatura de fusão de cristais (Tm) de polímeros parcialmente cristalinos (CANEVAROLO, 2003; MENDIETA-TABOADA et al., 2008).

Em curvas de tan õ em função da temperatura de blendas de amido e PLA é possível verificar 2 picos distintos em aproximadamente -35°C e 65°C. O primeiro está relacionado com a Tg do amido e o segundo com a Tg do PLA, indicando separação de fases e imiscibilidade entre os polímeros (WANG et al., 2010).

2.6.4 Ropriedades de Barreira

A capacidade de uma embalagem de resistir à sorção ou evaporação de gases e vapores, resistir à permeação de lipídios e à passagem de luz é definida como barreira. A determinação da quantidade máxima de umidade que pode permear através de uma embalagem é fundamental para a especificação de embalagens para produtos sensíveis ao ganho de umidade. A permeabilidade ao oxigênio é uma característica importante dos materiais flexíveis utilizados para proteção de produtos sensíveis ao oxigênio.

O processo de permeação aos gases e vapores em filmes acontece em três etapas: a) sorção e solubilização do permeante na superfície do material, b) difusão do permeante através do material devido à ação de gradiente de concentração e c) dessorção e evaporação do permeante na outra face do material (KESTER; FENNEMA, 1986; MILLER; KROCHTA, 1997; MAIA; PORTE; SOUZA, 2000).

A primeira e a terceira etapas do processo de permeação dependem da solubilização do permeante no polímero, ou seja, as interações (van der Waals ou ligações de hidrogênio) entre o permeante e as moléculas determinam a quantidade do permeante que irá dissolver. Na segunda etapa do processo, a

difusão envolve o transporte do permeante através das regiões não cristalinas do polímero, ou através dos espaços vazios formados pela movimentação das cadeias poliméricas.

Na ausência de rachaduras ou cavidades, o principal mecanismo para o fluxo de gases e vapor através do filme é por difusão molecular, que compreende a abertura de espaços vazios entre os segmentos das cadeias dos polímeros devido às oscilações dos segmentos, seguido do deslocamento do permeante dentro dos espaços vazios (KESTER; FENNEMA, 1986).

Dentre as propriedades de barreira, a mais discutida é a permeabilidade ao vapor de água (PVA) que, em filmes hidrofílicos é influenciada pelas características intrínsecas do material, pelo teor de plastificante e pelas condições ambientais de umidade relativa e temperatura às quais se encontram expostos. A Norma ASTM E96-00 define permeabilidade como sendo a taxa de transmissão de vapor de água por unidade de área do material plano, a uma determinada espessura, induzida pela diferença de pressão de vapor entre duas superfícies específicas, sob condições de temperatura definidas (ASTM E96-95, 1995).

2.6.5 Espectroscopia no Infravermelho

As propriedades mecânicas, ópticas e de barreira de um filme feito pela mistura de polímeros irão depender das interações e compatibilidade entre eles. Uma técnica bastante utilizada para a caracterização de misturas de polímeros é a espectroscopia no infravermelho com transformada de Fourier (FT-IR).

As técnicas espectroscópicas estão baseadas no princípio de que as moléculas e átomos podem interagir com a radiação eletromagnética e a partir disso, informações estruturais e físico-químicas de compostos sob estudo podem ser obtidas. A radiação infravermelha causa aumento na amplitude de vibração das ligações covalentes entre átomos e grupos de átomos de compostos orgânicos. Essas vibrações são quantizadas, e enquanto ocorrem, os compostos absorvem a energia em regiões particulares da porção infravermelha do espectro (SOLOMONS; FRYHLE, 2001).

A chamada radiação infravermelha corresponde à parte do espectro eletromagnético situada entre as regiões do visível e das micro-ondas. A porção de

maior utilidade está situada entre números de onda de 4.000 a 666 cm^{-1}, que corresponde a comprimentos de onda de 2,5 a 15,0 um. As regiões do infravermelho próximo, 14.290 - 4.000 cm^{-1}, e do infravermelho distante, 700 - 200 cm^{-1}, também são usadas para identificação de materiais plásticos (SARANTÓPOULOS, 2002; SILVERSTEIN; WEBSTER, 2000).

Se dois polímeros formam uma blenda imiscível, não há alterações apreciáveis no espectro FT-IR da blenda com relação à adição de cada componente. No entanto, se dois polímeros são compatíveis, uma interação química distinta (ponte de hidrogênio ou interação dipolar) deve existir entre as cadeias de um polímero e de outro causando alteração no espectro FT-IR (mudanças na banda e estiramento). Como resultado, o espectro FT-IR pode ser utilizado para identificar segmentos de interação e proporcionar informações sobre a relação de fase das blendas poliméricas.

O PLA possui pico definido em 1.749 cm^{-1}, referente ao estiramento do grupo carbonila. Com a adição de ATP e compatibilizante anidrido maleico, este pico deslocou-se para um número de onda menor (1.745 cm^{-1}). Isto significa que os grupos carbonila participaram da interação entre o PLA e ATP, resultando em deslocamento do estiramento da carbonila (C=O) do PLA. O mesmo fenômeno foi encontrado para C-O em CH-O (1.182 cm^{-1}) e C-O- em O-C=O (1.127, 1.082 e 1.044 cm^{-1}) do PLA em blendas de ATP e PLA (WANG; YU; MA, 2007).

2.6.6 Isotermas de Sorção

A relação entre a umidade relativa de equilíbrio e o conteúdo de água dos materiais a base de amido pode ser visualizada através das isotermas de sorção de água, as quais são de grande importância no estudo das propriedades de barreira necessárias para a embalagem do material (FENNEMA, 2003).

Em materiais produzidos a base de polímeros hidrofílicos como o amido, a importância na construção das isotermas está na predição de alterações que o material pode sofrer quando condicionado em diferentes umidades relativas. Estas alterações podem afetar as propriedades funcionais dos filmes, uma vez que maior conteúdo de água possibilita maior movimentação molecular e, portanto, diminuição da temperatura de transição vítrea, o que afeta a rigidez da estrutura dos filmes (MALI et al., 2005).

Poucos trabalhos relatam a determinação de isoterma em blendas de ATP e PLA, sendo mais comum encontrar estudos aplicados em filmes de amido. Diversos modelos descritos na literatura podem ser utilizados para descrever as isotermas de sorção de umidade de filmes, entre eles o mais utilizado é o de GAB (Guggenhein-Anderson-de Boer), um modelo cinético baseado em multicamadas e filmes condensados, pois é capaz de predizer os parâmetros de sorção em intervalos de atividade de água de 0,05 a 0,9 (MALI et al., 2005; TIMMERMANN, 2003).

O modelo de GAB, além de fornecer o valor da monocamada, fornece informações adicionais relativas ao calor de sorção da monocamada e multicamada, através de três parâmetros: C, *k* e m_0, onde *C* está representando o calor total de sorção da monocamada, *k* está relacionada ao calor de sorção da multicamada e *m0* representa o valor da monocamada, sendo este último importante por sua relação com a interação das moléculas de água com sítios polares específicos (GENNADIOS, 2002).

2.6.7 Microscopia Eletrônica de Varredura

O microscópio eletrônico de varredura é geralmente utilizado para o estudo de estruturas superficiais ou subsuperficiais de amostras com dimensões relativamente grandes. As imagens têm alta profundidade de foco, o que significa obter diferentes relevos da superfície da amostra simultaneamente em foco. Com esta técnica é possível, por exemplo, avaliar a presença de poros e rugosidade na superfície do filme e a partir da fratura vítrea realizada na presença de líquido criogênico pode-se observar a morfologia interna dos mesmos (CANEVAROLO, 2003).

A microscopia eletrônica de varredura é uma técnica versátil e para o caso de filmes e chapas a base de amido, a preparação das amostras e a obtenção das imagens é relativamente simples, necessitando de uma fratura em nitrogênio líquido, quando se deseja avaliar a área de fratura, e um recobrimento com partículas de ouro.

Imagens de microscopia eletrônica de varredura de blendas de ATP e PLA sem adição de plastificantes e compatibilizantes geralmente mostram uma

estrutura incompatível, com algumas cavidades que resultam da diferença de polaridade entre o amido e PLA que elevam a tensão interfacial.

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CAPÍTULO 3

DEVELOPMENT OF BIODEGRADABLE FLEXIBLE FILMS OF STARCH AND POLY(LACTIC ACID) PLASTICIZED WITH ADIPATE OR CITRATE ESTERS

Marianne Ayumi Shirai, Maria Victoria Eiras Grossmann, Suzana Mali, Fabio Yamashita, Patrícia Salomão Garcia, Carmen Maria Olivera Müller. **Carbohydrate Polymers,** v. 92, p. 19-22, 2013.

ABSTRACT: Biodegradable films were produced from blends contained a high amount of thermoplastic starch (TPS) and poly(lactic acid) (PLA) plasticized with different adipate or citrate esters. It was not possible to obtain pellets for the production of films using only glycerol as a plasticizer. The plasticization of the PLA with the esters and mixture stages added through extrusion was critical to achieve a blend capable of producing films by blow extrusion. Adipate esters were the most effective plasticizers because they interacted best with the PLA and yielded films with appropriate mechanical properties.

Keywords: Mechanical properties. Microstructure. Extrusion. Biodegradable polymer.

3.1 INTRODUCTION

The environmental problems caused by discarding non-biodegradable materials have led to the research and development of biodegradable materials with characteristics that allow for their use in the production of packaging on a commercial scale. In this context, the use of poly(lactic acid) (PLA) and starch blends is a promising option because in addition to being biodegradable, these materials are derived from renewable source.

Starch is an attractive biopolymer because of its abundance, low cost, and potential application in the production of biodegradable films in the form of thermoplastic starch (TPS). However, TPS film is limited due to its hydrophilic nature, which results in changes to its mechanical properties when exposure to high relative humidity (AVELLA et al., 2005; KALAMBUR; RIZVI, 2006; ZULLO; IANNACE, 2009).

PLA is an aliphatic, biodegradable, and hydrophobic polyester produced from the polymerization of lactic acid molecules and has properties comparable to those of plastics made from petroleum, such as transparency, good processability, and mechanical properties (GARLOTTA, 2001; MARTIN; AVEROUS, 2001). In general, PLA-based materials are rigid and brittle; thus, their properties

must be modified to produce flexible films. For this purpose, both adding plasticizers and blending with other biodegradable polymers has been examined (COLTELLI et al., 2008).

Plasticizers, such as glycerol and sorbitol, have been researched to increase the flexibility and improve the processability of starch/PLA blends; however, no significant improvement in the mechanical properties has been observed (LI; HUNEAULT, 2011; MARTIN; AVEROUS, 2001).

Several studies compared the plasticizing effect of different adipate and citrate esters and found that these substances efficiently reduced the glass transition temperature (Tg) and improved the mechanical properties of PLA by reducing the elastic modulus and the tensile strength and increasing the elongation, thus making it possible to obtain flexible films (LABRECQUE et al., 1997; LJUNGBERG et al., 2003; MARTINO et al., 2009; ZHANG; SUN, 2004).

The objective of this study was to produce TPS films by blow extrusion and evaluate the effect of adding PLA plasticized with adipate or citrate esters in the blend.

3.2 MATERIALS AND METHODS

3.2.1 Materials

This study used PLA Ingeo 3251D (Natureworks LLC, Cargill, USA), cassava starch (Indemil, Brazil), and commercial glycerol (Dinâmica, Brazil) as plasticizing for the starch; diisodecyl adipate (426.67 g/mol), diethyl adipate (202.25 g/mol), acetyl triethyl citrate (318 g/mol), acetyl tributyl citrate (402.49 g/mol), and tributyl citrate (360.44 g/mol) (Sigma Aldrich, Germany) were used as plasticizing for the PLA.

3.2.2 Production of Pellets and Films

The pellets were produced in two stages. In the first stage, mixtures containing 30% (w/w) of TPS and 70% (w/w) of PLA and plasticizer were extruded in a twin-screw extruder (BGM, D-20 model, Brazil) using the following processing conditions: a screw diameter of 20 mm, a screw speed of 120 rpm, a feeder speed of

40 rpm, and a temperature profile of 100 / 150 / 150 / 150 / 150°C. The concentrations of the plasticizers were 33 g glycerol / 100 g starch and either 11 g or 18 g of adipate or citrate ester / 100 g PLA. In the control formula, the ester was substituted with glycerol. The extruded cylindrical profiles were chilled in a water bath at room temperature and were pelletized.

In the next step, the pellets produced in the first stage were mixed at a proportion of 10% (w/w) pellets and 90% (w/w) TPS (33 g glycerol / 100 g starch) and were extruded in a twin-screw extruder, using a screw speed of 150 rpm, a feeder speed of 50 rpm, and a temperature profile of 100 / 140 / 140 / 140 / 140°C. The cylindrical profiles were pelletized and were extruded in a single-screw extruder (BGM, EL-25 model, Brazil) to produce films by blow extrusion under the following conditions: a screw diameter of 25 mm, a screw speed of 35 rpm and a temperature profile of 100 / 150 / 150 / 100°C. The final composition of each film is presented in Table 3.1.

Table 3.1 – Composition of the TPS and PLA films plasticized with citrate or adipate esters.

Formulation	Starch (%)	Glycerol (%)	PLA (%)	Adipate ester %)[a]	Citrate ester (%)[b]
C1	69.7	24	6.3	-	-
C2	69.7	24.3	6.0	-	-
DEA1 / DIA1	69.7	23.3	6.3	0.7	-
DEA2 / DIA2	69.7	23.3	6.0	1.0	-
ATE1 /ATB1 /TBC1	69.7	23.3	6.3	-	0.7
ATE2 / ATB2 / TBC2	69.7	23.3	6.0	-	1.0

C1 and C2 = Control; a = Diethyl adipate or Diisodecyl adipate; b = Acethyl triethyl citrate or Acethyl tributyl citrate or Tributyl citrate.

3.2.3 Mechanical Properties

The tensile strength tests were performed with a texture analyzer (Stable Micro Systems, TA XTplus model, England) based on the American Society for Testing and Material standards (ASTM D882-02, 2002). The samples were previously conditioned at 23 ± 2°C and 53 ± 2% RH for 48 hours. The properties measured were tensile strength (MPa), elongation at break (%), and Young's modulus (MPa).

3.2.4 Apparent Opacity

The apparent opacity (Y_{ap}) was determined using a colorimeter (BYK Gardner, USA), and was calculated based on the ratio of the luminosity (L* - CIELab system) of the system, which was measured with a black background (L_B*) and with a white background (L_w*), divided by the thickness of the film (pp). The results were expressed on an arbitrary scale (0 - 100 %. Mm^{-1}) according to equation 3.1.

$$Yap = [(L_B^*/L_W^*)/(P\ ]x100 \quad \text{(Eq. 3.1)}$$

3.2.5 Scanning Electron Microscopy (SEM)

The microstructure of the fractured films was analyzed with a scanning electron microscope (Philips, XL-30 model, Holland) with electron source of tungsten and detectors of secondary and back-scattered electrons. The films were immersed in liquid nitrogen and then broken. The samples were coated with gold using a sputter coater (BALTEC, SCD 005 model, Switzerland). All the samples were examined using an accelerating voltage of 10 KV.

3.2.6 Fourier Transform Infrared Spectroscopy (FT-IR)

The spectra were obtained with an FT-IR spectrophotometer (Shimatzu, IR-Prestige 21 model, Japan) equipped with a diffuse reflectance accessory. A resolution of 4 cm^{-1} was used for each spectrum, with 20 scans between 4000 and 700 cm^{-1}.

3.2.7 Statistical Analysis

The obtained results were evaluated using analysis of variance (ANOVA), and treatment means were compared using Tukey's test at the 5% significance level ($p<0.05$) with Statistica 7.0 software (Stat-Soft, Tulsa, OK, USA).

3.3 RESULTS AND DISCUSSION

3.3.1 Production of the Films

To produce the pellets of the blends of starch and PLA, two stages of mixture were necessary, due to the difficulty in preliminary tests in obtaining a homogenous blend by exclusively extruding all components together.

In general, all of the formulations displayed similar behavior during the film processing step without significant variations in the amperage (~ 8.0 A) of the extruder. The formulations displayed similar behavior because a majority of the film is composed of thermoplastic starch and an elevated amount of glycerol.

It was not possible to form the extruded profiles into pellets in the control formulation (Table 1) because the material was not homogenous, and after cooling, it became rigid, brittle, and sticky, which indicates that glycerol is not a good plasticizer for PLA, even though it is a good plasticizer for starch. The adipate and citrate esters plasticized the PLA and allowed homogenous pellets to be obtained for the production of films by blow extrusion.

The obtained films had a yellow surface, were homogenous, had irregularities in some spots, and were slightly sticky due to excess glycerol.

3.3.2 Mechanical and Optical Properties

The concentration and the type of ester plasticizer, either adipate or citrate, did not have a significant effect on the mechanical properties of the films produced from starch + PLA blends (Table 2). The films with adipate esters were characterized by greater elongation (120 to 148%), less tensile strength (0.6 to 0.9 MPa), and a lower Young's modulus (1.6 to 3.8 MPa) than the films made with citrate esters. The linear structure of these compounds probably facilitated the interaction with PLA, which led to efficient plasticization. The similarity of the chemical structures and the compatibility between the plasticizer and the polymer determine the plasticization efficiency. From a molecular perspective, the plasticizer should be miscible and should have solubility close to that of the polymer, thus requiring less energy to merge or solvate (MURARIU et al., 2008).

Table 3.2 – The thickness, mechanical and opacity properties of the TPS and PLA films plasticized with citrate or adipate esters.

Formulation *	YM (MPa)	T (MPa)	(%)	<P (Mm)	Yap (%.Mm^{-1})
F-DEA1	3.8 ± 1.0 ^{a}	0.9 ± 0.1 a	126 ± 17 $^{d.e}$	246 ± 30 ^{a}	0.19 ± 0.01 c
F-DEA2	3.6 ± 0.6 ^{a}	0.8 ± 0.1 a	146 ± 18 ^{e}	492 ± 104 ^{b}	0.08 ± 0.02 a,b
F-DIA1	1.6 ± 0.4 ^{a}	0.6 ± 0.1 a	148 ± 24 ^{e}	332 ± 76 ^{a}	0.16 ± 0.04 b,c
F-DIA2	2.9 ± 0.6 ^{a}	0.7 ± 0.1 a	120 ± 15 ^{c,d,e}	923 ± 163 ^{c}	0.05 ± 0.01 a
F-ATEC1	9.7 ± 1.8 ^{b,c}	1.2 ± 0.2 b	109 ± 17 ^{b,c,d}	621 ± 129 ^{b}	0.13 ± 0.03 ^{a,b,c}
F-ATEC2	8.2 ± 2.4 ^{b,c}	1.1 ± 0.2 b	98 ± 15 ^{a,b,c,d}	534 ± 175 ^{b}	0.11 ± 0.05 ^{a,b,c}
F-ATB1	10.8 ± 3.2 ^{c}	1.3 ± 0.2 b	92 ± 18 ^{a,b,c}	342 ± 71 ^{a}	0.16 ± 0.03 b,c
F-ATB2	10.6 ± 2.5 ^{c}	1.1 ± 0.1 b	86 ± 16 ^{a,b}	562 ± 139 ^{b}	0.11 ± 0.05 ^{a,b,c}
F-TBC1	7.0 ± 2.3 ^{b}	0.9 ± 0.2 a	72 ± 11 ^{a}	276 ± 38 ^{a}	0.20 ± 0.06 c
F-TBC2	6.8 ± 2.8 ^{b}	1.1 ± 0.2 b	103 ± 19 $^{b.c.d}$	303 ± 101 ^{a}	0.15 ± 0.03 $^{a.b.c}$

* The control formulations (F-C1 and F-C2) did not form films.
YM = Young's modulus; T = Tensile strength; £ = elongation; 9 = thickness; Yap = apparent opacity.
$^{a, b, c,d, e,}$ The means followed by the same letters in the same column do not exhibit differences at the 5% significance level according to Tukey's test.

Cassava TPS films (20 g glycerol / 100 g starch) produced by blow extrusion (COSTA, 2008) had a tensile strength of 13 MPa, an elongation of 13%, and a Young's modulus of 134 MPa. According to Martino et al. (2009), PLA films produced by injection molding exhibit reduced tensile strength and increased elongation when plasticized with 20% adipate ester (MW = 2,565 g/mol). A PLA-starch blend (55:45) made with maleic anhydride as compatibilizer and plasticized with acetyl triethyl citrate elongated approximately 130% (ZHANG; SUN, 2004).

In blow extrusion, thickness is mainly controlled by winding speed and airflow in the balloon matrix. The variation of thickness resulted from the differences in the formulation and processability of the blends.The increase in the concentration of DEA, DIA, and ATB increased the thickness of the films without altering the mechanical properties. The thickness also increased with the molecular mass of the esters used (DEA2 < ATB2 < DIA2), probably due to the increase in density. A similar pattern was observed in pea starch films plasticized with different monosaccharides and polyols (ZHANG; HAN, 2006).

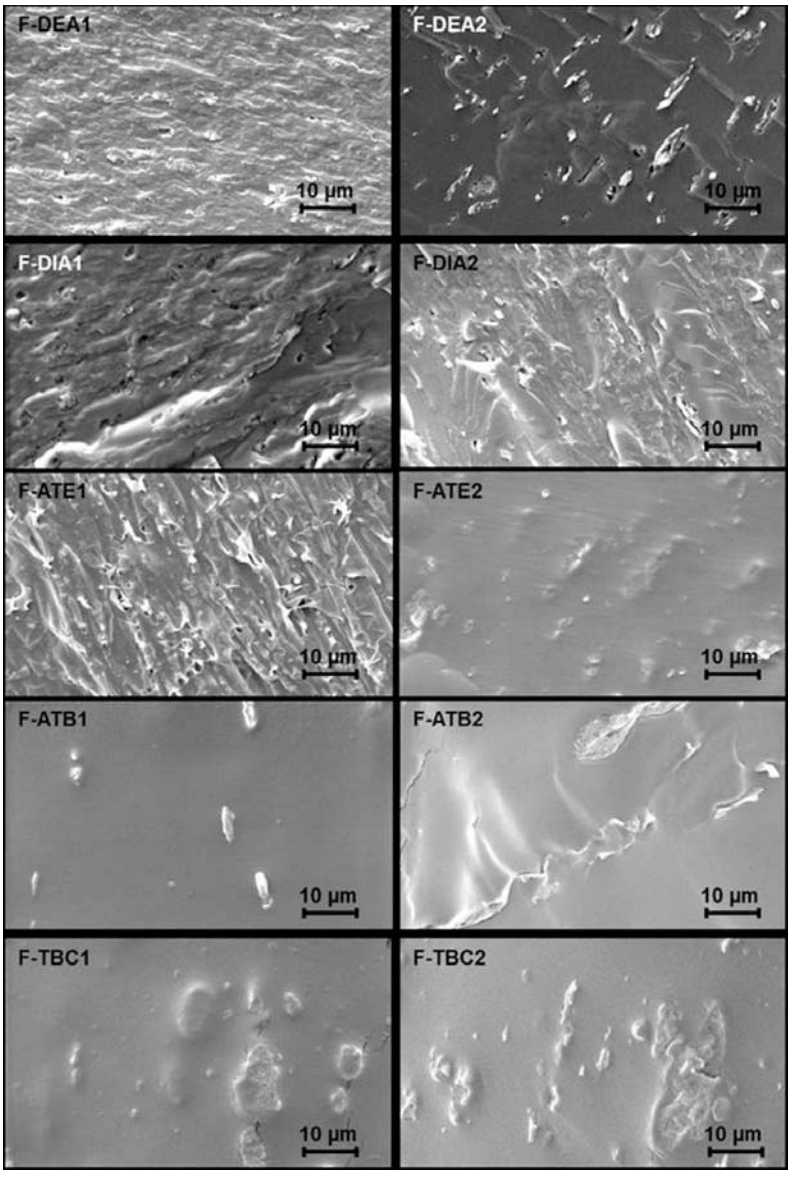
Increasing the concentration of adipate esters significantly decreased the opacity of the films, possibly due to the increased free volume resulting from the greater mobility of PLA chains and to the decrease in crystallinity. For the citrate esters, varying the concentration and type of plasticizer did not significantly alter opacity.

