Universidade Estadual de Londrina

JULIANO ZANELA

BLENDAS POLIMÉRICAS DE AMIDO E POLI (VINIL ÁLCOOL) – PVA: EFEITOS DO TIPO DE PVA, AMIDOS MODIFICADOS E USO DE FIBRAS NO DESENVOLVIMENTO DE MATERIAIS BIODEGRADÁVEIS

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

Orientador: Prof. Dr. Fabio Yamashita

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Dedico este trabalho a minha família, a todos os meus amigos, e em especial a Maira Casagrande pelo seu auxílio, compreensão e apoio durante toda minha jornada.

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“Nulla tenaci invia est via”

Para os persistentes nenhum caminho é impossível

ZANELA, Juliano. **Blendas poliméricas de amido e poli (vinil álcool) – PVA:** efeitos do tipo de PVA, amidos modificados e uso de fibras no desenvolvimento de materiais biodegradáveis. 2016. 192f. Tese (Doutorado em Ciência de Alimentos) – Universidade Estadual de Londrina, Londrina, 2016.

RESUMO

O objetivo do trabalho foi desenvolver materiais biodegradáveis de amido e poli (vinil álcool) (PVA) para substituir materiais produzidos com polímeros convencionais e, consequentemente, reduzir o impacto ambiental destes polímeros. Foi utilizado amido de mandioca nativo e modificado (fosfato de di-amido, fosfato de di-amido acetilado, adipato de di-amido acetilado e amido oxidado), amido catiônico com diferentes graus de substituição (0,019; 0,027 e 0,033 mol/mol), PVA com diferentes graus de hidrólise (hd) e tamanhos de cadeia, glicerol como plastificante e fibras da casca de aveia como reforço, e as blendas destas matérias primas foram produzidas por extrusão termoplástica. A partir destas blendas os materiais foram produzidos variando-se o tipo (extrusão plana e injeção termoplástica) e as condições de processo. Os materiais foram caracterizados através das propriedades mecânicas, permeabilidade ao vapor de água, microscopia eletrônica de varredura, difração de raios-X e espectroscopia no infravermelho com transformada de Fourier. De forma geral os componentes das blendas apresentaram boa compatibilidade e os materiais biodegradáveis produzidos a partir destas blendas apresentaram microestrutura homogênea, boa processabilidade e manuseabilidade. Foram obtidos materiais com tensão na ruptura de até 6,99 MPa, Módulo de Young de até 16,19 MPa e elongação na ruptura de até 642% quando utilizou-se PVA com alto hd e tamanho de cadeia, sendo observado que maiores hd promovem um aumento na rigidez do material, enquanto que o tamanho de cadeia aumenta a resistência à tração. O uso dos amidos modificados não alterou significativamente as propriedades dos materiais, não justificando seu uso em substituição ao amido nativo. Quanto ao emprego de fibras em materiais injetados, essas atuaram principalmente como carga inerte, não promovendo uma melhora significativa das propriedades mecânicas, mas servindo para a redução de custos do material. Portanto é possível produzir materiais biodegradáveis a partir de blendas de amido de mandioca nativo e PVA com características adequadas para substituir materiais semelhantes produzidos com polímeros petroquímicos convencionais.

Palavras-chave: Propriedades mecânicas. Extrusão termoplástica. Amidos modificados. Blendas biodegradáveis. Moldagem por injeção.

ZANELA, Juliano. **Polymer blends of starch and polyvinyl alcohol – PVA:** effects of PVA grade, modified starches and the use of fibers on the development of biodegradable materials. 2016. 192p. Thesis (Doctor Degree in Food Science) – Universidade Estadual de Londrina, Londrina, 2016.

ABSTRACT

The objective was to develop biodegradable materials using starch and poly (vinyl alcohol) (PVA) to replace materials produced with conventional polymers and thus reduce the environmental impact of these polymers. The biodegradable materials were produced with native or modified cassava starch (di-starch phosphate, di-acetylated starch phosphate, di-starch adipate acetylated and oxidized starch, cationic starch with different degrees of substitution - 0.019, 0.027 and 0.033 mole/mole), PVA with several degrees of hydrolysis (HD) and chain sizes, glycerol as plasticizer and oat hull fibers as reinforcement by thermoplastic extrusion. The materials were produced by varying the type (flat extrusion and thermoplastic injection) and process conditions, and they were characterized by means of mechanical properties, water vapor permeability, scanning electron microscopy, X-rays diffraction, and Fourier transform infrared spectroscopy. In general, the components of the blends showed good compatibility among them, and the biodegradable materials produced from these blends showed homogeneous microstructure, good processability and handleability. The biodegradable materials had stress at break up to 6.99 MPa, Young's Modulus up to 16:19 MPa and elongation at break up to 642% with PVA with high HD and chain length, and higher HD increased the material rigidity, whereas the high chain length increased the tensile strength. The use of modified starches did not significantly alter the materials properties, and it does not justify their use to replace native starch. The fiber used in injected materials acted mainly as a inert filler, and did not improve their mechanical properties, but it can reduce the material cost. Therefore, it is possible to produce biodegradable materials from starch and PVA blends with adequate characteristics for replacing similar materials produced with conventional petrochemical polymers.

Keywords: Mechanical properties. Thermoplastic extrusion. Modified starches. Polymeric blends. Injection molding.

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LISTA DE ABREVIATURAS E SIGLAS

ASTM	American Society for Testing and Material
DTG	Termogravimetria Derivada
FT-IR	Espectroscopia de Infravermelho com Transformada de Fourier
HD	Grau de hidrólise
MPa	Mega Pascal
MW	Massa Molecular
Op	Opacidade Aparente
PBAT	Poli (adipato co-tereftalato de butileno)
PCA	Análise de Componentes Principais
PHA	Poli(hidroxialcanoato)
PLA	Poli(ácido lático)
PVA	Poli(vinil álcool)
RH	Umidade Relativa
SEM	Microscopia Eletrônica de Varredura
TGA	Análise Termogravimétrica
TPS	Amido Termoplástico
WLW	Perda de Massa em Água
WVP	Permeabilidade ao vapor de água
XRD	Difração de Raios-X
ΔE^*	Diferença de Cor

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INTRODUÇÃO

Já se passaram mais de 100 anos desde o desenvolvimento do baquelite, que foi o primeiro plástico sintético criado em 1907 e, nesse curto período de tempo os plásticos se tornaram parte presente na vida moderna. Isso se deve ao desenvolvimento de uma grande quantidade novos polímeros, com uma ampla faixa de características e propriedades, dando uma grande versatilidade aos polímeros, aliado ainda ao baixo custo e disponibilidade. Atualmente, é possível encontrar os polímeros em inúmeras áreas, como na agricultura, embalagens, setor automotivo dentre outros ramos.

Segundo relatório da associação europeia das empresas produtoras de plástico – PlasticEurope (2015), entre os anos de 2004 e 2014, ocorreu um aumento na produção de plásticos no mundo, de 225 para 311 milhões de toneladas, sendo que a China foi o maior produtor de resinas plásticas em 2014, sendo responsável por 26% do total produzido no mundo. Já a Europa, respondeu por 20% da produção mundial, ao passo que a América Latina respondeu por apenas 5%. Esses dados demonstram que o mercado de resinas plásticas mesmo com as crises econômicas mundiais, continua em franco crescimento.

O relatório mostra, ainda, que o setor de embalagens é o maior consumidor de plásticos. Das 311 milhões de toneladas produzidas em 2014, 39,5% foi absorvida pelo setor de embalagens. Quanto aos tipos de resinas, o polipropileno foi a resina mais produzida em 2014, correspondendo a 19,2 % da produção total, seguida pelo polietileno de baixa densidade e polietileno linear de baixa densidade, que responderam por 17,2 %. Esses dados demonstram a importância econômica das resinas plásticas na economia, bem como a extensão de sua presença em nossa vida cotidiana.

Porém, esse grande volume no uso de plásticos vem causando sérios problemas ambientais, pois uma grande quantidade das resinas plásticas produzidas não é reciclada, se tornando um problema ambiental ao ser destinada a aterros sanitários ou disposta no meio ambiente, sem uma preocupação com suas consequências a longo prazo. De acordo com dados do CEMPRE – Compromisso Empresarial para Reciclagem (2015), no ano de 2011, cerca de 21,7 % do plástico foi reciclado no Brasil, representando 953 mil toneladas, sendo que o país campeão em reciclagem foi a Suécia, com 53 % dos polímeros reciclados. Isso demonstra que, mesmo em países desenvolvidos, a quantidade de reaproveitamento das resinas plásticas pode ser considerado baixo.

Esse fato, juntamente com o aumento da consciência ambiental e uma iminente crise do petróleo, fomentou a busca por substituintes as resinas plásticas convencionais, que sejam preferencialmente oriundas de fontes renováveis e que sejam totalmente biodegradáveis. Assim, ocorreu o surgimento de uma nova classe de polímeros biodegradáveis, sendo que alguns ainda são derivados do petróleo mas com modificações em suas cadeias carbônicas para que possam ser biodegradáveis, como o PBAT – Poli(butileno adipato co-tereftalato), ou o PVA – Poli(vinil álcool), outros polímeros obtidos por vias biotecnológicas como o PLA – Poli(ácido lático), ou a classe dos PHA's – Poli(hidroxi alcanoatos), que são um grande grupo de polímeros biodegradáveis originados de fermentação microbiana, mas uma classe muito importante é segundo Averous & Boquillon (2004) a dos agropolímeros ou biomassa de origem agrícola, que corresponde aos polissacarídeos como o amidoou pectina, bem como proteínas como a zeína. A principal vantagem dos agropolímeros é o fato de serem totalmente renováveis e biodegradáveis.

Dentre os agropolímeros, o amido é um polímero que se destaca, pois que apresenta baixo custo e grande escala de produção, bem como o fato de apresentar um comportamento semelhante ao dos polímeros termoplásticos convencionais, durante o processo de extrusão. Assim é uma opção economicamente viável para a substituição das resinas petroquímicas convencionais. Entretanto, os materias baseados somente em amido apresentam algumas desvantagens, sendo as principais uma baixa resistência à umidade e pobres propriedades mecânicas e de barreira, que acabam por inviabilizar seu uso. Para superar esses inconvenientes, uma opção é o desenvolvimento de blendas poliméricas entre o amido e outros polímeros, visando uma melhoria nas propriedades do material obtido. Na literatura é possível encontrar o amido em blendas com diversos polímeros como PBAT, PLA, PHB, PVA entre inúmeros outros.

Uma blenda que pode apresentar potencialidades é a de amido com PVA pois, ao contrário da maioria dos polímeros pesquisados para uso em blendas com amido, o PVA é hidrofílico. Assim, ocorre uma maior interação natural entre os polímeros, não sendo necessário o uso de compatilizantes, como em blendas com o PBAT (OLIVATOet al. 2013b) ou com o PLA (SHIRAI et al., 2016).

Porém os trabalhos com blendas de amido e PVA, processadas por extrusão termoplástica, são escassos na literatura, sendo necessário o desenvolvimento e um maior estudo do comportamento do PVA com o amido durante o processo de extrusão. Esse estudo já foi iniciado em trabalhos anteriores (ZANELA et al, 2015a; ZANELA et al., 2015b.

O objetivo deste trabalho foi o desenvolvimento de materiais biodegradáveis baseados em amido de mandioca e PVA, por técnicas de processamento de polímeros utilizados na indústria (extrusão e injeção de termoplásticos), visando a produção de materiais com melhores propriedades mecânicas e de barreira, que tornem esses novos materiais biodegradáveis uma opção aos termoplásticos convencionais. Foram estudadas variáveis de processo como temperatura e velocidades de rosca, diferentes formulações, bem como a influência de PVA com diferentes tamanhos de cadeia e graus de hidrólise nas propriedades dos materiais obtidos, sendo ainda avaliado o uso de amidos com diferentes modificações em blendas com o PVA e, pôr fim, a formulação de compósitos de amido e PVA, com a adição de fibras de aveia como reforço, e obtidos por injeção.

Este trabalho está subdividido em nove capítulos organizados da seguinte forma:

- Capítulo 1: Revisão bibliográfica;
- Capítulo 2: Caracterização das diferentes amostras de poli (vinil álcool) e amido utilizados no decorrer deste trabalho, e descrição dos equipamentos de extrusão utilizados;
- Capítulo 3: Avaliação das propriedades mecânicas de perfis cilíndricos de amido com cinco diferentes amostras de poli (vinil álcool) através de análise multivariada para seleção do PVA com melhores propriedades mecânicas para a próxima etapa do trabalho;
- Capítulo 4: Uso de planejamento de mistura para avaliar as propriedades de blendas com diferentes proporções de amido, poli (vinil álcool) e glicerol obtidos por extrusão plana.
- Capítulo 5: Avaliação do efeito da massa molecular do PVA e do perfil de temperatura de extrusão nas propriedades de laminados biodegradáveis obtidos por extrusão em blendas de amido e poli (vinil álcool);
- Capítulo 6: Avaliação do efeito do grau de hidrólise e tamanho de

cadeia do PVA em laminados biodegradáveis de amido/poli (vinil álcool), obtidos por extrusão;

- Capítulo 7: Efeito do uso de diferentes amidos modificados em blendas com poli (vinil álcool) nas propriedades de laminados biodegradáveis obtidos por extrusão;
- Capítulo 8: Efeito do uso de amidos catiônicos com diferentes graus de substituição em blendas de amido e poli (vinil álcool) nas propriedades de laminados biodegradáveis obtidos por extrusão;
- Capítulo 9: Efeito da adição de fibras de aveia no desenvolvimento de materiais biodegradáveis baseados em blendas de amido nativo e catiônico com poli (vinil álcool), obtidos pelo processo de injeção termoplástica.

CAPÍTULO 1 – REVISÃO BIBLIOGRÁFICA

1. POLÍMEROS BIODEGRADÁVEIS

Há uma busca crescente pela redução dos resíduos plásticos em quase todos os países, visando reduzir os impactos da poluição ambiental causada pelos plásticos, motivado também por uma eminente crise do petróleo que é a matéria prima dos polímeros convencionais. Uma solução para esse problema é a substituição desses polímeros por outros que sejam totalmente biodegradáveis e, consequentemente, não causem danos ao meio ambiente. Entretanto, esses novos polímeros têm custos mais elevados, além de apresentarem alguns inconvenientes para o seu uso quando comparados aos termoplásticos convencionais, fazendo-se necessária a melhoria de algumas características desses novos polímeros para que se tornem competitivos frente aos polímeros convencionais (BORDES, POLET & AVÉROUS, 2009). Dentre as alternativas para a redução dos custos desses polímeros, uma que se mostra promissora é a blenda de polímeros biodegradáveis de menor custo como o amido, por ser uma macromolécula abundante, de baixo custo frente aos polímeros petroquímicos biodegradáveis, renovável e biodegradável (OLIVATO et al., 2014; MALI et al., 2010).

De acordo com Chandra & Rustigi (1997), vários órgãos internacionais de normatização produziram definições para plásticos biodegradáveis, segundo a ISO 472:1988: o plástico para ser considerado biodegradável deve ser passível de sofrer alterações significativas em sua estrutura química sob condições ambientais específicas, que resultem na perda das propriedades desse material. As mudanças na estrutura química do material são resultantes da ação de microrganismos de ocorrência natural. A norma D6400 da ASTM traz duas definições distintas, para plásticos biodegradáveis e para plásticos compostáveis, definindo os plásticos biodegradáveis como materiais que são degradados pela ação de microrganismos, de ocorrência natural, como bactérias, fungos e algas. Já os materiais compostáveis são aqueles em que a degradação ocorre por um processo biológico durante a compostagem, produzindo CO_2, água, compostos inorgânicos e biomassa, em uma taxa consistente com outros materiais compostáveis, resultando em resíduos não distinguíveis e tóxicos.

Os polímeros biodegradáveis normalmente são degradados por um mecanismo de hidrólise seguida de um processo de oxidação. Inicialmente ocorre a desintegração, depois a quebra em moléculas de tamanho menor, formando como produtos finais CO_2 em condições aeróbicas (ou CH_4 em condições anaeróbicas), água e energia para os microrganismos (KRZAN et al., 2006). Porém a cinética de biodegradação dos polímeros é dependente do tipo de polímero utilizado (massa molecular, cristalinidade e estrutura) e dos aditivos utilizados (por exemplo, o plastificante utilizado) (GUILBERT & GONTARD, 2005), bem como do ambiente em que esse material foi disposto, em um aterro sanitário ou corpo hídrico por exemplo.

Avérous & Boquillon (2004) propuseram a subdivisão dos polímeros biodegradáveis em quatro grupos, levando-se em conta a sua origem biológica e tecnológica: como biomassa de origem agrícola (agropolímeros): subdivididos em polissacarídeos como o amido ou proteínas como a gelatina; produtos de fermentação microbiana (obtidos por extração): nesse grupo se enquadram os polihidroxialcanoatos (PHA) como o polihidroxibutirato (PHB); produtos biotecnológicos: são produzidos por via biotecnológica, mas que necessitam de uma etapa de síntese ou polimerização convencional como, por exemplo, o poli (ácido lático); Produtos de origem petroquímica: são produzidos por processos de síntese convencional a partir de monômeros sintéticos, como por exemplo a policaprolactonas (PCL) e os co-poliésteres aromáticos como o poli (adipato co-tereftalato de butileno) (PBAT).

O maior empecilho no uso extensivo de polímeros biodegradáveis está em seu alto custo quando comparado aos polímeros petroquímicos convencionais, sendo assim as aplicações reais ainda são limitadas a nichos de mercado, devido ao marketing ambiental ou a uma propriedade em particular do material. Entretanto, novas pesquisas estão surgindo, demonstrando a possibilidade de uso dos polímeros biodegradáveis com vantagens em comparação aos polímeros convencionais, como por exemplo, na agricultura, para produção de filmes biodegradáveis de cobertura de solo (mulch film) que apresenta como vantagem o fato de não necessitar ser retirado do solo após a colheita (BILCK et al., 2010) e sacos para mudas, que pode ser plantada em seu saco, reduzindo uma etapa no plantio e evitando a geração de resíduos (BILCK et al., 2014).

O uso de sacolas biodegradáveis também pode ser uma vantagem funcional importante, pois geralmente essas sacolas são utilizadas para se depositar lixo para a coleta urbana. Olivato et al. (2013a) produziram sacolas plásticas baseadas em amido de mandioca e PBAT, as sacolas produzidas atenderam plenamente as normas brasileiras de qualidade, podendo assim serem utilizadas sem maiores problemas de resistência.

A indústria de alimentos é uma área onde os materiais biodegradáveis podem encontrar um grande número de aplicações, por exemplo, em redes de "fast food" onde o tempo de uso das embalagens antes da disposição é muito curto, ou como embalagens ativas, carregando componentes antimicrobianos ou antioxidantes por exemplo (BIERHALZ, da SILVA & KIECKBUSCH, 2012; FLORES et al.; 2010; ANDRADE-MOLINA et al., 2013; SALGADO et al., 2010).

A opção mais pesquisada para a redução de custos dos polímeros biodegradáveis é sua blenda com outros polímeros biodegradáveis, mas de fontes naturais e renováveis, que apresentem ainda custos mais baixos, como por exemplo, o amido, que pode ser originado de várias espécies de tuberosas ou cereais amiláceos, sendo as principais fontes de amido o milho e a mandioca. Essas blendas com o amido podem resultar em materiais com menor custo, que possam ter melhores condições de competir com os polímeros petroquímicos convencionais.

2. AMIDO

O amido é a principal fonte de reserva de carbono das plantas, sendo o produto final da fotossíntese, é armazenado no interior de estruturas denominadas de amiloplastos. Quimicamente, o amido é um carboidrato polimérico constituído de unidades de glicose unidas por ligações glicosídicas. Entretanto o amido apresenta diferenças significativas em sua estrutura dependendo de qual a sua fonte botânica, sendo possível observar variações dentro das mesmas fontes, o amido é um biopolímero de glicose constituído por duas cadeias distintas, uma linear (amilose) constituída por monômeros de glicose unidos por ligações α-(1-4) e uma ramificada (amilopectina), que é altamente ramificada e formada por cadeias α-(1-4) curtas unidas por ligações α-(1-6) nas ramificações.

A Figura 1 apresenta as estruturas químicas e a representação esquemática das cadeias de amilose e amilopectina.

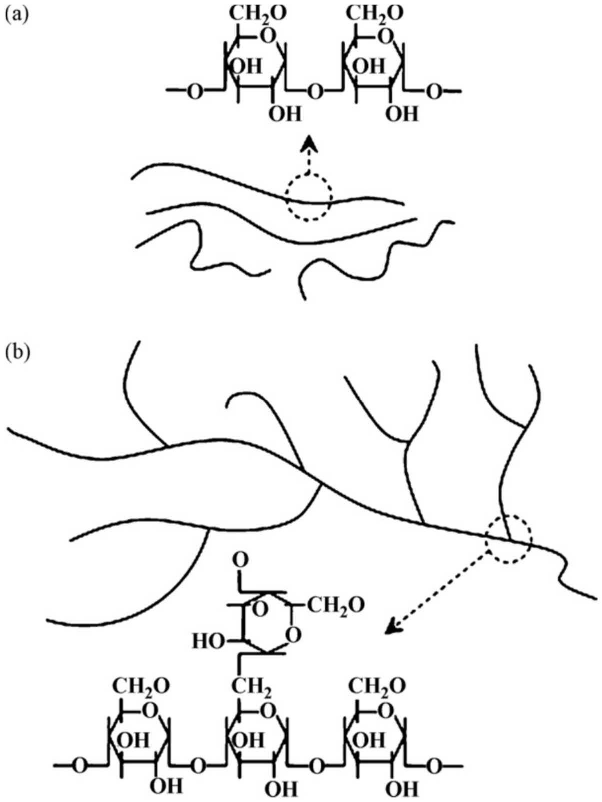


Figura 1. Estruturas químicas e representações esquemáticas da amilose (a) e amilopectina (b). (Fonte: LIU et al., 2009)

A estrutura linear da amilose concede a ela um comportamento mais próximo ao obtido nos polímeros sintéticos. Já a amilopectina é um polímero ramificado muito maior que a amilose, com massa molecular na casa de milhões de g.mol^{-1}. Devido à alta massa molecular e a estrutura ramificada da amilopectina, ocorre a redução da mobilidade das cadeias poliméricas, interferindo com a tendência das cadeias estarem próximas o suficiente para permitir níveis significantes de pontes de hidrogênio entre elas (LIU et al., 2009). Essa diferença estrutural faz com que as cadeias de amilose e a amilopectina se distribuem em camadas sucessivas no entorno do núcleo, conferindo ao grânulo de amido um caráter semicristalino, com a presença de regiões mais ordenadas devido a uma maior concentração de amilopectina (regiões cristalinas da molécula), e regiões onde a amilose encontra-se em maior quantidade (região amorfa).

Diversas fontes botânicas de amido já foram pesquisadas na literatura para a produção de materiais biodegradáveis, sozinhos ou em blendas com outros polímeros, como o amido de mandioca (LARONTONDA et al., 2005; RHAMAN et al., 2010; MÜLLER, YAMASHITA & LAURINDO, 2008; OLIVATO et al., 2014, ZANELA et al., 2015b), milho (LÓPEZ et al., 2011; GALICIA-GARCÍA et al., 2011; REDDY & YANG, 2010), batata (CYRAS, ZENKLUSEN & VAZQUEZ, 2006; HU, CHEN & GAO, 2009), ervilha (CHEN et al., 2008; CANO et al., 2015), aveia (GALDEANO et al., 2009) dentre outros.

A Nigéria é o maior consumidor de mandioca do mundo atualmente, com uma estimativa de consumo de 67.100 mil toneladas no ano de 2015 (TONUKARI et al, 2015), sendo a África como um todo um grande produtor e consumidor de mandioca. Porém uma diferença da África com as outras regiões produtoras é a destinação, onde aproximadamente 60% da mandioca é utilizada diretamente para consumo humano, sendo a industrialização ainda incipiente, ao contrário das outras regiões produtoras (SEAB, 2015).

No ano de 2013 o Brasil produziu aproximadamente 21,5 milhões de toneladas de raiz, respondendo por 7,8% da produção mundial. Sendo que a estimativa de safra brasileira de raiz de mandioca para o ano de 2015 é de 24.108 mil toneladas, e para o estado do Paraná a estimativa para o ano de 2015 é uma produção de 4.212 mil toneladas que correspondem a 17,5% da produção nacional, sagrando o estado como o maior produtor nacional. Para a fécula de mandioca a estimativa de produção do ano de 2015 no Brasil é de 730 mil toneladas, sendo o Paraná o estado com maior produção, representando no ano de 2014 por 70% da produção brasileira de fécula. Os principais consumidores de fécula de mandioca no ano de 2014 foram a panificação (21,6%), atacadistas (21,3%), papel e papelão (18,8%) e frigoríficos (11,8%) (SEAB, 2015).

Segundo relatório do CEPEA (2015), o preço médio praticado no Paraná para o período de 23 – 27 de novembro de 2015 para a tonelada de raiz e fécula de mandioca foi de R$ 217,73 e R$ 1.425,94 respectivamente. O valor da fécula mostra a potencialidade para seu uso na produção de materiais biodegradáveis, pois seu preço (R$ 1,42 / kg) é muito inferior ao das resinas plásticas biodegradáveis disponíveis atualmente no mercado.

2.1 Amidos Modificados

A realização de modificações na molécula de amido é necessária quando o amido nativo não apresenta propriedades adequadas para o uso desejado, como viscosidade, temperatura de gelatinização ou retrogradação, assim, as modificações no amido aumentam sua gama de aplicações seja para usos alimentares ou não.

As modificações em amidos podem ser feitas por métodos físicos ou químicos, os métodos físicos são feitos com o uso de calor e umidade (amidos pré-gelatinizados, por exemplo), já as modificações químicas dos amidos envolvem a introdução de grupos funcionais nas moléculas de amidos (esterificação ou presença de ligações cruzadas no amido, por exemplo) ou de decomposições (amidos hidrolisados ou oxidados, por exemplo) (LÓPEZ, ZARITZKI & GÁRCIA, 2010). A modificação química envolve a introdução de grupos funcionais na molécula de amido, porém, sem afetar a morfologia ou a distribuição de tamanho dos grânulos (ALCÁZAR-ALAY & MEIRELES, 2015).

Algumas das diversas modificações químicas que podem ser realizadas em amidos estão sucintamente discutidas abaixo:

Fosfato de di-amidos: Consiste na reticulação (formação de ligações cruzadas) e ocorre quando uma cadeia que pode ser linear ou ramificada é covalentemente ligada a outra cadeia de amido; os reagentes utilizados nessa reação formam ligações éter ou éster com o grupamento hidroxipropila da molécula de amido. Essa modificação aumenta a rigidez estrutural do amido pelo aumento da rede polimérica tridimensional das cadeias de amilose e amilopectina, promovendo ainda o aumento do grau de polimerização e da massa molecular e reduzindo a solubilidade em água do amido (ALCÁZAR-ALAY & MEIRELES, 2015). De acordo com Singh, Kaur & MacCarthy (2007), os reagentes utilizados para a esterificação do amido é o trimetafosfato de sódio ou oxicloreto de fósforo.

Fosfato de di-amido acetilado: a acetilação é a modificação da molécula de amido pela adição de grupos funcionais acetil (CH_3CO) que reagem com os grupos hidroxilas livres presentes nas cadeias ramificadas do amido para a formação de um éster. A acetilação modifica o grânulo de amido, reduzindo a tendência a retrogradação, e aumentando a solubilidade e a viscosidade da pasta de amido (ALCÁZAR-ALAY & MEIRELES, 2015). O fosfato de di-amido acetilado consiste em uma modificação dupla do amido, baseado na esterificação com trimetafosfato de sódio ou oxicloreto de fósforo (formação do fosfato de di-amido) combinado com a esterificação com anidrido acético ou acetato de vinila (acetilação do amido) (SING, KAUR & MAcCARTHY, 2007).

Adipato de di-amido acetilado: De acordo com Singh, Kaur & MacCarthy (2007) a formação do adipato de di-amido acetilado consiste na esterificação do amido com anidrido acético e anidrido adípico. Essas modificações no amido de acordo com Gonzáles & Pérez (2002) e Mali & Grossmann (2001), promovem um aumento da viscosidade, solubilidade, coesividade, adesividade, e ainda a redução da temperatura inicial de gelatinização do amido.

Amidos oxidados: Os amidos oxidados têm atraído atenção nos últimos anos devido ao fato de serem utilizados em diversas aplicações tanto para alimentos como para usos em outras áreas. A oxidação do amido envolve a introdução dos grupos funcionais carboxila e carbonila e subsequentemente a despolimerização do amido (ASHOGBON & AKINTAYO, 2014). O hipoclorito de sódio é o agente oxidante mais utilizado na produção de amidos oxidados, mas muitos outros oxidantes podem ser utilizados, como peróxido de hidrogênio, permanganato de potássio, ácido peracético, persulfatos, dicromatos dentre outros (MOAD, 2011; ALCÁZAR-ALAY & MEIRELES, 2015).

Amidos Catiônicos: os amidos catiônicos são utilizados principalmente na indústria de papel e celulose, sendo utilizados para dar resistência a seco ao papel. Os amidos catiônicos são geralmente produzidos pela reação entre o amido e compostos contendo sais terciários ou quaternários de amônio, grupamentos amina, fosfato dentre outros (ALCÁZAR-ALAY & MEIRELES, 2015). O processo de cationização pode ser realizado por via seca ou úmida, e geralmente o processo por via úmida produz amidos catiônicos com graus de substituição mais elevados (ASHOGBON & AKINTAYO, 2014). Segundo os mesmos autores, geralmente as propriedades físico-químicas e a morfologia do grânulo de amido costuma ser alterado após a cationização, principalmente quando se usa graus maiores de substituição. Amidos catiônicos costumam apresentar tipicamente baixas temperaturas e altas viscosidades de pasta (KUO & LAI, 2007).

3. PROCESSO DE EXTRUSÃO

A extrusão termoplástica é um processo térmico, que pela combinação de calor, umidade e trabalho mecânico provoca mudanças substanciais nas matérias-primas, alterando suas formas, estruturas e características funcionais.

Segundo Manrich (2005), durante o processo de extrusão ocorre a mistura e o transporte do material por meio de uma rosca sem-fim. O movimento da rosca é capaz de fundir, homogeneizar e plastificar o polímero. É devido ao movimento, e consequente cisalhamento sobre o material, que uma extrusora monorosca gera cerca de 80% da energia térmica e mecânica necessária para transformar os polímeros, sendo que o restante da energia é obtido por meio de aquecedores externos.

A Figura 2 apresenta uma representação esquemática de uma extrusora monorosca.

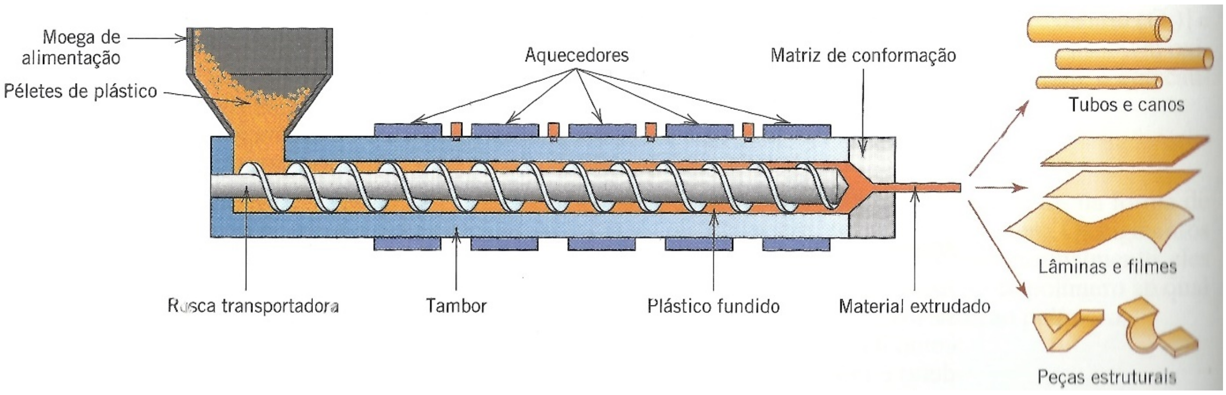


Figura 2. Representação esquemática de uma extrusora monorosca. (Fonte: CALLISTER & RETHWISCH, 2012).

O material a ser processado, que pode ser na forma de pó, grânulo ou pellet, é introduzido na extrusora pelo funil (ou moega). O canhão e a rosca são responsáveis pela homogeneização e a transferência de calor para o material a ser processado, devendo os mesmos possuir tamanho adequado para possibilitar a completa fusão do material, o aquecimento externo complementar do polímero é feito por meio de resistências elétricas fixadas na parte externa do barril. A rosca é a responsável pelo cisalhamento, compressão e homogeneização do polímero, sendo que há várias configurações de roscas dependendo do tipo de material e do objetivo final. Segundo Mercier (1994), o tipo de rosca mais utilizada é o sistema de três zonas que é apresentado esquematicamente na Figura 3. A primeira é a zona de entrada (função de transporte do material), a segunda é a zona de compressão (promovendo a compactação e fusão do material devido ao atrito entre as cadeias poliméricas a rosca e o barril) e a última é a zona de calibragem ou de dosagem onde o material é homogeneizado e elevado à temperatura de processamento desejado. Uma característica importante é a relação entre comprimento e diâmetro da rosca (relação L/D), que permite estimar a potência da rosca.

Figura 3. Esquema de uma rosca com três zonas de aquecimento. (Fonte: RODA, 2015).

A função de cada uma das três zonas de uma rosca de termoplásticos é dada abaixo de acordo com Oréfice (2012):

Zona de alimentação: região da extrusora onde o polímero geralmente em forma de pellet é introduzido, promove o aquecimento e o transporte do material para as outras zonas. Em geral, o sulco da rosca é constante;

Zona de compressão: nessa região da rosca a profundidade do canal tende a ser reduzida ao longo do parafuso, sua função é retirar o ar entre os pellets, aumentar a condução térmica, já que o contato aumenta entre o material e a parede e a compressão do material (aumento da pressão);

Zona de calibragem: o sulco do parafuso tem uma profundidade constante, sua função é a de homogeneizar a massa polimérica fundida e manter o material em condições de temperatura e pressão constantes.

Ao final da rosca é necessário que haja uma restrição para gerar pressão, evitando que o material saia distorcido ou espiralado, devido ao movimento da rosca. No cabeçote (conjunto que fica à frente da rosca) se encontra a matriz, que é responsável pelo perfil do extrudado. A ação da passagem do material em estado fundido pela matriz, em conjunto com o trabalho da linha de acabamento (tracionadores, bobinas e injeção de ar comprimido) são fatores importantes para as formas e propriedades do produto final.

São várias as formas de processamento de polímeros pelas indústrias, sendo as mais utilizadas a extrusão por sopro em balão, extrusão plana (calandragem) e a injeção.

No processo de extrusão plana, após sair da extrusora, o polímero fundido é forçado através de uma matriz plana, que em conjunto com a tração aplicada pela calandra determina a espessura e a largura do filme. O material ainda em estado fundido passa pela calandra, que é formada por cilindros metálicos e tem a função de resfriar e dar polimento ao filme. Há ainda outros periféricos de extrusão como os puxadores e bobinadeiras, que podem ser vistos na representação esquemática de uma planta de extrusão plana (Figura 4).

Após o polímero passar pela matriz, ele é tracionado por uma curta distância e resfriado rapidamente ao entrar em contato com os rolos da calandra, que recebem resfriamento, promovendo a solidificação do polímero. O controle da espessura e da largura do material pode ser difícil dependendo das condições de operação, pois a velocidade de saída do material da matriz é inferior a velocidade dos rolos da calandra, assim, a calandra promove uma força elongacional no material fundido, e qualquer mudança na razão de saída do material da matriz promoverá alterações na espessura e largura do material final. Os defeitos durante o processo de calandragem 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 (SOLLOGOOG, DEMAY & AGASSANT, 2006; SAKAKI et al., 1996).

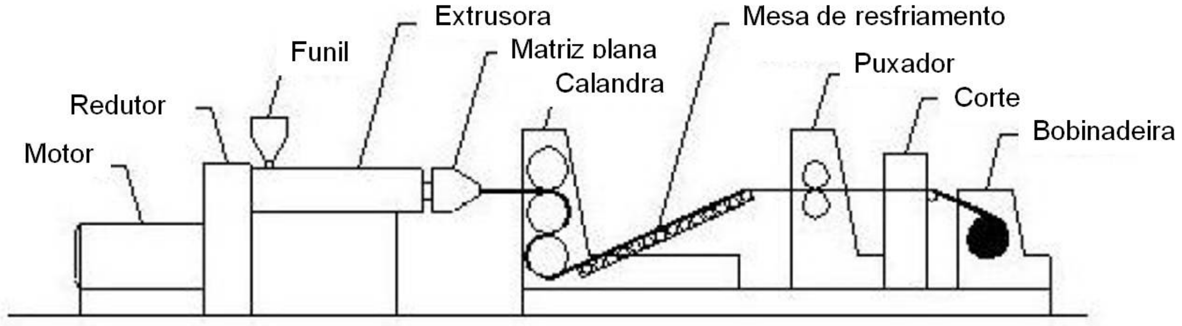


Figura 4. Representação esquemática de uma extrusora plana. (Fonte: VIDAL, 2011).

O processo de produção de materiais poliméricos por extrusão plana apresenta como vantagem quando comparado com a extrusão por sopro em balão a possibilidade da produção de materiais com maior espessura e o processamento de materiais que não apresentam resistência mecânica suficiente para o processo de formação por sopro em balão, pois as forças elongacionais sofridas pelo material fundido na calandra são inferiores às sofridas no processamento por balão.

Galicia-García et al. (2011) produziu pelo processo de extrusão plana filmes biodegradáveis de amidos nativos de milho, milho ceroso, batata e amido fosforilado de milho, 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. Resultados semelhantes foram obtidos por Zanela et al. (2015a) e Zanela et al. (2015b), em filmes de amido de mandioca e álcool polivinílico plastificados com glicerol e obtidos por extrusão plana acoplada a um extrusora dupla rosca.

Outra forma de processamento de materiais poliméricos é a moldagem por injeção, que de acordo com Askeland & Phulé (2008), consiste no aquecimento do material termoplástico acima da sua temperatura de fusão por meio de uma extrusora e injetado sob pressão em uma matriz para a produção de uma peça moldada, um pistão a ar ou um mecanismo de rosca pressiona o polímero em estado fundido para dentro da matriz. Segundo Callister & Rethwisch (2012), uma característica dessa técnica é a alta velocidade na qual as peças podem ser produzidas, para os materiais termoplásticos, a solidificação da carga injetada é quase imediata, consequentemente os tempos de ciclo são curtos (na ordem de 10 a 30 segundos).

Oréfice (2012) cita como vantagens da moldagem por injeção a grande velocidade de injeção e volume de produção, baixo custo com mão-de-obra por unidade, a possibilidade de utilizar automação nos equipamentos, produção de peças com tamanhos e formas variadas, e como desvantagens do método podem ser citadas o custo elevado dos moldes e equipamentos de injeção, o controle de processo e qualidade dos produtos finais é dependente de capacitação técnica.

Uma diferença do processamento por sopro em balão ou calandragem quando comparados com o processo de injeção é devido ao fato de que o processo de injeção é cíclico e não contínuo como os outros dois processos mencionados.

Um ciclo completo de injeção consiste segundo Oréfice (2012) nas seguintes operações:

- O parafuso empurra (sem rodar) o polímero fundido para o molde, ficando nessa posição até o resfriamento do polímero no canal de injeção;

- O parafuso começa a girar para o carregamento do parafuso com o polímero sólido que irá se fundir, enquanto o parafuso é carregado a peça no interior do molde está sendo resfriada;

- Após o completo resfriamento o molde é aberto e a peça é ejetada com a ajuda de pinos ejetores;

- Ocorre o fechamento do molde e o ciclo é reiniciado.

A Figura 5 apresenta um esquema de uma injetora de termoplásticos, onde é possível visualizar suas principais partes, o polímero é alimentado por um funil que faz o carregamento da rosca, após a completa fusão do polímero no interior da rosca a mesma promove a injeção no molde, deslocando-se para frente funcionando como um êmbolo e injetando o polímero no molde que se encontra fechado, o molde promove o resfriamento da peça e posterior ao resfriamento ele se abre e ejeta a peça pronta.

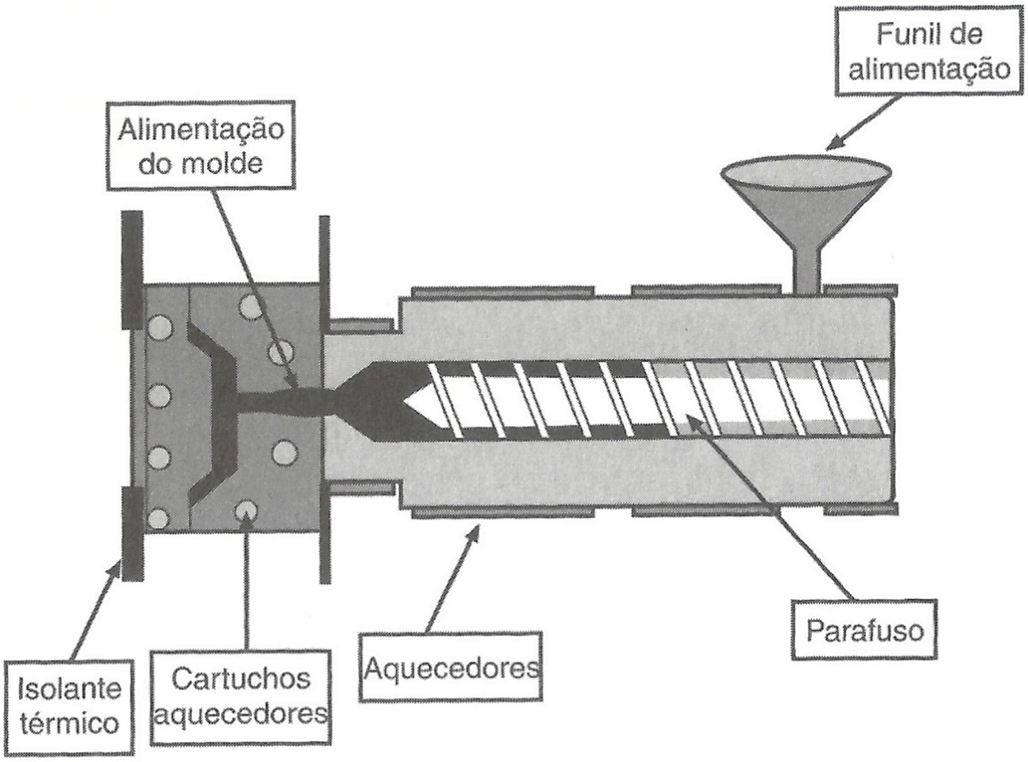


Figura 5. Representação esquemática de uma injetora de termoplásticos. (Fonte: ORÉFICE, 2012).