3.3.3 Scanning Electron Microscopy

From the fracture micrographs of the films (Figure 3.1), there was no phase separation between the TPS and PLA plasticized with citrate or adipate esters, probably because of the small concentration of PLA relative to TPS. For the films containing adipate esters, particles on the surface, which were non-gelatinized starch granules or PLA droplets dispersed in the matrix, and micropores were observed.

The micrographs support the conclusion that the mixture stages by extrusion used in this study were efficient, both in the plastification of the starch and in the plastification of PLA.

Figure 3.1 – Micrographs of the fracture (x 1600) of the TPS and PLA films plasticized with citrate or adipate esters.



3.3.4 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra (not shown) reveal that all of the samples displayed peaks of absorption in the same regions but no bands that could indicate interactions between the starch and the PLA.

Absorption bands were observed at approximately 1,020 and 995 cm^{-1}, which were related to the C-O fracture strain of the C-O-C group in the anhydroglucose ring that developed because of the starch. A broad band was observed at approximately 3,300 cm^{-1}, which is related to the hydrogen interactions due to the presence of hydroxyl groups in the ends of the PLA chain, in the glycerol and in the starch.

A low-intensity absorption peak was observed at approximately 1,750 cm^{-1}, which corresponds to the vibration of the C=O bond of PLA and of the adipate and citrate esters as a result of the presence of the ester. This spike was not intense because the concentration of PLA and of the esters in the formulation was low (7%).

3.4 CONCLUSION

The plasticization of PLA with citrate or adipate esters, the high concentration of glycerol in the TPS, and the inclusion of mixture stages with twin-screw extrusion allowed the production of TPS+PLA films with low PLA concentration using blow extrusion.

Adipate esters at a low concentration, in particular DEA, which has a linear structure and the smallest molecular weight, were the best plasticizers for PLA. It was possible to produce films with mechanical properties that are appropriate for various types of applications.

3.5 ACKNOWLEDGEMENTS

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CAPÍTULO 4

THERMOPLASTIC STARCH/POLYESTER FILMS: EFFECTS OF EXTRUSION PROCESS AND POLY(LACTIC ACID) ADDITION

Marianne Ayumi Shirai, Juliana Bonametti Olivato, Patrícia Salomão Garcia, Carmen Maria Olivera Müller, Maria Victoria Eiras Grossmann, Fabio Yamashita. **Materials Science and Engineering C,** v. 33, p. 4112-4117, 2013

ABSTRACT: Biodegradable films were produced using the blown extrusion method from blends that contained cassava thermoplastic starch (TPS), poly(butylene adipate-co-terephthalate) (PBAT) and poly(lactic acid) (PLA) with two different extrusion processes. The choice of extrusion process did not have a significant effect on the mechanical properties, water vapor permeability (WVP) or viscoelasticity of the films, but the addition of PLA decreased the elongation, blow-up ratio (BUR) and opacity and increased the elastic modulus, tensile strength, and viscoelastic parameters of the films. The films with 20% PLA exhibited a lower WVP due to the hydrophobic nature of this polymer. Morphological analyses revealed the incompatibility between the polymers used.

Key–words: Biodegradable film. Viscoelasticity. Mechanical properties. Water vapor permeability. Blown extrusion.

4.1 INTRODUCTION

The development of biodegradable materials has received considerable interest in recent years with the primary goal of reducing the consumption of non-biodegradable petroleum-based polymers in various applications (Yeh et al., 2010). There are currently several biodegradable polymers commercially available, and they exhibit a wide range of properties and can compete with non-biodegradable polymers in different industrial fields.

Biodegradable films composed of thermoplastic starch (TPS) and poly(butylene adipate-co-terephthalate) (PBAT) with good mechanical properties and adequate water vapor barrier properties have been obtained by Bilck et al. (2010), Brandelero et al. (2011), and Olivato et al. (2012). PBAT is a flexible co-polyester that can fully biodegrade within a few weeks, but it is derived from petroleum.

In this context, TPS/PBAT blends with poly(lactic acid) (PLA) are a promising option because in addition to being biodegradable, both TPS and PLA are derived from renewable resources. PLA is an aliphatic and hydrophobic polyester

that is produced from the polymerization of lactic acid molecules, and it has properties that are comparable to those of plastics produced from petroleum, such as polypropylene (PP) and poly(ethylene terephthalate) (PET) (GARLOTTA, 2001; MARTIN; AVEROUS, 2001). However, the high brittleness, slow crystallization, low toughness, and hydrolysis properties limit the usage of PLA in the production of flexible films (YEH et al., 2010).

The production of films of blends of TPS/PLA using the blown extrusion method is difficult because PLA is rigid and brittle. In addition, the weak interfacial affinity between these polymers results in poor mechanical properties. The brittle properties of PLA can be modified by reactive extrusion using dicumyl peroxide as a radical initiator and with the addition of PBAT (KANZAWA; TOKUMITSU, 2011; SIRISINHA; SOMBOON, 2012). Ren et al. (2009) also reported that blending the PLA/TPS blend with another flexible polymer, such as PBAT, could be a useful method for obtaining new types of materials with excellent integrated properties.

Jiang et al. (2006) studied PLA/PBAT blends and observed that the blends exhibited a decreased tensile strength and modulus; however, the elongation and toughness of these blends significantly increased when PBAT was added. Coltelli et al. (2008) studied the effect of adding acetyl tributyl citrate (ATBC) as a plasticizer to the PLA/PBAT blends, and they observed that the blend with 20% ATBC with respect to PLA resulted in films with strains at break that were 30% greater than the PLA/PBAT blend.

There are a few studies on the production of ternary blends of TPS, PLA and PBAT with citric acid and magnesium stearate and their use in films obtained by blown extrusion. Citric acid, naturally present in vegetables and employed in food processing, has shown interesting effect as compatibilizer on TPS/PBAT blends improving the interaction between the polymeric phase (OLIVATO et al., 2012). Furthermore, there are few reports about viscoelastic characterization of the films and their correlation with extrusion process. Ren et al. (2009) produced binary and ternary blends of TPS, PLA and PBAT using a one-step extrusion process, but they did not employed these blends in film production.

Some studies have demonstrated that the blend production method and the processing technique influence the mechanical, morphological and barrier properties of the obtained films (ALTSKÃR et al., 2008; BRANDELERO et al., 2011).

The aim of this work was to evaluate the effect of the type of the extruder (single- or a twin-screw extruder) used in the preparation of the blends and the addition of PLA on the functional properties of TPS/PBAT films produced using the blown extrusion method.

4.2 MATERIALS AND METHODS

4.2.1 Materials

This study used PLA Ingeo 3251D (Natureworks LLC, Cargill, USA), native cassava starch (Indemil, Brazil), poly(butylene adipate-co-terephthalate) (PBAT) (BASF, Germany) under the commercial name Ecoflex®, glycerol (Dinâmica, Brazil), citric acid (Nuclear, Brazil),and magnesium stearate (Sigma, Brazil).

4.2.2 Preparation of Pellets and Films

The blends were prepared using a single- (BS) or a twin-screw extruder (BT). PLA was added at concentrations of 10, 20 and 30% as a substitute for TPS in the blends, and in the control samples (CS and CT), PLA was not added. The samples were labeled according to the PLA content and the type of extruder used during the production of the blends (Table 4.1). Citric acid and magnesium stearate were used to improve the processability of the films, because they act as compatibilizer and plasticizer, respectively.

In BS, the blends were processed in a pilot single-screw extruder (BGM, EL-25 model, Brazil) with screw diameter of 25 mm, screw length of 28D, screw speed of 35 rpm and a temperature profile of 130 / 150 / 150 / 150°C. In the preparation of BT, a pilot co-rotating twin-screw extruder (BGM, D-20 model, Brazil) was used with the following processing conditions: screw diameter of 20 mm, screw length of 35D, screw speed of 100 rpm, feeder speed of 30 rpm, and a temperature profile of 100 / 150 / 150 / 150 / 150°C. All of the extruded cylindrical profiles were pelletized and were extruded in a single-screw extruder (BGM, EL-25 model, Brazil) to produce films with the blown extrusion method under the following conditions: screw speed of 35 rpm, barrel temperature profile of 100 / 140 / 140/ 140°C and a 50 mm film-blowing die. The winding speed and airflow in the matrix that formed the

balloon was adjusted for each formulation to allow the formation of the balloon without tearing or cracking.

Table 4.1 – Composition of the films from blends processed in a single- (BS) or twin-screw (BT) extruder.

Film	PBAT (%)	*TPS (%)	PLA (%)	Citric acid (%)	Magnesium stearate (%)
CS / CT	40	59.49	0	0.01	0.5
BS-10 / BT-10	40	49.49	10	0.01	0.5
BS-20 / BT-20	40	39.49	20	0.01	0.5
BS-30 / BT-30	40	29.49	30	0.01	0.5

*TPS = 32 g glycerol / 100 g starch
CS = Control blend prepared by single-screw extruder; CT = Control blend prepared by twin-srew extruder

4.2.3 Blow-up Ratio

The blow-up ratio (BUR) is the ratio between the film and the diameter of the die, and this ratio was used to express the film elongation capacity (Pelissari et al., 2011). The results were expressed as the arithmetic means of ten random measurements.

4.2.4 Mechanical Properties

The tensile strength tests were performed using a texture analyzer (Stable Micro Systems, TA XTplus model, England) based on the American Society for Testing and Material standards (ASTM D882-02, 2002). The films were previously conditioned for 48 hours at 23 ± 2°C and 53 ± 2% relative humidity. The measured properties included the tensile strength (MPa), elongation at break (%), and the Young's modulus (MPa). The tests were repeated ten times for each formulation.

4.2.5 Apparent Opacity

The apparent opacity of the films were determined using a colorimeter (BYK Gardner, USA) with an illuminant D_{65} (day light) and a visual angle of 10°. The apparent opacity (Y_{ap}) was calculated according to Eq. 4.1, which is based on the film luminosity (L* - CIELab system).

$$Yap = [(L^*_B / L^*w) / cp] \times 100 \quad \text{(Eq. 4.1)}$$

Y_{ap}: apparent opacity (%.um^{-1})
L^*_B: L* measured against a black background
L^*_w: L* measured against a white background
cp: film thickness (um)

4.2.6 Water Vapor Permeability

The water vapor permeability (WVP) of the films was determined gravimetrically, according to the American Society for Testing and Material Standards (ASTM E96-00, 1996), under a relative humidity gradient of 33 - 64%.The tests were performed in duplicate.

4.2.7 Moisture Sorption Isotherm

The moisture sorption isotherms of the films were obtained using the static gravimetric method, and saturated saline solutions were used to create different relative humidities. The GAB (Guggenhein-Anderson-de Boer) model (Eq.4.2) was used to fit the experimental data. In this equation, the parameter X_w is the equilibrium moisture content (g water/g dry solid) at a water activity (aw), mo is the monolayer water content, C is the Guggenheim constant, which represents the sorption heat of the first layer, and k is the sorption heat of the multilayer. The parameters of the GAB model were determined using non-linear regression with the Statistica 7.0 software (Stat-Soft, Tulsa, OK, USA).

$$Xw = moCkaw / (1 - kaw)(1 - kaw + Ckaw) \quad \text{(Eq. 4.2)}$$

4.2.8 Stress Relaxation Test and Viscoelastic Properties

The stress relaxation test was performed using a texture analyzer (Stable Micro Systems, TA XTplus model, England), and the test samples (25 mm x 130 mm) were conditioned for 48 hours at 23 ± 2°C and 53 ± 2% relative humidity. The initial distance between the grips was 100 mm, and the films were stretched at

0.8 mm/s until 1% deformation was achieved, which was maintained for 60 seconds. The force required to maintain the deformation was measured at intervals of 0.04 seconds. This deformation value was selected to ensure that the behavior of the material remained in the linear viscoelastic region.

Linear viscoelastic models for the static relaxation test are generally developed from two elements, a spring and a hydraulic dashpot. The spring is considered to obey Hooke's law, whereas the second element obeys Newton's law. A spring and a dashpot assembled in series constitute Maxwell's model. The generalized Maxwell modelis obtained from summing the Maxwell model and the simplest representation consistsof the two units in parallel.

In our study, the viscoelastic properties were determined from the Peleg model (Eq.4.3), the Maxwell model (Eq.4.4) and the generalized Maxwell equation (Eq. 4.5), according to Chandra and Sobral (2000), Müller et al. (2009), Nobrega et al. (2012a) and Nobrega et al. (2012b), using non-linear regression and the Statistica 7.0 software (Statsoft, Tulsa, OK, USA). The validity of the model was evaluated based on the coefficient of determination (R^2).

$$o(t) = 1 - [(C1 \times t) / (C2 + t)] \text{ (Eq. 4.3)}$$

$$o(t) = £0\ [E1 \times \exp(-t/Á1) + Ee] \text{ (Eq. 4.4)}$$

$$a(t) = £_0\ [E_1 \times \exp(-t/A_1) + E_2 \times \exp(-t/A_2) + E_e] \text{ (Eq. 4.5)}$$

where a(t) is the stress at time t, $£_0$ is the deformation, E_1 and E_2 are the elastic modulus, E_e is the equilibrium elastic modulus, and A_1 and A_2 are the relaxation times. The viscous moduli (n and n_2) were obtained from A = n/E. In the Peleg model, (1 - C_1) can be viewed as the "degree of solidity", and the ratio C_1/C_2 represents the initial rate of the stress decay.

4.2.9 Scanning Electron Microscopy

The microstructure of the films was analyzed using a scanning electron microscope (Philips, model FEI Quanta 200, Japan). The films were fractured after being immersed in liquid nitrogen and then coated with gold using a sputter coater (Bal-Tec, model SCD-050, Balzers, Liechtenstein). All samples were examined using an accelerating voltage of 20 kV, and the magnification was 1600x.

4.2.10 Statistical Analysis

The obtained results were evaluated using the analysis of variance (ANOVA) method, and the treatment means were compared using Tukey's test at the 5% significance level ($p<0.05$) with the Statistica 7.0 software (Statsoft, Tulsa, OK, USA).

4.3 Results and Discussion

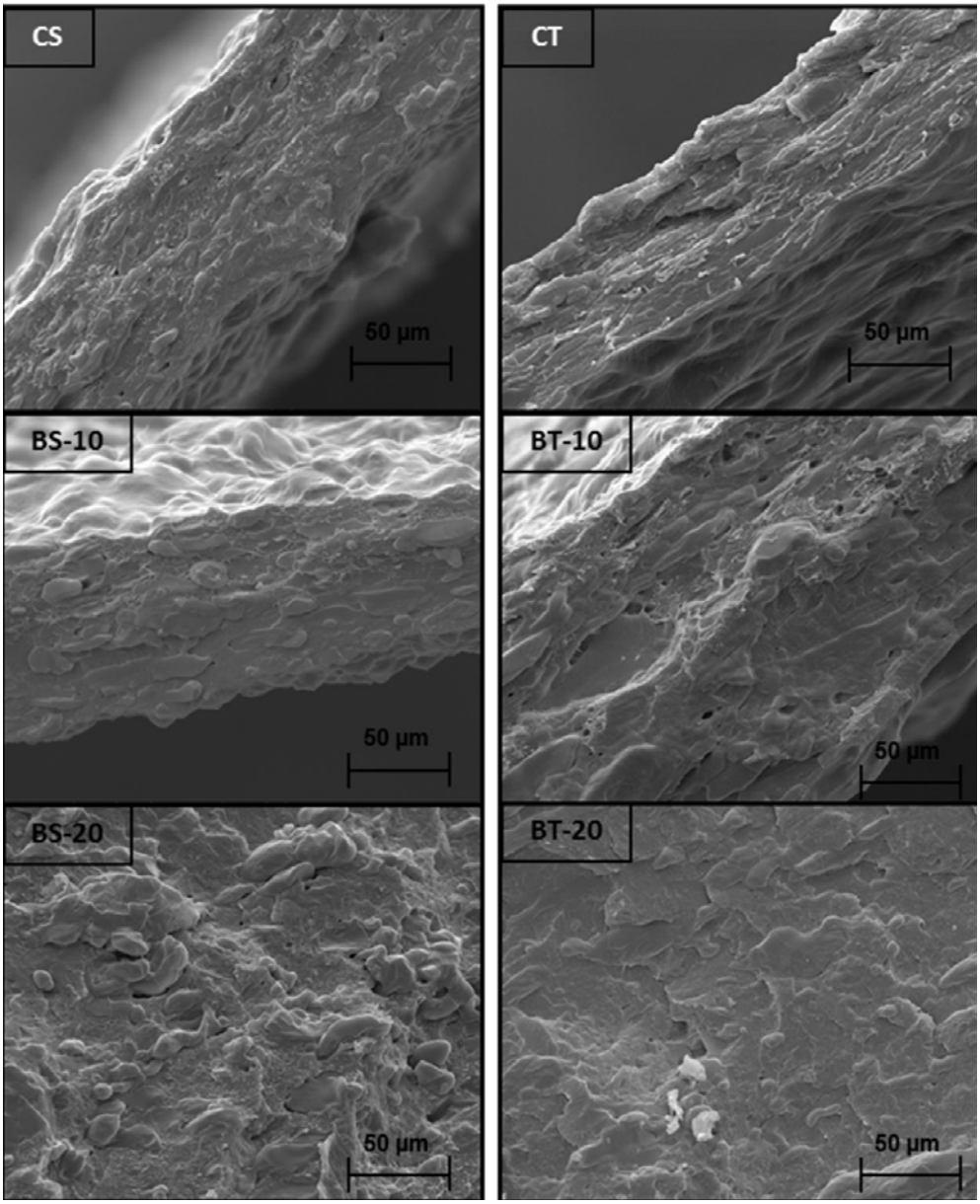
4.3.1 Scanning Electronic Microscopy

Producing films using the blown extrusion method with blends that contained 30% of PLA was not possible because the pellets were too rigid and brittle. All films exhibited an opaque surface due to the alignment of the chains and the subsequent crystallization. The control films exhibited good homogeneity and no tendency to tear, but the films with PLA were fragile, prone to tearing and possessed a rougher surface due to the presence of the non-melted PLA agglomerates.

The fracture micrographs of the films with and without PLA are shown in Figure 4.1. The high interfacial tension generated by the difference in the polarity between hydrophilic starch and hydrophobic PBAT and PLA could account the presence of micropores observed in the films micrographs. PLA and PBAT formed a continuous phase while the starch granules were distributed in the matrix, which confirms the incompatibility of the starch with the PBAT/PLA and the increase in the Young's modulus, which will be discussed below.

The micrographs confirm that the extrusion process (single- or twin-screw extruder) did not affect the functional characteristics of the films.

Figure 4.1 – Micrographs of the fracture of the TPS/PBAT films with and without PLA.



4.3.2 Mechanical Properties and Blow-Up Ratio

The incorporation of PLA affected the mechanical properties and thicknesses of the films (Table 4.2). In general, the films that contained PLA exhibited a higher Young's modulus and tensile strength and lower elongation at break than the control films, regardless of the extrusion process used, which is most likely due to the lack of compatibility between PLA and TPS/PBAT. Ren et al. (2009) observed the same tendency in 40% PBAT + 10% PLA + 50% TPS blends, which exhibited a 6% elongation at break and a tensile strength of 6MPa. Thellen et al. (2005) produced

films of PLA and montmorillonite plasticized with acetyltriethyl citrate, and the films exhibited elongations and tensile strengths that ranged from approximately 5.5 to 7.0% and 23 to 30 MPa, respectively.

Table 4.2 – Mechanical properties and thicknesses of the TPS/PBAT films with and without PLA.

Film	**YM** (MPa)	**T** (MPa)		**BUR**	**P** (Mm)
CS	28 ± 4 [c]	4.7 ± 0.4 [b]	395 ± 49 [a]	5.55 ± 0.07 [a]	94 ± 6 [b]
BS-10	75 ± 10 [b]	3.2 ± 0.4 [c]	39 ± 13 [b]	4.54 ± 0.06[b]	135 ± 25 [b]
BS-20	109 ± 10 [a]	5.1 ± 0.4 [a,b]	27 ± 9 [b]	1.00 ± 0.05 [c]	411 ± 66 [a]
CT	21 ± 1 [c]	3.6 ± 0.3 [c]	405 ± 29 [a]	5.94 ± 0.02 [a]	103 ± 9 [b]
BT-10	73 ± 20 [b]	3.2 ± 0.7 [c]	55 ± 26 [b]	4.67 ± 0.22 [b]	131 ± 10 [b]
BT-20	121 ± 10 [a]	5.7 ± 0.7 [a]	36 ± 7 [b]	1.07 ± 0.02 [c]	405 ± 59 [a]

YM = Young's modulus; T = tensile strength; £ = elongation; BUR = blow-up ratio; 9 = thickness.
a,b,c The means followed by the same letters in the same column do not exhibit differences at the 5% significance level according to Tukey's test.

The films with PLA did not exhibit differences in their elongation values, but the BS-10 and BT-10 films were thinner and capable of continuously forming larger diameter balloons, which was indicated by their higher BUR values. For the production of the BS-20 and BT-20 films, the airflow and winding speed had to be reduced to produce the balloon and support the vertical stretch, which caused the BUR values to decrease, and increase in the thickness. Higher BUR values (5.14 to 12.61) were obtained for the active starch/chitosan film (PELISSARI et al., 2011).

The type of extruder (single- or twin-screw) used to produce the blends did not have an influence on the resulting mechanical properties, BUR values or thicknesses of the films. Complete melting of the initial crystalline structure of the blend materials and subsequent homogenization is desirable because any remaining crystals will have a negative impact on the extensibility of the polymer melt (ALTSKAR et al., 2008). During the second extrusion employed for the film production, the pellets were resubmitted to thermal-mechanical processing, and this can be responsible for the gelatinization of the residual starch granules and melting of PBAT. This fact could explain the equal functional properties of the films. In the extruded blown films of zein plasticized with oleic acid, the preparation of the blend in the single- and twin-screw extruders provided similar tensile properties (WANG; PADUA, 2003).