O uso de amido no processo de injeção apresenta algumas dificuldades, principalmente devido a sua alta viscosidade e propriedades de fluxo pobres, além disso, é difícil de obter parâmetros de injeção confiáveis, pois as formulações podem sofrer variações devido à presença, por exemplo, de água que se evapora durante o aquecimento, dificultando o entendimento do comportamento de fluxo da massa polimérica fundida durante o processo de injeção (LIU et al., 2009).

3.1 Amido Termoplástico (ATp)

O amido não é considerado um termoplástico verdadeiro, mas em presença de um plastificante como a água, temperatura e forças de cisalhamento adequadas fazem com que o amido se funda, permitindo seu uso em injetoras ou extrusoras, semelhantemente aos polímeros sintéticos, após o amido passar por esse processamento, recebe a denominação de amido termoplástico - ATp. Através da alteração da umidade ou da concentração de plastificantes, razão entre amilose e amilopectina na matéria prima, pelo controle da temperatura e pressão na extrusora é possível a obtenção de amidos termoplásticos com diferentes viscosidades, forças mecânicas, solubilidades e taxas de absorção de água (MOHANTY; MISRA & HINRICHEN, 2000).

A perda da estrutura organizada do grânulo de amido é a principal responsável pela conversão do amido em um material termoplástico (LIU et al., 2009). O processamento térmico de materiais baseados em amido envolve múltiplas reações químicas e físicas, como difusão de água, expansão do grânulo, gelatinização, fusão e cristalização.

As propriedades do ATp são dependentes do conteúdo de umidade do material, pois a água age como um excelente plastificante para o amido, portanto o comportamento de um material a base de amido muda de acordo com o teor de umidade presente (VILPOUX & AVÉROUS, 2003).

O processo de perda da estrutura organizada do grânulo de amido é dependente principalmente da temperatura e do conteúdo de umidade do material. Em condições de altos níveis de água presentes no meio o processo de gelatinização ocorre pela atuação direta da água que penetra nos grânulos de amido. Mas devido ao processo de extrusão envolver condições de altas taxas de cisalhamento e alta pressão, a desestruturação do grânulo de amido ocorre com baixos teores de umidade, mas desde que sejam alcançadas forças de cisalhamento fortes o suficiente para romper as estruturas granulares, permitindo uma rápida transferência de água para o interior das cadeias do amido. Portanto, a perda de cristalinidade durante a extrusão não se deve à penetração de água, mas sim pela ruptura mecânica de interações moleculares, provocadas devido às forças de cisalhamento presentes no interior da extrusora. Durante a extrusão com baixo teor de umidade, pequenas quantidades de amido gelatinizado e fundido, bem como a fragmentação do amido coexistem (LIU et al., 2009).

Os principais objetivos da maioria das técnicas de processamento do amido estão baseados na fusão e homogeneização do material, sendo os parâmetros do processo ajustados para minimizar a degradação das cadeias de amido. Entretanto, a fragmentação devido às forças de cisalhamento é inevitável, e o grau de fragmentação durante a extrusão tem relação direta com a velocidade e a configuração da rosca, temperatura, conteúdo de umidade e o tipo de amido processado (LIU et al., 2009). Davidson et al. (1984) observaram que o grau de fragmentação da amilopectina diminuiu com a redução da velocidade da rosca ou do conteúdo de umidade, e aumentou com o aumento da temperatura, corroborando com os resultados obtidos por Wen; Rodis & Wasserman (1990).

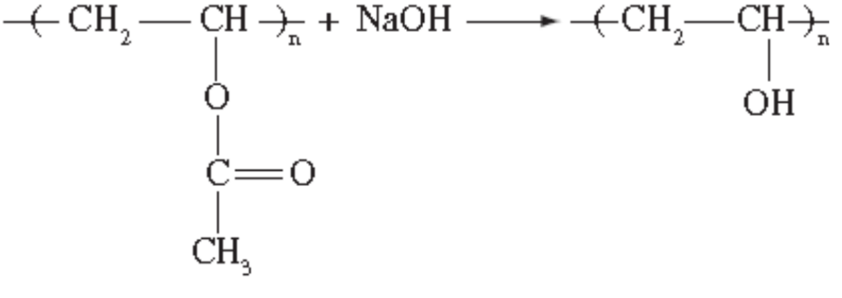
Em escala industrial, usualmente são realizadas duas etapas de processamento para a obtenção dos produtos finais, a primeira etapa de extrusão consiste na produção de pellets onde as resinas, plastificantes e demais aditivos são processados na forma de pellets, e em uma segunda etapa de extrusão, reprocessados para a obtenção do produto final, seja pelo uso de calandra, sopro em balão, injeção ou outra forma de processamento. Podem ainda ocorrer novas etapas de extrusão, caso o material sofra a reciclagem por exemplo. De maneira geral, as resinas termoplásticas convencionais costumam apresentar boa estabilidade após várias etapas de processamento, já o amido, devido a sua estrutura granular, e de grande massa molecular, é passível de sofrer alterações irreversíveis durante o processamento, embora Zanela (2013), observou que não houve perda das propriedades mecânicas após uma segunda etapa de extrusão de filmes de amido de mandioca e poli (vinil álcool) plastificados com glicerol e processados em extrusora dupla-rosca.

O amido termoplástico (ATp) puro não é adequado para produção de materiais biodegradáveis devido sua alta hidrofilicidade e propriedades mecânicas pobres em comparação com os polímeros convencionais (AVÉROUS & BOQUILLON, 2004; MALI et al., 2005). Como a água atua como plastificante, as propriedades do ATp mudam de acordo com a umidade relativa do ar, através de um mecanismo de sorção e dessorção (VILPOUX & AVÉROUS, 2003; MÜLLER, YAMASHITA & LAURINDO, 2008), assim, as propriedades dos materiais obtidos a base de ATp são dependentes das condições do ambiente em que as mesmas se encontram, sendo isso um possível problema. Uma possível solução é a produção de blendas de ATp com outros polímeros biodegradáveis, como por exemplo o poli (vinil álcool) (PVA), visando melhorar as propriedades mecânicas e reduzir o caráter hidrofílico do material obtido.

4. POLI (VINIL ÁLCOOL) (PVA)

O poli (vinil álcool) – PVA (sendo muitas vezes utilizada a sigla PVOH) é uma resina sintética primeiramente obtida por Herrman e Haehnel em 1924, e uma característica que a diferencia da maioria das resinas convencionais é o fato do PVA ser solúvel em água. O PVA é obtido através da hidrólise do poli (vinil acetato), sendo esta a forma de obtenção utilizada até hoje. Suas propriedades básicas são dependentes de seu grau de polimerização e de hidrólise.

O PVA não é obtido por polimerização direta de seu monômero correspondente, pois o álcool vinílico tende a converter-se espontaneamente para a forma enol de acetaldeído. Assim, o PVA é obtido através da polimerização do acetato de vinila, seguida da reação de hidrólise alcalina em solução alcoólica do poli (vinil acetato) levando a formação do poli (vinil álcool) pela eliminação dos grupos acetato na forma de ácido acético. A representação esquemática simplificada da reação está representada na Figura 6.



$$-\!\!(\,CH_2-\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{\underset{O}{|}}{CH}\,)_n + NaOH \longrightarrow -\!\!(\,CH_2-\underset{\underset{OH}{|}}{CH}\,)_n$$

Figura 6. Obtenção do PVA através da hidrólise alcalina do poli (vinil acetato).

A figura 7 apresenta a cadeia do poli (vinil álcool) totalmente hidrolisado.

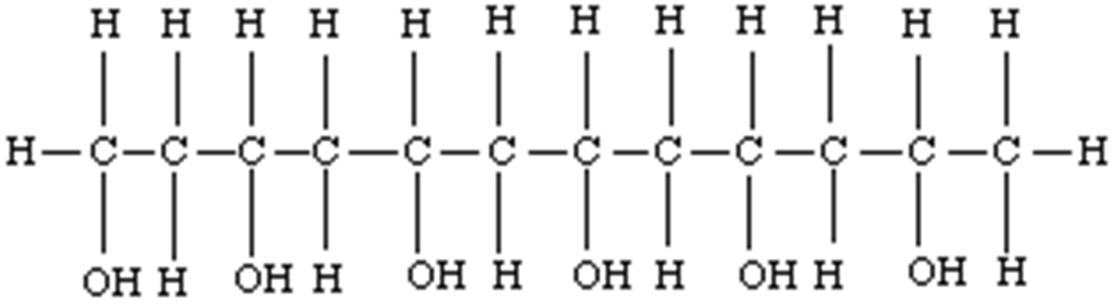


Figura 7. Representação da estrutura do PVA totalmente hidrolisado.

O grau de hidrólise (HD) do PVA é dado como sendo a relação entre o percentual de hidroxilas e o número inicial de radicais ácido acético no copolímero final, muitas propriedades do PVA são dependentes de seu grau de hidrólise. O aumento do HD implica em redução de solubilidade em água, associada ainda a estabilização energética promovida pelas pontes de hidrogênio intra- e inter-cadeias do polímero, no aumento da adesão em superfícies hidrofílicas, viscosidade e resistência à tração (MANSUR & MANSUR, 2008 apud COSTA JÚNIOR & MANSUR, 2008). Outra característica que apresenta influência nas propriedades do PVA é seu grau de polimerização, que se refere ao número de monômeros interligados em cada cadeia polimérica.

PVAs com diferentes especificações são produzidos industrialmente, possuindo diferentes graus de hidrólise (GH) e graus de polimerização (P*n*). Quanto ao grau de hidrólise, geralmente são classificados em parcialmente hidrolisados (acima de 88%) ou altamente hidrolisados (98-99%), e quanto ao grau de polimerização, em baixa viscosidade (até 5 cP), média viscosidade (20-30 cP) e alta viscosidade (40-50 cP) (FINCH, 1973 apud ARANHA & LUCAS, 2001). A Figura 8 apresenta o efeito da massa molecular e do grau de hidrólise nas propriedades de materiais elaborados a base de poli (vinil álcool).

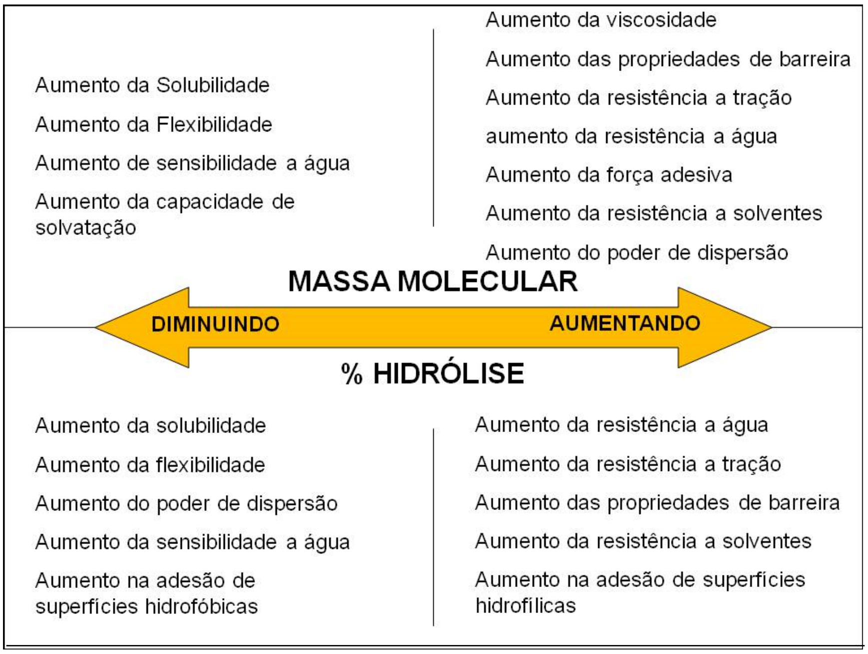


Figura 8. Efeito da massa molecular e do grau de hidrólise sobre as propriedades do PVA. (Fonte: SEKISUI, 2015).

O PVA parcialmente hidrolisado contém grupos residuais de acetato em suas cadeias, que reduzem seu grau de cristalinidade, devido a um impedimento estérico, apresentando geralmente baixos pontos de fusão, melhor processabilidade, menor resistência mecânica e solubilidade em água a temperaturas mais baixas quando comparados com os polímeros totalmente hidrolisados (TANG & ALAVI, 2011).

A natureza cristalina do PVA é de certa forma incomum, uma vez que ele é um polímero atático linear, ou seja, o posicionamento dos grupamentos álcool nas cadeias laterais secundárias é totalmente aleatório, e esta característica, de forma geral, impossibilitaria a formação de cristais entre as cadeias poliméricas. O poli (vinil acetato) não é cristalino devido à presença de grupos acetato, que são maiores que os grupos hidroxila do PVA, ou seja, os grupos acetato impossibilitam a cristalização da molécula devido à dificuldade de arranjo organizado para promover interações entre as cadeias dos polímeros (impedimento estérico), o que não ocorre na molécula de PVA pela presença somente de grupos hidroxila que possuem um menor volume quando comparados aos grupos acetatos, tornando o PVA cristalino. Entretanto, a presença de grupos acetato residuais diminui o grau de cristalinidade e de ligações de hidrogênio devido à sua estrutura mais volumosa (GOODSHIP, 2009), assim, PVAs com menores GH apresentam uma redução de seu grau de cristalinidade quando comparados a polímeros com maior GH.

O PVA tem baixa taxa de biodegradação quando não está em solução e alta permeabilidade ao vapor de água quando comparado com os polímeros convencionais, como polietileno e polipropileno (GOODSHIP, 2009; TANG & ALAVI, 2011).

O PVA é biodegradável quando em solução, mas em geral é biologicamente estável em seu estado sólido. Sua solubilidade é depende de diversos fatores, como os graus de polimerização e de hidrólise. O grau de hidrólise é particularmente importante devido à estrutura química inerente do polímero. A presença de muitos grupos hidroxila significa uma elevada afinidade pela água, porém a presença dos grupos hidroxila leva a formação de ligação de hidrogênio entre os grupos hidroxila do polímero que acarretam em dificultar a hidratação e consequente solubilidade do PVA. Em contraste, os polímeros parcialmente hidrolisados contêm grupos residuais de acetato que promovem um enfraquecimento das ligações de hidrogênio inter-cadeias pelos grupos hidroxila, promovendo o aumento da solubilidade, existindo uma relação diretamente proporcional entre a temperatura de solubilidade com a presença de grupos acetato. Portanto, o PVA apresenta um comportamento complexo quando em solução (GOODSHIP, 2009).

O PVA é utilizado em diversas aplicações industriais, tendo como características o fato de ser inodoro, atóxico, apresentar boa capacidade emulsificante, adesiva e de formação de filme. Seus filmes apresentam boa resistência a gases, óleos e uma série de solventes, além de boas propriedades mecânicas, com alta resistência à tração, compressão, abrasão e boa flexibilidade. As boas propriedades de barreira a gases do PVA são devidas a sua estrutura cristalina monoclínica pequena e densamente empacotada (AKCELRUD, 2007). Entretanto, todas estas propriedades são dependentes do conteúdo de umidade, pois a água atua como um plastificante para o PVA, aumentando, por exemplo, o alongamento e reduzindo a resistência à tração.

Industrialmente, o PVA pode ser utilizado na forma de fibras, adesivos, emulsificantes, protetores de coloides na indústria têxtil e de papel (OKAYA, SUZUKI & KIKUCHI, 1999), imobilização de enzimas (UHLICH, ULBRICHT & TOMASCHEWSKI, 1996). O PVA encontra aplicações também na área médica por ser um polímero atóxico, biocompatível e elástico, podendo ser utilizado na fabricação de lentes de contato, na engenharia de tecidos ou na liberação controlada de fármacos (LI, WANG & HU, 1998; COSTA JÚNIOR & MANSUR, 2008), como carreadores para a liberação de agentes antimicrobianos para embalagens de alimentos (MUPPALLA et al., 2014; JIPA et al., 2012) e na agricultura como filmes de cobertura de solo ("mulch films") (BRIASSOULIS, 1996).

Um fator limitante para uma aplicação mais ampla do PVA é seu custo elevado quando em comparação a outras resinas petroquímicas convencionais como, por exemplo, o polietileno e o polipropileno (TANG & ALAVI, 2011). Assim, uma forma de superar esse problema é o uso do PVA em blendas com outros polímeros biodegradáveis, mas de um menor custo, como o amido, por exemplo, sendo essa uma alternativa que pode viabilizar um uso mais extensivo no PVA com o desenvolvimento de novos nichos de mercado.

5. BLENDAS DE AMIDO E PVA

Blendas poliméricas são definidas de acordo com a IUPAC como uma mistura macroscopicamente homogênea de duas ou mais espécies diferentes de polímeros (WORK et al., 2004).

A blenda de duas ou mais resinas poliméricas com características e propriedades diferenciadas, é feita visando à obtenção de um produto final com propriedades físicas e/ou químicas superiores as que seriam obtidas nos respectivos polímeros puros. O amido tem sido um polímero natural muito estudado e utilizado em blendas com outros polímeros devido ao fato de ter um baixo custo e uma grande disponibilidade no mercado (GOODSHIP, 2009).

O amido já foi inserido com diferentes graus de sucesso em blendas com diversos polímeros biodegradáveis, como o poli (ácido lático) (PLA) (SHIRAI et al., 2013; SHIRAI, ZANELA & YAMASHITA, 2014; YOKESAHACHART & YOKSAN, 2011;); poli (adipato co-tereftalato de butileno) (PBAT) (REIS et al., 2014; BRANDELERO, YAMASHITA & GROSSMANN, 2010; OLIVATO et al., 2012; OLIVATO et al., 2013b; NOBREGA et al., 2013); poli (succinato co-adipato de butileno) (PBSA) (SAKANAKA, 2007; BOCCHINI; BATTEGAZZORE & FRACHE, 2010); polihidroxialcanoatos (PHA), como por exemplo o polihidroxibutirato-co-hidroxivalerato (PHB-HV) (REIS et al., 2008), polihidroxibutirato (PHB) (GODBOLE et al., 2003); policaprolactona (PCL) (ROSA et al., 2004; AVELLA et al., 2000) e poli (vinil álcool) (PVA) (ZANELA et al., 2015a; ZANELA et al., 2015b; CHEN et al., 2008; SIN et al., 2011; TANG & ALAVI, 2012; BRANDELERO et al., 2015).

De acordo com Rahmat et al. (2009), a adição de amido em polímeros sintéticos polares, como o caso do PVA demonstrou uma melhoria nas propriedades físico-químicas dos produtos obtidos.

O amido e o PVA apresentam uma boa compatibilidade quando em blendas poliméricas desses dois polímeros, e isso se deve ao fato de ambos serem substâncias polares e de possuírem grande quantidade de grupamento hidroxila em suas estruturas químicas, que leva a uma tendência a formação de ligações de hidrogênio inter e intramoleculares, melhorando assim a integridade da blenda (TANG & ALAVI, 2011).

Sin et al. (2010c) estudaram as interações em blendas de PVA/amido de mandioca obtidos por *casting* utilizando modelagem computacional e espectroscopia no infravermelho, e observaram que as ligações de hidrogênio entre o PVA e o amido só se formam com uma distância mínima de 3,2 Å, e um ângulo máximo de ligação de 120° e que as interações apresentam altos valores de energia de ligação, demonstrando assim a alta afinidade química entre esses componentes.

De acordo com Tang & Alavi (2011), os primeiros estudos de blendas de PVA e amido foram realizados pela metodologia de *casting*, por ser uma metodologia simples para ser realizada em laboratório. Do ponto de vista econômico, a produção de filmes por *casting* não é viável, principalmente pelo alto custo adicional de processamento e a baixa eficiência do processo quando comparado ao processo de extrusão termoplástica. Entretanto o PVA pode ser degradado no processo de extrusão devido às altas temperaturas e pressões utilizadas no processo. Isso se deve segundo Tsuchiya & Sumi (1969), ao fato do PVA não ser considerado um termoplástico verdadeiro, pois a sua temperatura de fusão excede sua temperatura de degradação. O PVA não plastificado se degrada a aproximadamente 180 °C, enquanto que seu ponto de fusão varia de 180 °C a 240 °C, dependendo do grau de hidrólise. Porém, com o uso de plastificantes adequados, a temperatura de fusão do PVA pode ser reduzida e controlada, melhorando a estabilidade térmica do material e permitindo seu processamento por extrusão termoplástica para a produção de materiais biodegradáveis (BASTIOLI et al., 1995; TANG & ALAVI, 2011).

Os plastificantes mais comumente utilizados são o glicerol e a água, mas muitos outros compostos químicos como, por exemplo: sorbitol, ureia, ácido cítrico bem como plastificantes complexos já foram empregados com sucesso em blendas de amido e PVA (TANG & ALAVI, 2011).

Rhaman et al. (2010) estudaram o comportamento térmico e as interações em blendas de amido de mandioca e PVA plastificados com glicerol e obtidos pelo método de *casting*, e observaram que o glicerol promoveu a redução das temperaturas iniciais e finais de fusão das blendas, a explicação segundo os autores é devido ao fato do glicerol promover uma lubrificação interna entre as cadeias de polímeros reduzindo a rigidez das cadeias e consequentemente a temperatura de fusão.

Mohsin, Hossin & Haik (2011) avaliaram a influência de diferentes percentuais de sorbitol como plastificante (0; 0,5; 1 e 2% m/m) sobre as propriedades térmicas e mecânicas de filmes de PVA produzidos por *casting*. Os autores observaram que as temperaturas de transição vítrea, fusão e decomposição diminuíram proporcionalmente ao aumento das concentrações de sorbitol, variando de 152,9 a 80,2 °C; 230,1 a 200,4 °C e de 331,0 a 296,8 °C quando o sorbitol variou de 0 a 2% respectivamente.

Jang & Lee (2003), avaliaram o comportamento das temperaturas de fusão e cristalização em pellets de PVA com diferentes GH e plastificados com glicerol. Os autores observaram que o pico de temperatura de cristalização do PVA totalmente hidrolisado sofreu uma redução com o aumento do conteúdo de glicerol, enquanto que o PVA parcialmente hidrolisado não apresentou uma mudança significativa desse valor. Os autores observaram ainda que com o aumento do conteúdo de glicerol ocorre a redução da temperatura de fusão, sendo atribuído ao aumento da mobilidade das cadeias de PVA e redução das regiões cristalinas do PVA. Entretanto, com o aumento do conteúdo de glicerol na blenda, a magnitude da redução da temperatura de fusão diminui gradualmente; esse efeito é interpretado como uma redução do efeito plastificante do glicerol com o aumento da concentração presente. Em uma amostra de PVA totalmente hidrolisada esse fenômeno ocorre a cerca de 40 g/100g de polímero (28,57% m/m), já para uma amostra de PVA parcialmente hidrolisado esse fenômeno começa a ocorrer em concentrações de glicerol de 65 g/100g de polímero (39,40 % m/m).

Sin et al. (2010b) determinaram o calor específico por meio da técnica de calorimetria diferencial de varredura (DSC) do PVA totalmente hidrolisado (grau de hidrólise de 99,4 – 99,8%, viscosidade 25 – 30 cP) nativo e plastificado com 40 g/100 g de polímero de glicerol (28,57% m/m). A temperatura de fusão do PVA plastificado (177 °C) foi reduzida em 30 °C quando comparada ao PVA puro (207 °C) devido ao glicerol, que diminuiu a rigidez do material pelo enfraquecimento das interações intermoleculares entre as cadeias de PVA, promovendo uma redução na cristalinidade do material, necessitando assim, de menos energia para alcançar o estado fundido. Entretanto, a energia de aquecimento global do PVA plastificado foi maior que a do PVA nativo. Sendo atribuído segundo os autores à alta rigidez estrutural das moléculas do PVA nativo, que apresentam consequentemente um baixo nível de vibrações moleculares. O glicerol é capaz de reduzir a rigidez estrutural do PVA por atuar como um plastificante, o que acaba por induzir uma maior vibração das moléculas aumentando assim os valores de calor específico para que ocorra a fusão. O calor específico na faixa de temperatura de 57 a 257 °C variaram de 2.293 a 7.718 e de 3.261 a 14.677 $J.g^{-1}.K^{-1}$ para o PVA nativo e plastificado, respectivamente.

Já ao avaliar o calor específico de blendas de PVA e amido de mandioca plastificados com glicerol (40 g/100 g de polímero) com o PVA nas proporções de 30 e 40 % em relação à massa total de polímero, Sin et al. (2010a) observaram que a blenda com 40 % de PVA requereu mais energia para alcançar o estado fundido, porém globalmente a blenda com 30 % de PVA apresentou os maiores valores de calor específico. A explicação para o fenômeno, de acordo com os autores, é a menor rigidez das cadeias poliméricas e consequentemente maior mobilidade vibracional devido aos menores percentuais de PVA na blenda. Para a faixa de temperatura de 57 a 257 °C o calor específico variou de 2.963 a 14.995 e de 2.517 a 14.727 $J.g^{-1}.K^{-1}$ para as blendas com 30 e 40% de PVA respectivamente, valores finais superiores quando comparados com o PVA puro, e semelhantes ao PVA plastificado, sendo possível observar que a blenda de amido e PVA possui menor rigidez molecular quando comparado com o PVA puro, sendo necessária maior quantidade de energia para promover a fusão do material.

Sin et al. (2010d) estudaram a reologia e o estado de transição de fases de blendas de PVA e amido de mandioca, utilizando um PVA totalmente hidrolisado (99,4 a 99,8% de hidrólise e viscosidade 25-30 cP) processados por extrusão em um reômetro capilar. Foi observado que o amido promoveu uma redução no nível de cristalinidade do PVA, corroborando com a afirmação de que o PVA é um polímero que pode melhorar a processabilidade do amido termoplástico.

Yoon, Chough & Park (2006) estudaram o efeito de plastificantes com diferentes grupos funcionais sobre as propriedades físicas de blendas de amido de milho e PVA feitos por *casting*, aos filmes contendo 5% de cada polímero (m/m), foram adicionados glicerol (3 grupos hidroxila), ou ácido succínico (2 grupos ácido carboxílico), ou ácido málico (1 grupos hidroxila e 2 grupos ácido carboxílico) ou ácido tartárico (2 grupos hidroxila e 2 grupos ácido carboxílico), e um tratamento com adição simultânea de glicerol e ácido succínico. Através das análises de tensão na ruptura e elongação observou-se que ambos os grupos funcionais melhoraram a flexibilidade e a resistência dos filmes. Sendo observado, além disso, que quando grupos hidroxila e ácido carboxílico são adicionados simultaneamente, a resistência à tração e a elongação dos filmes aumentam em comparação a filmes contendo somente glicerol que possui apenas grupamentos hidroxila.

Resultados semelhantes foram observados por Park et al. (2005) ao avaliarem as propriedades mecânicas de filmes formados por *casting* de blendas de amido de milho e PVA (5% m/m de cada polímero) com a adição de glicerol, sorbitol e ácido cítrico (0, 10, 20, 30, 40 e 50% m/m do total de polímeros). A resistência à tração e o alongamento foram superiores nos filmes contendo ácido cítrico como plastificante, sendo atribuído esse aumento a presença de grupos hidroxila e carboxila que aumentam as interações inter e intramoleculares entre o amido e o PVA.

O ácido cítrico tem dupla função, podendo atuar também como um reticulante, conforme observado no trabalho de Reddy & Yang (2010), que obtiveram filmes de amido de milho por *casting*, plastificados com glicerol e reticulados com ácido cítrico utilizando hipofosfito de sódio como catalisador. Os filmes obtidos mostraram uma diminuição em sua solubilidade em água e resistência à tração até 150% superior de que os filmes não reticulados. Zhou et al. (2009) reticularam superficialmente com radiação ultravioleta filmes de PVA e amido de milho utilizando benzoato de sódio como fotossensibilizador. A reticulação superficial reduziu a hidrofilicidade superficial do material, e promoveu um aumento na resistência à tração e módulo de Young dos filmes, e reduziu a elongação na ruptura e a solubilidade em água.

Shi et al. (2008) estudaram os efeitos do ácido cítrico sobre as propriedades mecânicas de blendas de PVA e amido de milho elaboradas por *casting* a alta temperatura. Foi utilizado PVA totalmente hidrolisado (99%) e amido de milho que foram misturados na proporção de 3:1 (m/m) respectivamente, sendo adicionados glicerol (20% m/m base seca dos polímeros) e ácido cítrico (5 – 20% m/m em base seca dos polímeros), as amostras foram secas em estufa com ventilação forçada a 140 °C por uma hora. Através da análise de FT-IR foi observado a ocorrência de reticulação com o ácido cítrico e que esta ocorreu preferencialmente com o amido, com o ácido cítrico residual atuando como plastificante. Ao comparar os grupos hidroxila do glicerol com os grupos carboxila do ácido cítrico, os grupos carboxila foram capazes de formar ligações de hidrogênio mais fortes entre as cadeias de polímeros. A adição de 5% de ácido cítrico promoveu um aumento na tensão de ruptura de 39 para 48 MPa, mas quando 30% de ácido cítrico foi adicionado a tensão de ruptura diminuiu para 42 MPa e o alongamento na ruptura aumentou de 102 para 208%, devido ao efeito plastificante do ácido cítrico residual.

Zou, Jin & Xin (2008) observaram os efeitos da adição de glicerol, ácido cítrico, água e bórax em filmes de amido de milho e PVA, com a concentração de amido variando de 30 a 70% (m/m), os materiais foram processados em extrusora monorosca, sendo que a concentração de amido foi o fator de maior influência sobre as propriedades térmicas e morfológicas dos filmes, seguidas pela concentração do ácido cítrico e do bórax. Através das análises térmicas foi possível observar que o ácido cítrico e o bórax podem atuar tanto como plastificantes quanto como reticulantes para a blenda, podendo melhorar as propriedades mecânicas e reduzir a sorção de água pelos materiais, sendo que a sorção de água é diretamente influenciada pelo aumento da concentração de amido. Concentrações de PVA superiores a 30% melhoraram a compatibilidade com o amido, sendo a melhor dispersão em proporção de 50%.

Corroborando com os resultados acima expostos, Sin et al. (2010c) avaliaram as interações entre as ligações de hidrogênio em filmes de PVA e amido de mandioca obtidos por *casting*, através da análise de FT-IR. Os autores observaram que as ligações de hidrogênio entre o PVA e o amido são estáveis, e que altas concentrações de PVA em relação ao amido pode tornar o sistema mais estável e compatível.

Maria et al. (2008) utilizaram PVA com 5 graus de hidrólise distintos, de 88 a 99,7% e diferentes proporções de glicerol em filmes a base de gelatina e obtidos por *casting*, os filmes obtidos se mostraram incolores e pouco opacos. As análises térmicas foram típicas de materiais parcialmente cristalinos, com 2 picos endotérmicos. De acordo com os autores não foi possível observar uma relação direta entre o grau de hidrólise do PVA e as propriedades mecânicas dos filmes. As propriedades observadas foram dependentes principalmente da concentração de glicerol presente na blenda.

Zanela et al. (2015b), utilizaram um planejamento de misturas para produzir laminados biodegradáveis a base de amido de mandioca e PVA plastificados com glicerol e obtidos em extrusora duplarosca, foi possível observar que o PVA foi o principal responsável pela melhora das propriedades mecânicas dos materiais, sendo que o glicerol apresentou um comportamento oposto. Os autores observaram ainda através de FT-IR e MEV uma boa compatibilidade entre os componentes da blenda, não tendo sido observada separação de fases, poros ou rachaduras no material.

6. USO DE FIBRAS NATURAIS COMO REFORÇO EM MATERIAIS A BASE DE AMIDO E PVA

Em diversas aplicações é necessário um aumento da resistência ou rigidez mecânica do material e o uso de fibras é uma forma de conseguir esse aumento. As fibras naturais vêm atraindo a atenção de pesquisadores devido as vantagens que elas apresentam sobre os materiais de reforço convencionais (NABI SAHEB & JOG, 1999) e estas fibras podem serem aplicadas tanto em materiais convencionais como em biodegradáveis.

Fontes de fibras oriundas de produtos agrícolas como palha de trigo, arroz, caules ou sabugos de milho dentre outras espécies são boas fontes de fibras celulósicas. Devido à grande disponibilidade desses resíduos agrícolas de baixo custo, essas fibras naturais se fazem adequadas para produção de compósitos (PANTHAPULAKKAL, ZERESHKIAN & SAIN, (2006).

A fonte de fibra pode ser considerada como primária ou secundária, dependendo da forma de utilização principal da planta. As fontes primárias são aquelas em que as plantas são cultivadas com o objetivo de produzir fibras, como por exemplo, o sisal. As fontes secundárias de fibras são aquelas em que as fibras são um co-produto da produção, como por exemplo fibras milho ou aveia. (FARUK et al., 2012).

O uso de fibras naturais em compósitos apresenta como vantagens o fato de apresentarem baixa densidade, baixo custo, alta rigidez e o fato de serem biodegradáveis. Estas vantagens fazem das fibras naturais potenciais substitutos para as fibras sintéticas, como por exemplo a fibra de vidro em compósitos, sendo que algumas fibras apresentam propriedades mecânicas capazes de superar a fibra de vidro por exemplo (LI, TABIL & PANIGRAHI, 2007; FARUK et al., 2012). Principalmente em materiais biodegradáveis é interessante que as fibras também sejam biodegradáveis, para que se tornem uma alternativa lógica para a melhora das propriedades mecânicas e manter a biodegradabilidade do material (GIRONÈS et al., 2012).

Quando fibras naturais são utilizadas em uma matriz de amido termoplástico, é esperado um aumento das propriedades mecânicas do compósito resultante, isso se deve à similaridade química entre o amido e as fibras que contém alto conteúdo celulósico, promovendo assim, uma boa compatibilidade entre o amido e a fibra (MA, YU & KENNEDY, 2005).

Muitos fatores influenciam na performance de fibras naturais utilizadas como reforço em compósitos, como a fração de volume das fibras, a razão de aspecto (comprimento da fibra dividido pelo seu diâmetro), adesão da fibra na matriz, interface de transferência de stress e orientação das fibras na matriz. Sendo que nas propriedades do compósito obtido, a tensão na ruptura do material é principalmente dependente da matriz polimérica, enquanto que o módulo de Young depende principalmente das propriedades da fibra empregada na produção do compósito (KU et al., 2011; NABI SAHEB & JOG, 1999).

Diversos autores produziram materiais contendo fibras naturais como reforço em matriz de amido e PVA, ou em outros polímeros utilizando diferentes técnicas de produção. Müller, Laurindo & Yamashita (2009) adicionaram fibras celulósicas em filmes de amido produzidos por casting, a adição de fibras promoveu um aumento na tensão na ruptura e no módulo de Young e reduziu a elongação.

Cinelli, Chiellini & Imam (2008) produziram laminados termoformados baseados em PVA/amido/glicerol com a adição de fibras de bagaço de laranja e maçã e de cana. Os autores observaram uma ampla variação nas propriedades mecânicas com relação à fonte de fibras utilizada, sendo que as fibras oriundas dos bagaços de maçã e de cana apresentaram os maiores valores das propriedades mecânicas. De acordo com os autores, essa variação foi devida ao formato e a composição das fibras.

Além das características intrínsecas de cada tipo de fibra, as propriedades dos materiais obtidos podem estar diretamente relacionadas ao processo de produção dos materiais. Chiellini et al. (2001) utilizaram as mesmas fibras e matrizes poliméricas utilizadas por Cinelli, Chiellini & Imam (2008), mas produziram os filmes pelo método de casting. Os resultados foram significativamente diferentes quando comparados os trabalhos, sendo que as fibras oriundas de bagaço de laranja apresentaram as melhores propriedades mecânicas.

Cinelli et al. (2006), em compósitos injetados contendo PVA e amido de milho com adição de fibras de milho observaram que esses materiais apresentaram boa processabilidade no processo de injeção na presença de plastificantes adequados, a adição de amido levou a uma pequena redução das propriedades do material, porém promoveu uma redução significativa do custo do material.

Isso demonstra que o uso de fibras naturais como reforço em materiais biodegradáveis é viável, porém é dependente de várias condições, sendo a forma de processamento e a fonte ou características da fibra muito importantes na definição das propriedades finais dos materiais obtidos.

Pelos trabalhos demonstrados acima é possível observar que a blenda de PVA com amido apresenta boa compatibilidade entre os polímeros, compatibilidade também com o processo de extrusão e é uma alternativa viável para o desenvolvimento de materiais biodegradáveis com a função de substitutos aos polímeros petroquímicos convencionais. Porém ainda são necessários trabalhos mais amplos que auxiliem no entendimento dos efeitos do tamanho de cadeia e graus de hidrólise do PVA sobre o comportamento dos materiais obtidos.

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CAPÍTULO 2 – CARACTERIZAÇÃO DOS AMIDOS E POLI (VINIL ÁLCOOIS) UTILIZADOS NOS EXPERIMENTOS E ESPECIFICAÇÃO DOS EQUIPAMENTOS DE EXTRUSÃO

Para a realização da parte experimental da tese foram utilizados cinco tipos de poli (vinil álcool) (com diferentes graus de hidrólise e tamanho de cadeia) e oito tipos de amido (um amido nativo de mandioca e sete tipos de amidos modificados) e estas matérias primas foram caracterizadas física e quimicamente.

Para a realização das diferentes etapas de produção dos materiais biodegradáveis desenvolvidos na elaboração da tese fez-se o uso de extrusoras monorrosca, duplarrosca e de uma injetora para termoplásticos. Neste capítulo são apresentadas suas principais características e, nos capítulos subsequentes, estão descritas as condições de operação utilizadas em cada experimento.

1. EXPERIMENTAL

1.1 Difração de Raios X

A análise de difração de raios X foi realizada utilizando um difratomêtro (Panalytical X’Pert PRO MPD, Holanda), emitindo radiação de cobre kα ($\lambda = 1.5418$ angstrom). A radiação de ânodo foi gerada a 40 kV e 50 mA, e monocromatizada usando uma corrente de 20 mA. As medidas da intensidade de difração foram realizadas na faixa 2θ de 5 a 50° a temperatura ambiente. A cristalinidade relativa de cada amostra foi calculada pela divisão da área dos picos pela área total da região cristalina (a área total da curva menos a região amorfa).

1.2 Espectroscopia no Infravermelho com Transformada de Fourier – FT-IR

As amostras foram secas em cloreto de cálcio por uma semana e analisadas em um espectrofotômetro de infravermelho com trasnformada de Fourier – FT-IR (IR Prestige 21, Shimadzu, Japão), as amostras foram pastilhadas em brometo de potássio, e a análise foi realizada na faixa espectral de 4000 a 450 cm^{-1}.

1.3 Análise viscoamilográfica

Para a análise dos perfis viscoamilográficos das amostras de amido foi utilizado um viscoamilógrafo Brabender, a pasta de amido na concentração de 5% (m/v) foi aquecida de 30 a 95 °C a uma taxa de aquecimento de 1,5 $°C.min^{-1}$ e mantida a 95 °C por 10 minutos, posteriormente foi resfriada na taxa de 1,5 $°C.min^{-1}$ até atingir 45 °C. Foi mantida agitação constante de 60 RPM durante a execução do ensaio e os dados foram obtidos em duplicata e expressos em unidades Brabender de viscosidadade (BU).

2. CARACTERIZAÇÃO DOS POLI (VINIL ÁLCOOIS) – PVA

Os poli (vinil álcoois) foram adquiridos da Sekisui Chemical Co. Ltda. (Japão) com nome comercial de Selvol™. A Tabela 1 apresenta as principais características de cada amostra, de acordo com as informações constantes nos laudos que acompanham cada lote do produto.

Tabela 1. Especificação dos poli (vinil alcoóis) – PVA utilizados nos experimentos.

PVA	Grau de Hidrólise (%)	Viscosidade (cP)*	Grau de polimerização	Faixa de massa molecular média
Selvol 203	88,14	4,10	150 – 300	1300 – 2300
Selvol 523	87,84	24,50	1000 – 1500	85000 – 124000
Selvol 540	88,04	49,40	1600 – 2200	146000 – 186000
Selvol 107	98,30	6,00	350 – 650	31000 – 50000
Selvol 325	98,42	31,40	1600 – 2200	146000 – 186000

*Solução aquosa a 4 %, 20 °C
**Incluindo a água

2.1 Difração de Raios X dos Poli (Vinil Álcoois) – PVA

Na Figura 1 é apresentando o gráfico da análise de Difração de Raios X (DRX). É possível observar picos característicos de difração nos ângulos de: 19,6; 22,5 e 40,2 °, resultados semelhantes aos observados por Das et al. (2010) que obtiveram picos em 19,8; 22,6 e 40,6 °. Os índices de cristalinidade, de acordo com Zanela (2013), para as mesmas amostras e lotes de PVA, variaram de 26 – 32%, não observando assim um efeito significativo do tamanho de cadeia ou do grau de hidrólise, sobre o índice de cristalinidade das diferentes amostras de PVA.

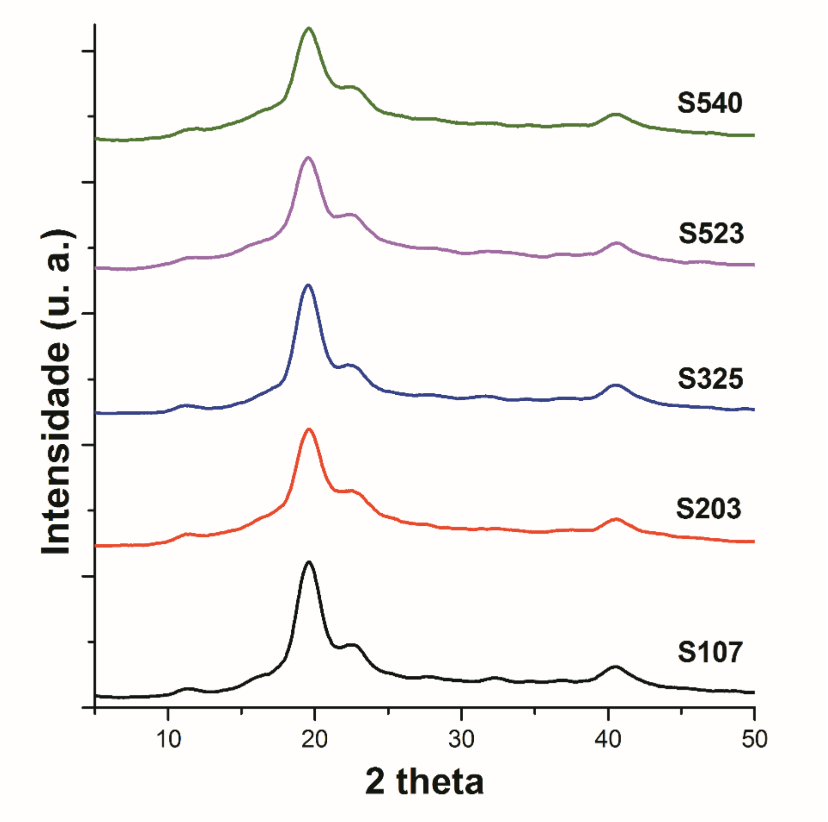

Figura 1. Difratogramas das amostras de PVA.