4.3.3 Water Vapor Permeability (WVP) and Opacity

The WVP of the films decreased by approximately 60% when 20% PLA was added because PLA is more hydrophobic than starch and PBAT, which hinders the permeation of water (Table 4.3). The WVP was independent of the mixture processes (single- or twin-extruder), which suggests that the permeation of water is controlled by the components of the blend and their concentrations.

Table 4.3 – Water vapor permeability (WVP) and apparent opacity (Y_{ap}) of the TPS/PBAT films with and without PLA.

Film	WVP ($g.m^{-1}.Pa^{-1}.day^{-1}$) (x 10^{-6})	Y_{ap} ($\%.\mu m^{-1}$)
CS	5.9 ± 0.4 [a,b]	0.67 ± 0.05 [a]
BS-10	6.5 ± 0.2 [a]	0.50 ± 0.12 [a,b]
BS-20	3.7 ± 0.2 [c]	0.25 ± 0.01 [c]
CT	7.2 ± 0.2 [a]	0.59 ± 0.07 [a,b]
BT-10	6.3 ± 0.3 [a,b]	0.49 ± 0.01 [b]
BT-20	5.0 ± 0.7 [b,c]	0.29 ± 0.06 [c]

[a,b,c] Means followed by the same letters in the columns do not exhibit differences at a 5% significance level according to Tukey's test.

According to Bilck et al. (2010), films composed of cassava starch/PBAT (30:70) exhibited similar WVP values (4.72 x 10^{-6} $g.m^{-1}.Pa^{-1}.day^{-1}$) when the same relative humidity gradient (33-64%) was used to determine the permeability. Brandelero et al. (2011) measured the WVP of cassava starch/PBAT films with 30% glycerol and obtained lower values that ranged from 1.83x 10^{-7} to 6.75 x 10^{-7} $g.m^{-1}.Pa^{-1}.day^{-1}$. The neat PLA film and PLA films with synthetic phenolic antioxidants produced by casting (JAMSHIDIAN et al., 2012) exhibited lower WVP values than the films produced in this study (2.7 x 10^{-15} and 3 x 10^{-15} $kg.m.m^{-2}.s^{-1}.Pa^{-1}$, respectively) due to the absence of hydrophilic polymers such as starch.

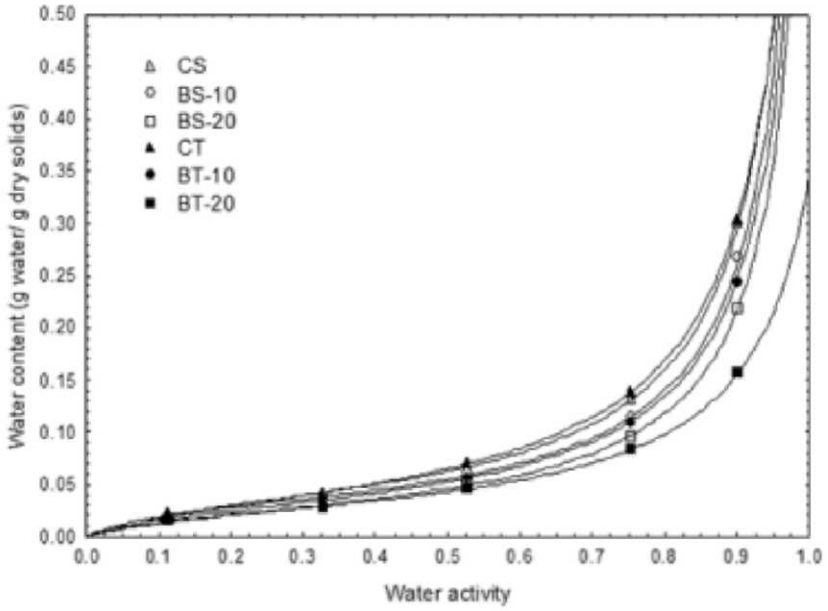
Increasing the concentration of PLA significantly decreased the opacity of the films due to the semi-crystallinity and transparency of PLA. The lack of compatibility between the polymers prevents the crosslinking reaction, which decreases the compaction of the polymeric chains. The less compact polymeric chains allow light to travel through the matrix, which results in less opaque films. Similar opacity values were observed in the starch/PBAT films compatibilized with citric acid and maleic anhydride and produced using the blown extrusion method

(OLIVATO et al., 2012). Pelissari et al. (2011) obtained more opaque starch/chitosan films with values that ranged from 45.42 to 66.60 %.Mm^{-1}.

4.3.4 Moisture Sorption Isotherm

Figure 4.2 presents the water sorption isotherms obtained at 25°C for the TPS/PBAT and TPS/PBAT/PLA films produced using either the single- or twin-screw extruder. The GAB parameters (m_o, C and K) are provided in Table 4.4.

Figure 4.2 – Moisture sorption isotherm for the TPS/PBAT films with and without PLA.



All samples exhibited sorption isotherms that had a sigmoidal shape, which is typical of water sorption in hydrophilic materials, and the isotherms were influenced by the concentration of PLA. When the PLA content was increased in the blend, the equilibrium moisture content decreased in the evaluated water activity range. This result may be associated with the hydrophobic character of PLA and PBAT, which was observed in the WVP measurements.

Table 4.4 – Estimated parameters for the GAB model for the TPS/PBAT films with and without PLA.

Film	GAB parameters [a]		
	m_o (g water /g dry solids)	K	C
CS	0.036	0.977	8.70
BS-10	0.031	0.980	11.01
BS-20	0.027	0.975	7.36
CT	0.040	0.968	5.79
BT-10	0.031	0.973	7.30
BT-20	0.027	0.923	7.13

[a] Coefficient of determination R2 > 0.99 for all fitted models.
mo = monolayer water content; C = Guggenheim constant; K = sorption heat of the multilayer.

The GAB model fitted the experimental data well with R^2>0.99, and it is adequate for describing the water sorption isotherms of the TPS films (MALI et al., 2005; MULLER et al. 2011) and the TPS/PBAT films (BRANDELERO et al., 2011). The films with 20% PLA exhibited the lowest monolayer values (0.027 g water/g solids) due to the hydrophobic characteristics of PLA, which decreased the water binding capacity of the film.

According to Figure 4.2, at water activities greater than 0.53, the films that contained PLA and were produced in the twin-screw extruder exhibited an equilibrium moisture content that was slightly lower than that of the films produced in the single-screw extruder; however, their mo values were equal.

The parameter K was not influenced by the composition of the blends, as observed by Mali et al. (2005) and Muller et al. (2011). The parameter C also was not influenced by the composition of the blends, and the obtained values were less than those observed in the TPS/PBAT films (BRANDELERO et al., 2011) and the cassava starch films plasticized with glycerol and sorbitol (MALI et al., 2005).

4.3.5 Viscoelastic Properties

The stress relaxation test shows the decay of the stress over the time, and this is an important characteristic for winding processes, which need to maintain a constant stretch, without significant reduction in the stress.

The stress relaxation curves of the films exhibited viscoelastic behavior, with the residual tension decreasing to an asymptotic value. Similar studies have been performed on starch films (MULLER et al., 2009), films of myofibrillar

proteins from fish (CHANDRA; SOBRAL, 2000; CUQ et al., 1996), and TPS/PBAT films (NOBREGA et al., 2012a; NOBREGA et al., 2012b).

All of the stress relaxation curves were modeled using the Peleg, Maxwell and generalized Maxwell models. Neither the Peleg model or the Maxwell models fit the experimental data well, specifically at the initial stress decay rate (0 to approximately 10 s), which is in contrast to the behavior observed by Muller et al. (2009) and Chandra and Sobral (2000).

The generalized Maxwell model fitted well the experimental data, with a coefficient of determination of $R^2 > 0.99$, and the model parameters are presented in Table 4.5. The elastic modulus (E) is related to the energy required to deform angle and bonds distance between atoms of the polymeric chains. The more rigid the polymer chain, greater E value. The viscous modulus (nj is related to the friction generated between polymer molecules during deformation, and the high n value means more friction occurrence. The PLA content influenced the viscoelastic properties of the films because, regardless of the extrusion process, the films that contained 20% PLA exhibited 1% n_2 and E_{eq} values that were approximately 2-, 2- and 4-times greater, respectively, than the control films. These results indicate that the addition of PLA caused an increase in the elasticity of the films.

The addition of PLA increased the rigidity and partially hindered the relaxation of the films. This result could explain the lower relaxation time of the control sample than that of the films with added PLA because a lower relaxation time corresponds to a greater film relaxation rate.

Cuq et al. (1996) observed that the viscoelastic properties of films were independent of their thicknesses. In addition, Chandra and Sobral (2000) reported a positive correlation between the thickness and the viscoelastic parameters of the film, and this behavior was also observed in this study. Therefore, the increase in the concentration of PLA was responsible for the increased elasticity (stiffness), thicknesses and viscoelastic properties of the samples.

Table 4.5 – Viscoelastic parameters calculated according to the generalized Maxwell model for the starch/PBAT films with and without PLA.

Film	E_1 (MPa)	n_1 (MPa.s)	A_1 (s)	E_2 (MPa)	n_2 (MPa.s)	A_2 (s)		E_e (MPa)
CS	16 ± 2 ^{a,b}	228 ± 39 ^{b}	14 ± 2 ^{b}	12 ± 2 ^{b}	16 ± 3 ^{c,d}	1.3 ± 0.1	a	33 ± 4 ^{d}
BS-10	14 ± 2 ^{b,c}	327 ± 67 ^{a,b}	23 ± 2 ^{a}	13 ± 3 ^{b}	21 ± 3 ^{b,c}	1.7 ± 0.1	a	57 ± 15 ^{c}
BS-20	18 ± 1 ^{a}	438 ± 71 ^{a}	24 ± 3 ^{a}	18 ± 2 ^{a}	30 ± 5 ^{a}	1.6 ± 0.1	a	120 ± 8 ^{a}
CT	11 ± 2 ^{c}	181 ± 37 ^{c}	17 ± 2 ^{b}	7 ± 1 ^{c}	10 ± 1 ^{d}	1.4 ± 0.1	a	27 ± 2 ^{d}
BT-10	17 ± 2 ^{a}^{b}	348 ± 41 ^{a}	20 ± 2 ^{a}	16 ± 2 ^{a}	25 ± 3 ^{a,b}	1.5 ± 0.2	a	87 ± 5 ^{b}
BT-20	19 ± 1 ^{a}	410 ± 63 ^{a}	22 ± 3 ^{a}	16 ± 1 ^{a}	27 ± 3 ^{a}	1.7 ± 0.1	a	132 ± 8 ^{a}

E1 and E2 = elastic modulus; r|1 and r|2 = viscous moduli; A1 and A2 = relaxation times; Ee = equilibrium elastic modulus.
^{a,b,c,d} Means followed by the same letters in the columns do not exhibit differences at a 5% significance level according to Tukey's test.

4.4 CONCLUSIONS

The incorporation of PLA into the TPS/PBAT blends had a significant effect on the opacity and the mechanical, barrier and viscoelastic properties of the films produced using the blown extrusion method. The micrographs of the films confirmed the incompatibility of PLA and PBAT with starch and that the extrusion process (single- or twin-screw extruder) did not affect the properties of the films.

The films with 20% PLA had presented a good barrier to water vapor, but due to their mechanical properties and thicknesses ,it is not possible to use these films as flexible packaging. Therefore, the results of this study suggest the use of adequate plasticizers to reduce the stiffness caused by the PLA and to improve the processability of the films.

4.5 ACKNOWLEDGEMENTS

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CAPÍTULO 5

ADIPATE AND CITRATE ESTER AS PLASTICIZERS FOR POLY(LACTIC ACID) / THERMOPLASTIC STARCH SHEETS

ABSTRACT: Poly(lactic acid) (PLA) and thermoplastic starch (TPS) sheets plasticized with different adipate and citrate esters were produced by calendering-extrusion process. The incorporation of plasticizers reduced significantly the glass transition temperature (Tg) and increased the PLA chain mobility, thus improving the mechanical properties. Among the plasticizer employed, diethyl adipate (DEA) increased significantly the elongation, and slightly increased the water vapor permeability. Micrographs revealed the incompatibility between starch and PLA, and there were no plasticizers phase separation, suggesting that the plasticizers concentration was adequate. The incorporation of adipate or citrate esters improves the mechanical properties and processability of PLA/TPS sheets produced by calendering-extrusion in pilot-scale process.

Key-words: Extrusion. Calendering. Mechanical properties. Glass transition. Crystallinity.

5.1 INTRODUCTION

Poly(lactic acid) (PLA), a polymer produced from renewable biobased feedstock, has been extensively studied with the main alternative to synthetic non-biodegradable materials. It is characterized by excellent optical properties and high tensile strength, biocompatibility, and biodegradability which make it appropriate for packaging end-use applications. Unfortunately, there are some issues, such as cost, rigidity, and brittleness at room temperature, due to its glass transition temperature (Tg) close to 55°C (LIM et al., 2008; NAJAFI et al., 2012).

The cost of PLA is higher than that for conventional thermoplastic such as polyethylene and polypropylene. To overcome these limitations, other polymers, minerals and biobased materials have been incorporated in PLA to produce composites with enhanced properties. Blending PLA with thermoplastic starch (TPS) can reduce the material cost, improve the water vapor barrier properties, and increase their biodegradation rate. However, PLA/starch composites are extremely brittle because of the coarse structure and lack of interfacial adhesion (KOZLOWSKI et al., 2007, LIM et al., 2008; MARTIN; AVÉROUS, 2001; WANG et al., 2007).

Addition of adequate plasticizer can improve the processability and flexibility of PLA/TPS blend. Several PLA plasticizers have been studied such as glycerol, sorbitol, lactic acid oligomers, citrate esters, poly(ethylene glycol), and poly(propylene glycol) (JAMSHIDIAN et al., 2010; MURARIU et al., 2008). Typically, amounts from 10 to 20 wt% plasticizers are required to provide a substantial reduction of the glass transition temperature (Tg) of the PLA matrix, increasing the mobility of polymer chains, and improving their flexibility by reducing intermolecular forces. Depending on the plasticizer, the addition of more than 20-30 wt% of plasticizers into the PLA matrix leads to a phase separation (HASSOUNA et al., 2012; LJUNGBERG et al., 2003; ROMERO-BATISTA et al., 2005). The polymers degree of plasticity is largely dependent on the chemical structure of the plasticizer, including chemical composition, molecular weight and functional groups (VIEIRA et al., 2011).

According to Murariu et al. (2008), adipate and citrate esters have demonstrated as interesting plasticizer for PLA. Low molecular weight plasticizers like bis(2-ethylhexyl) adipate, glyceryl triacetate and acetyl tributyl citrate interacted well with PLA and improved crystallization rates, and mechanical properties.

Labrecque et al. (1997) compared the plasticizing effect of different citrate esters (triethyl citrate, tributyl citrate, acetyl triethyl citrate, and acetyl tributyl citrate), and found that these substances efficiently reduced the Tg and improved the elongation of PLA films. Similar results were obtained by upon plasticizing PLA with triacetin and tributyl citrate (LJUNGBERG et al., 2003). In PLA/starch/maleic anhydride blends plasticized with acetyl triethyl citrate, the elongation increased when concentrations of plasticizers above 8% were used (ZHANG; SUN, 2004).

Adipate esters were also responsible to improve the mechanical properties of PLA by reducing the elastic modulus and the tensile strength, and increasing the elongation, thus making it possible to obtain flexible films. The effect of organo-modified layered montmorillonite on PLA plasticized with polyadipate was also studied, and significant properties improvement were observed such as oxygen barrier performance and elastic modulus increase, and elongation decrease (MARTINO et al., 2009; MARTINO et al., 2010).

In order to improve PLA/TPS properties, and to reach new application fields, the main objective of this study was to evaluate the effect of

adipate and citrate ester as plasticizer on the performance of PLA/TPS sheets produced by extrusion and calendering process.

5.2 MATERIAL AND METHODS

5.2.1 Materials

The biodegradable material (sheet) were produced with PLA Ingeo 4043D (Natureworks LLC, Cargill, USA), native cassava starch (Indemil, Brazil), and commercial glycerol (Dinâmica, Brazil), which was used as plasticizing for the starch. The diisodecyl adipate (426.67 g/mol), diethyl adipate (202.25 g/mol), acetyl triethyl citrate (318 g/mol), acetyl tributyl citrate (402.49 g/mol), and tributyl citrate (360.44 g/mol) (Sigma Aldrich, Germany) were used as plasticizing agents for the PLA.

5.2.2 Sheets Production

The formulation of the sheets was 70 wt% (w/w) of (PLA + plasticizer) and 30 wt% of TPS (starch + glycerol). The concentration of plasticizers was 33 g glycerol / 100 g starch and 10 g adipate or citrate ester / 100 g PLA. In the control formulation, adipate and citrate ester were not added. The formulations were labeled according to the adipate and citrate esters as diethyl adipate (DEA), diisodecyl adipate (DIA), acetyl triethyl citrate (ATE), acetyl tributyl citrate (ATB), and tributyl citrate (TBC).

All the components, PLA, starch, glycerol, adipate and citrate ester were manually mixed, and extruded as cylindrical strands in a pilot twin-screw extruder (BGM, model D-20, Brazil) with screw diameter of 20 mm (L/D = 35), screw speed of 100 rpm, feed speed of 30 rpm, and temperature profile of 100 / 180 / 180 / 180 / 180°C at the 5 zones.

The cylindrical strands were pelletized and then extruded in the same twin-screw extruder coupled with a calender (AX-Plasticos, Brazil) for sheet production. The temperature profile was 100 / 170 / 170 / 170 / 175°C, and the screw speed and feed speed were maintained. In the calender, the distance between the rolls was 0.8 mm, and the rolls speed was adjusted depending on the formulation to maintain continuous process.

5.2.3 Thickness and Density

Sheet thickness was measured with a digital micrometer (Starrett, Brazil) at ten different points. To determine the sheet density, samples of 20 mm * 20 mm were kept in a desiccator with anhydrous calcium chloride (0% RH) for 2 weeks and weighed, according described by Muller, Laurindo and Yamashita (2011).

5.2.4 Mechanical Properties

The tensile strength tests were performed with a texture analyzer (Stable Micro Systems, TA XTplus model, England) based on the American Society for Testing and Material standards (ASTM D882-02, 2002). The sheets were condicioned at 23 ± 2°C and 53 ± 2% RH for 48 hours before the test. The properties measured were tensile strength (MPa), elongation at break (%), and Young's modulus (MPa). The tests were repeated ten times for each formulation.

5.2.5 Water Vapor Permeability

The water vapor permeability (WVP) of the sheets was determined gravimetrically, according to the ASTM E96-00 (2000) standard, under a relative humidity gradient of 0 - 75%. The tests were conducted in duplicate.

5.2.6 Moisture Sorption Isotherm

The moisture sorption isotherms of the sheets were obtained using the static gravimetric method, and saturated saline solutions were employed to obtain different relative humidity. The GAB (Guggenhein-Anderson-de Boer) model (Eq. 5.2) was used to fit the experimental data. In this equation, the parameter X_w is the equilibrium moisture content (g water/g dry solid) at a water activity (aw), mo is the monolayer water content, C is the Guggenheim constant, which represents the sorption heat of the first layer, and k is the sorption heat of the multilayer. The parameters of the GAB model were determined using non-linear regression, with the Statistica 7.0 software (Stat-Soft, Tulsa, OK, USA).

$$Xw = mo.C.K.aw/(1 - K.aw)(1 - K.aw + C.K.aw) \quad \text{(Eq. 5.2)}$$

5.2.7 X-ray Diffraction

The crystallinity of the sheets were investigated by X-ray diffraction. The analysis was performed with a Philips X'Pert diffractometer, using copper radiation Ka (A = 1.5418 A), a voltage of 40 kV, and operation current of 30 mA. All essays were performed from 29 =2° to 29 =70° ramping at 0.05°/s. The relative crystallinity index (CI) was estimated from the relative areas of crystalline and amorphous regions, according described by Kóksel et al. (1993) and Müller et al. (2011).

5.2.8 Scanning Electron Microscopy

The microstructure of the sheets was analyzed with a scanning electron microscope (Philips, FEI Quanta 200 model, Japan). The sheets were fractured after immersing in liquid nitrogen and gold coated using a sputter coater (Bal-Tec, SCD-050 model, Balzers, Liechtenstein). All the sheets were examined using an accelerating voltage of 20 kV and the magnitude of the observation was 100x.

5.2.9 Dynamic Mechanical Analysis

A Dynamical Mechanical Analyser (DMA-Q800, TA Instruments, USA) was used to determine the storage modulus (MPa) and loss factor (tan5) of the sheets. The samples were subjected to a sinusoidal strain in traction mode and scanned from -50°C to 150°C with a heating rate of 3°C/min and fixed frequency of 1 Hz.

5.2.10 Statistical Analysis

The obtained results were evaluated using the analysis of variance (ANOVA), and the treatment means were compared using Tukey's test at the 5%

significance level ($p<0.05$) with the Statistica 7.0 software (STATSOFT, TULSA, OK, USA).

5.3 RESULTS AND DISCUSSION

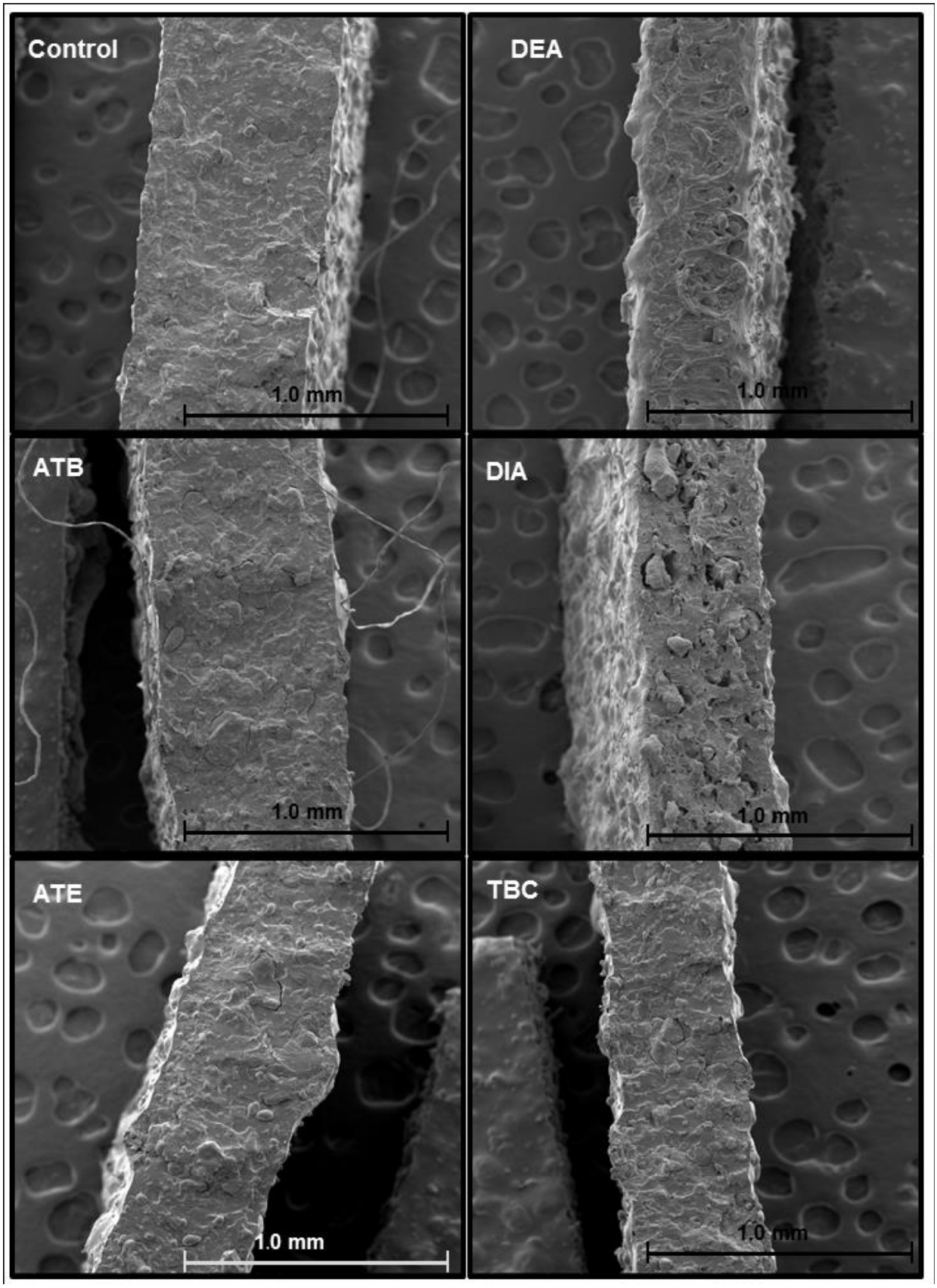
5.3.1 Sheets Morphology

All the PLA/TPS materials (sheets) were rigid, opaque due to the presence of starch, and their surface was rough. The morphology structure of PLA/TPS sheets plasticized with adipate or citrate ester was studied by scanning electron microscopy, and the images of the fracture (x 100) are presented in Figure 5.1.

All sheets micrographs revealed that the polymer blends are immiscible, with starch granules of various sizes dispersed in a continuous PLA matrix, and some cavities, which were more intense in sheets plasticized with adipate esters. The incompatibility between PLA and TPS was reported by other authors (KOZLOWSKI et al., 2007; MARTIN; AVEROUS, 2001; MULLER et al., 2012; SHIN et al., 2011; WANG et al., 2007; WOOTTHIKANOKKHAN et al., 2012; ZHANG; SUN, 2004).

Phase separation between plasticizer and PLA was not observed, suggesting that these compounds were homogeneously dispersed by extrusion process, and the concentration employed was adequate.

Figure 5.1 – Fracture micrographs of the PLA/TPS sheets with and without adipate or citrate ester (100x magnification).



5.3.2 Mechanical Properties, Thickness and Density

The Table 5.1 shows the mechanical properties, thickness and density of the PLA/TPS sheets. The sheets thickness ranged from 786 ± 57 to 906 ± 69 ^m, similar to the distance between the calender rolls (0.8 mm), and there was no significant difference between the formulations. Uniform material thickness is required for reliability of measured properties, and validity of comparisons between thickness-dependent properties of different materials (GENNADIOS et al., 1993).

Table 5.1 – Mechanical properties, thickness and density of PLA/TPS sheets plasticized with adipate or citrate ester.

Formulation	TS (MPa)	ε (%)	YM (MPa)	φ (μm)	ρ (g/cm^3)
Control	28.0 ± 1.1 ^{a}	7.1 ± 1.4 ^{c}	602 ± 27 ^{a}	906 ± 69 ^{a}	1.20 ± 0.05 ^{a}
DEA	11.6 ± 0.5 ^{d}	104.4 ± 57.9 ^{a}	311 ± 10 ^{d}	847 ± 24 ^{a}	1.04 ± 0.02 ^{b}
DIA	14.3 ± 0.5 ^{c}	39.5 ± 7.6 ^{b}	494 ± 19 ^{b}	819 ± 12 ^{a}	1.19 ± 0.04 ^{a}
ATE	19.1 ± 0.6 ^{b}	10.1 ± 3.4 ^{c}	478 ± 15 ^{b,c}	866 ± 55 ^{a}	1.11 ± 0.04 ^{a,b}
ATB	18.9 ± 0.7 ^{b}	8.0 ± 0.9 ^{c}	482 ± 11 ^{b,c}	877 ± 39 ^{a}	1.14 ± 0.03 ^{a}
TBC	17.5 ± 1.4 ^{b}	9.8 ± 2.3 ^{c}	455 ± 33 ^{c}	786 ± 57 ^{a}	1.04 ± 0.04 ^{b}

YM = Young's modulus; T = tensile strength; £ = elongation; p = density; 9 = thickness.
^{a,b,c} The means followed by the same letters in the same column do not exhibit differences at the 5% significance level according to Tukey's test.

The sheets with DEA and TBC showed lower density values, probably due to the lower molecular mass of these plasticizers that increased the intermolecular distance between the PLA chains, and thus decreased the density. The density values were lower than cassava starch films plasticized with glycerol and sorbitol prepared by casting, and TPS films with nanoclays produced by extrusion and thermopressing (MULLER et al., 2008; MULLER et al., 2012).

The adipate and citrate esters affected the mechanical properties of the sheets, reducing the Young's modulus (YM) and the tensile strength (TS), and only the adipate ester promoted a significant elongation (£) increasing. The plasticizer effect of the adipate esters on PLA have been reported in previous studies (MARTINO et al., 2009; MARTINO et al., 2010; SHIRAI et al., 2013).

The more compact structure of the control and citrate plasticized sheets, observed by SEM, allowed better load transfer under stress condition, and contributed to the higher YM. The voids in the sheets with adipate esters would

concentrate stress and act as crack initiators and could be responsible for the significant reduction in tensile strength.

The linear structure of adipate esters probably facilitated the interaction with PLA, which led to efficient plasticization. The chemical structures similarity and the compatibility between the plasticizer and the polymer determine the plasticization efficiency. From a molecular perspective, the plasticizer should be miscible and should have solubility close to that of the polymer (MURARIU et al., 2008).

The results also suggest that, among the plasticizers studied, DEA with lower molecular mass was more effective, because reduced about 50% the YM and TS values, and the elongation was 15 times greater than control. Compounds with smaller chain (molecular mass) can penetrate between the PLA chains most easily, interacting and thus plasticizing them. Martino et al. (2009) observed different behavior, where polyadipate (2565 g/mole) with higher molar mass was the most efficient plasticizer than the lower ones.

It is also important to emphasize that the plasticizing effect should be examined on a molar basis, i.e. when used at same mass basis, the number of moles of DEA incorporated in the sheets were higher than the DIA ones, and this is important to the plasticizing effect.

Compared with the mechanical properties of pure PLA (TS of 36 MPa) (WANG et al., 2008), the blends produced with TPS in our study had lower TS, which could be ascribed to the poor interfacial adhesion between starch and PLA as also observed by SEM. In the study of Wang et al. (2008) TPS/PLA blend (50/50) had lower TS than observed in our study, because of the lower content of PLA and higher concentration of glycerol and water as plasticizer for starch (40 g/ 100 g dry starch).

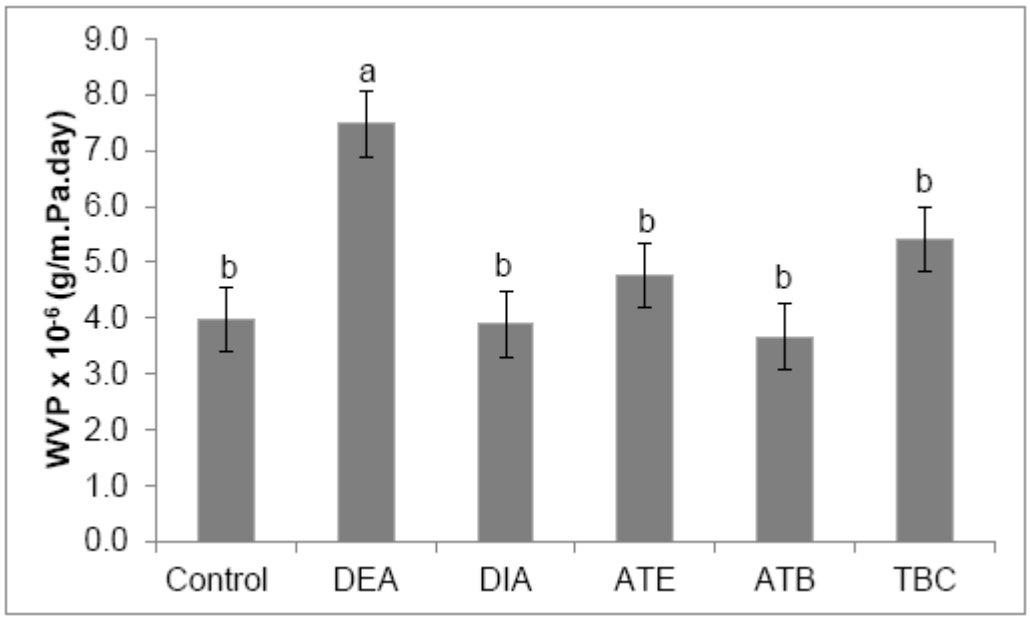
5.3.3 Water Vapor Permeability

The water vapor permeability (WVP) of PLA/TPS sheets plasticized with adipate or citrate are shown in Figure 5.2, and ranged from $3.7\pm1.2 \times 10^{-6}$ to $7.5\pm0.4 \times 10^{-6}$ $g.m^{-1}.Pa^{-1}.day^{-1}$. The PLA plasticization with DIA and citrate ester did not alter the WVP, but the addition of DEA significantly increased the WVP. As describing before, DEA plasticized better PLA, increasing the free volume and the

molecular chain distance, and these facts could facilitated the permeation of water molecules.

PLA films added with synthetic phenolic antioxidants (JAMSHIDIAN et al., 2012) had lower WVP than observed in our study, due to the absence of hydrophilic polymer like starch, which increased the amount of hydroxyl groups available for interaction with water.

Figure 5.2 – Water vapor permeability of PLA/TPS sheets plasticized with adipate or citrate esters.



5.3.4 Moisture Sorption Isotherm

The moisture sorption isotherms of PLA/TPS sheets with and without plasticizer are displayed in Figure 5.3, and the GAB model parameters are show in Table 5.2. All formulations presented sigmoid sorption isotherms (Type II), because of presence of hydrophilic materials like TPS.

Figure 5.3 – Water sorption isotherm of PLA/TPS sheet with adipate or citrate ester.

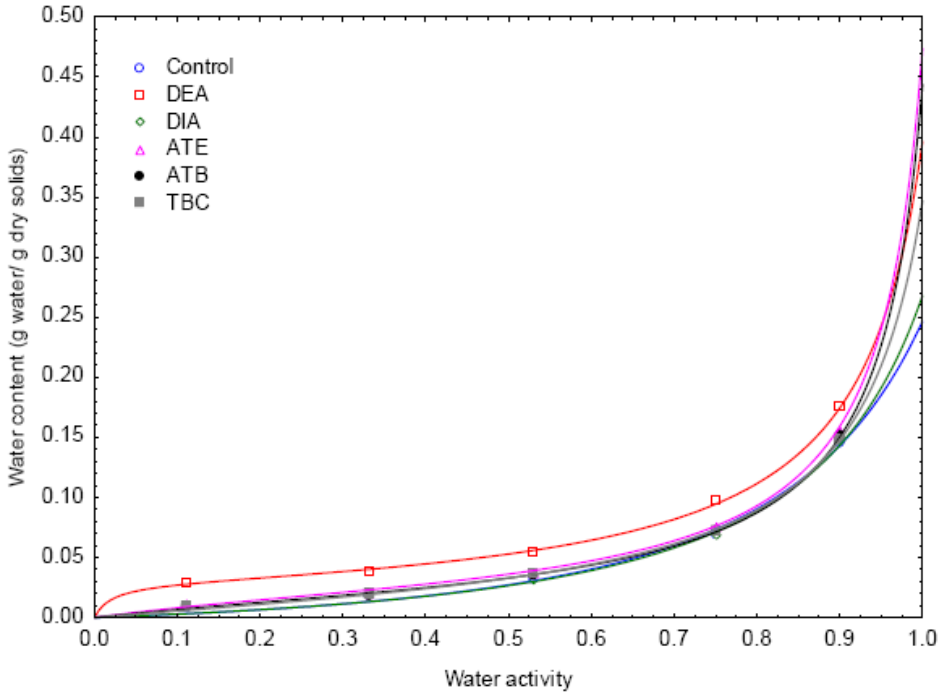


Table 5.2 – GAB model estimated parameters for the PLA/TPS sheets plasticized with adipate or citrate esters.

Formulation	GAB parameters [a]		
	m_o (g water/g dry solids)	*K*	*C*
Control	0.022	0.949	3.18
DEA	0.029	0.927	52.76
DIA	0.021	0.959	3.73
ATE	0.023	0.951	4.56
ATB	0.023	0.949	3.38
TBC	0.024	0.943	3.89

a Coefficient of determination R2 > 0.99 for all fitted models.
Diethyl adipate (DEA), diisodecyl adipate (DIA), acetyl triethyl citrate (ATE), acetyl tributyl citrate (ATB), and tributyl citrate (TBC).

The water activity from 0.5 to 0.9 caused an increase in moisture content of all sheets, and this behavior is associated with a "water clustering" phenomenon (GODBILLOT et al., 2006; MÜLLER et al., 2012; PENG et al., 2007; ZEPPA et al., 2009). This phenomenon was more intense in the sheets containing DEA.

The GAB model represented well the experimental data ($R^2 > 0.99$) and it is adequate for describing the water sorption isotherms of the TPS films (MALI et al., 2005; MÜLLER et al. 2008; MÜLLER et al., 2012) and the TPS/PLA blends (MÜLLER et al., 2012).

The monolayer moisture content (mo) indicates the amount of water strongly adsorbed by the material, and it is related with the material hygroscopicity and hydrofilicity. The formulation containing DEA had slightly higher mo value (0.029 g water/g dry solids) indicating higher moisture adsorption capacity. This result corroborates with higher equilibrium moisture content in the evaluated water activity range and with WVP values previously observed.

The better plasticizing effect of DEA increased the intermolecular distance between the polymer chains, and hence facilitated the penetration of water into the polymer matrix. Furthermore, the presence of the voids and cracks, observed in SEM images, allowed water to penetrate more easily and interact with starch. PLA/TPS sheets showed lower mo values than TPS films (MALI et al., 2005; MÜLLER et al., 2008), due to the more hydrophobic character of PLA than TPS.

The type of plasticizer did not influence the parameter K, which is related to the sorption heat of the multilayer, and the values were in accordance to other reports (MALI et al., 2005; MÜLLER et al., 2008; MÜLLER et al., 2012). The parameter C, which is associated with the sorption heat of the monolayer, was higher for DEA sheets, and the magnitude of this parameter was in accordance with values reported by other studies for PLA/TPS blends (MÜLLER et al., 2012).

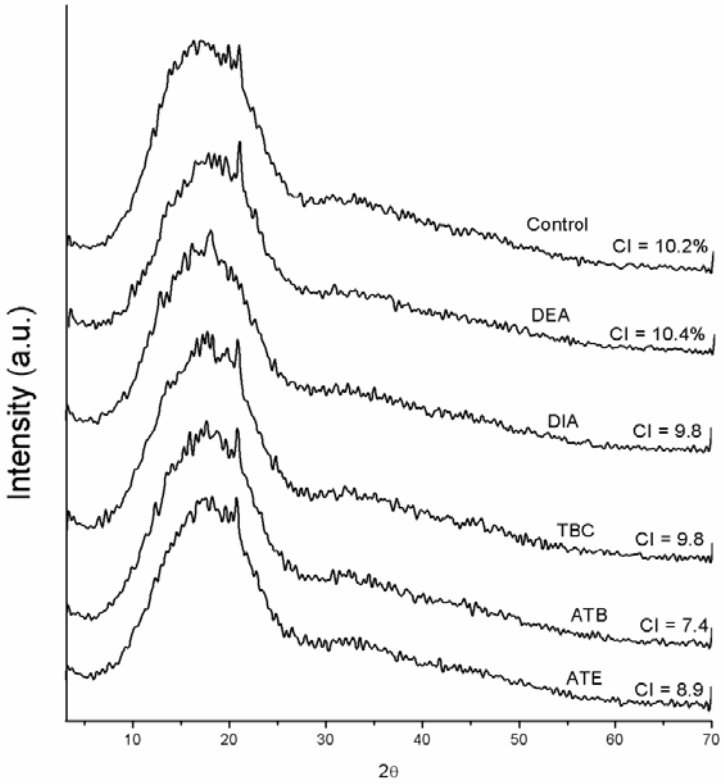
5.3.5 X-ray Diffraction

The X-ray diffraction (XRD) diffractograms of the PLA/TPS sheets plasticized with adipate or citrate ester with the respective relative crystallinity index (CI) are show in Figure 5.4. The CI of the sheets varied from 7.4 to 10.4%, suggesting that plasticizers had little effect on the crystallinity, and the rapid cooling of the sheets by the calender chilled rolls was responsible for the low degree of crystallinity. Ke and Sun (2001) observed that the processing procedure affect significantly the crystallinity of the PLA/TPS blends; the blends prepared by injection molding and extrusion had lower CI than those the blends produced by compression molding.

All XRD diffractograms presented peaks at the same angle, and the intensity of the peaks decreased when plasticizers were introduced. These results indicated that plasticized PLA did not modify the crystalline structure of PLA, but reduced the intensity of diffraction peak as also observed by Xiao et al. (2009) in PLA plasticized with triphenyl phosphate.

Diffractions peaks at about 29 = 18° and 19° corresponding to crystallinity of PLA, as also observed by Ke and Sun (2001). The peaks at 29 = 13° and 20.8° are related to VA-type crystallinity due induced crystallization of the starch with glycerol by extrusion process (MA; YU, 2004).

Figure 5.4 – Diffractogram of PLA/TPS sheets plasticized with adipate or citrate ester.

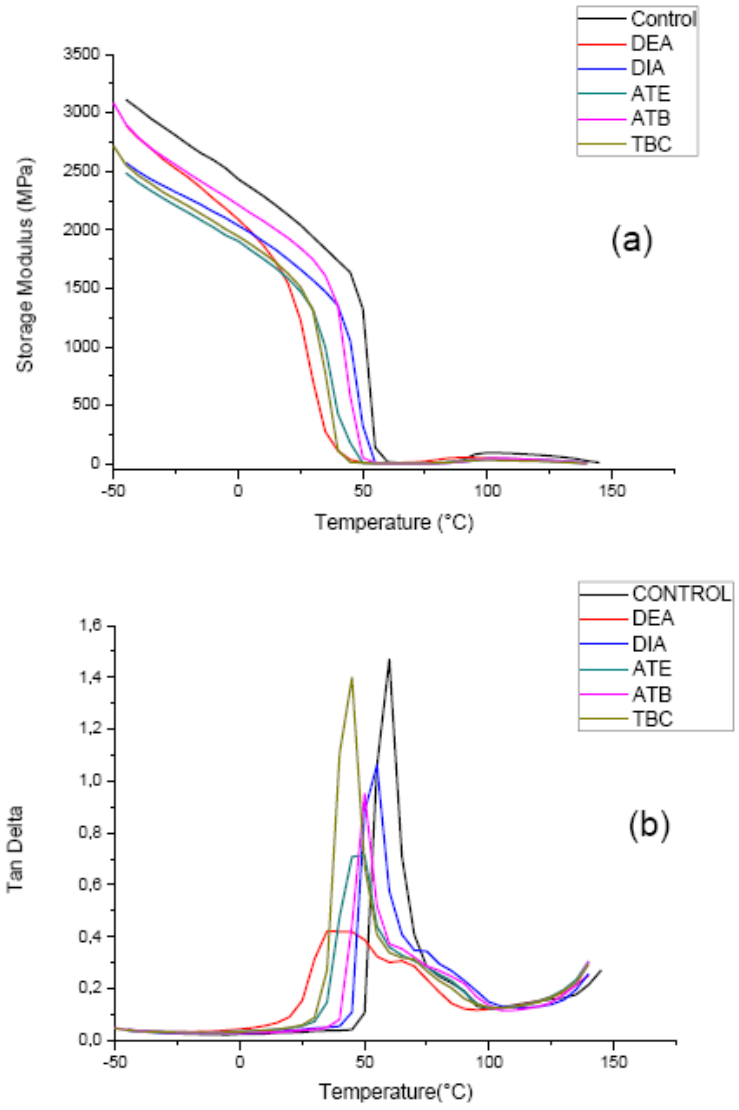


5.3.6 Dynamic Mechanical Analysis (DMA)

DMA was used to measure the temperature dependence of the storage moduli of the PLA/TPS blends plasticized with adipate or citrate ester, and is show in Figure 5.5 - a. The temperature dependence of storage modulus of all the blends showed similar patterns. The lower storage modulus of the PLA/TPS sheets

plasticized with adipate or citrate ester compared to Control formulation, indicated a decrease in the rigidity, as observed previously in the mechanical properties (Table 5.1). The plasticizers considerably decreased the viscosity of polymer compositions through the replacement of polymer-polymer interaction by polymer-plasticizer interaction, increasing chains mobility, and decreasing sheets rigidity. The slightly increase of storage modulus around 80 - 120°C was related to PLA cold-crystallization as described by Chabrat et al. (2012), Hassouna et al. (2012), and Ljungberg et al. (2003), explaining the residual crystallinity observed in the diffractograms.

Figure 5.5 – DMA of PLA/TPS sheets plasticized with adipate or citrate ester. (a) Storage modulus, and (b) Tan Delta. Diethyl adipate (DEA), diisodecyl adipate (DIA), acetyl triethyl citrate (ATE), acetyl tributyl citrate (ATB), and tributyl citrate (TBC).



The relaxation peak around 60°C correspond to PLA glass transition (Figure 5.5 - b), and the peak attributed to the glass transition of starch-rich phase was not observed. Wootthikanokkhan et al. (2012) also did not observe the peak related to the starch in PLA/Maleated TPS blends, when the concentration of starch was 30%.

The incorporation of plasticizers shifted Tg to a lower temperature, as observed in Figure 5.5-b and Table 5.3, indicating an increased chain mobility of the PLA matrix. It was responsible for the significant decrease of the elasticity (rigidity) observed previously. Other authors (HASSOUNA et al., 2012; LABRECQUE et al., 1997; LJUNGBERG et al., 2003; MARTINO et al., 2009) observed similar results.