A semelhança entre os graus de cristalinidade não seria esperada, pois de acordo com Tang & Alavi (2011), nas moléculas de PVA parcialmente hidrolisadas, devido ao fato de possuírem maior quantidade de grupos acetato residuais em suas cadeias, esses grupos promovem uma repulsão estérica, dificultando assim a sobreposição e arranjo das cadeias poliméricas em uma estrutura ordenada que permita a formação de cristais de polímeros.

2.2 Espectroscopia no Infravermelho com Transformada de Fourier – FT-IR das amostras de Poli (álcool vinílico) – PVA

A Tabela 2 apresenta as principais bandas de absorção dos grupos funcionais observados tanto para o PVA quanto para o amido.

Tabela 2. Bandas de absorção no infravermelho do PVA e do amido.

Ligação ou função	Faixa de absorção (cm^{-1})	Comentário
O-H	3550 – 3200	Hidroxilas participando de ligações de hidrogênio intermoleculares e intramoleculares.
C-H	3000 – 2850	Estiramentos simétricos e assimétricos de ligação C-H de grupos CH_3, CH_2 e CH de alcanos.
C=O	1733 – 1710	Estiramentos de grupos carbonila em acetatos residuais do PVA
C-O-C	1150 – 1085	Banda alargada típica

Fonte: Barbosa, (2007); Mansur et al., (2008); Chen et al., (2008)

A Figura 2 apresenta os espectros de FT-IR para as amostras de PVA puro.

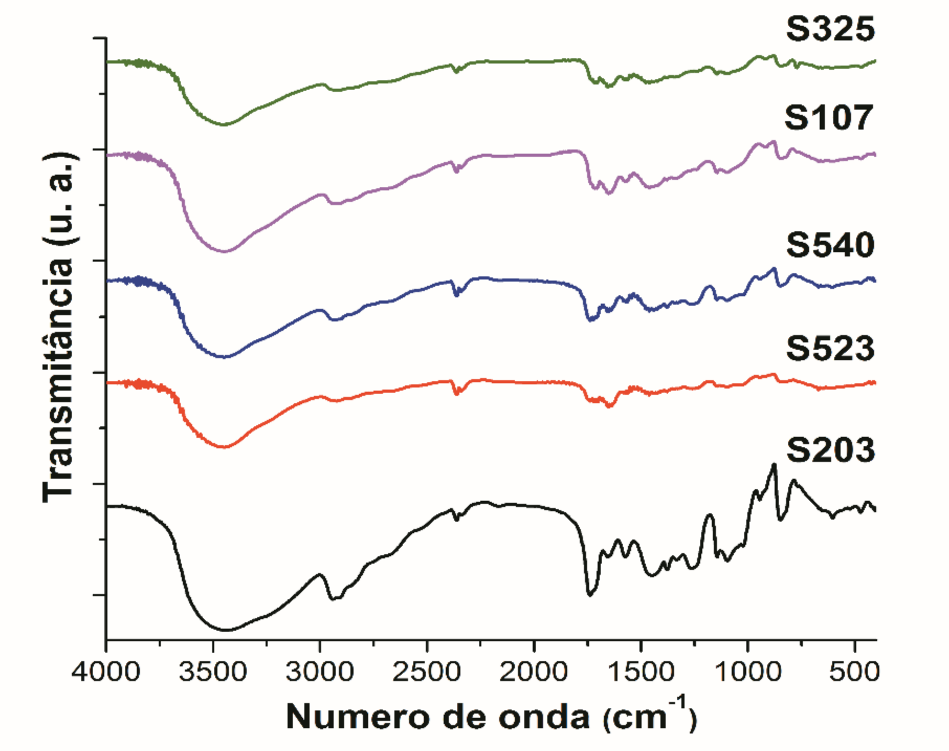

Figura 9. Espectro de FT-IR das amostras de PVA.

É possível observar que todas as amostras de PVA possuem uma banda de absorção na região de 3440 cm^{-1}, grande e alargada, que é atribuída às hidroxilas que formam as ligações de hidrogênio inter e intramoleculares, sendo esperado o aparecimento dessa banda devido à grande quantidade de hidroxilas presentes na estrutura do PVA devido ao seu caráter hidrofílico. A banda na região de 1730 cm^{-1} é atribuída ao estiramento dos grupos carbonila presentes nos grupos acetato residuais do PVA, sendo observada uma maior intensidade dessa banda nas amostras S203 e S540, devido ao fato de possuírem menores graus de hidrólise e, consequentemente, maiores quantidades de grupos acetato residuais. A amostra S523, apesar de ter médio grau de hidrólise (87,23 %) não apresentou essa banda.

3. CARACTERIZAÇÃO DAS AMOSTRAS DE AMIDO

Para a execução do presente trabalho foram utilizados um total de 8 diferentes tipos de amidos de mandioca. Uma amostra de amido nativo, fornecida pela empresa Indemil (Brasil), e sete amostras de amidos modificados de mandioca fornecidas pela empresa Agrícola Horizonte (Brasil), e as principais características de cada amostra de amido modificado estão apresentadas abaixo:

Supercorp 51: Amido modificado (fosfato de di-amido);
Supercorp 52: Amido modificado (fosfato de di-amido acetilado);
Supercorp 75: Amido modificado (adipato de di-amido acetilado);
HC 50: Amido oxidado;
Superion 150, 250 e 300: amidos catiônicos, com diferentes graus de substituição.

A Tabela 3 apresenta as principais características de cada amido, sendo as informações retiradas diretamente das fichas de análise que acompanham cada lote do produto, exceto a umidade que foi determinada nos laboratórios da UEL logo após o recebimento das amostras.

Tabela 3. Especificação das amostras de amido utilizados nos experimentos.

Amido	Umidade* (g/100g)	pH**	Grau de substituição (Ds) mol/mol	Viscosidade (cP)
Nativo	12,22			
Supercorp 51	12,85	5,44		
Supercorp 52	13,26	5,98		
Supercorp 75	12,88	5,18		
HC 50	12,90	5,76		47,8
Superion 150	12,27	5,20	0,019	
Superion 250	13,44	5,02	0,027	
Superion 300	12,57	5,10	0,033	

*Método IAL 012/IV – Secagem direta em estufa a 105 °C.
**Solução com 20% de sólidos.

3.1 Difração de Raios X – DRX das amostras de amido

O amido apresenta uma natureza cristalina bem definida devido à estrutura ordenada das moléculas de amilopectina dentro dos grânulos de amido (MOORTHY, 2002).

A Figura 3 apresenta os difratogramas das amostras de amido nativo e modificados. É possível observar que todas as amostras apresentaram um perfil de difração muito semelhante, com três principais picos identificáveis nos ângulos de: 15,2, 17,6 e 23,2 °, valores semelhantes os apresentados por Moorthy (2002), indicando um padrão de difração do tipo A para todas as amostras. O índice de cristalinidade não apresentou grande variação entre as amostras, apresentando valores entre 17 e 21%.

É possível ainda observar que as modificações produzidas não causaram alterações estruturais significativas nos grânulos de amido, ao contrário do observado por Chi et al. (2008) que, ao estudar o efeito da acetilação no amido de milho, observou que altos graus de substituição promoveram uma perda da estrutura cristalina dos grânulos de amido.

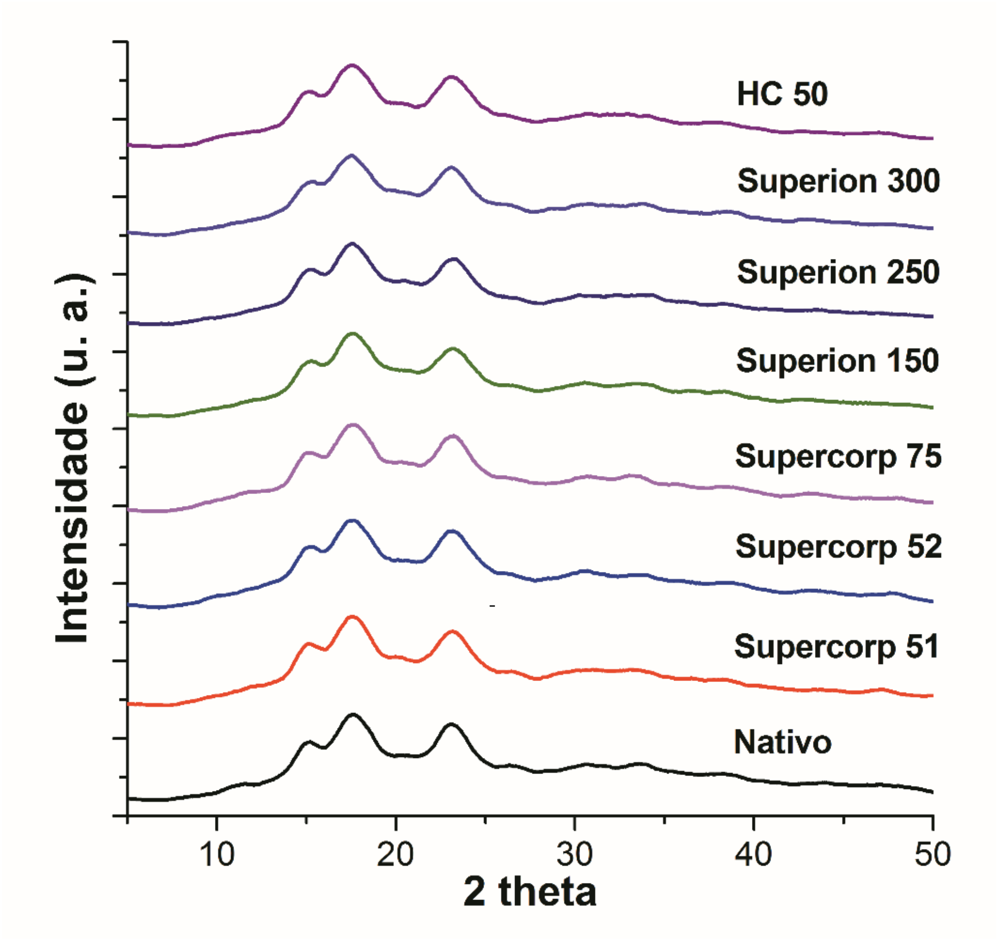

Figura 10. Difratogramas das amostras de amido.

3.2 Espectroscopia no Infravermelho com Transformada de Fourier – FT-IR das amostras de amido

Todos os espectros se mostraram muito semelhantes, com uma banda alargada na região de 3400 cm^{-1} correspondente aos grupos hidroxila, que são abundantes na estrutura do amido. A única diferença perceptível nos espectros é na região de 1730cm^{-1} e 1245 cm^{-1}, que foi observada somente nas amostras Supercorp 52 e Supercorp 75 (regiões demarcadas no gráfico) e são relativas ao estiramento das ligações C=O e C-O respectivamente, que são atribuídos ao grupamento acetil presente nesses dois amidos (fosfato de di-amido acetilado e adipato de di-amido acetilado, respectivamente). Essas bandas estão de acordo com o observado na literatura (FRINGANT et al., 1996; DEMIANTE et al., 2000 e SILVA et al., 2006).

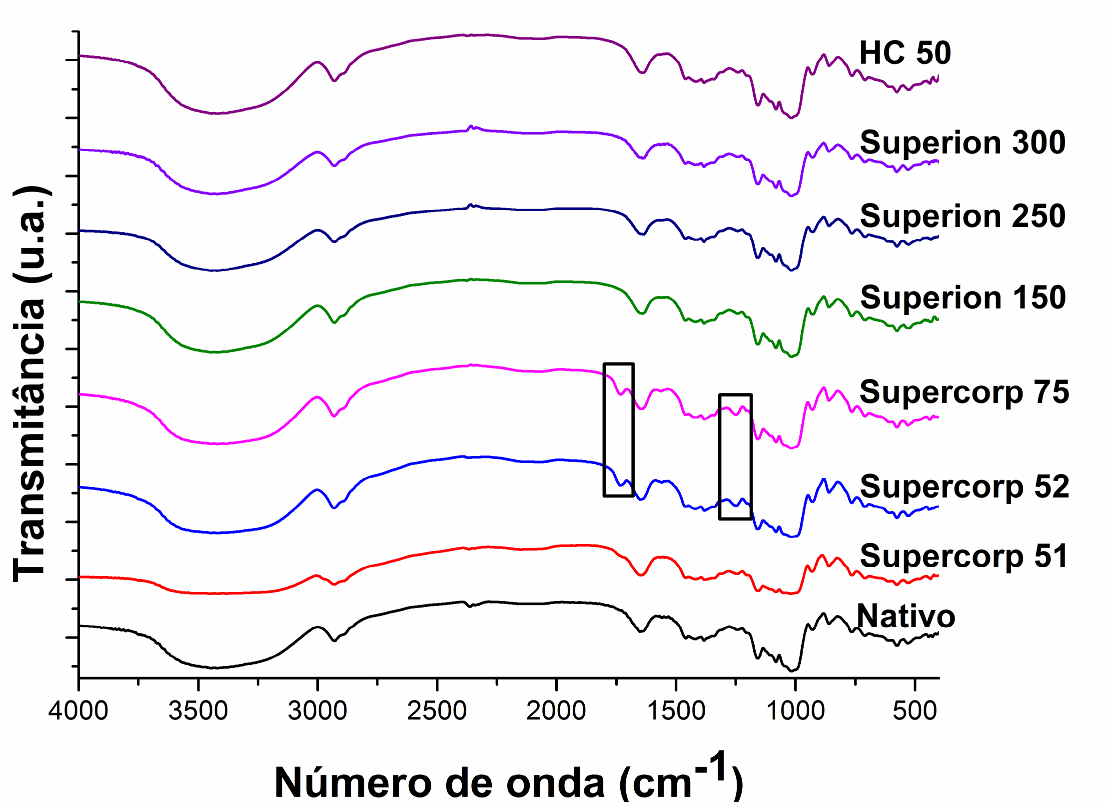

Figura 11. Espectro de FT-IR das amostras de amido.

3.3 Perfis viscoamilográficos das amostras de amido

A Figura 5 apresenta as curvas obtidas em amilógrafo Brabender e a Tabela 4 apresenta as propriedades de pasta das amostras de amido, sendo possível observar grandes diferenças entre as amostras, dependendo do tipo de modificação sofrida pelo amido.

Os amidos catiônicos (Superion 150, 250 e 300) apresentaram as menores temperaturas de pasta e as maiores viscosidades máximas, comportamento típico para esse tipo de modificação, segundo observado na literatura (KUO e LAI, 2007). Essa característica, segundo Kweon, Sosulski e Han (1997), é atribuída ao fato de que os amidos catiônicos permitirem uma maior e mais rápida absorção de água nos grânulos de amido, a temperaturas mais baixas de que seu respectivo amido nativo, aumentando assim o intumescimento do grânulo.

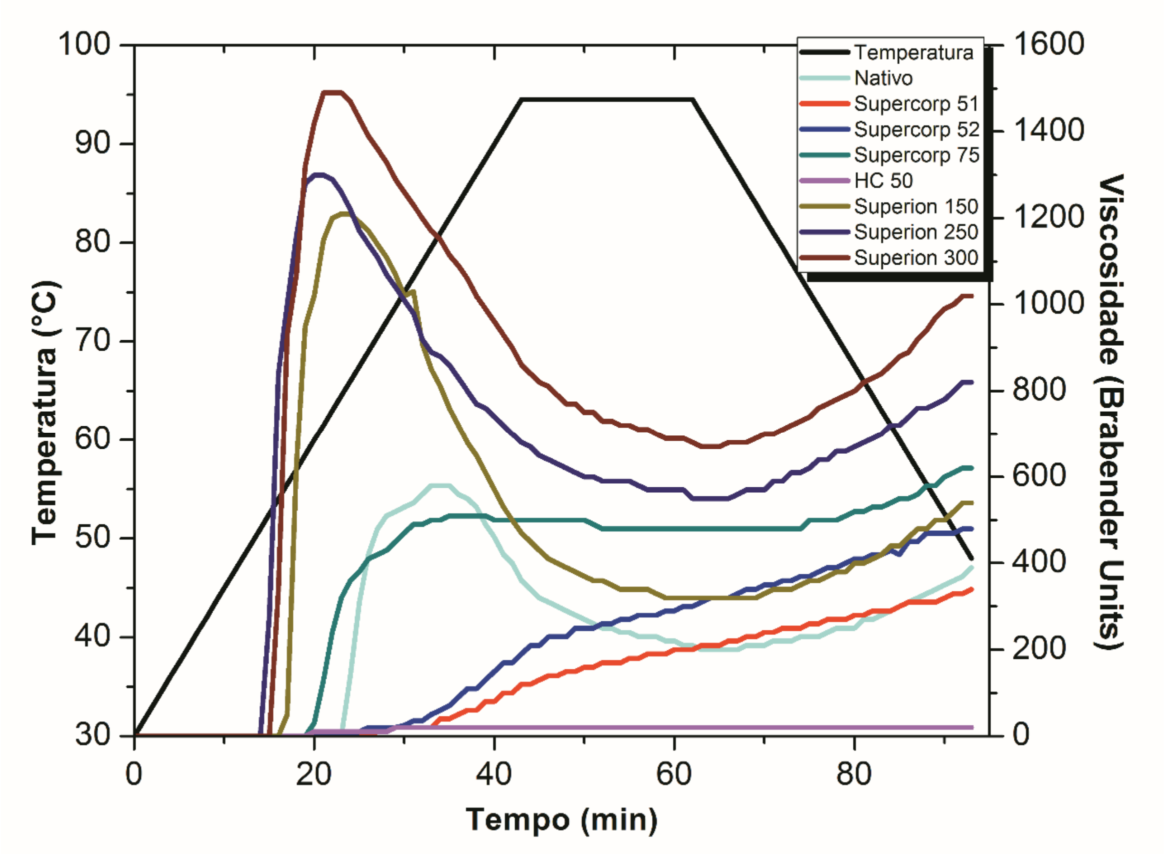

Figura 12. Amilogramas das amostras de amido.

O amido oxidado (HC 50) apresentou viscosidade extremamente baixa, durante toda a análise, provavelmente devido ao processo de modificação ter promovido a clivagem das moléculas de amilose e amilopectina em cadeias relativamente curtas (KUAKPETOON e WANG, 2001).

Tabela 4. Propriedades de pasta das amostras de amido nativo e modificados.

Amido	Temperatura de Pasta °C	Viscosidade Máxima (B.U.)	Viscosidade Final (B.U.)	Quebra (B.U.)	Setback (B.U.)
Nativo	66,0	580	390	380	190
Supercorp 51	70,5	340	340	-	-
Supercorp 52	67,5	480	480	-	-
Supercorp 75	60,0	620	620	30	140
HC 50	60,0	20	20	-	-
Superion 150	55,5	1210	540	890	220
Superion 250	52,5	1300	820	750	270
Superion 300	54,0	1490	1020	820	350

Os amidos modificados Supercorp 51 e 52 (fosfato de di-amido e fosfato de di-amido acetilado, respectivamente) apresentaram comportamento semelhante, com um aumento da viscosidade constante durante todo o ciclo de análise, apresentando o maior valor de viscosidade somente ao final da análise, com o amido Supercorp 52 apresentando maiores valores de viscosidade. Esse comportamento é devido às ligações cruzadas entre as moléculas de amido que reduzem a mobilidade das cadeias amorfas dos grânulos de amido, promovendo a redução da retrogradação e o aumento da temperatura de gelatinização (SINGH, KAUR e McCARTHY, 2007). Já o amido Supercorp 75 (adipato de di-amido acetilado) apresentou um acréscimo muito rápido de viscosidade em temperatura de pasta relativamente baixa (60,0 °C), e manteve sua viscosidade quase constante durante todo o ciclo de análise. Esse comportamento é atribuído, segundo Gonzáles e Pérez (2002), ao fato de a acetilação do amido promover um aumento da viscosidade, solubilidade, coesividade, adesividade e transparência do gel e reduzir a temperatura inicial de gelatinização do amido.

4. ESPECIFICAÇÃO DOS EQUIPAMENTOS UTILIZADOS PARA A PRODUÇÃO DOS MATERIAIS BIODEGRADÁVEIS

Para a produção dos materiais biodegradáveis desenvolvidos nos capítulos posteriores foram utilizados três equipamentos em escala piloto, uma extrusora monorrosca utilizada na produção de pellets, uma extrusora duplarrosca corrotante, utilizada na produção de pellets ou acoplada a uma matriz plana e a calandra para a produção de laminados e uma injetora de termoplásticos. As principais características de cada equipamento são descritas abaixo, sendo que os parâmetros e equipamentos utilizados em cada experimento serão descritos nos capítulos seguintes.

Todos os equipamentos estão alocados no Laboratório de Tecnologia, do Departamento de Ciência e Tecnologia de Alimentos da Universidade Estadual de Londrina.

A importância da utilização desses equipamentos no trabalho se deve ao fato de que eles se assemelham muito aos utilizados nas indústrias processadoras de polímeros, sendo assim, uma possível transferência de tecnologia para a indústria seria mais fácil, necessitando-se fazer os ajustes para o aumento de escala produtiva.