Table 5.3 – Glass transition temperature (Tg) of PLA/TPS sheets and plasticizing capacity of adipate and citrate ester.

Formulation	Molar Mass (MM) of plasticizers (g/mol)	Hydrogen bond capacity (H)	H/MM (x 10^3)	Tg (°C)
Control	-	-	-	60
DEA	202.25	2	9.9	36
DIA	426.67	2	4.7	54
ATE	318.00	4	12.6	47
ATB	402.49	4	9.9	50
TBC	360.44	4	11.1	45

In order to assist the discussion of the results and to conclude which is the best plasticizer for PLA/TPS sheets, the plasticizing capacity was calculated. According to Table 5.3, sheets with DIA had lower value (4.7 x 10^{-3}) of plasticizing capacity and this fact explain the higher YM and Tg. DEA had similar plasticizing capacity to others, but presented different comportment and this fact can be related to the high hygroscopicity of this component as observed in WVP and isotherm results. Sheets with DEA were more plasticized by water and therefore presented lower Tg, T and YM and higher elongation, as observed previously. As discussed before, the linear chemical structure and lower molar mass associated with the plasticizing capacity of DEA are the most responsible for the greatest improvement in sheets properties.

The plasticizing capacity of glycerol (control sheets) was not calculated because previous studies (MARTIN; AVEROUS, 2001; SHIRAI et al.,

2013) demonstrated that this was an effective plasticizer for starch but not for PLA. Furthermore, the Tg of control sheets was near to the pure PLA, confirming again that glycerol did not plasticize PLA.

5.4 CONCLUSION

The incorporation of adipate or citrate esters improves the mechanical properties and processability of PLA/TPS sheets produced by calendering-extrusion in pilot-scale process.

Among the plasticizer tested, the adipate esters, mainly DEA, provided higher values of elongation and lower TS and YM suggesting better plasticization effect. On the other hand, this compound elevated the WPV values.

The plasticizers reduced the Tg, but no significant difference was observed for crystallinity index. The SEM micrographs revealed the incompatibility between starch and PLA, suggesting new studies to introduce an adequate compatibilizer in the blend.

5.5 ACKNOWLEDGEMENTS

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CAPÍTULO 6

PRODUCTION AND CHARACTERIZATION OF POLY(LACTIC ACID) / THERMOPLASTIC STARCH SHEETS PLASTICIZED WITH ADIPATE ESTER

ABSTRACT: Blends of poly(lactic acid) (PLA) and thermoplastic starch (TPS) (60/40, 50/50, 40/60, 30/70, 20/80 and 10/90 w/w) plasticized with adipate esters with different molar masses were used to produce sheets by calendering-extrusion process, and their mechanical, barrier, thermal and morphological characterization were performed. The increase of TPS content affected the mechanical properties of the sheets, increasing elongation and decreasing rigidity. TPS conferred more hydrophilic character to the sheets as observed by water vapour permeability and isotherm. The crystallinity of the sheets was affected by TPS. The diisodecyl adipate (DIA) with higher molar mass was more effective as plasticizer, because the sheets had better mechanical and barrier properties than diethyl adipate (DEA) plasticized ones. According to confocal laser microscopy, with a higher PLA content, the higher roughnesses of the sheets were observed, which could be related with the incompatibility between starch and PLA. Scanning electron microscopy also confirmed this fact.

Key-words: Extrusion. Calendering. Biodegradable material. Plasticizer.

6.1 INTRODUCTION

The interest in developing plastic materials produced from natural resources is considerably increasing as the need for reduction of the amount of plastic waste in the environment becomes urgent (BASTOS et al., 2009). Due to its biodegradability, low cost, and worldwide availability, starch in the form of thermoplastic starch (TPS) has been extensively studied as main component in the production of biodegradable films. TPS is usually obtained by destroying the crystalline structure of native starch by an extrusion process in presence of plasticizers, such as glycerol (AVÉROUS et al., 2001; LIU et al., 2009; ZULLO; IANNACE, 2009).

Because of its hygroscopic nature, the TPS must be blended with another polymer to produce materials for packaging and industrial applications (LI; HUNEAULT, 2011). In this context, the blend of TPS with poly(lactic acid) (PLA) is promising because in addition to be biodegradable, PLA is produce from renewable resource. PLA has been receiving much attention as the most innovative alternative to conventional petroleum-based polymers, and has been intensively studied due to its environmentally-friendly characteristics, biocompatibility, sustainability, as well as,

potentially useful physical and mechanical properties. Adding TPS into a PLA matrix can also decrease the material cost and increase its biodegradation rate (LI; HUNEAULT, 2011; MARTIN; AVÉROUS, 2001).

There are several reports about the production of TPS/PLA blends by extrusion. TPS/PLA materials are known to be extremely brittle because of the coarse structure and lack of interfacial adhesion (KOZLOWSKI et al., 2007; LI; HUNEAULT, 2011; LIM et al., 2008; MARTIN; AVÉROUS, 2001; ZHANG; SUN, 2004; WANG et al., 2007). Addition of adequate plasticizer can improve processability and flexibility of PLA, making possible their blend with starch to produce sheets with adequate mechanical properties.

In our previous work (SHIRAI et al., 2013) we observed that adipate esters improved the mechanical properties of TPS/PLA materials by reducing the elastic modulus and the tensile strength, and increasing the elongation modulus. Adipate esters were also researched by other authors (MARTINO et al., 2009; MARTINO et al., 2010), making possible the production of flexible PLA films.

The objective of this work was to evaluate the effect of adipate ester with different molar mass as plasticizer on the performance of PLA/TPS blends to produce biodegradable sheets by extrusion and calendering process.

6.2 MATERIAL AND METHODS

6.2.1 Materials

This study employed PLA Ingeo 4043D (Natureworks LLC, Cargill, USA), native cassava starch (Indemil, Brazil), and commercial glycerol (Dinamica, Brazil), which was used as plasticizing for the starch. The diisodecyl adipate (426.67 g/mol), and diethyl adipate (202.25 g/mol) (Sigma Aldrich, Germany) were used as plasticizing agents for the PLA.

6.2.2 Sheets Production

Sheets with different proportion of PLA and TPS (60/40, 50/50, 40/60, 30/70, 20/80 and 10/90) were produced, and the concentration of glycerol was 33 g / 100 g starch. Two different adipate ester, diisodecyl adipate (DIA) and diethyl

adipate (DEA) were used and the concentration employed was 10 g adipate ester / 100 g PLA.

All the components, PLA, starch, glycerol, adipate ester were manually mixed, and processed using a pilot twin-screw extruder (BGM, D-20 model, Brazil) with a screw diameter of 20 mm (L/D = 35). The screw speed employed was 100 rpm, feed speed of 30 rpm, and a temperature profile of 100 / 180 / 180 / 180 / 180°C.

The extruded cylindrical profiles were pelletized and extruded in the twin-screw extruder coupled with a calender (AX-Plasticos, Brazil) for sheet production. The temperature profiles were 100 / 170 / 170 / 170 / 175°C, and the distance between the calendar rolls was 0.8 mm, and the rolls speed was adjusted for each formulation to maintain the continuous process.

6.2.3 Thickness and Density

Film thickness was measured using a digital micrometre (Starrett, Brazil) at ten different points of the film. To determine the film density, samples of 20 mm x 20 mm were kept in a desiccator with anhydrous calcium chloride (0 % RH) for two weeks and weighed, as described by Muller, Laurindo and Yamashita (2012).

6.2.4 Mechanical Properties

Tensile tests were performed with a texture analyser (Stable Micro Systems, TA XTplus model, England) based on the American Society for Testing and Material standards (ASTM D882-02, 2002). The speciments were previously conditioned at 23 ± 2°C and 53 ± 2% for 48 hours, and the properties measured were tensile strength (MPa), elongation at break (%), and Young's modulus (MPa). The tests were repeated ten times for each formulation.

6.2.5 Water Vapour Permeability

The water vapour permeability (WVP) of the sheets was determined gravimetrically, according to the ASTM E96-00 (2000) standard, under a relative humidity gradient of 0 - 75 %.The tests were conducted in duplicate.

6.2.6 Moisture Sorption Isotherm

The moisture sorption isotherms of the films were obtained using a moisture sorption isotherm generator (Aquasorp, Decagon Devices, USA). The Guggenhein-Anderson-de Boer (GAB) model (Eq. 6.1) was used to fit the experimental data, where X_w is the equilibrium moisture content (g water / g dry solid) at a water activity (a_w), m_o is the monolayer water content, C is the Guggenheim constant, which represents the sorption heat of the first layer, and K is the sorption heat of the multilayer. The parameters of the GAB model were determined using non-linear regression, with the Statistica 7.0 software (Statsoft, USA).

$$Xw = mo.C.K.aw/(1 - K.aw)(1 - K.aw + C.K.aw) \quad \text{(Eq. 6.1)}$$

6.2.7 X-Ray Diffraction

The crystallinity of the films was investigated by X-ray diffraction using a X'Pert PRO diffractometer (PANalytical, The Netherlands), with copper Ka radiation (A = 1.5418 A), a voltage of 40 kV, and an operation current of 30 mA. All essays were performed from 29=2° to 29=70°, with ramping at 0.05°/s. The relative crystallinity index (RCI) was estimated from the relative areas of crystalline and amorphous regions, according to Koksel et al. (1993), and Muller, Laurindo and Yamashita (2011).

6.2.8 Scanning Electron Microscopy

The microstructure of the films was analysed with a scanning electron microscope (Philips, FEI Quanta 200 model, Japan). The films were fractured after immersing in liquid nitrogen and gold coated using a sputter coater (Bal-Tec, SCD-050 model, Balzers, Liechtenstein). All the samples were examined using an accelerating voltage of 20 kV and the magnitude of the observation was 400x.

6.2.9 Confocal Laser Microscopy

A Confocal Laser Scanning Microscope (Olympus LEXT, OLS400 model, Germany) was used to obtain the surface images of the sheets.

6.2.10 Thermogravimetric Analysis

The thermal stability of the PLA/TPS sheets was measured by a TGA-Q50 instrument (TA Instruments, USA). The samples were analysed under nitrogen atmosphere (100 mL/min), and heated from 25°C to 600°C at a heating rate of 10°C/min. Derivatives of the TG curves were obtained using Origin 8.0 software (OriginLab, USA) in order to verify the maximum temperature degradation.

6.2.11 Differential Scanning Calorimetry

The differential scanning calorimetry (DSC) (TA Instruments, DSC-Q20 model, USA) was also used to determine the thermal properties of PLA/TPS sheets. The samples were heated up to 250°C at rate of 10°C/min, and the sample cell was kept under nitrogen flow of 50 mL/min. The glass transition (Tg), crystallization (Tc), and melting (Tm) temperatures were obtained. The crystallinity index (Xc) is defined as the enthalpy difference between melting and crystallization peaks divided by the enthalpy of 100% crystalline PLA (93.6 J/g), according to Eq. 6.2, and described by Fisher et al. (1973) cited by Xiong et al. (2013). In this equation AH_{m1}, AH_{m2}, and AH_c are the enthalpies (J/g) of fusion at higher melting temperature and crystallization of the blend, respectively, and 5_{PLA} is the PLA content in the blend.

$$Xc = [(AHm1 + AHm2 - AHc) / (93.6 \times 5_{PLA})] \times 100 \quad \text{(Eq. 6.2)}$$

6.2.12 Statistical analysis

The obtained results were evaluated using the analysis of variance (ANOVA), and the treatment means were compared using Tukey's test at the 5% significance level ($p<0.05$) with the Statistica 7.0 software (STATSOFT, USA).

6.3 RESULTS AND DISCUSSION

6.3.1 Thickness and Density

It was not possible to produce sheets with PLA/TPS proportions of 20/80 and 10/90, because the extruded materials were too stiff, and did not have enough flexibility to be processed through the calendar rolls. The others formulations had good processability, and the sheets showed slightly rough surface, and increasing starch amount, the colour became more yellowish.

The thickness of the sheets ranged from 431 to 815 um (Table 6.1) and the thickness of the sheets produced with DEA as plasticizer were less influenced by the TPS content than the DIA ones. The sheets with DIA were less thick than the ones with DEA for the same TPS/PLA compositions, and this could be related to DIA plasticizing effect that contributed to enhance the materials flexibility and allowed then to be more stretched by the calender rolls. During the calendaring process, the sheets thickness is controlled by the distance between the rolls, speed of the rolls, and stretching capacity of the formulation.

The density of the sheets ranged from 1.12 to 1.44 g/cm^3 (Table 6.1), and increasing TPS concentration did not increase the density of the materials plasticized with DEA, but the sheets with DIA were highly influenced by the TPS content. The effect of the molar mass of the adipate ester on the density also could be considered, because lower molar mass usually is related with lower density values. The slightly greater density of the sheets with DIA was due to their higher molar mass than DEA. Similar densities were observed in TPS films incorporated with nanoclays, produced by extrusion and thermopressing (MÙLLER; LAURINDO; YAMASHITA, 2011; MÙLLER; LAURINDO; YAMASHITA, 2012), and lower values were verified in the PLA/TPS blends obtained by extrusion and thermopressing (MÙLLER; PIRES; YAMASHITA, 2012).

Table 6.1 – Thickness and density of PLA/TPS sheets plasticized with adipate ester.

PLA/TPS	Thickness (urn)	Density (g/cm^3)
DEA 60/40	764 ± 2^{b}	1.22 ± 0.05^{b,c}
DEA 50/50	749 ± 8^{b}	1.25 ± 0.07^{b}
DEA 40/60	753 ± 9^{b}	1.28 ± 0.04^{b}
DEA 30/70	815 ± 21^{a}	1.31 ± 0.03^{b}
DIA 60/40	538 ± 7^{d}	1.27 ± 0.03^{b}
DIA 50/50	431 ± 69^{e}	1.12 ± 0.02^{c}
DIA 40/60	619 ± 5^{c}	1.20 ± 0.07^{b,c}
DIA 30/70	736±31^{b}	1.44 ± 0.08^{a}

^{a,b,c,d,e} Means in the same column with different letters are significant different ($p < 0.05$) by Tukey test.

6.3.2 Mechanical Properties

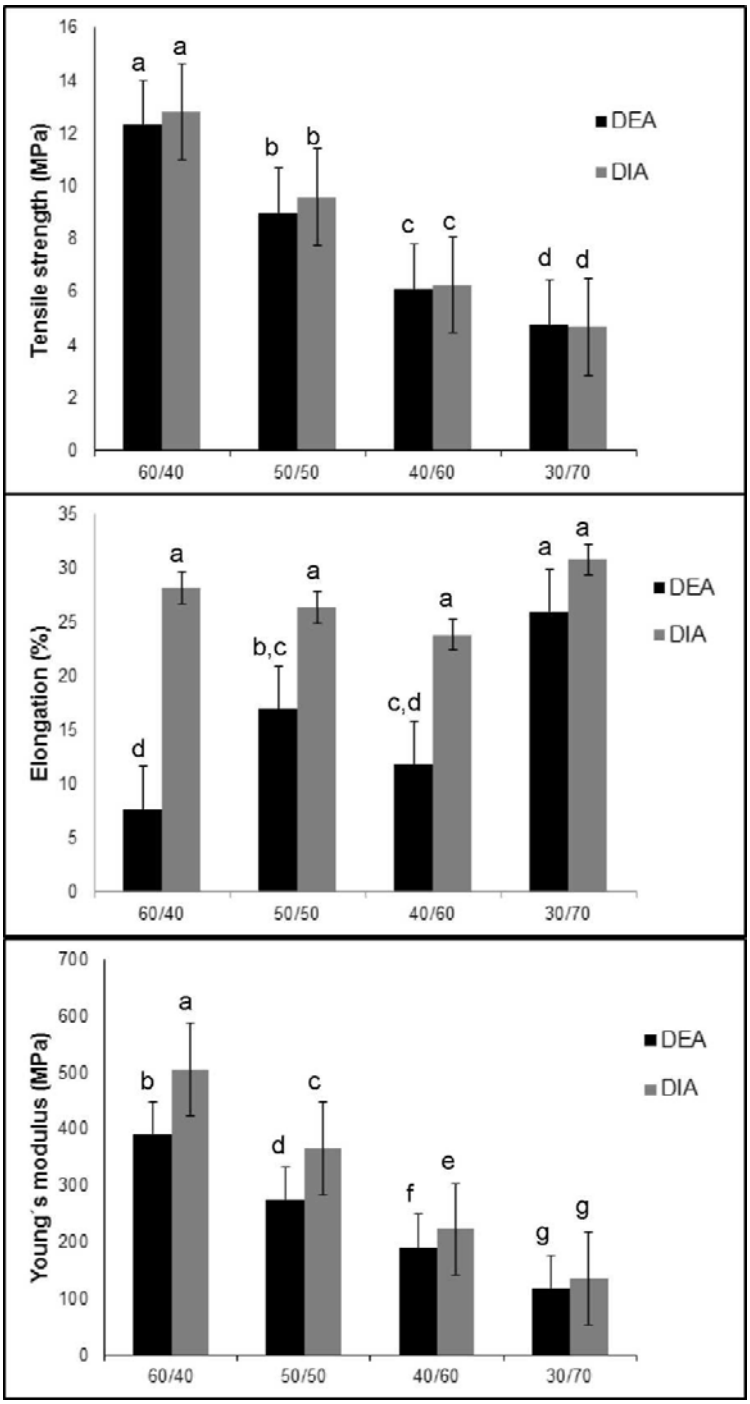
The Figure 6.1 shows the mechanical properties of PLA/TPS sheets plasticized with adipate esters. About the loaded tests, it is possible to observe that increasing TPS concentration there are a significantly decrease in the tensile strength and Young's modulus for all the sheets. The increase in the elongation at break was significant only in the DEA added sheets. Ke, Sun and Seib (2003) evaluated the effect of the amylose content in PLA/starch blends containing more than 60% of starch and reported a decreased tensile strength and elongation at break of the films. According to Teixeira et al. (2012), neat PLA had higher tensile modulus and strength values than TPS, and the TPS had higher elongation at break.

These results can also be explained by the lack of compatibility between PLA and starch that generate poor interfacial adhesion between the faces of the both polymers, impairing the load transfer under stress condition. The tensile strength and elongation at break of the composites are directly linked to interfacial adhesion between the solid particulate and the polymer matrix (HUNEAULT; LI, 2007). Zhang and Sun (2004) also reported similar results for PLA/starch blends plasticized with acetyl triethyl citrate.

Comparing the effect of the adipate ester, DIA promoted higher values of elongation at break and Young's modulus, however for tensile strength the same values were observed for the two plasticizers. It is possible to conclude that adipate with higher molar mass promoted more flexible materials as observed by Martino, Jiménez and Ruseckaite (2009), which used polyadipate as plasticizer for PLA film. We suppose that this result is related to the higher hydrocarbon content of the polymer chain (polyadipate), which is capable of accommodating loads during stress tests.

The mechanical properties of the samples PLA/TPS 30/70 were similar. Lower values of tensile strength, Young's modulus and elongation at break were observed in the PLA/TPS (30g PLA / 100g TPS) films produced by extrusion and thermopressing (MÜLLER; PIRES; YAMASHITA, 2012). More resistant PLA/TPS films (20% TPS) were produced by Teixeira et al. (2012).

Figure 6.1 – Mechanical properties of PLA/TPS sheets plasticized with DEA and DIA.

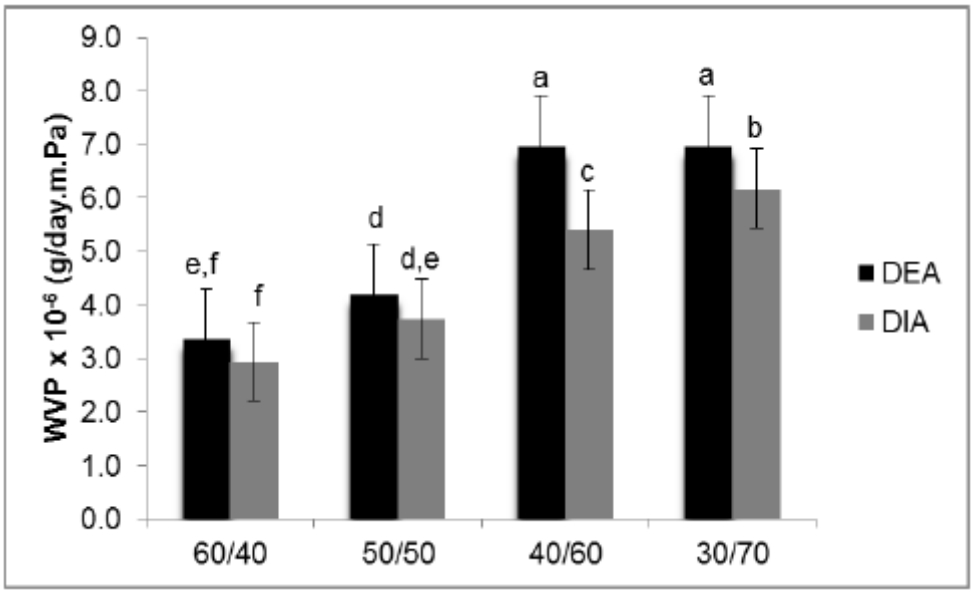


Different letters represent significant difference ($p < 0.05$) between the means obtained by Tukey test.

6.3.3 Water Vapour Permeability (WVP)

The WVP of the sheets are shown in Figure 6.2 and ranged from 2.94 x 10^{-6} to 6.98 x 10^{-6} g.day"^{1}m"^{1}.Pa"^{1}. The values obtained are lower than those found for cassava starch films (ALVES et al., 2007, MÜLLER et al., 2012) and PLA/TPS films (MÜLLER; PIRES; YAMASHITA, 2012), and closer to those of PBAT/TPS films (BILCK; GROSSMANN; YAMASHITA, 2010). The PLA inclusion promoted a hydrophobic character to the material and was responsible for WVP decreasing because the material permeability is strongly influenced by the hydrophobic or hydrophilic nature of its components.

Figure 6.2 – Water vapour permeability of PLA/TPS sheets plasticized with DEA and DIA.



Different letters represent significant difference ($p < 0.05$) between the means obtained by Tukey test.

The increase of TPS concentration (from 40% to 70% wt) increased the WVP because of the hydrophilic character of the starch. Furthermore, at high starch content, water could saturate the blends surface easily, and also penetrated into these through voids and being quickly absorbed by the starch, resulting in higher water permeation (KE; SUN;SEIB, 2003).

PLA/TPS sheets plasticized with DIA had WVP values lower than plasticized with DEA probably due to the higher molar mass and longer chain of the DIA enhancing the sheets hydrophobicity.

PLA films added with synthetic phenolic antioxidants (JAMSHIDIAN et al., 2012) had lower WVP than observed in our study, due to the absence of hydrophilic polymer like starch, which increased the amount of hydroxyl groups available for interaction with water.