4.1 Extrusora monorrosca BGM EL – 25

A extrusora de escala piloto de laboratório monorrosca modelo EL – 25 (BGM, Brasil), é composta de rosca com diâmetro de 25 mm, L/D = 30, com velocidade máxima do parafuso de 70 RPM, equipada com motor de 5 CV, três zonas de aquecimento na rosca e uma na matriz. A matriz para produção de perfis cilíndricos (para posterior peletização) é composta por seis orifícios de 1 mm de diâmetro cada. Pode ainda ser acoplada na extrusora uma matriz cilíndrica para a produção de filmes por sopro em balão (não utilizado no presente trabalho). A Figura 6 apresenta uma foto da extrusora.

Figura 13. Extrusora monorrosca com os periféricos para a extrusão por sopro em balão ou para a produção de perfis cilíndricos. (Fonte: o autor).

4.2 Extrusora duplarrosca BGM D – 20

A Extrusora duplarrosca de laboratório em escala piloto modelo D – 20 (BGM, Brasil) é composta de duas roscas corrotantes, com diâmetro de rosca de 20 mm, razão L/D = 35; cinco zonas de aquecimento podendo ser utilizados duas matrizes diferentes, uma matriz para produção de perfis cilíndricos, composta de cinco orifícios de 2 mm cada, ou uma matriz plana do tipo “flat die” com abertura regulável e comprimento de 350 mm que pode ser utilizada acoplada com uma calandra de três rolos resfriada com água (AX-Plásticos, Brasil), para a produção de laminados.

A Figura 7 mostra a extrusora duplarrosca com a matriz plana em funcionamento juntamente com a calandra para a produção de laminados.

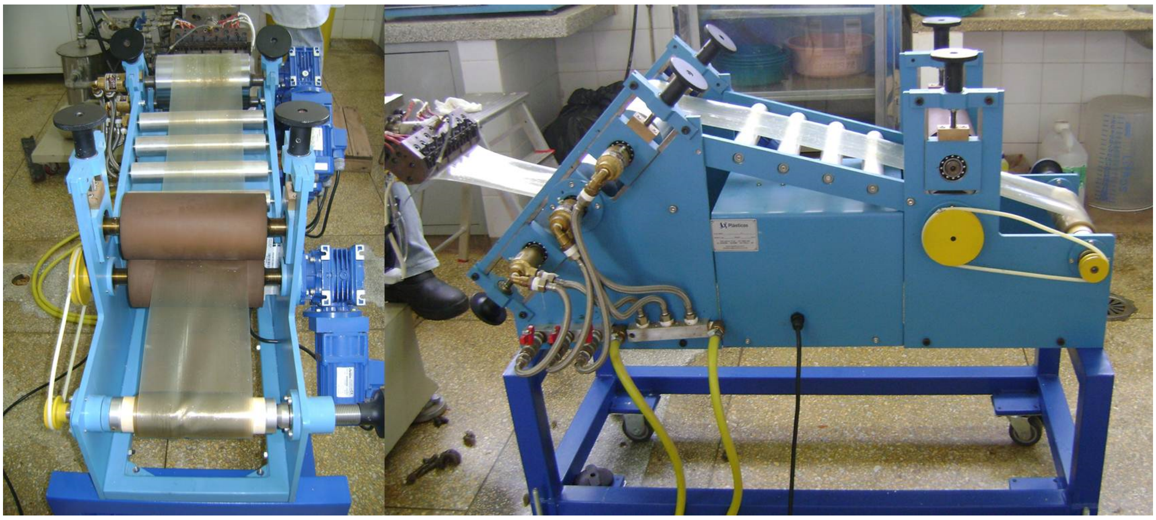

Figura 7. Funcionamento da extrusora duplarrosca acoplada com a calandra para a produção de laminados biodegradáveis (Fonte: Zanela, 2013).

A Figura 8 mostra em detalhes a produção de perfis cilíndricos e de laminados com as duas matrizes disponíveis.

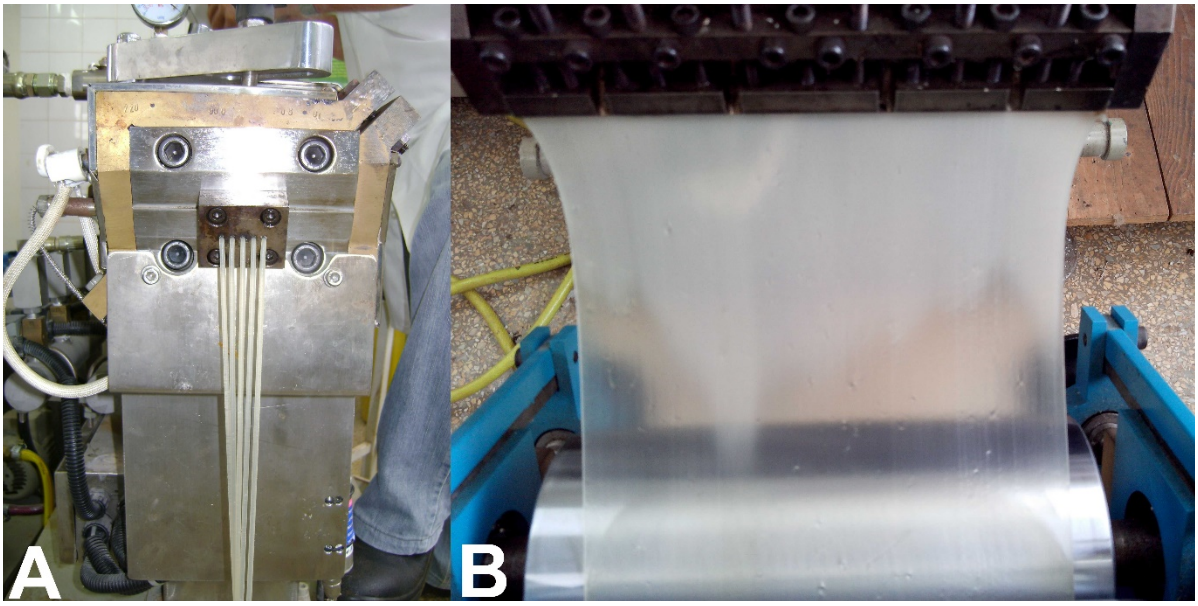

Figura 14. Detalhes da matriz para a produção de perfis cilíndricos (A), e matriz plana do tipo “flat die” (B) para a produção de laminados acoplado a calandra. (Fonte: o autor).

4.3 Injetora de plásticos AX16I

A injetora de laboratório modelo AX16I (AX-Plásticos, Brasil), é constituída de uma rosca recíproca com diâmetro de 16 mm e razão L/D = 24, velocidade da rosca variável de 10 a 200 RPM, curso máximo da rosca de 90 mm, volume máximo de injeção de 22 cm^3, velocidade de injeção de 30 $cm^3.s^{-1}$ e força de fechamento de 22 kN. O aquecimento é feito por resistências elétricas e a placa do molde é refrigerada a água; possui uma capacidade máxima de injeção de 12 g de polímero (em base do poliestireno) e força de fechamento do molde de 55 kN. O molde para corpo de prova segue a norma ASTM 680 tipo IV (gravata), conjugado com barra para teste de flexão.

A figura 9 apresenta uma imagem da injetora.

A Figura 10 mostra o painel de controle da injetora, onde é possível visualizar alguns dos parâmetros de processo que podem ser alterados. Os principais parâmetros que controlam a injeção são a temperatura do barril e do molde, velocidade de carregamento e de avanço do parafuso para a injeção, e do carregamento, que deve permitir um completo preenchimento da rosca para o próximo ciclo de injeção.

Figura 15. Injetora em escala piloto de termoplásticos utilizada no desenvolvimento do trabalho (Fonte: o autor).

Fase | Fecham. molde | Amortec.
Veloc. 80 % | 20 %
Ret. 0.00 seg
Dur. 0.99 seg | 1.50 seg
Habilita curso relativo 0 s/n

Fase | Amortec. | Abertura molde
Veloc. 80 % | 20 %
Ret. 0.00 seg | 0.00 seg

Zona 4: 20 °C, 20 oC, 0
Zona 3: 155 °C, 160 oC, 0
Zona 2: 152 °C, 160 oC, 0
Zona 1: 118 °C, 120 oC, 0

Pré-Avançamento
Número de pré-avanços 0 qtd
Duração pré-avanço 0.00 seg

Aquecimento
Liga aquecimento 0 s/n
Banda de alarme 30 °C
Banda de resfriamento 20 °C

Extrator | Recuo | Avanço
Retardo 0.00 | 0.00 seg
Duração 0.50 seg
Número de movimentos 1 qtd

Unid. Injeção | Avanço | Recuo
Retardo 0.00 seg | 0.00 seg
Duração 0.00 seg
Habilita recuo unidade injeção 0 s/n

Figura 1016. Imagem do painel de comando da injetora (Fonte: o autor).

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CAPÍTULO 3 – BIODEGRADABLE BLENDS OF STARCH/POLYVINYL ALCOHOL/GLYCEROL: MULTIVARIATE ANALYSIS OF THE MECHANICAL PROPERTIES

ABSTRACT: The aim of the work was to study the mechanical properties of extruded starch/polyvinyl alcohol (PVA)/glycerol biodegradable blends using multivariate analysis. The blends were produced as cylindrical strands by extrusion using PVAs with different hydrolysis degrees and viscosities, at two extrusion temperature profiles (90/170/170/170/170 °C and 90/170/200/200/200 °C) and three conditioning relative humidities of the samples (33, 53, and 75%). The mechanical properties showed a great variability according to PVA type, as well as the extrusion temperature profile and the conditioning relative humidity; the tensile strength ranged from 0.42 to 5.40 MPa, elongation at break ranged from 10 to 404% and Young's modulus ranged from 0.93 to 13.81 MPa. The materials produced with medium chain size PVA, independently of their hydrolysis degree (Selvol 325 and 523), presented better mechanical properties. The multivariate analysis was a useful methodology to study the mechanical properties behavior of starch/PVA/glycerol blends, and it can be used as an exploratory technique to select of the more suitable PVA type and extrusion temperature to produce biodegradable materials.

Keywords: Biodegradable material, extrusion, principal component analysis.

1. INTRODUCTION

The environmental concerns about the plastic wastes are increasing, promoting the development of suitable alternatives for petroleum based polymers, and starch is a promisor biopolymer from renewable resources to produce biodegradable materials. However, the mechanical properties of these materials are poor, being necessary the development of blends with others biodegradable polymers to improve its mechanical and barrier properties.

Polyvinyl alcohol (PVA) is a biodegradable polymer with vast use in paper and textile industry; it is available industrially with several hydrolysis degree and molecular weight, and these characteristics can affect the properties of the materials produced with PVA blends (LINPAN et al., 2012; MARIA et al., 2008), and PVA can be processed by thermoplastic extrusion (TANG & ALAVI, 2011).

Blending starch with polyvinyl alcohol (PVA) can improve the mechanical properties and maintain the biodegradability of starch-based materials as observed in many works (ZANELA et al., 2015; SIN et al., 2011; TANG & ALAVI, 2012; BRANDELERO et al., 2015).

To produce biodegradable material by extrusion it is necessary to extrude the blend components producing cylindrical strands, to pelletize the strands, and then to extrude these pellets to produce the material by blown extrusion or flat die extrusion-calendering process. According to Nobrega et al. (2012), the mechanical and viscoelastic properties of extruded cylindrical strands from biodegradable polymer blends (starch/poly (butylene adipate co-terephthalate)/glycerol) were correlated with their capacity to form films by blown extrusion process.

The aim of this work was to study the behavior of the mechanical properties of starch/polyvinyl alcohol/glycerol blends using multivariate analysis. The blends were produced as cylindrical strands by extrusion with different polyvinyl alcohol types, and extrusion temperature profiles.

2. MATERIAL AND METHODS

2.1 Material

The polyvinyl alcohol (PVA) with different degree of hydrolysis (HD) and viscosities (4% aqueous solution) were provided by Sekisui Chemical (Japan): Selvol™ 203 (HD: 88.14%, viscosity: 4.10 cP); Selvol™ 523 (HD: 87.84%, viscosity: 24.50 cP); Selvol™ 540 (HD: 88.04%, viscosity: 49.40 cP); Selvol™ 107 (HD: 98.30%, viscosity: 6.00 cP) and Selvol™ 325 (HD: 98.42%, viscosity: 31.40 cP). The native cassava starch was provided by Indemil (Brazil) and the technical grade glycerol by Dinamica (Brazil).

2.2 Cylindrical strands production

The PVA, starch, and glycerol (20:40:40% w/w) were manually homogenized and conditioned in vacuum oven (model Q819V2, Quimis, Brazil) with a vacuum pressure of 0.085 MPa for 90 min at 85 °C to incorporate the glycerol, according the method adapted from Jang & Lee, (2003). The blends were extruded in a co-rotating twin-screw extruder (model D-20, BGM, Brazil) with a six holes (2 mm) die to produce the cylindrical strands, and a screw diameter of 20 mm (L/D = 35). The screw speed was set at 100 rpm and it was used two extrusion temperature profiles: 90/170/170/170/170 °C and 90/170/200/200/200 °C, totaling 10 different formulations (5 PVA types x 2 extrusion temperature profiles).

2.3 Mechanical characterization

The tensile strength, Young's modulus and elongation at break tests were performed according to ASTM D882-02 (2002) using a texture analyzer (model TA.XT2i, Stable Micro Systems, England) with an initial distance between grips of 30 mm and a crosshead speed of 0.8 mm/s.

Ten samples from each treatment (50 mm in length) were conditioned at different relative humidity (33±2%, 53±2%, and 75±2% RH) for 72 hours at 23±2ºC before analysis.

2.4 Statistical analyses

The multivariate exploratory techniques, Principal Components Analysis (PCA) and Hierarchical Cluster Analysis, were performed using STATISTICA 7.0 software (Statsoft, USA). For PCA, the mechanical parameters (tensile strength, Young's modulus, and elongation at break) were used as active variables in the derivation of the principal components, and the supplementary variables (temperature, hydrolysis degree, viscosity, and relative humidity) were projected onto the factor space. The PCA analysis was performed using the covariance matrix. The hierarchical tree was obtained considering the same active variables applied to PCA. The formulations were joined by single linkage as linkage rule, and considering the Euclidean distance as the coefficient of similarity

3. RESULTS AND DISCUSSIONS

The results of the cylindrical strands mechanical properties are presented in Table 1. Tensile strength ranged from 0.42 to 5.40 MPa, elongation at break ranged from 10 to 404% and Young's modulus ranged from 0.93 to 13.81 MPa, showing a great variability according to PVA type, as well as the extrusion temperature profile and the conditioning relative humidity.

The Figure 1a presents the Principal Component Analysis (PCA) plot of active and supplementary variables for mechanical properties of cylindrical strands, and is possible to observe that the two principal components explained 97.28% of total variance.

The tensile strength was positively correlated with the extrusion temperature profile, probably because the extrusion process was more efficient at the higher temperature profile, permitting a better interaction among the components (starch/PVA/glycerol).

The PVA hydrolysis degree correlated well with Young's modulus, probably because the higher the hydrolysis degree the higher the number of hydroxyl groups in substitution of the acetate groups, enabling more interactions by hydrogen bonds with starch molecules, so increasing their rigidity. The PVA viscosity correlated well with the elongation at break of the strands, probably because the longer PVA chains.

The conditioning relative humidity had a negative correlation with the mechanical properties, due to the hydrophilic characteristic of starch/PVA-based materials. The water acts as plasticizer, consequently materials conditioned at high RH absorb more water, decreasing their mechanical properties (MAO et al., 2002; CHEN et al., 1997).

In the scatterplot (Figure 1b), the samples could be grouped in two distinct clusters considering the groups suggested by the dendogram of the hierarchical cluster analysis (Figure 1c). The cluster '1' is composed by the strands produced with Selvol 523 and 325 at the higher extrusion temperature profile (90/170/200/200/200 °C) and the three conditioning relative humidities (33, 53 and 75% RH), and with Selvol 107 at the higher temperature profile and 33% RH. The cluster '2' is composed by the remaining strands (below the cutting line of the dendogram) based in their similarities.

Table 1. Mechanical properties of PVA/starch/glycerol cylindrical strands.

PVA	**Extrusion Temperature Profile (ºC)**	**Relative Humidity (%)**	**Tensile Strength (MPa)**	**Elongation at Break (%)**	**Young's Modulus (MPa)**
Selvol 203	90/170/170/170/170	33%	1.44 ± 0.11	61 ± 7	5.46 ± 0.37
		53%	0.83 ± 0.16	32 ± 5	4.09 ± 0.75
		75%	0.60 ± 0.25	10 ± 4	0.93 ± 0.60
	90/170/200/200/200	33%	1.38 ± 0.20	92 ± 14	4.4 ± 0.72
		53%	0.72 ± 0.10	41 ± 12	3.11 ± 0.38
		75%	0.42 ± 0.06	39 ± 6	2.50 ± 0.38
Selvol 523	90/170/170/170/170	33%	2.20 ± 0.34	166 ± 48	5.25 ± 0.91
		53%	2.39 ± 0.48	186 ± 47	5.40 ± 1.07
		75%	1.12 ± 0.43	155 ± 94	2.48 ± 0.54
	90/170/200/200/200	33%	4.56 ± 0.79	391 ± 91	7.97 ± 0.71
		53%	2.77 ± 0.40	404 ± 95	4.84 ± 0.35
		75%	1.78 ± 0.19	347 ± 85	3.38 ± 0.89
Selvol 540	90/170/170/170/170	33%	1.46 ± 0.17	119 ± 22	2.64 ± 0.61
		53%	0.95 ± 0.18	108 ± 32	1.88 ± 0.49
		75%	1.18 ± 0.23	86 ± 15	2.60 ± 0.88
	90/170/200/200/200	33%	2.46 ± 0.35	149 ± 35	5.27 ± 0.70
		53%	1.83 ± 0.25	136 ± 27	4.05 ± 0.42
		75%	1.41 ± 0.37	131 ± 24	2.84 ± 0.81
Selvol 107	90/170/170/170/170	33%	1.67 ± 0.23	62 ± 16	7.60 ± 0.52
		53%	1.28 ± 0.25	47 ± 6	6.58 ± 0.97
		75%	0.82 ± 0.08	39 ± 12	4.33 ± 0.75
	90/170/200/200/200	33%	2.57 ± 0.15	95 ± 16	13.30 ± 0.93
		53%	1.52 ± 0.11	52 ± 8	9.56 ± 0.71
		75%	1.40 ± 0.11	98 ± 17	8.35 ± 0.95
Selvol 325	90/170/170/170/170	33%	1.90 ± 0.21	83 ± 14	5.79 ± 0.74
		53%	1.49 ± 0.19	81 ± 16	4.18 ± 0.64
		75%	1.40 ± 0.14	81 ± 16	4.18 ± 0.39
	90/170/200/200/200	33%	5.40 ± 0.58	262 ± 24	13.81 ± 1.57
		53%	4.06 ± 0.52	219 ± 47	11.63 ± 1.63
		75%	3.47 ± 0.47	236 ± 88	9.03 ± 1.12

According to the dendogram, the higher extrusion temperature profile was more adequate for extrusion process of PVA, and PVA with medium chain size (Selvol 325 Selvol 523) resulted in materials with better mechanical properties.

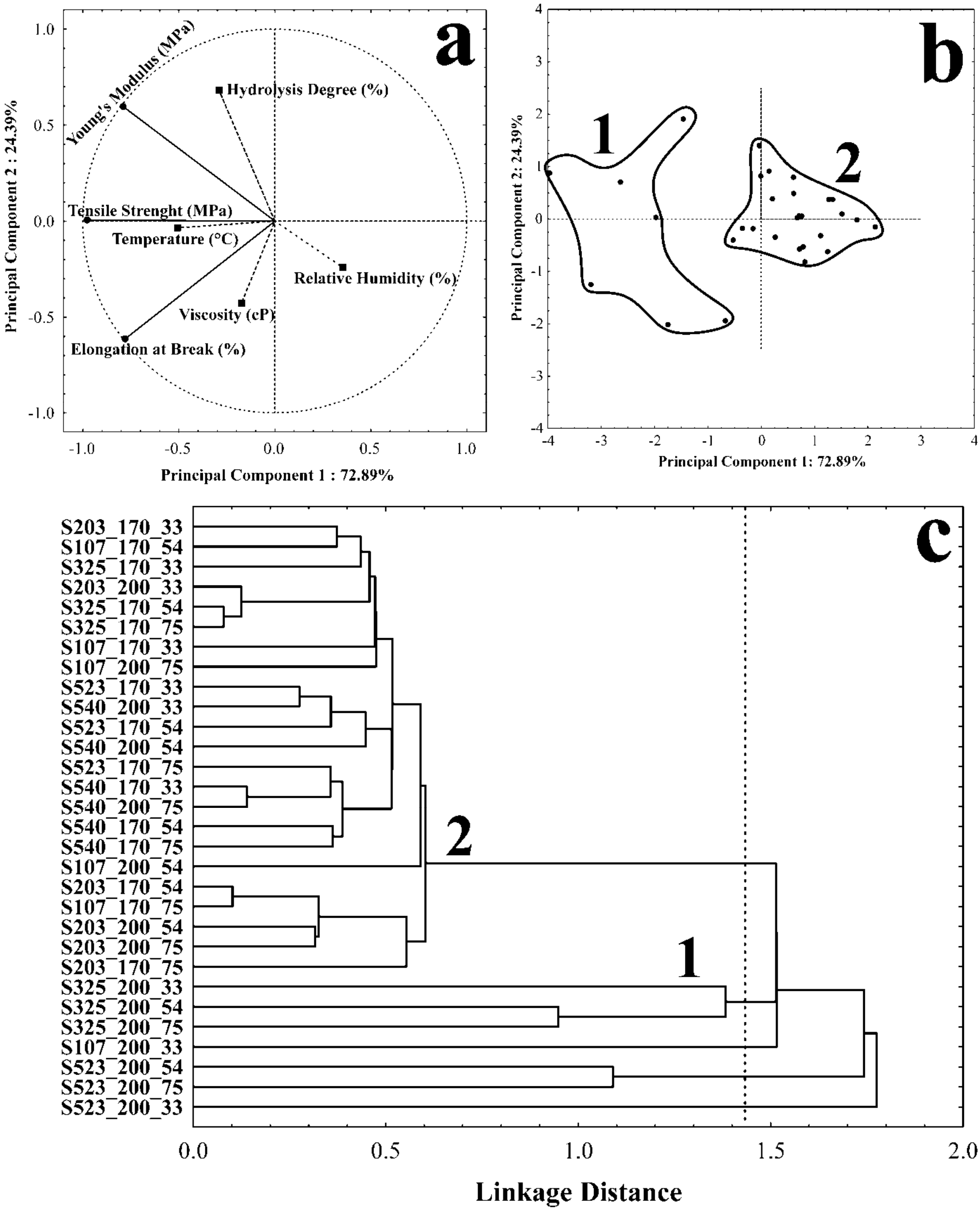

Figure 1. Classification of the formulations by mechanical parameters. (a) Variable projection by PCA: —— active variable, ------- supplementary variable, (b) Scatterplot for the formulations by PCA with grouping suggested by HCA and (c) Dendogram by HCA analysis.