6.3.4 Moisture Sorption Isotherm

The moisture sorption isotherms of PLA/TPS sheets plasticized with adipate esters presented sigmoid sorption isotherms (graph not shown), because of presence of hydrophilic materials like TPS. The GAB model parameters are shown in Table 6.2. The GAB model represented well the experimental data (R^2> 0.99) and it is adequate for describing the water sorption isotherms of the TPS films (MALI et al., 2005; MÜLLER; LAURINDO; YAMASHITA, 2008; MÜLLER; LAURINDO; YAMASHITA, 2012) and the TPS/PLA blends (MÜLLER; PIRES; YAMASHITA, 2012).

Table 6.2 – GAB model estimated parameters for the PLA/TPS sheets plasticized with adipate esters.

Formulation	GAB parameters [a]		
	m_o(g water/g dry solids)	*K*	*C*
DEA 60/40	0.0042	1.11	0.333
DEA 50/50	0.0083	1.10	0.163
DEA 40/60	0.0097	1.15	0.443
DEA 30/60	0.0174	1.04	0.002
DIA 60/40	0.0024	0.24	0.736
DIA 50/50	0.0049	1.09	0.449
DIA 40/60	0.0099	1.12	0.371
DIA 30/70	0.0088	1.04	0.036

[a]Coefficient of determination R^2> 0.99 for all fitted models. m_o = monolayer water content; C = Guggenheim constant; k = sorption heat of the multilayer.

The monolayer moisture content (m_o) indicates the amount of water strongly adsorbed by the material, and it is related with the material hygroscopicity and hydrofilicity. Independent of plasticizer used m_o values increased with increasing starch content, showing greater availability of hydroxyl groups to interact with water.

Samples with DIA had lower value than with DEA and this may be related to the hydrophobic character provided by DIA, as previously discussed.

The parameter K is related to the sorption heat of the multilayer, and did not influence by the composition of the blends, but the values are lower than reported in other studies (MALI et al., 2005; MÜLLER; LAURINDO; YAMASHITA, 2008, MÜLLER; LAURINDO; YAMASHITA, 2012). A clear trend was not observed with the C parameter, which is associated with the sorption heat of the monolayer.

6.3.5 X-ray Diffraction (XRD)

X-ray diffractograms of the sheets are presented in Figure 6.3. The PLA spectra showed a small peak at 29 = 15°, and the spectra were composed mainly with the amorphous region. According to Martino, Jimenez and Ruseckaite (2009), the rapid cooling rate during calendaring process is sufficient to produce materials mainly amorphous. Ke and Sun (2001) also reported the influence of the process in the PLA crystallinity.

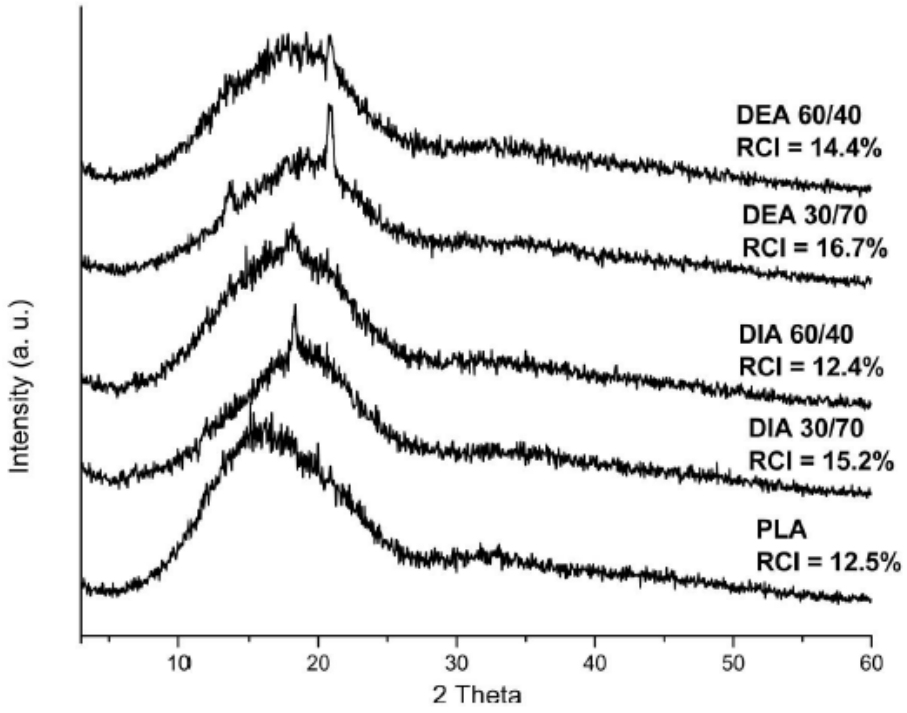
In the presence of plasticizers, the native starch was disrupted under heating and shearing conditions, which broke the hydrogen bonds in starch, so-destroying partially its initial crystalline nature (RAQUEZ et al., 2008). The crystallinity forms induced by thermomechanical processing of several native starches with glycerol as a plasticizer are called VH-, VA-, or EH that depend on the composition of starch, the plasticizer and the process parameters (MA; YU, 2004).

The peaks at 29 = 13.6° and 20.8 for the sheets plasticized with DEA, and at 29 = 12.0 and 18.5 in sheets added with DIA are indicative of V_A-type crystallinity caused by the fast recrystallization of amylose complexed with glycerol into single-helical structures as described by RAQUEZ et al. (2008) and ZULLO and IANNACE (2009).

The relative crystallinity index (RCI) ranged from 29 = 11.4° to 16.7° and the increase in these values was affected by TPS, according to Figure 6.3, and the DEA adipate ester promoted higher RCI. According to Ljungberg and Wesslen (2003), for PLA films the more plasticized, the higher degree of crystallinity, although the differences were small. Therefore, the plasticizer with the lower molar mass, like DEA, probably was better incorporated in the amorphous part of the PLA, and induced the crystallinity. The values of RCI obtained in this study are in agreement

with those observed by Ke and Sun (2001) in TPS/PLA blends produced by extrusion.

Figure 6.3 – Diffractograms of PLA and PLA/TPS sheets plasticized with adipate esters.



6.3.6 SEM

When two polymers are mixed together by extrusion, it is interesting that the dispersion and the distribution of the particles occur, forming a single polymeric phase. Poor dispersal could result in the formation of clusters from the entanglement of the polymer chains, which reduces the transmission of tension interfering in the mechanical properties of the material (BRADELERO; GROSSMANN; YAMASHITA, 2011).

The micrographs of the PLA/TPS sheets at 400x magnification (Figure 6.4) shows that the extrusion process promoted good mixture of the components of the blends. In the sheets 50/50 (w/w), for example, there were starch granules with different size distributed in the PLA matrix, and some cavities were evident proving the incompatibility between starch and PLA. Other authors (KOZLOWSKI et al., 2007; MARTIN; AVEROUS, 2001, MÜLLER; LAURINDO;

YAMASHITA, 2012; SHIN et al., 2011; WANG et al., 2007; WOOTTHIKANOKKHAN et al., 2012; ZHANG; SUN, 2004) reported the incompatibility between PLA and TPS.

PLA phase was continuous at low starch content (40 - 50 %) but became discontinuous when the starch content is increased to 70 %. Ke et al. (2003) also observed this behavior in blends of PLA and starch with varied amylose content. The amount of starch particle size increased remarkably, when the starch content was increased from 20 to 30 pph. This morphological change contributed to the decrease in the tensile properties of the blends as were discussed earlier. Similar trends were observed by Shin et al. (2011) in a study on mechanical and morphological properties of blends of PLA and chemically modified corn starch.

Phase separation between plasticizer and PLA was not observed, suggesting that these compounds were homogeneously dispersed by extrusion process, and the concentration employed was adequate.

6.3.7 Confocal Laser Microscopy

Confocal laser microscopy was used to study the surface properties of the PLA/TPS sheets plasticized with DEA or DIA. Figure 6.5 shows just the confocal images of the sheets with higher and lower content of starch, and plasticized with DEA or DIA.

Sheets with higher proportion of PLA had more roughened surface that can suggest a certain phase separation of the obtained blend. This idea is supposed that there is a chain-chain PLA/TPS repulsion in the cooling process, causing a disordered phase separation and addition, increasing the surface roughness.

Figure 6.4 – SEM (400 X) of PLA/TPS sheets plasticized with adipate esters.

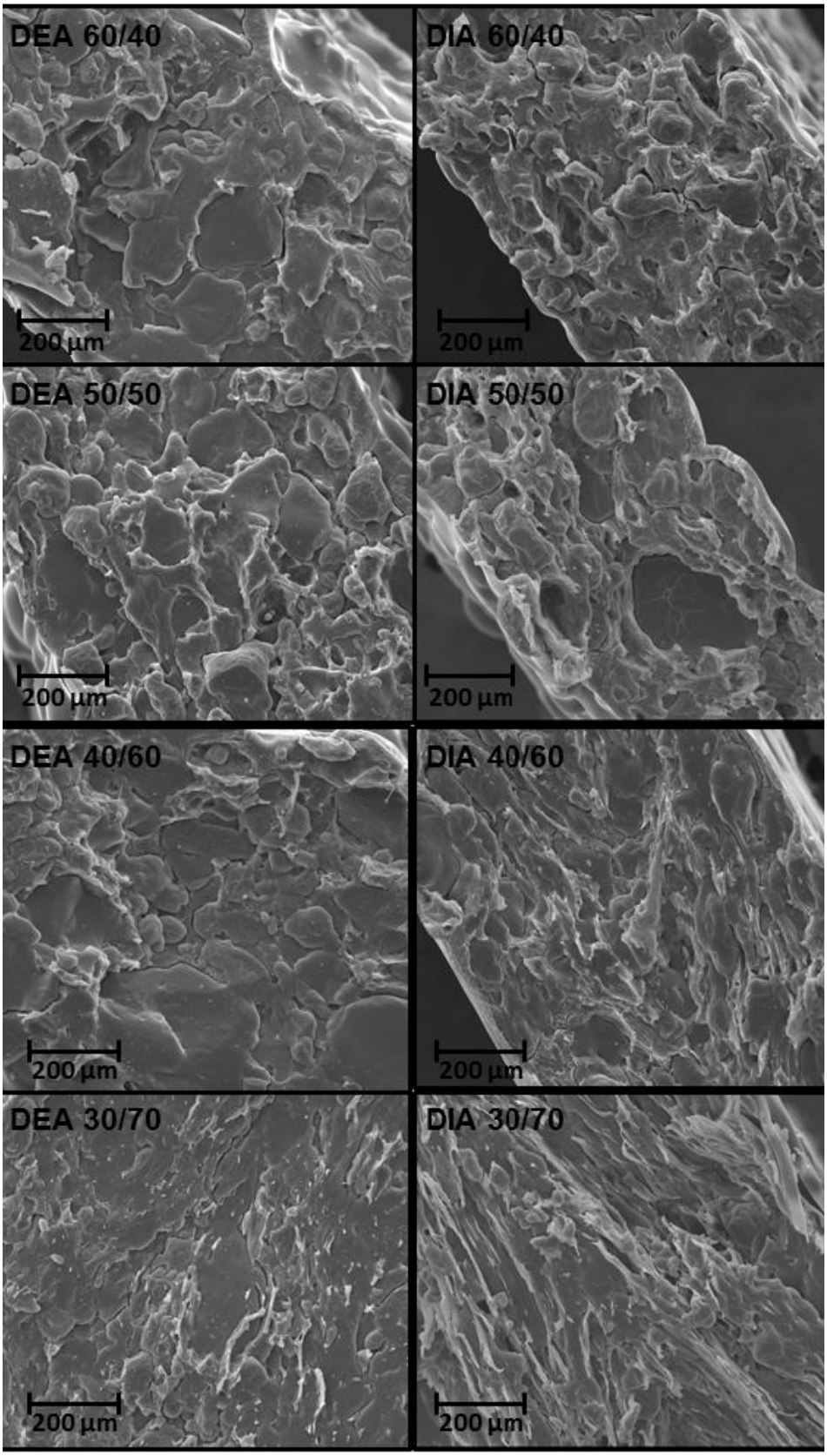
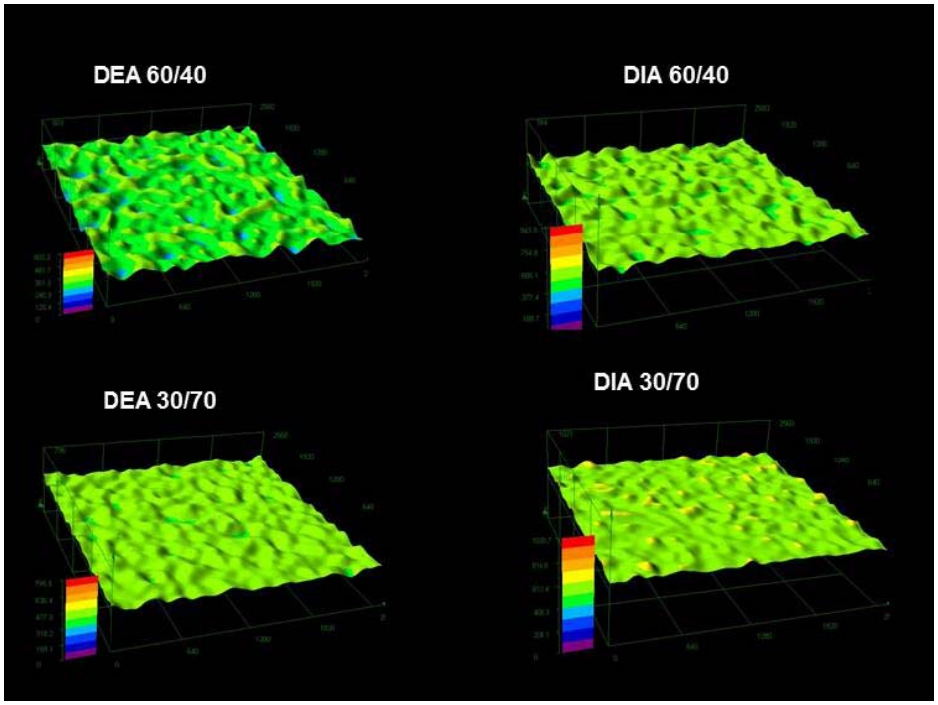


Figure 6.5 – Confocal microscopy images of PLA/TPS sheets plasticized with adipate esters.



6.3.8 TGA

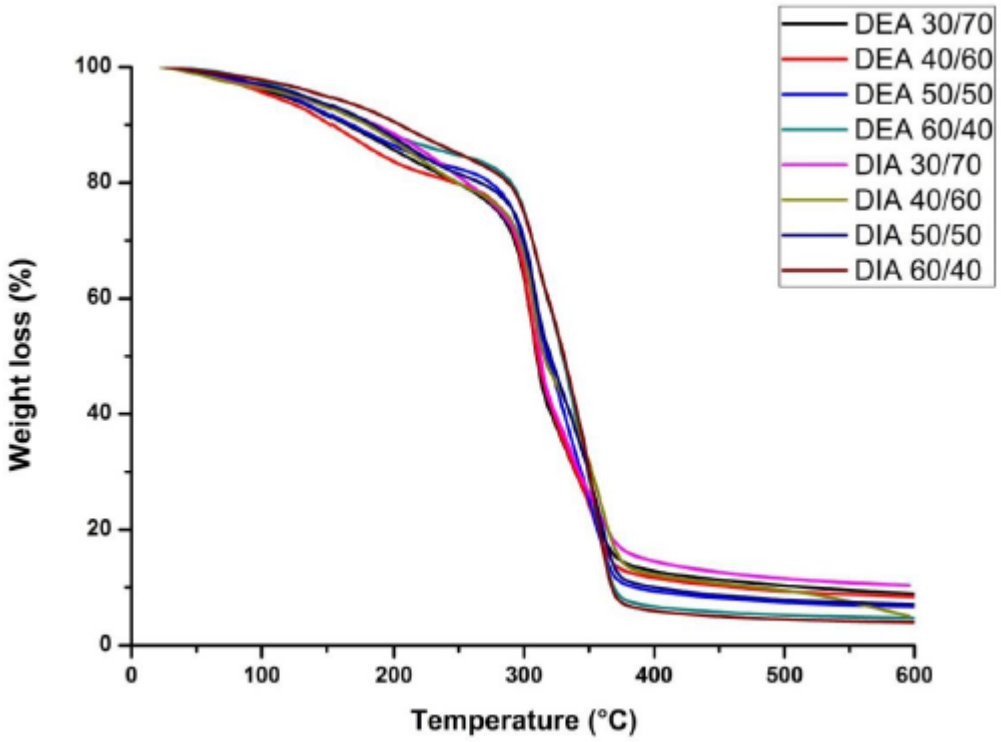
Thermal stability of PLA/TPS sheets plasticized with adipate ester were studied by TGA under inert atmosphere (nitrogen), and the weight loss due to the degradation of the components was monitored as a function of temperature. As shown in Figure 6.6, all the sheets demonstrated similar behaviour. Different comportment was observed by Wang et al. (2007), which the blends with higher content of PLA were more thermostable, proving that the addition of PLA can improve the thermostability of the TPS.

The temperature at the maximum rate of weight loss (Tmax), which is related to the maximum decomposition temperature (Tmax) of each component (PLA, TPS and adipate ester) were determined by derivatives of the TG curves (graph not shown). The sheets decomposed in well-defined three step processes, and for all samples, no significant difference was observed in Tmax. In general, the maximum degradation rate at 305°C was related to adipate esters, at 330°C refers to TPS and at 350°C was related to PLA degradation.

It was also possible to conclude that the temperature (180°C) employed during the extrusion was adequate and did not cause significant

degradation of the components and volatilization of the plasticizers, because the maximum degradation temperature of the blends is around 300°C.

Figure 6.6 – TG curves for PLA/TPS sheets plasticized with adipate esters.



6.3.9 DSC

The thermal properties of PLA/TPS sheets plasticized with adipate ester were also investigated by DSC, and summarized in Table 6.3. The pure PLA had Tg at 60°C, Tc at 117°C, and Tm at 164°C (XIONG et al., 2013). The blends of PLA with TPS, and the inclusion of adipate ester presented a significant modification in the thermal properties with the reduction of these temperatures.

The Tg and Tc did not vary with the TPS content, but the Tg and Tc of the sheets with DIA were higher than the sheets with DEA. According to Martino, Jiménez and Ruseckaite (2009), because a chain mobility increased due to the higher amount of plasticizer and/or its lower molar mass, the crystallization and melting temperatures of the blends were all shifted to lower temperatures. In this study, DEA with low molar mass had a better plasticization with PLA, explaining the lower Tg and Tc obtained. The better plasticizing effect of DEA is correlated with the

mechanical properties previously discussed (Figure 6.1) by significant decrease in the rigidity (Young's modulus) of the sheets.

The crystallinity index (X_C) increased with TPS inclusion and might be due to the effect of starch on induced crystallization of PLA matrix in PLA/TPS blends (KE; SUN, 2003; SCHWACH; SIX; AVEROUS, 2008; XIONG et al., 2013). This phenomenon was more intense in sheets plasticized with DIA, despite the DEA is a better plasticizer than DIA, which could provide more chain mobility, facilitating the rearrangement of molecules, and consequently the crystallization.

The PLA/TPS sheets had two melting temperatures (Tm), which Tm1 was related to TPS and Tm2 to PLA. Tm1 did not vary with TPS inclusion and type of adipate ester, but T_{m2} was higher in sheets with 60% (w/w) of PLA. As observed in the TG curves, this variation occurred because PLA has a higher thermal stability than TPS, so the addition of PLA improves the thermal stability of the blend.

Table 6.3 – Thermal data for PLA/TPS sheets plasticized with adipate ester.

Sample (PLA/TPS)	T_g (°C)	T_c (°C)	ΔH_c ($J.g^{-1}$)	T_{m1} (°C)	ΔH_{m1} ($J.g^{-1}$)	T_{m2} (°C)	ΔH_{m2} ($J.g^{-1}$)	X_c (%)
DEA 30/70	40	77	3.36	141	5.59	161	2.35	15.2
DEA 40/60	40	76	6.90	141	7.31	163	4.82	14.0
DEA 50/50	40	72	8.02	141	9.45	162	3.18	9.9
DEA 60/40	40	76	10.4	142	11.2	169	3.08	6.8
DIA 30/70	55	86	4.41	143	6.68	163	2.79	18.0
DIA 40/60	55	81	6.54	142	9.82	165	2.75	16.1
DIA 50/50	54	83	7.19	143	11.4	163	2.74	14.9
DIA 60/40	54	86	10.6	142	14.3	169	4.29	14.2

Tg: glass transition temperature; Tc: crystallization temperature; ΔHc: enthalpy crystallization; Tm1: low melting temperature; Tm2: high melting temperature; ΔHm1: melting fusion enthalpy; ΔHm2: high melting fusion enthalpy; Xc: crystallinity index.

6.4 CONCLUSION

The calendaring-extrusion was a feasible way to produce PLA/TPS sheets at pilot scale. The inclusion of TPS in the sheets modified the mechanical, barrier and thermal properties.

Adipate ester could be used as a plasticizer for PLA in PLA/TPS sheets, and between them DEA with low molar mass plasticized better PLA, because greater reduce in T_g and rigidity were observed. On the other hand, sheets with this component presented more hydrophilic character.

Micrographs of the sheets revealed the incompatibility between PLA and TPS suggesting the necessity of a compatibilizer to improve the mechanical and thermal properties.

6.5 ACKNOWLEDGEMENTS

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CAPITULO 7

ADDING CARBOXYLIC ACIDS TO POLY(LACTIC ACID) / THERMOPLASTIC STARCH SHEETS PRODUCED BY CALENDERING-EXTRUSION

ABSTRACT: Poly (lactic acid) (PLA) and thermoplastic starch (TPS) sheets with citric and adipic acid additives were produced through a calendering-extrusion process, and their mechanical, barrier, thermal and morphological characteristics were determined. According to the micrographs, citric acid improved the fragmentation and dispersion of starch granules by facilitating interactions with PLA chains and increasing interfacial adhesion. Citric acid also induced a significant increase in the tensile strength and elongation at rupture, reduced the water vapour permeability, increased the crystallinity, and raised the thermal stability. Adipic acid did not demonstrate the same efficiency, even when mixed with citric acid. The FT-IR spectra did not exhibit any absorption signals that suggested an interaction between the TPS and PLA.

Key-words: Compatibilizer. Interfacial adhesion. Extrusion. Calendaring. Biodegradable material.

7.1 INTRODUCTION

Poly (lactic acid) (PLA) and starch blends have been extensively studied as primary substitutes for non-biodegradable materials. Blends of PLA and starch offer cost-performance benefits alongside increased biodegradability without compromising the environment. Starch can enhance biodegradability and reduce costs while PLA offers superior mechanical properties (JANG et al., 2007). However, PLA and starch are non-miscible, and the resultant composites are brittle due to their coarse structure and lack of interfacial adhesion (KOZLOWSKI et al., 2007; LI; HUNEAULT, 2011; LIM et al., 2008; MARTIN; AVÉROUS, 2001; ZHANG; SUN, 2004; WANG et al., 2007).

Compatibilisers generally exhibit interfacial activity in heterogeneous polymer blends, and the compatibilising effect is usually attributed to increased interfacial adhesion and the presence of small, dispersed particles, leading to improved mechanical properties. The compatibiliser reacts with the components of a blend, reducing the difference in their polarity and, consequently, the interfacial tension between them. Different strategies for compatibilisation can be distinguished in the literature (IMRE; PUKANSZKY, 2013; RAQUEZ et al., 2008; SCHWACH; SIX; AVEROUS, 2008).

The compatibility between starch and PLA can be improved with reactive compatibilisers or coupling agents that reduce interfacial tension, such as maleic anhydride, acrylic acid, and methylene diphenyl diisocyanate (ZHANG; SUN, 2004; WANG; SUN; SEIB, 2002). However, these compatibilisers are toxic, limiting their use in food packaging. In this context, organic acids, such as citric and adipic acids, are an interesting option because they are naturally present in fruits and vegetables and are synthesised by microorganisms during the fermentation process.

Citric acid has been used as an additive in corn starch films to promote cross-linking (REDDY; YANG, 2010); it has also been used in TPS / poly (butylene adipate co-terephthalate) (PBAT) blends to improve the interactions between the polymeric phases via cross-linking reactions (esterification, hydrogen bonding) to produce materials with better mechanical and barrier properties (GARCIA et al., 2011; GARCIA et al., 2014; OLIVATO et al., 2012; OLIVATO et al, 2013).

The influence of citric acid on PLA/TPS (Wang et al., 2010; Teixeira et al., 2012) and PLA/wheat flour blends (CHABRAT et al., 2012) has been reported. These materials' properties are improved because the citric acid partially de-polymerises the starch, improving its distribution in the PLA matrix. In addition to its role as a compatibiliser, citric acid has been reported to increase the plasticisation and melt processing properties of TPS by accelerating the fragmentation and dissolution of the starch granules (SHI et al., 2007). The plasticisation of starch in a mixture of glycerol and citric acid increases the starch's plasticisation, facilitating partial esterification and generating chains with a lower molecular weight (CHABRAT et al., 2012).

Few studies report using adipic acid as a compatibiliser in PLA/TPS blends, even though this component was employed in TPS/PBAT blends to improve the functional properties of films produced by blown extrusion (SILVA et al., 2013).

Previous studies (SHIRAI et al., 2013) have demonstrated that plasticising PLA with diisodecyl adipate (DIA) improved its processability (extrusion) when blended with TPS. The aim of this study was to evaluate the effect of adding adipic and citric acids to TPS/PLA plasticised with DIA sheets produced through a calendering-extrusion process.

7.2 MATERIALS AND METHODS

7.2.1 Materials

The sheets were produced with PLA Ingeo 4043D (Natureworks LLC, Cargill, USA), native cassava starch (Indemil, Brazil), and commercial glycerol (Dinamica, Brazil), which was used as plasticizing for the starch. The technical grade diisodecyl adipate (426.67 g/mole) (Sigma Aldrich, Germany) was employed as plasticizing agents for the PLA, commercial citric acid (Nuclear, Brazil) and adipic acid (Nuclear, Brazil) as additives.

7.2.2 Sheet Production

The formulation of the sheets was 50% (w/w) of (PLA + diisodecyl adipate) and 50% of TPS (starch + glycerol). The concentration of plasticizers was 33 g glycerol / 100 g starch and 10 g diisodecyl adipate (DIA) / 100 g PLA. Citric acid (CA) and adipic acid (AA) were used as aditives, according Table 7.1.

Table 7.1 – Formulation of PLA/TPS sheets added of citric and adipic acids.

Formulation	PLA + DIA (wt%)	Starch + Glycerol (wt%)	Citric acid (wt%)	Adipic acid (wt%)
Control	50	50	0	0
CA 0.75	50	49.25	0.75	0
CA 1.50	50	48.50	1.50	0
AA 0.75	50	49.25	0	0.75
AA 1.50	50	48.25	0	1.50
CA + AA 0.75	50	49.25	0.375	0.375
CA + AA 1.50	50	48.25	0.75	0.75

AA: adipic acid; CA: citric acid; DIA: diisodecyl adipate; PLA: poly (lactic acid); TPS: thermoplastic starch

All components were manually mixed and extruded as cylindrical strands in a pilot twin-screw extruder (BGM, model D-20, Brazil) with a screw 20 mm in diameter, a 100 rpm screw speed, a 30 rpm feed speed, and a temperature profile of 100 / 180 / 180 / 180 / 180°C at the 5 zones.

The cylindrical strands were pelletised and extruded in the same twin-screw extruder coupled with a calendar (AX Plásticos, Brazil) to produce sheets. The temperature profile was 100 / 170 / 170 / 170 / 175°C, while the same screw and feed speeds were maintained. In the calender, the distance between the rolls was 0.8 mm, and the roll speed was adjusted depending on the formulation to maintain a continuous process.

7.2.3 Thickness and Density

The sheets thicknesses were measured with a digital micrometre at ten different points. To determine the sheet density, 20 mm * 20 mm samples were stored in a desiccator with anhydrous calcium chloride (0% RH) for 2 weeks and weighed, according to the procedure described by Müller, Laurindo and Yamashita (2011).

7.2.4 Mechanical Properties

Tensile strength tests were performed with a texture analyser (Stable Micro System, TA XTplus model, England) and were based on the guidelines of the American Society for Testing and Material standards (ASTM D882-02, 2002). The specimens were conditioned at 52.9 % relative humidity and 25 °C for 48 hours. The measured properties included tensile strength (MPa), elongation at break (%), and Young's modulus (MPa). The tests were repeated ten times for each formulation.

7.2.5 Water Vapor Permeability

The water vapor permeability (WVP) of the sheets was determined gravimetrically, according to the ASTM E96-00 (2000) standard under a relative humidity gradient of 0 - 75%. The specimens were previously conditioned at 53 % of relative humidity and 25°C for 48 hours, and the tests were conducted in duplicate.

7.2.6 Moisture Sorption Isotherm

The moisture sorption isotherms of the sheets were obtained using the static gravimetric method, and saturated saline solutions were employed to obtain different relative humidities. The GAB (Guggenheim-Anderson-de Boer) model (Eq. 7.1) was used to fit the experimental data. In this equation, the parameter X_w is the equilibrium moisture content (g water/g dry solid) at a known water activity (a_w), m_o is the monolayer water content, C is the Guggenheim constant (representing the sorption heat of the first layer), and k is the sorption heat of the multilayer. The parameters of the GAB model were determined using non-linear regression performed with the Statistica 7.0 software.

$$Xw = mo.C.K.aw/(1 - K.aw)(1 - K.aw + C.K.aw) \quad \text{(Eq. 7.1)}$$

7.2.7 Scanning Electron Microscopy

The microstructure of the sheets (surface and fracture) was analysed with a scanning electron microscope (Philips, FEI Quanta 200 model, Japan). The sheets were fractured after immersing them in liquid nitrogen; the samples were coated in gold using a sputter coater (Bal-Tec, SCD-050 model, Balzers, Liechtenstein). All sheets were examined using a 20 kV accelerating voltage, and the magnitude of the observation was 100x.

7.2.8 FT-IR

The analyses were performed using a Fourier Transform Infrared Spectrometer (FT-IR) (IRPrestige-21 model, Shimadzu, Japan) equipped with a reflectance attenuator (ATR) (ATR-8200HA model, Shimadzu, Japan). Each spectrum was collected using 100 scans covering 4000 to 750 cm^{-1}. The samples were previously conditioned in a desiccator containing anhydrous calcium chloride (~0 % RH) for 7 days.

7.2.9 TGA

The thermal stability of the PLA/TPS blends was measured with a TGA-Q50 instrument (TA Instruments, USA). The samples were analysed under a nitrogen atmosphere (100 mL/min) and heated from 25 °C to 600 °C at 10 °C/min. The derivatives of the TG curves were obtained using the Origin 8.0 software (OriginLab, USA) to verify the maximum temperature degradation.

7.2.10 DSC

The glass transition (Tg), crystallisation (Tc), and melting (Tm) temperatures of the sheets were determined with a differential scanning calorimeter (DSC-Q20, TA Instruments, USA). The samples were heated to 250 °C at 10 °C/min under 50 mL/min nitrogen. The crystallinity indexes (Xc) of the sheets were calculated according to Eq. 7.2, and Xc is the enthalpy difference between the melting and crystallisation peaks divided by the enthalpy of 100% crystalline PLA (93.6 J/g) (FISHER et al., 1973 *apud* XIONG et al., 2013). The variables AHm1, AHm2, and AH_c are the enthalpies (J/g) of fusion at two higher melting temperatures and crystallisations of the blend, respectively, and 5_{PLA} is the PLA content in the blend.

$$Xc = [(AHm1 + AHm2 - AHc) / (93.6 \times 5_{PLA})] \times 100 \quad \text{(Eq. 7.2)}$$

7.2.11 Statistical Analysis

The results were evaluated using analysis of variance (ANOVA), and the treatment means were compared using Tukey's test at the 5% significance level ($p<0.05$) using the Statistica 7.0 software.

7.3 RESULTS AND DISCUSSION 7

7.3.1 Thickness and Density

All formulations exhibited good processability, and the sheets containing citric acid (CA) had a smoother surface and a better appearance than the other formulations, suggesting that these materials had a better processability. Adipic acid (AA) did not exert the same effect.

In general, the poly (lactic acid) (PLA)/thermoplastic starch (TPS) sheets had a highly variable thickness (Table 7.2), and except for the CA + AA 0.75 sample, all sheets with CA were thinner than the other sheets. During the calendering process, the sheets' thickness was controlled by the distance between the rolls, the speed of the rolls, and the stretching capacity of the formulation. The inclusion of CA generated thinner sheets, possibly due to its plasticising effect, that enhanced the material's flexibility, allowing further stretching by the calender rolls.

Table 7.2 – Thickness and density of PLA/TPS sheets added of adipic and citric acids.

Formulation	Thickness (um)	Density (g/cm^3)
Control	703 ± 45^{b}	1.12 ± 0.02^{c}
CA 0.75	460± 117^{e}	1.35 ± 0.01^{a}
CA 1.50	521 ± 131de	1.24 ± 0.06^{b}
AA 0.75	663 ± 41^{b,c}	0.90 ± 0.03^{d}
AA 1.50	745 ± 50^{b}	1.07 ± 0.01^{c}
CA + AA 0.75	901 ± 70^{a}	1.31 ± 0.02^{a,b}
CA + AA 1.50	572 ± 54^{c,d}	1.32 ± 0.03^{a}

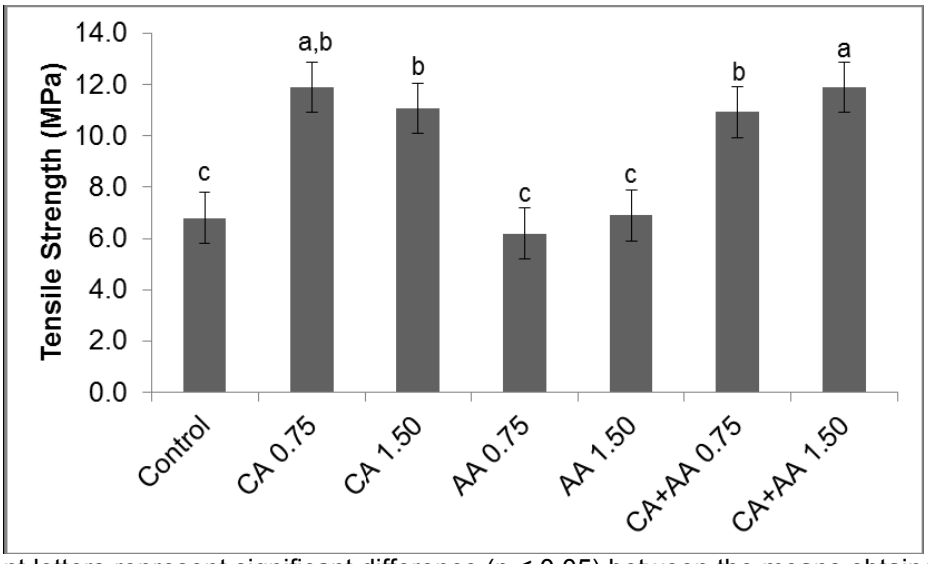
^{a,b,c,d} Different letters represent significant difference ($p < 0.05$) between the means obtained by Tukey test in the same column.

The density of the sheets ranged from 0.90 to 1.35 g/cm^3 (Table 2). Including CA increased the material's density, and the samples containing AA exhibited densities similar to those of the controls. CA most likely improved the interfacial adhesion between the TPS and PLA chains, forming a more compact and dense structure. Similar densities were observed in TPS films incorporating nanoclays and produced by extrusion and thermopressing (MÙLLER; LAURINDO; YAMASHITA, 2011, MÙLLER; LAURINDO; YAMASHITA, 2012) and in PLA/TPS blends obtained by extrusion and thermopressing (MÙLLER; PIRES; YAMASHITA, 2012).

7.3.2 Mechanical Properties

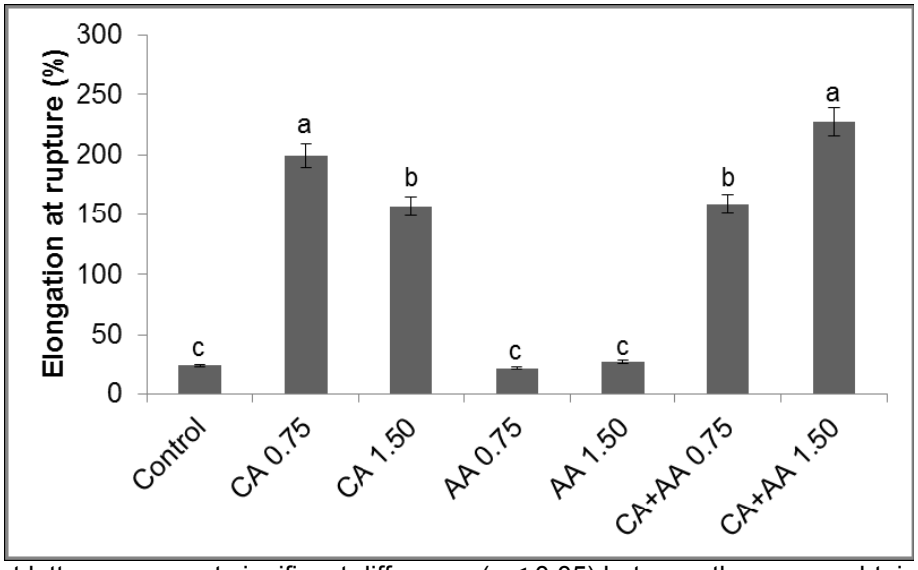
According to Figures 7.1, 7.2 and 7.3, adding CA significantly affected the mechanical properties by increasing the tensile strength and Young's modulus, and the elongation at rupture for the CA+AA 1.50 sample increased approximately 800% relative to the other samples. The same was not observed for the sheets with AA, and the experimental sheets did not differ from the controls.

Figure 7.1 – Tensile strength of PLA/TPS sheets added of adipic and citric acids.



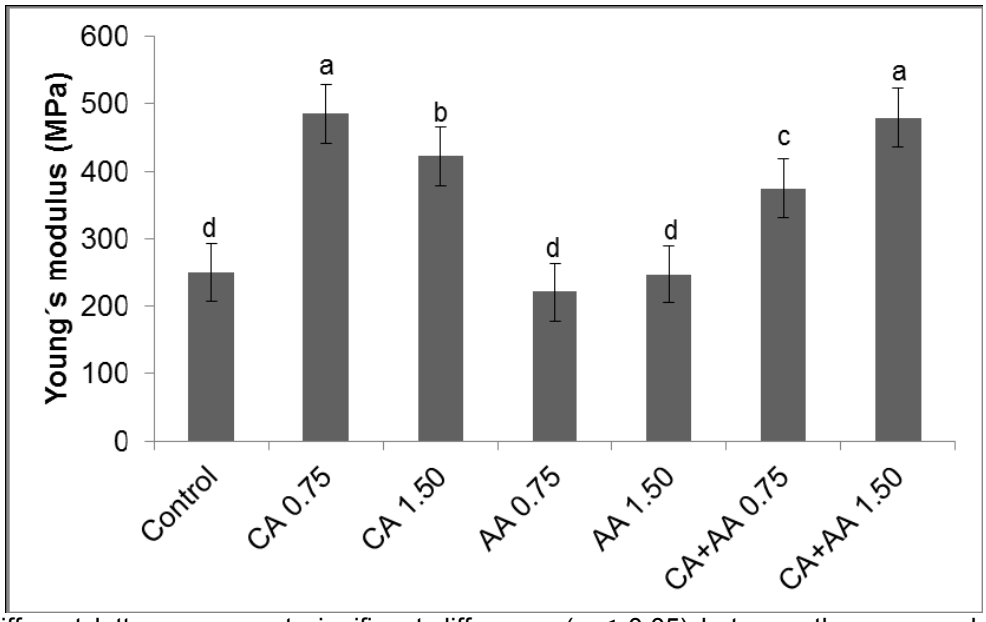
a,b,c Different letters represent significant difference ($p \leq 0.05$) between the means obtained by Tukey test.

Figure 7.2 – Elongation at rupture of PLA/TPS sheets added of adipic and citric acids.



a,b,c Different letters represent significant difference ($p \leq 0.05$) between the means obtained by Tukey test.

Figure 7.3 – Young´s modulus of PLA/TPS sheets added of adipic and citric acids.



a,b,c,d Different letters represent significant difference ($p \leq 0.05$) between the means obtained by Tukey test.

According to Wang et al. (2010), the tensile strength of the PLA/TPS blends increased with CA addition due to the increased PLA/TPS dispersion, which improved the interfacial adhesion. The authors also concluded that high CA concentrations (approximately 3 wt%) depolymerised the PLA and starch, deteriorating the mechanical properties of the blend.

Adding CA to the wheat flour/PLA and the TPS/PE blends decreased the Young's modulus and increased both the elongation at break and tensile strengths; these observations were attributed to the improved affinity between the phases (CHABRAT et al., 2012; WANG et al., 2007).

We postulated that citric acid modified the starch, introducing new groups such as carboxylates and esters into their structures, making starch more hydrophobic and facilitating the interactions and approximation with the hydrophobic PLA chain. According to Olivato et al. (2012), these new groups are potentially reactive points for the crosslinking reactions that can improve the compatibility between the polymeric molecules and generate more resistant films.

The AA concentration (0.75 - 1.5 wt%) had no effect on the sheets' mechanical properties. Different results were observed in PBAT/TPS films produced by blown extrusion: adding 0.5 - 1.5 wt% AA generated more resistant and flexible films (SILVA et al., 2013).

7.3.3 Water Vapour Permeability (WVP) and Moisture Sorption Isotherm

The WVP values of the sheets are presented in Table 7.2 and range between 4.55 x 10^{-6} and 20.1 x 10^{-6} g.day^{-1}m^{-1}.Pa^{-1}. Sheets containing CA exhibited the lowest WVP values, most likely due to the reduction of the mobility of the polymeric chains caused by the better interactions between the starch and PLA chains, which impaired water diffusion across the sheet. The higher CA concentration (1.50 wt%) did not continue to improve the evaluated properties, suggesting that this component is efficient at lower concentrations (0.75 wt%), where it increases the interfacial adhesion without hydrolysing the starch and PLA molecules.

The WVP of the CA 0.75 and CA+AA 1.50 sheets were the same, confirming that AA was not a compatibiliser in PLA/TPS sheets at the tested concentrations. More studies are necessary to determine whether higher or lower concentrations of AA can act as compatibilisers in PLA/TPS blends. Other researchers have reported significant WVP decreases in starch (REDDY; YANG, 2010) and PBAT/TPS films (OLIVATO et al., 2012; OLIVATO et al., 2013; SILVA et al., 2013) after adding carboxylic acids.

Table 7.3 – Water vapor permeability (WVP) and GAB model parameters of the PLA/TPS sheets.

Formulation	WVP (x10^6) (g/m.Pa.day)	GAB parameters*		
		m_o (g water/g dry solids)	*K*	*C*
Control	16.3 ± 1.17^a	0.051	0.85	8.5
CA 0.75	4.55 ± 0.78^b	0.039	0.88	7.1
CA 1.50	9.12 ± 0.84^b	0.037	0.67	14.0
AA 0.75	20.1 ± 4.46^a	0.041	0.93	16.1
AA 1.50	18.0 ± 0.68^a	0.049	0.94	20.3
CA + AA 0.75	7.52 ± 0.38^b	0.037	0.94	13.2
CA + AA 1.50	4.82 ± 0.45^b	0.039	0.92	14.3

a,b Different letters represent significant difference ($p \leq 0.05$) between the means of WVP obtained by Tukey test.
* Coefficient of determination R2> 0.99 for all fitted models.
mo = monolayer water content; C = Guggenheim constant; k = sorption heat of the multilayer.

The moisture sorption isotherms of the PLA/TPS sheets with added CA and AA exhibited a sigmoid pattern because of the hydrophilic materials, such as TPS. The GAB model parameters (m_o, C and K) are listed in Table 7.2. The GAB model represented the experimental data well (R^2> 0.99), making it adequate for

describing the water sorption isotherms of the TPS films (MALI et al., 2005; MULLER; LAURINDO; YAMASHITA, 2008; MULLER; LAURINDO; YAMASHITA, 2012), the TPS/PLA blends (MULLER; PIRES; YAMASHITA, 2012), and the TPS/PBAT/PLA films (SHIRAI et al., 2013).

The monolayer moisture content (mo) describes the amount of water strongly adsorbed by the material and is related to the material's hygroscopy and hydrophilicity. The lowest values were observed for sheets with CA (0.037 to 0.039 g water/g dry solids), in accordance with the WVP values. Adding CA modified starch that substitutes hydroxyl groups for esters and carboxyl groups, decreases the amount of hydroxyl groups available to interact with water, diminishing the hydrophilicity and permeability of the sheets. The obtained mo values were slightly larger than were encountered during our previous studies using PLA/PBAT/TPS films (SHIRAI et al., 2013) because of the higher TPS content in the sheets.

The K parameter is related to the sorption heat of the multilayer, and the C parameter is associated with the sorption heat of the monolayer. No clear trend was observed, and it was difficult to establish a correlation between the additions of CA and AA in PLA/TPS sheets. The values of K and C are closer than were reported in other studies (MALI et al., 2005; MULLER; LAURINDO; YAMASHITA, 2008, MÜLLER; LAURINDO; YAMASHITA, 2012).