4. CONCLUSIONS

The multivariate analysis was a useful methodology to study the mechanical properties behavior of starch/PVA/glycerol blends, and it can be used as an exploratory technique to select of the more suitable PVA type and extrusion temperature to produce biodegradable materials. The PVA with medium chain size, independently of their hydrolysis degree (Selvol 325 and 523), presented the more adequate mechanical properties, and they are promising polymers for future studies.

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CAPÍTULO 4 – MIXTURE DESIGN APPLIED FOR THE DEVELOPMENT OF FILMS BASED ON STARCH, POLYVINYL ALCOHOL AND GLYCEROL[1]

ABSTRACT: Starch and polyvinyl alcohol (PVA) are biodegradable materials with potentiality to replace the conventional polymers in some applications. The aim of this work was produce biodegradable films of PVA, cassava starch and glycerol by thermoplastic extrusion using a mixture design to evaluate the effects of each component in the blend properties. Six formulations were prepared using a twin-screw extruder coupled with a calender. All of the materials were visually homogeneous and presented good processability. Mechanical properties were dependent on both the relative humidity conditioning and the formulation; higher relative humidities detracted the mechanical properties, which was associated to plasticiser effect of the water. Furthermore, the mechanical properties were better when higher concentrations of PVA were used, resulting in films with lower opacity, lower water vapour permeability and higher thermal stability, according to TGA. Biodegradable materials based on starch, PVA and glycerol have adequate mechanical and processing properties for commercial production.

Keywords: mechanical properties; thermoplastic starch, eco-friendly polymers, extrusion.

1. INTRODUCTION

The environmental concerns about the plastic wastes are increasing, because the plastics polymers are widely used in several areas, and they are an important industrial sector worldwide. Plastics are widely used in packaging because they are inexpensive, lightweight, durable and easily processed into desired shapes. However, the widespread use of plastics in applications with short life cycles results in the accumulation of millions of tons of plastic waste per year, resulting in serious environmental problems (RAHMAT et al., 2009). Therefore, the search for substitutes

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[1] Zanela, J., Olivato, J. B., Dias, A. P., Grossmann, M. V. E., & Yamashita, F. (2015). Mixture design applied for the development of films based on starch, polyvinyl alcohol, and glycerol. *Journal of Applied Polymer Science*, 132(43), 42697. doi:10.1002/app.42697

for conventional plastics is increasing.

Starch was one of the first biodegradable polymers used as a substitute for conventional plastics and it is still widely studied because it is inexpensive, easily renewable and fully biodegradable. However, the use of pure starch has some drawbacks, such as poor mechanical properties, water barrier properties and low thermal stability and processability (TANG & ALAVI, 2011). To overcome the problems associated with conventional plastics and starch-based plastics, one alternative is to develop novel polymeric composite materials based on starch and other polymers that can be degraded by microorganisms in soil and water, and this area is attracting the increasing attention of researchers (PARK et al., 2005).

There are currently many biodegradable polymers that have properties similar to those of conventional polymers (polyethylene, polypropylene etc.), such as polyvinyl alcohol (PVA), poly (butylene adipate-co-terephthalate) (PBAT), and poly (lactic acid) (PLA), but these polymers are expensive compared to conventional ones. Thus, one alternative to reduce the production costs of biodegradable materials is to develop starch blends, in which the starch is responsible for reducing the production costs and another polymer is responsible for reinforcing the structural integrity of the blend.

PVA is a material that has high technological potential due to its excellent optical and physical properties, and because PVA possess many hydroxyl groups in its structure, PVA is highly compatible with starch and can be used in starch blends to produce biodegradable materials as an alternative to non-biodegradable plastics (TANG & ALAVI, 2011; CHI et al., 2012).

The aim of this work was to develop biodegradable materials based on cassava starch, PVA and glycerol produced by extrusion using mixture design to understand the effects of each component on the properties of the blends. Mixture design is a statistical tool that allows evaluating the influence of each component in the mixture, as well as the interactions between them, which is important in the study of polymer blends, because the mathematical models obtained are predictive, allowing the optimization of the material properties as desired.

The biodegradable films of cassava starch and PVA have adequate mechanical, microstructural and thermal properties, indicating a good miscibility between the starch and the PVA. The mechanical properties are also dependent on the relative humidity. Biodegradable materials based on starch, PVA and glycerol blends have adequate properties and processability for commercial production.

2. EXPERIMENTAL

2.1 Materials

Selvol™ 523 PVA (degree of hydrolysis: 87.84%; viscosity of 4% aqueous solution: 24.50 cP) (Sekisui Chemical, Japan), cassava starch (Indemil, Brazil) and pure glycerol (Dinamica, Brazil) as a plasticiser were used.

2.2 Methods

2.2.1 Mixture designs

A mixture design with upper and lower limits defined by preliminary tests was used, and the independent variables of the experimental design were the concentrations of starch, PVA and glycerol. The limits refer to the maximum and minimum concentration of each component necessary to produce the films by thermoplastic extrusion. The response variables were analysed with STATISTICA 7.0 (Statsoft, USA) using the aforementioned mixture design. Linear (eq. 1) and quadratic (eq. 2) models were used because they provided the best fits to the experimental data.

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 \qquad (1)$$

$$y = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \qquad (2)$$

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

The pseudo-components were calculated using eq. 3.

$$Ps_x = (C_x - a_y)/(1 - \sum a_y) \qquad (3)$$

Where Ps_x is the pseudo-component of each component, C_x is the real concentration of the component, a_y is the lower limit of the real component, and Σa_y is the sum of the lower limits of the three components in the mixture design.

Table 1 shows the real concentrations and the pseudo-components of each mixture.

Table 1. Concentration of the components according to the mixture design

Formulation	**Component (wt. %)**			**Pseudo-component** [a]		
	Starch	**PVA**	**Glycerol**	**Ps_1**	**Ps_2**	**Ps_3**
F1	20.0	50.0	30.0	0.000	1.000	0.000
F2	40.0	30.0	30.0	1.000	0.000	0.000
F3	20.0	40.0	40.0	0.000	0.500	0.500
F4	20.0	45.0	35.0	0.000	0.750	0.250
F5	30.0	30.0	40.0	0.500	0.000	0.500
F6	32.5	32.5	35.0	0.625	0.125	0.250

[a] Ps_1 = starch, Ps_2= PVA, Ps_3 = glycerol.

2.2.2 Film production

Each formulation (Table 1) was manually homogenized and placed in a vacuum oven (model Q819V2, Quimis, Brazil) with a vacuum pressure of 0.085 MPa for 90 minutes at 85 °C to incorporate the glycerol using a method adapted from Jang & Lee (2003). After this step, the blends were extruded in a co-rotating twin-screw extruder (model D-20, BGM, Brazil) with a screw diameter of 20 mm (L/D = 35), a screw speed of 100 RPM and a temperature profile of 90/200/200/200/200 °C from the feeder zone until the flat die zone. The feed velocity was 33 RPM, and the extruder was equipped with a six holes (2 mm) die to produce cylindrical strands. After pelletisation of the strands, the pellets were extruded in the same extruder and under the same conditions cited above using a flat die with a 0.8 mm aperture and 320 mm length, and a 3-roll water-cooled calender (AX Plásticos, Brazil) to produce the films.

2.2.3 Mechanical properties

The tensile strength, Young's modulus and elongation at break were determined according to ASTM D882-02 (2002) method, with some modifications. Ten samples from each treatment (50 mm in length and 20 mm in width) were conditioned in a desiccator with three controlled relative humidities (33±2%, 53±2% and 75±2%) and a temperature of 23±2 °C for a minimum of 72 hours before analysis. The samples were then analysed in a texture analyser (model TA.XT2i, Stable Micro Systems, England) with an initial distance between the grips of 30mm and a crosshead speed of 0.8 $mm.s^{-1}$.

For puncture analysis, ten replicates from each treatment were conditioned as described above and were then attached to a support and punctured perpendicularly with a 6.35-mm-diameter cylindrical probe at a velocity of 2.0 $mm.s^{-1}$. The puncture strength was obtained by dividing the maximum force by the film thickness. The puncture elongation was the maximum elongation supported by the film, expressed in mm.

2.2.4 Apparent opacity (Op)

The apparent opacities of the films were measured using a colorimeter (BYK Gardner, Germany) according to the method described by Maria et al. (2008), using the illuminant D65 (daylight) and a visual angle of 10°. Opacity (Op) was determined as the ratio of the opacity of the sample over a black standard Op_b and the opacity over a white standard Op_w being represented on an arbitrary scale (0-100%), and the analyses were performed in triplicate according to eq. 4.

$$\mathrm{Op} = (\mathrm{Op_b}/\mathrm{Op_w}) \times 100 \qquad (4)$$

2.2.5 Weight loss in water (WLW)

The analysis of weight loss in water (WLW) was performed as described by Olivato et al. (2012a) The weight loss in water measurements were performed in triplicate and expressed as the percentage of the original mass (M_i) and the final mass (M_f) of the film after immersion in water for 48 hours at 25 °C, according to eq. 5.

$$\mathrm{WLW} = [(\mathrm{M_i} - \mathrm{M_f})/\mathrm{M_i}] \times 100 \tag{5}$$

2.2.6 Water vapour permeability (WVP)

Water vapour permeability was determined gravimetrically according to the ASTM E96-00 (2009) standard. The measurements were performed in triplicate using a relative humidity gradient of 33 - 64%.

2.2.7 Scanning Electron Microscopy (SEM)

Scanning electron micrographs were recorded using a scanning electron microscope (FEI Quanta 200, USA). The films were fractured in liquid nitrogen, attached to aluminium supports and coated with gold (BAL-TEC SCD 050 sputter coater, Leica Microsystems, Germany) (40-50 nm in thickness) at 25 °C and a pressure of 2.105 Torr for 180 seconds. The surface and the fracture surface of the films were analysed.

2.2.8 Fourier Transform Infrared Spectroscopy (FT-IR)

The samples were dried over anhydrous calcium chloride salt for one week and analysed in a Fourier transform infrared spectrophotometer (FT-IR) (IRPrestige 21, Shimadzu, Japan) using a horizontal attenuated total reflection (ATR) module operating over the spectral range of 4000 cm^{-1} - 750 cm^{-1}.

2.2.9 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a TGA – 50 (Shimadzu, Japan). The samples were dried over anhydrous calcium chloride salt and analysed from 25 °C to 600 °C with a 10 °C.min^{-1} heating rate under a nitrogen atmosphere (20 mL.min^{-1}).

3. RESULTS AND DISCUSSION

All of the films were uniform, visually homogeneous, and easy to handle. The average thickness of the films was 771(±176) µm. The influence of the components (PVA, glycerol and starch) on film properties was evaluated based on the modelling coefficients, considering the isolated effect of each component (β_1, β_2 and β_3) and their interactions (β_{12}, β_{13} and β_{23}). All of the coefficients of determination (R^2) were greater than 0.70, most of them higher than 0.90, demonstrating an adequate fit of the models to the experimental data. These R^2 values were useful to discuss the influence of each component (PVA, glycerol and starch), and their interactions, on the properties of the starch/PVA films, as can be noted considering the observed and predict results showed at Tables 3, 4, 5, 7, 8 and 9, for all properties. For all models, the lack of fit was not significant ($p>0.05$).

3.1 Mechanical properties

The coefficients of the mixture design models for the mechanical properties (tensile strength, Young’s modulus and elongation-at-break) of the films under different relative humidities are shown in Table 2.

According to Table 3, 4 and 5, the tensile strengths ranged from 2.6 to 11.0 MPa, the Young's moduli ranged from 3.1 to 12.3 MPa, and the elongation-at-break ranged from 377 to 698% for all of the formulations and relative humidities tested.

Table 2. Regression coefficients for the mechanical properties in different relative humidities.

Coef[a]	**Tensile Strength (MPa)**			**Young's Modulus (MPa)**			**Elongation at Break (%)**		
	Relative Humidity (%)								
	33	54	75	33	54	75	33	54	75
β_1	5.78	4.86	3.30	8.04	6.56	4.75	586	566	402
β_2	10.42	8.92	8.35	12.15	9.83	7.42	714	702	652
β_3	0.69	1.14	1.83	-5.70	1.76	0.51	273	227	105
β_{12}	-	ns[b]	ns	-19.57	-	-	-1725	ns	ns
β_{13}	-	ns	ns	15.95	-	-	ns	ns	474
β_{23}	-	6.39	-7.53	11.46	-	-	ns	831	ns
R^2	0.82	0.90	0.90	0.99	0.99	0.95	0.73	0.85	0.81

[a] β_1 = starch, β_2= PVA, β_3 = glycerol, β_{12} = interaction starch:PVA, β_{13} = interaction starch:glycerol, β_{23} = interaction PVA:glycerol

[b] ns = not significant.

Table 3. Observed and predicted data for tensile strength in different relative humidities.

Formulation	**Tensile Strength (MPa)**					
	33% RH		54% RH		75% RH	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	11.0±1.6	10.4	7.8±0.9	8.9	8.7±0.9	8.4
F2	6.8±0.9	5.8	4.8±0.5	4.9	3.3±0.4	3.3
F3	6.1±1.0	5.6	6.0±0.8	6.6	3.5±0.3	3.2
F4	9.1±1.0	8.0	8.0±1.0	8.2	5.2±0.8	5.3
F5	3.5±0.4	3.2	3.1±0.4	3.0	2.6±0.2	2.6
F6	4.1±0.4	5.1	4.0±0.3	4.6	2.9±0.4	3.3

Table 4. Observed and predicted data for Young modulus in different relative humidities.

Formulation	Young's Modulus (MPa)					
	33% RH		54% RH		75% RH	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	12.3±0.3	12.2	9.9±0.3	9.8	7.0±0.3	7.4
F2	7.9±0.5	8.0	6.2±0.4	6.56	4.7±0.3	4.8
F3	6.1±0.4	6.1	5.5±0.3	5.8	4.0±0.3	4.0
F4	9.9±0.5	9.8	8.0±0.3	7.8	5.9±0.2	5.7
F5	5.3±0.2	5.2	4.5±0.3	4.2	3.1±0.4	2.6
F6	6.2±0.3	6.4	5.4±.02	5.8	3.8±0.2	4.0

Table 5. Observed and predicted data for elongation at break in different relative humidities.

Formulation	Elongation at Break (%)					
	33% RH		54% RH		75% RH	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	643±80	714	646±54	702	655±26	693
F2	628±64	586	543±50	566	407±40	416
F3	565±71	494	614±56	672	377±32	390
F4	649±49	604	699±72	739	514±68	506
F5	416±60	430	417±71	397	383±53	394
F6	403±56	389	467±44	524	419±60	422

Increasing the relative humidity caused a slight decrease in the coefficients of PVA and starch (Table 2), thereby reducing the tensile strength and the Young's modulus. The role of water as plasticiser was already fully studied (TANG & ALAVI, 2011; VILPOUX & AVÉROUS, 2004). Considering the plasticiser effect and the hydrophilic character of the PVA and starch, when the material is conditioned into a higher relative humidity, the presence of water in the matrix increases the molecular mobility of the polymeric chains and results in a less rigid structure, which can explain the above mentioned results.

Similar behaviour was observed in casting films of PVA (completely hydrolysed and medium size chain) and corn starch (1:1 wt%) plasticised with glycerol (0 – 50 wt%), in which increasing the relative humidity promoted a reduction in the tensile strength and Young's modulus (LEE et al., 2007).

Mao et al. (2000) produced extruded films of corn starch containing 9.1 wt% PVA (completely hydrolysed to medium chain size) and plasticised with glycerol, and the tensile strengths of the films ranged from 47 (0% glycerol) to 9 MPa (35% glycerol) at 30% RH and from 12 (0% glycerol) to 2 MPa (35% glycerol) at 50% RH. Under the same conditions, the maximum elongations were 250 and 150%, respectively. These results demonstrate the plasticising effect of the water in PVA/starch films, i.e., with increasing water content, the films exhibited a decrease in tensile strength and an increase in elongation; the same behaviour was observed with increasing glycerol content in the blends.

Ramaraj (2007) produced casting films of potato starch and PVA (medium degree of hydrolysis and chain size). The tensile strengths of the films ranged from 8.02 to 13.00 MPa, the elongation at break ranged from 94 to 398%, and the Young's modulus ranged from 4 to 43 MPa depending on the starch concentration (0 - 50 wt%). According to the authors the main component responsible to increase the tensile strength and Young’s modulus properties was the PVA, in contrast to the behaviour observed in our study. Also considering 33% RH (Table 2), the coefficients showed a positive effect for starch and PVA in the blends ($\beta 1 = 8.04$, $\beta 2 = 12.15$) and a negative effect for glycerol ($\beta 3 = -5.70$) for Young’s modulus. Based on this, higher glycerol content decreased the Young’s modulus and higher starch and mainly PVA concentrations increased the rigidity of the films (greater Young’s modulus). The same authors attributed the increase of Young’s modulus to a filler effect promoted by the addition of starch in the blends, with the starch granules acting as reinforcement.

Limpan et al. (2010) produced casting films with maize starch and 10 to 40 wt% PVA (fully hydrolysed and chain size of 100,000 - 146,000) without plasticisers. The tensile strength of the films ranged from 70 to 20 MPa and the elongation at break ranged from 7 to 48% depending on the RH (20 to 100%), and according to the authors the RH effect was due to the plasticising effect of water

Coefficients of the mixture design models for the puncture strength and puncture elongation of the films under different relative humidities are shown in Table 6.

Table 6. Regression coefficients for the puncture analysis.

Coefficient [a]	**Puncture Strength** (N/mm)			**Puncture Elongation** (mm)		
	33% RH	54% RH	75% RH	33% RH	54% RH	75% RH
β_1	180	107	80	17.18	16.92	17.67
β_2	208	152	98	19.79	23.11	23.42
β_3	10	-71	-168	23.69	16.46	24.57
β_{12}	-264	-339	-504	35.05	-20.08	-
β_{13}	ns[b]	205	355	ns	22.06	-
β_{23}	ns	242	379	ns	17.04	-
R^2	0.98	0.98	0.95	0.66	0.97	0.70

[a] β_1 = starch, β_2= PVA, β_3 = glycerol, β_{12} = interaction starch:PVA, β_{13} = interaction starch:glycerol, β_{23} = interaction PVA:glycerol.

[b] ns = not significant.

The puncture strengths ranged from 40.5 to 201.4 N/mm, and the puncture elongations ranged from 17.7 to 24.7 mm (Table 7 and 8).

The main component coefficients of the puncture strength model decreased with increasing moisture content and this effect was due to the plasticising effect of water, and increasing the concentration of PVA in the blend improved the puncture properties of the materials. This behaviour was similar to the mechanical properties; therefore, the same previous discussions are valid.

Table 7. Observed and predicted data for puncture strength in different relative humidities.

Formulation	Puncture Strength (MPa)					
	33% RH		54% RH		75% RH	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	201±20	208	156±13	152	100±9	98
F2	163±17	180	102±7	107	69±9	80
F3	105±10	109	87±12	101	64±9	60
F4	164±10	158	148±12	141	100±5	102
F5	94±4	95	68±5	69	40±5	44
F6	119±6	120	80±3	81	46±4	48

Table 8. Observed and predicted data for puncture elongation in different relative humidities.

Formulation	Puncture Elongation (mm)					
	33% RH		54% RH		75% RH	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
F1	19.6±1.6	19.8	21.9±2.3	23.1	22.0±2.2	23.4
F2	17.8±1.5	17.2	17.7±0.9	16.9	17.7±1.2	17.7
F3	21.6±1.4	21.7	21.9±2.1	24.0	22.1±3.7	24
F4	21.8±1.3	20.8	24.7±0.8	24.6	23.3±0.8	23.7
F5	21.6±0.9	20.4	21.2±1.6	22.2	22.0±1.4	21.1
F6	21.8±1.1	21.9	20.0±0.6	20.0	19.7±0.9	20.1

3.2 Weight loss in water

The weight loss in water of the biodegradable films ranged from 54.4 to 75.4% (Table 9), and high values of weight loss were expected because all of the blend components were hydrophilic, and as shown in Table 10, the PVA component (β2) had the greatest effect on weight loss. Lee et al. (2007), in PVA:corn starch films plasticised with glycerol (0-50 wt%),obtained values of solubility in water from 20 to 60 %, which are less than those obtained in this work; however, the methodology employed by the authors was different. A high solubility of biodegradable materials is important for accelerating the biodegradation process when the materials are disposed of in sanitary landfills, aquatic environments, or in specific agricultural uses; thus, a high solubility is a good characteristic of the material.