7.3.4 Scanning Electron Microscopy (SEM)

The micrograph of the control sheet fracture (Figure 7.4) reveals differently sized starch granules distributed in the PLA matrix, proving the incompatibility between starch and PLA. Other authors reported that the incompatibility between PLA and TPS was caused by the high interfacial tension between non-polar and highly polar polymers (KOZLOWSKI et al., 2007; MARTIN; AVEROUS, 2001; MÜLLER; LAURINDO; YAMASHITA, 2012; SHIN et al., 2011; WANG et al., 2007; WOOTTHIKANOKKHAN et al., 2012; ZHANG; SUN, 2004).

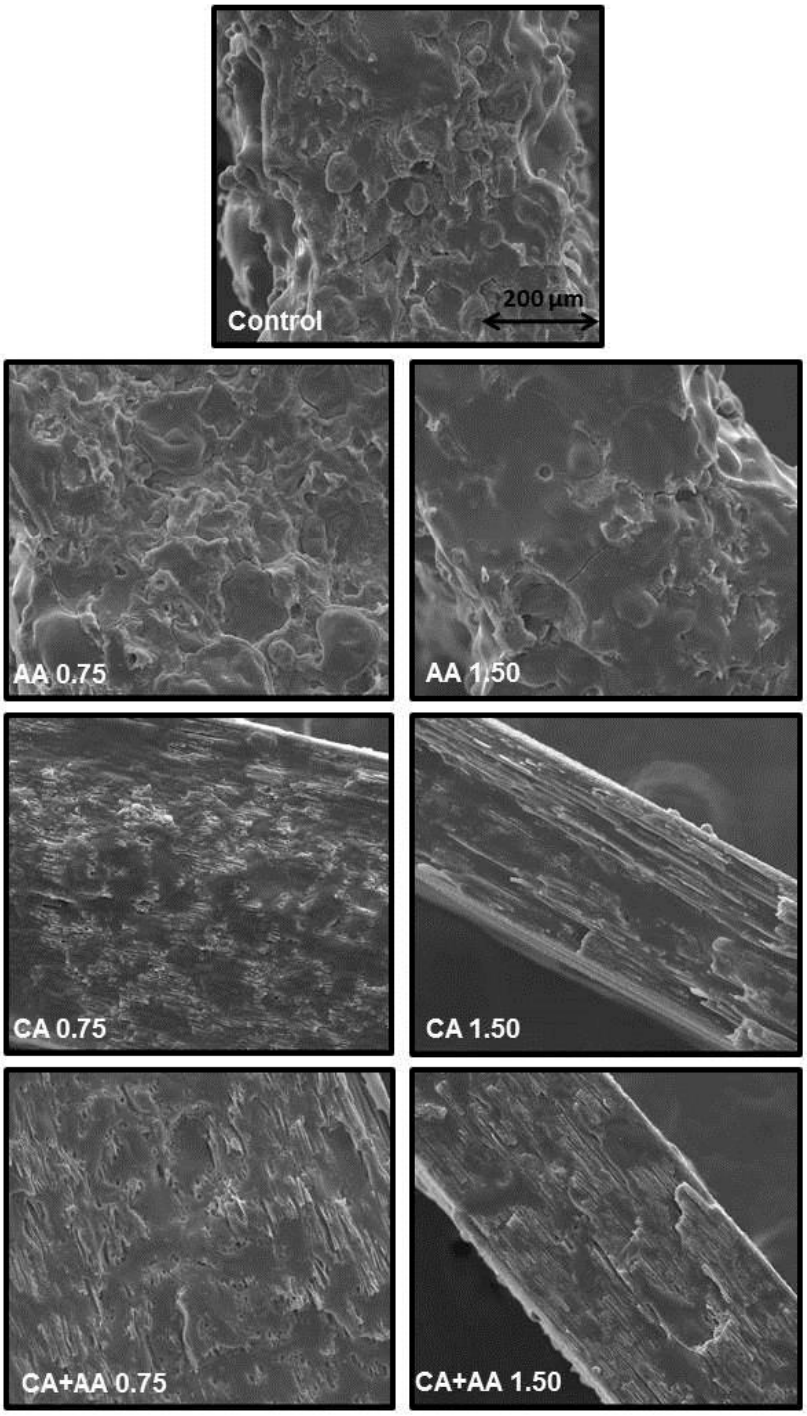
In contrast to the control sample, when CA was added, TPS and PLA formed a more homogeneous and compact structure, while starch granules were not evident, suggesting that CA increases the plasticisation and affects the melt process of TPS by accelerating the fragmentation and dissolution of the starch granules (SHI et al., 2007). The micrographs of the AA 0.75 sheets revealed cavities between the

starch granules and PLA, but the AA 1.50 micrograph exhibited better dispersion of the two polymeric phases, indicating that higher AA concentrations could promote better starch dispersion and fragmentation.

The surface micrographs (not shown) of the control, AA 0.75 and AA 1.50 sheets revealed a rough surface that was most likely due to partial phase separation. The chain-chain PLA/TPS repulsion during cooling could cause a disordered phase separation, increasing the surface roughness. Conversely, CA-added sheets exhibited smoother surfaces because the starch became more hydrophobic due to the esterification with CA, allowing approximation with the PLA chains and increasing the interfacial adhesion to form a compact structure.

Adding carboxylic acids was the main contributor to the improved mechanical properties because these properties are related to the polymer blend's morphology.The more compact structure formed after CA was added, and the absence of cracks and voids decreased the WVP values. According to Andersson (2008), molecular transport through a polymer film occurs mainly through defects in the film, such as cracks and voids where the gas molecules have free passage through the film or diffuse through the amorphous regions.

Figure 7.4 – SEM (400 X) of the PLA/TPS sheets with added carboxylic acids.



7.3.5 TGA

The thermal stability of the PLA/TPS sheets with added AA and CA were studied by TGA under an inert atmosphere (nitrogen), and the weight loss due to the degradation of the components was monitored relative to their temperature (Figure 7.5). The temperature at the maximum rate of weight loss (Tmax) was related

to the maximum decomposition temperature (Tmax) of each component (PLA, TPS and DIA) and was determined by deriving the TG curves (Figure 7.6).

During the first step (from 25 to 300 °C), the mass loss was slow, indicating that the sheets were thermally stable and had a slower degradation rate; concurrently, the mass loss below 100 °C was ascribed to water loss. The mass loss from 100°C until the onset decomposition temperature (305°C) is attributed to water and glycerol volatilization as observed by Jiang et al. (2006) and Garcia et al. (2014).

Compared with the control sample, the thermal stability of the sheets with added carboxylic acids decreased slightly due to acidic depolymerisation of starch and PLA, as described by Wang et al. (2010). For all sheets, two peaks were evident in the TG derivative curves that were different from those observed during our previous work with PLA/TPS blends plasticised with different adipate esters; three peaks appeared and were ascribed to the adipate ester, the starch and the PLA. The maximum degradation rate at 305 °C was related to the starch rich phase; every sample exhibited the same value. The second degradation peak, observed at approximately 330 °C, was attributed to the PLA+DIA and decreased slightly after the acids were added. For example, the control sheets exhibited a degradation peak at about 350 °C, while the acids added sheets exhibited a peak at 332 °C.

Figure 7.5 – TG curves for PLA/TPS sheets with added adipic and citric acids.

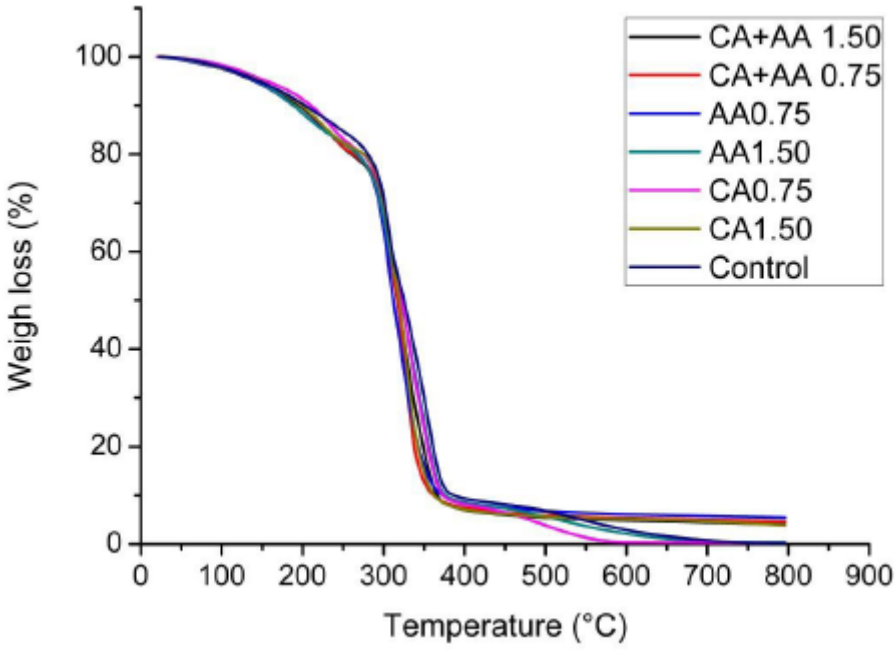
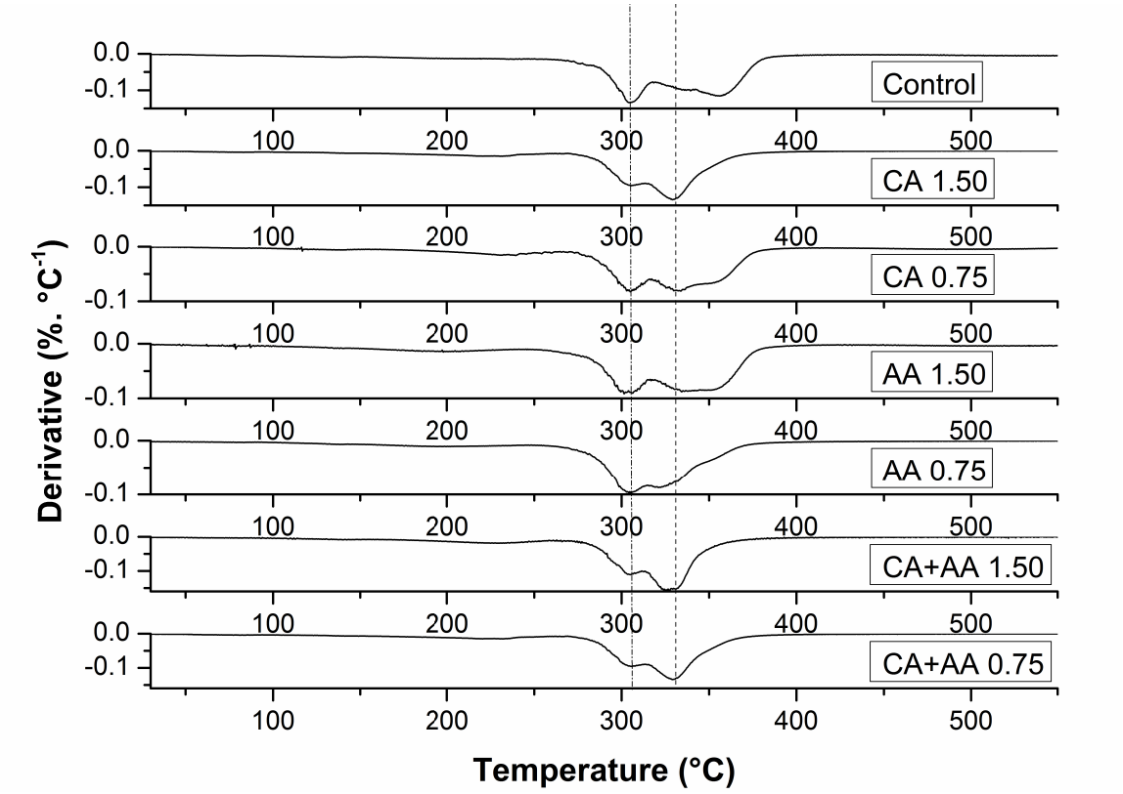


Figure 7.6 – DTG curves for PLA/TPS sheets added with adipic and citric acids.



7.3.6 DSC

The thermal properties of the PLA/TPS sheets with added AA and CA were also investigated by DSC, and the results are summarised in Table 7.3. According to Xiong et al. (2013), the pure PLA has Tg at 60°C, Tc at 117°C, and Tm at 164°C, while the blends of PLA with TPS, the plasticisation of PLA with DIA, and the inclusion of AA and CA significantly modified the thermal properties.

The Tg of TPS was not observed because the heat capacity variations at the Tg transitions are rather small. Because the PLA/TPS blends are not miscible, the T_g at approximately 53-55 °C can be attributed to the PLA phase (MARTIN; AVEROUS, 2001; SCHWACH; SIX; AVEROU, 2008). Generally, adding the acids slightly lowered Tg and increased Tc and Tm2. A slight decrease in Tm1 was only observed in the samples with CA. The Tg shift could be linked to PLA degradation (thermomechanical or through acidolysis) or plasticisation (SCHWACH; SIX; AVEROU, 2008) by acids. In addition, CA and AA can react during extrusion with glycerol to form a citrate and an adipate, respectively; these groups are

plasticisers for PLA (SHIRAI et al., 2013). Even in small amounts, these compounds could be formed, plasticising PLA and reducing Tg.

The crystallinity index (XC) increased as the acids were added. AA and CA possibly acted as plasticisers for PLA or citrate, while the adipate ester formed during extrusion, explaining the decrease in Tg and the increases in Tc and Tm2. Similar comportment was observed in the PLA/starch composites plasticised with epoxidised soybean oil (XIONG et al., 2013). According to Ljungberg and Wesslen (2003), PLA films with greater plasticity result in higher chain mobility, which facilitates the crystallisation and increases XC.

For the CA-added sheets, the changes in mechanical properties agreed with the changes in XC. Increases in XC were also associated with increases in the material's strength and stiffness, as reported in other studies. Crystalline domains may act as physical crosslinks between the polymer chains, improving the interfacial adhesion and therefore the material's strength (ARIAS et al., 2013, SCHWACH; SIX; AVEROUS, 2008).

Table 7.4 – Thermal data for PLA/TPS sheets added of citric and adipic acids.

Formulation	T_g (°C)	T_c (°C)	ΔH_c (J.g-1)	T_{m1} (°C)	ΔH_{m1} (J.g-1)	T_{m2} (°C)	ΔH_{m2} (J.g-1)	χ_c (%)
Control	55	87	7.17	144	12.1	162	1.42	13.5
CA 0.75	53	88	7.49	143	12.9	172	3.59	19.3
CA 1.50	54	92	7.69	143	12.3	175	4.91	20.2
AA 0.75	54	89	7.46	144	13.3	173	4.21	21.4
AA 1.50	54	91	9.57	144	15.2	174	3.09	18.6
CA + AA 0.75	54	88	7.19	144	12.7	185	5.93	24.5
CA + AA 1.50	53	88	7.85	143	13.3	175	5.96	24.4

Tg: glass transition temperature; Tc: crystallization temperature; ΔHc: enthalpy of crystallization; Tm1: low melting temperature; Tm2: high melting temperature; ΔHm1: low melting fusion enthalpy; ΔHm2: high melting fusion enthalpy; Xc: crystallinity index.

7.3.7 FT-IR

Table 7.4 lists the peak band wavenumbers in the FT-IR spectrum for the PLA/TPS sheets with added AA and CA. The absorption bands observed at approximately 1018 and 993 cm^{-1} were related to the C-O fracture strain of the C-O-C group in the anhydroglucose ring that originated in the starch. A broad band was observed at approximately 3300 cm^{-1} that was related to the hydrogen interactions

and the hydroxyl groups present in every component (PLA, glycerol, acids and starch). The peak at 1180 cm^{-1} was related to the C-O bond of C-O-H (PLA and TPS), while the peaks at 1037 cm^{-1}, 1080 cm^{-1} and 1128 cm^{-1} corresponded to the C-O bond of O-C=O present in PLA and DIA.

The strong carbonyl stretching absorption at approximately 1749 cm^{-1} corresponded to the vibration of the C=O bond in PLA and the adipate esters. The peaks for the samples with acids were more intense, and we did not observe any shifts in the bands toward different wavenumbers. According to Wang et al. (2010), shifts toward lower wavenumbers suggest that the functional groups of TPS and PLA interacted via esterification and transesterification reactions. In our study, we could not conclude whether these reactions occurred during the extrusion process.

Table 7.5 – The FT-IR spectrum wavenumber of the PLA/TPS sheets with added citric and adipic acids.

Formulation	Vibration wavenumber (cm^{-1})			
	-C=O	-C-O of –C-O-H-	-C-O- of –O-C=O	C-O of C-O-C in starch
Control	1749	1180	1037, 1080, 1128	991, 1018
CA 0.75	1749	1180	1037, 1080, 1128	993, 1016
CA 1.50	1749	1180	1037, 1080, 1128	991, 1014
AA 0.75	1749	1180	1037, 1080, 1128	991, 1018
AA 1.50	1749	1180	1037, 1080, 1128	991, 1018
CA + AA 0.75	1749	1180	1037, 1080, 1128	991, 1018
CA + AA 1.50	1749	1180	1037, 1080, 1128	991, 1018

7.4 CONCLUSION

Citric acid is an effective additive for poly (lactic acid)/thermoplastic starch sheets produced by calendering-extrusion. The material with added citric acid is more resistant and flexible with lower WVP than the control materials. Comparatively, adipic acid did not exhibit the same performance, even when mixed with citric acid.

Morphological analyses revealed that citric acid increased the interaction between the polymers and consequently their interfacial adhesion to improve their mechanical and barrier properties.

Citric and adipic acids decreased the Tg and increased the crystallinity index of the sheets, most likely due to their plasticising effect and the partial degradation of PLA and TPS via thermomechanical effects and acidolysis.

7.5 ACKNOWLEDGEMENTS

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CAPÍTULO 8
CONCLUSÃO

Para a produção de filmes de PLA e ATP por extrusão-sopro em balão é necessária a utilização de altas concentrações de ATP na blenda, plastificação do PLA com ésteres de adipato e citrate e emprego dos processos de mistura com a extrusora dupla rosca.

A adição de PLA em blendas de ATP e PBAT diminui a permeabilidade ao vapor de água, aumenta a rigidez dos filmes e o limite de incorporação de PLA à blenda é de 20%.

A mudança do processo de extrusão-sopro em balão para a extrusão plana juntamente com a mudança no tipo de PLA, permitiu a produção em escala piloto de chapas planas com altas concentrações de PLA.

A plastificação do PLA com adipato de diisodecila somada à incorporação de ácido cítrico como compatibilizante torna a estrutura das chapas mais compacta e com a superfície mais lisa em virtude da maior adesão interfacial causada pelo ácido cítrico, diminuindo a permeabilidade ao vapor de água, elevando a elongação e a resistência à tração, sem alterar a temperatura de degradação térmica.

É possível produzir materiais biodegradáveis a base de PLA e ATP plastificado com éster de adipato e adicionado de ácido cítrico em escala piloto e com grande viabilidade para produção em escala comercial.

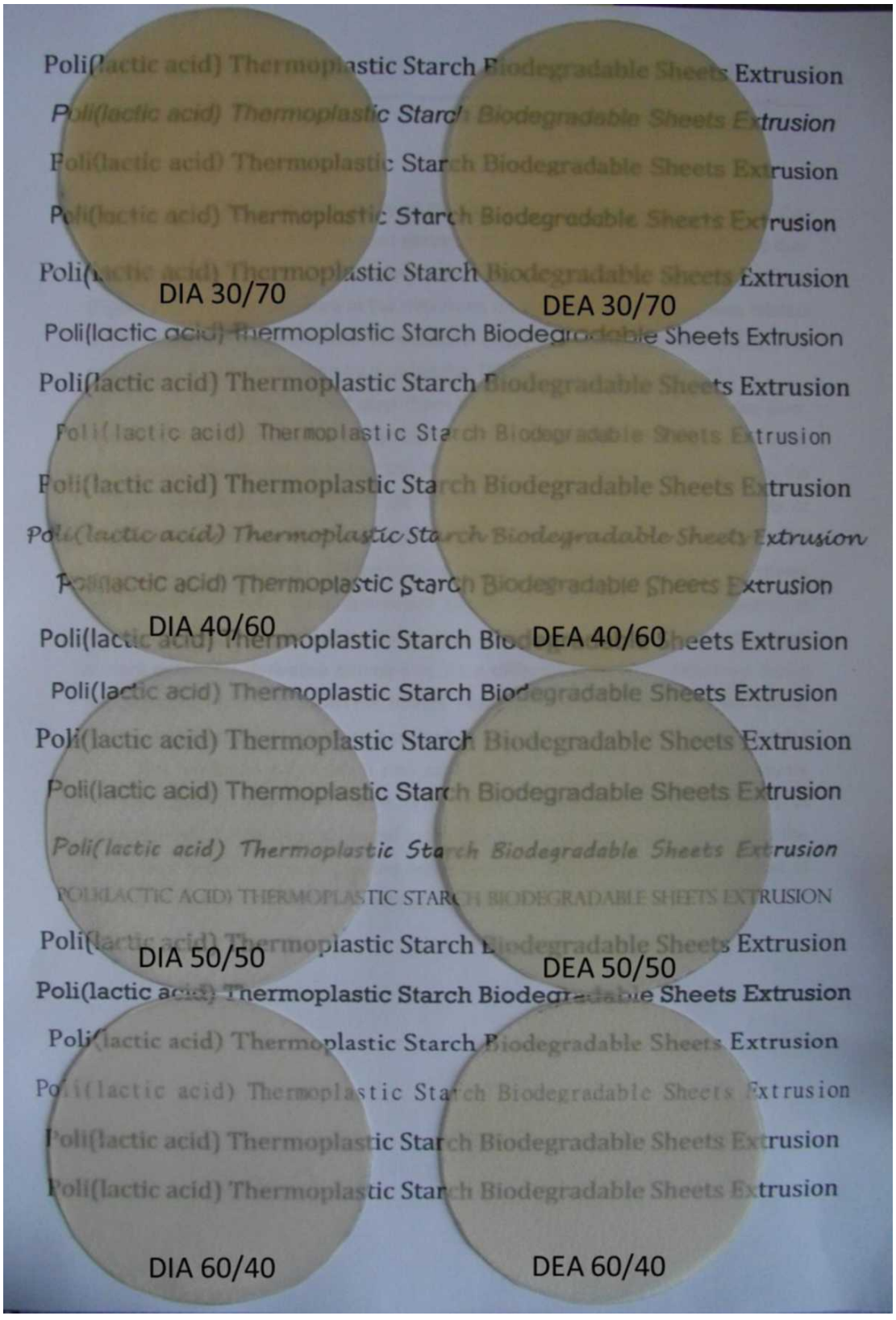
ANEXOS

ANEXO A

Chapas de PLA/TPS plastificados com ésteres de adipato e citrato (Capítulo 5)

ANEXO B

Chapas de PLA/TPS plastificados com adipato de diisodecila (DIA) e adipato de dietila (DEA) (Capítulo 6)



ANEXO C

Chapas de PLA/TPS adicionados de ácidos cítrico (CA) e ácido adípico (AA) (Capítulo 7)