Table 9. Observed and predicted data for the apparent opacity, weight loss in water and water vapour permeability of the films.

Formulation	**Apparent Opacity** (%)		**Weight Loss in Water** (%)		**Water Vapour Permeability** ($g.m^{-1}.s^{-1}.kPa^{-1}$) ($x10^{10}$)	
	Observed	Predict	Observed	Predict	Observed	Predict
F1	42.4±6.9	38.6	75.4±8.9	80.6	2.1±0.2	2.1
F2	40.4±7.1	40.4	69.1±1.6	69.1	2.8±0.9	2.7
F3	23.8±2.6	22.4	54.4±0.2	54.7	4.7±0.2	4.4
F4	42.9±7.4	42.9	63.4±4.1	63.2	3.0±0.2	3.3
F5	28.6±2.7	28.6	67.1±5.0	67.1	4.5±0.7	4.7
F6	28.2±4.0	28.2	62.0±2.0	62.0	3.7±0.2	3.6

Table 10. Regression coefficients for the apparent opacity, weight loss in water and water vapour permeability of the films.

Coefficient[a]	**Apparent Opacity** (%)	**Weight Loss in Water** (%)	**Water Vapour Permeability** ($g.m^{-1}.s^{-1}.kPa^{-1}$) **(**$x10^{10}$)
β_1	40.41	69.09	2.73
β_2	38.56	80.65	2.13
β_3	-93.19	65.03	6.62
β_{12}	-245.06	-66.60	-
β_{13}	220.04	ns[b]	-
β_{23}	198.66	-72.39	-
R^2	0.77	0.89	0.77

[a] β_1 = starch, β_2= PVA, β_3 = glycerol, β_{12} = interaction starch:PVA, β_{13} = interaction starch: glycerol, β_{23} = interaction PVA:glycerol.

[b] ns = not significant.

3.3 Water vapour permeability

The water vapour permeability (WVP) of the films ranged from 2.14 to 4.74 $x10^{-10}$ $g.m^{-1}.s^{-1}.kPa^{-1}$ (Table 9), and the glycerol component (β_3) showed the greatest effect on increasing the permeabilities of the films (Table 10). Limpan et al. (2010; 2012) produced casting films with fish myofibrillar protein and different types and proportions of PVA plasticised with glycerol (50 wt%), and the WVP ranged from 8 to 12 $x10^{-10}$ $g.m^{-1}.s^{-1}.kPa^{-1}$, higher than those obtained in the present study. Xianda et al. (1987) produced PVA casting films, non-plasticised and plasticised with 30% of glycerol, and the WVP were 3.80 and 15.8 $x10^{-11}$ $g.m^{-1}.s^{-1}.kPa^{-1}$, respectively. Higher glycerol concentration increases the WVP because glycerol enhances the film hygroscopicity, and consequently the WVP (MÜLLER et al., 2008).

3.4 Scanning electron microscopy (SEM)

As shown in Figure 1, the surfaces and fracture surfaces of the films were both homogeneous, without the presence of domains or visible cracks, demonstrating that starch and the PVA had a good compatibility.

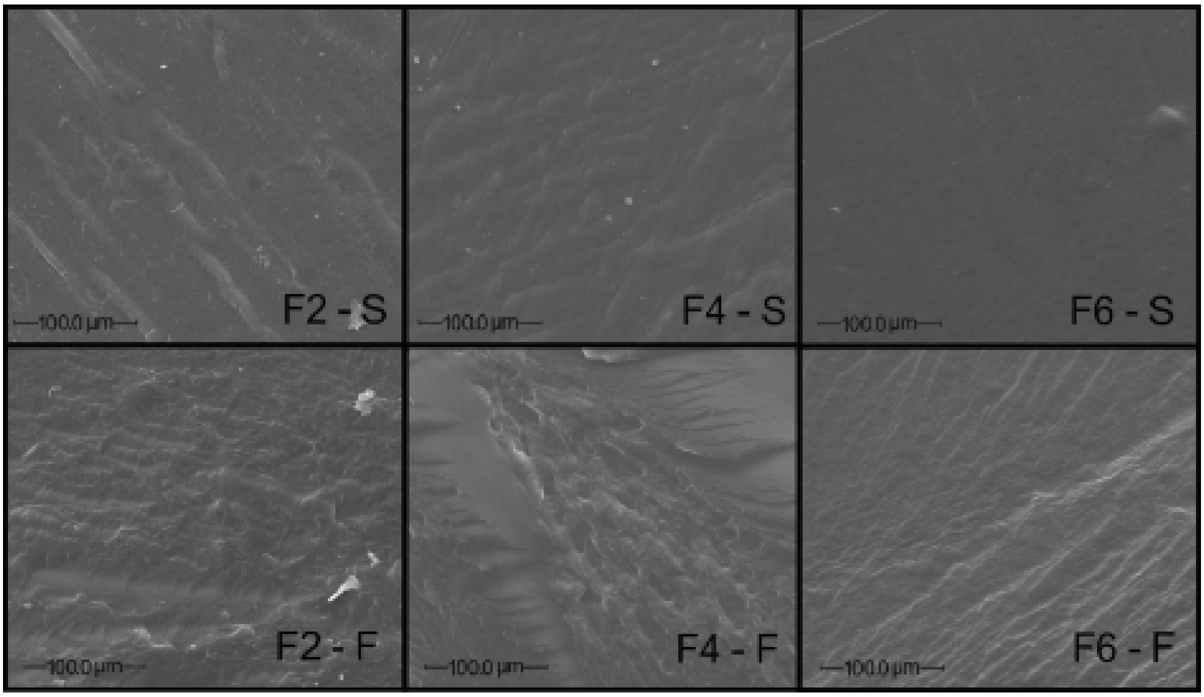

Figure 1. Scanning electron microscopy micrographs of the fracture surfaces (F) and unaltered surfaces (S) with magnification at 800 x.

Similar results were obtained with wheat starch + PVA films produced by extrusion (ZHIQIANG et al. 1999), with corn starch + PVA + glycerol films (LUO et al. 2012) and with PVA + pea starch films obtained by casting (CHEN et al. 2008). All of the authors obtained good miscibility between the polymers, and they observed a trend in which the surface became rougher with increasing starch concentration; this behaviour was also observed in this study, as shown by the scanning electron micrograph of film F2, which had the highest starch concentration.

3.5 Apparent opacity

Apparent opacities of the films ranged from 23.8 to 42.9% (Table 9).

Considering the most significant effects showed at Table 10, it was observed positive effects for the coefficients of the interactions starch:glycerol (β_{13} = 220.04) and PVA:glycerol (β_{23} = 198.66), which resulted in higher opacities. A negative effect was observed for the starch:PVA (β_{12} = -245.06) interaction that led to more translucent materials (lower apparent opacity).

The increasing opacity can be attributed to the good adhesion between the polymeric phases that difficult the light to pass through the matrix (OLIVATO et al, 2012b), as discussed in SEM analysis (Figure 1).

3.6 Fourier transformed infrared spectroscopy (FT-IR)

Because the formulations are composed of polymers that have various common functional groups, their spectra were very similar (Figure 2).

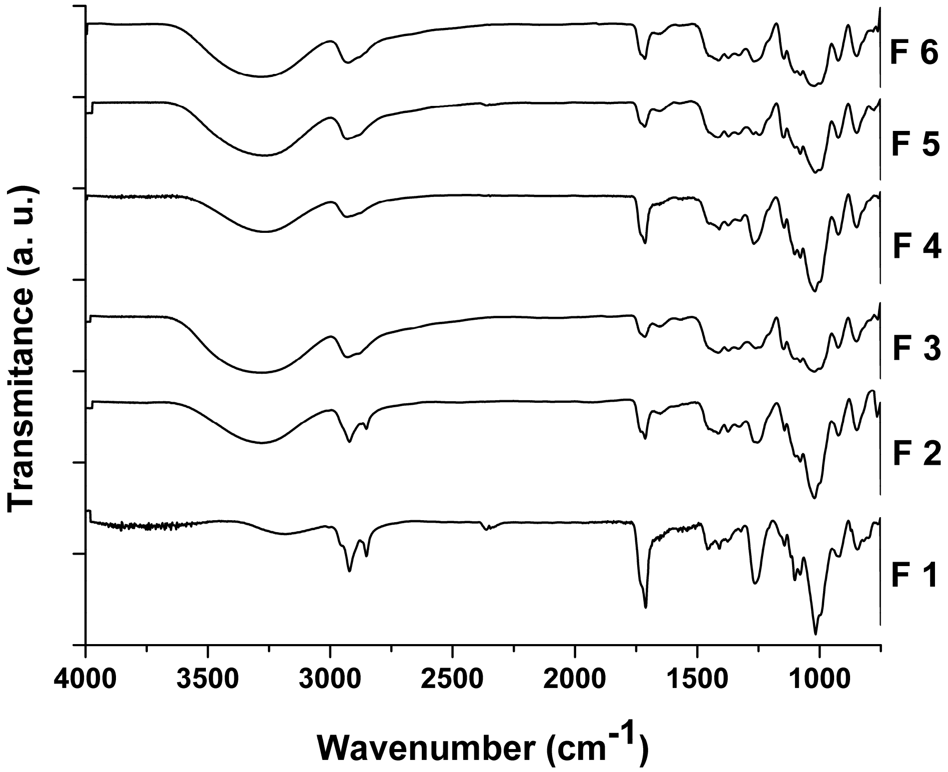

Figure 2. FT-IR analysis of the mixture designed sheets.

There was a large absorption band at 3400 cm^{-1} due to the stretching of hydroxyls present in the three components of the blend, and the region of 3000 - 2850 cm^{-1} showed bands for the stretching of -CH groups. These data are consistent with those observed by another authors (DAS et al. 2010; JAYASEKARA et al, 2003).

The absorption band at 1730 cm^{-1} was attributed to the stretching of carbonyl groups present in the residual acetate groups of the PVA molecule (JAYASEKARA et al. 2003), the absorption band at 1275 cm^{-1} was attributed to secondary alcohol presents in PVA molecules. Both absorption bands exhibited good correlation with the percentage of PVA present in the blend.

3.7 Thermogravimetric analysis (TGA)

Figure 3 shows the weight loss versus temperature curves of the films, and the mass loss at 300 °C was primarily related to the glycerol concentration, ranging from 48.98% (formulation F3 – glycerol content of 40%) to 68.64% (formulation F2 – glycerol content of 30%).

Thermal degradation occurred between 150 – 450 °C, which is the same range observed with corn starch + PVA (average degree of hydrolysis) films plasticised with glycerol and urea (TUDORACHI et al. 2000).

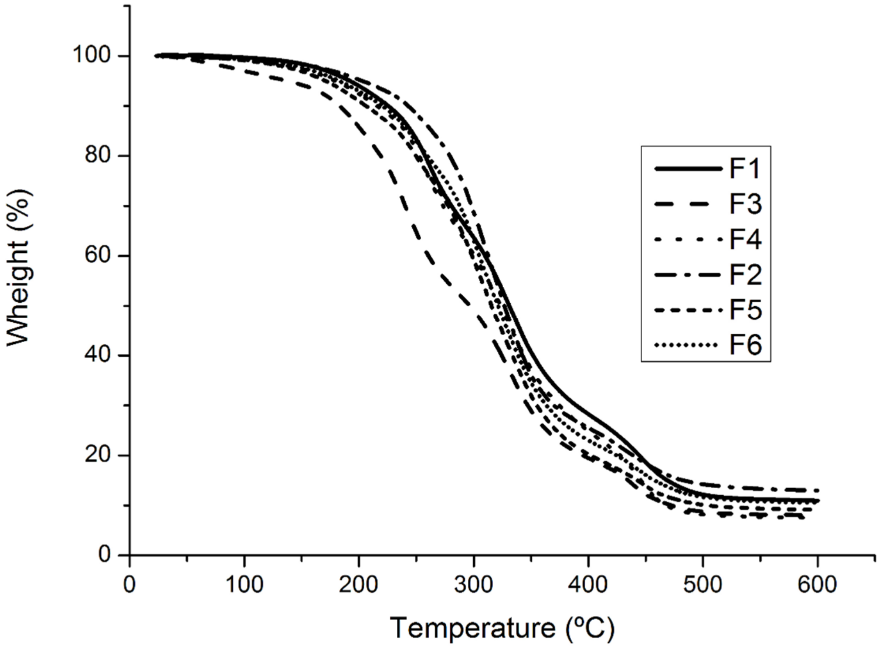

Figure 3. TGA analysis of the mixture designed sheets.

According to the DTG analysis (Figure 4), the films showed two or three pronounced steps. Films F2, F5 and F6 showed only two steps, most likely because the missing step (~250°C) is related to the initial degradation of the PVA, which had a lower concentration in the above formulations.

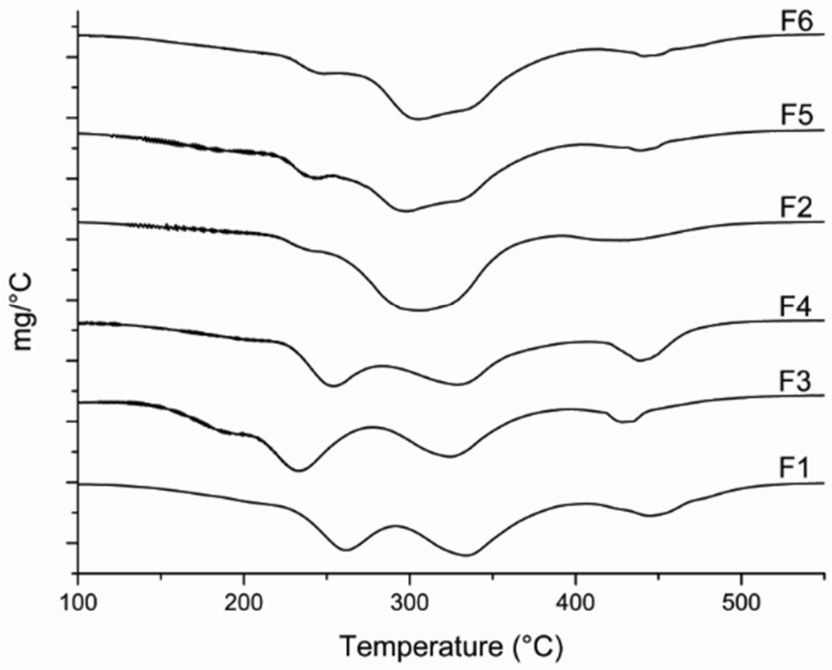

Figure 4. DTGA analysis of the mixture designed sheets.

Ray et al. (2009), in starch + PVA casting films plasticised with glycerol, observed that the degradation rates decreased compared with the pure components and that the position of the highest degradation peak shifted to higher temperatures, mainly at higher PVA concentrations. Similar behaviour was observed in our study, in which the formulations containing the highest PVA concentrations showed degradation peaks at higher temperatures. The hydrogen bonds between the components of the blend increase the thermal stability of the material (SIN et al., 2011).

It was observed similar behaviour in films of PVA + corn starch plasticised with glycerol, with three distinct onset regions; the first was due to the loss of volatiles, such as water and glycerol; the second degradation region was attributed to either starch and PVA; and the third region was due to carbonisation of the material (LUO et al., 2012).

In produced casting films with cassava starch + PVA (fully hydrolysed), and the mass loss curves also showed three stages (stage 1 - below 200°C; stage 2 -

between 200-500 °C, and stage 3 - above 500 °C). The authors observed that PVA decomposed faster than the starch and that the PVA had two stages of degradation: at ~200 °C and at ~450 °C (SIN et al., 2011). The intensities of the thermogravimetric steps observed at ~450°C correlated with the concentration of PVA present in the blends, which is consistent with the result obtained in this work.

4. CONCLUSIONS

The biodegradable films of cassava starch and PVA has adequate mechanical, microstructural and thermal properties, indicating a good miscibility between the starch and the PVA. All of the formulations exhibited good processability and extrudability, and the materials were visually homogeneous. The mechanical properties are influenced by formulation and by relative humidity of conditioning.

In general, a higher PVA concentration in the blend improves the mechanical and barrier properties of the biodegradable films. In contrast, a higher glycerol concentration and a higher relative humidity decrease the mechanical and barrier properties of the materials.

Biodegradable materials based on starch, PVA and glycerol blends has adequate properties and processability when compared with previous works.

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CAPÍTULO 5 – EFFECT OF MOLECULAR WEIGHT OF POLYVINYL ALCOHOL (PVA) AND THE EXTRUSION TEMPERATURE PROFILE ON THE PROPERTIES OF STARCH/PVA BIODEGRADABLE SHEETS

ABSTRACT: The aim of this work was to study the relationship of chain size of partially hydrolyzed PVA blended with starch in properties of biodegradable sheets produced by thermoplastic extrusion. It was also studied the effect of extrusion temperature profile to determine the better PVA concentration and temperature profile to produce biodegradable sheets through a factorial design. The processability, and the mechanical, thermal, optical, and microstructural properties of the biodegradable sheets were adequate, indicating that PVA/cassava starch blends has potential to replace conventional non-biodegradable polymers in large scale. It was not possible to state a conclusive relationship between PVA molecular weight and the materials properties, but in general, PVA with medium molecular weight and high extrusion temperature profile promote an increasing of mechanical properties of the sheets.

Keywords: mechanical properties, calendering, experimental design.

1. INTRODUCTION

Petroleum based plastics are used worldwide in a crescent number of application areas, and the disposal of plastics residues is an environmental problem. In the last years, several researchers have studied new eco-friendly materials preferentially from renewable resources to replace conventional petrochemical polymers (PARK et al., 2005; SINGHA & KAPOOR, 2014).

Starch is one of more studied biopolymer for biodegradable materials production, due to its low cost, biodegradability, and from renewable sources (TANG & ALAVI, 2011), but pure starch presents some drawbacks to replace conventional polymers due to its inherent brittleness, poor mechanical properties, high hydrophilicity and lower processability than conventional polymers. These drawbacks can be overcome by blending starch with other biodegradable polymers like polyvinyl alcohol - PVA (AYDIN & ILBERG, 2016).

PVA is an odorless, nontoxic, water-soluble, and fully biodegradable polymer that presents good film-forming capacity, resistance to greases and oil, good mechanical properties, and good barrier to oxygen and aroma (TANG & ALAVI, 2011).

According to Majdzadeh-Ardakani & Nazari (2010), the co-processing of starch with polar polymers, as PVA, can improve the mechanical properties and processability when compared to pure starch materials, and several studies reported a good compatibility of these polymers in starch/PVA blends. Mao et al. (2002) produced sheets by extrusion using cornstarch plasticized with glycerol (30% w/w), with tensile strength of 1.8 MPa and elongation at break of 113%, and adding PVA (9.1% w/w) the tensile strength and elongation at break were enhanced to 4 MPa and 150% respectively. According to the authors, the material with PVA had no cracks, unlike that observed by SEM in materials without PVA. Similar results was observed by Ray et al. (2009), that produced casting films with starch:PVA:glycerol of 60:40:30 and 50:50:30 (wt%). Films with higher PVA content had better mechanical properties and the polymers dispersion in the blend was improved, creating a more homogeneous network as observed by SEM and FT-IR. Therefore, PVA and starch has a good compatibility for the production of biodegradable materials.

Zanela et al. (2015b) produced extruded sheets based in different proportions of starch, PVA and glycerol through a mixture design. The authors observed that all formulations were homogeneous, without visible cracks by SEM, demonstrating a good compatibility between both polymers, and with the increasing the level of PVA present in the blends, the mechanical and barrier properties of the sheets were increased.

There are several PVA grades, with different molecular weights and chain sizes, due their large field of application, so it is important to study how these characteristics affect the properties of the films. Limpan et al. (2012) evaluate the influence of PVA with different hydrolysis degree and molecular weight in properties of fish myofibrillar protein/PVA blends with glycerol as plasticizer. The author observed that PVA with higher molecular weight improves tensile strength and elongation at break, and PVA with higher hydrolysis degree led to films that were more rigid.

Silva et al. (2008) produced films by casting using PVA with different hydrolysis degree and pigskin gelatin, and they observed that the hydrolysis degree influenced the properties of the films, but they were unable to find a relationship of the hydrolysis degree with the physical properties of the films.

The aim of this work was to study the relationship of chain size of partially hydrolyzed PVA blended with starch in properties of biodegradable sheets produced by thermoplastic extrusion. It was also studied the effect of extrusion temperature profile to determine the better PVA chain size and temperature profile to produce biodegradable sheets through a factorial design.

2. EXPERIMENTAL

2.1 Materials

It was used three PVA grades (Sekisui Chemical, Japan) with similar degrees of hydrolysis (DH) and different chain sizes (based on their viscosity in 4% aqueous solution): Selvol™ 203 (DH: 88.14%, viscosity 4.10 cP); Selvol™ 523 (DH: 87.84%, viscosity: 24.50 cP) and Selvol™ 540 (DH: 88.04 %, viscosity: 49.40 cP); native cassava starch (Indemil, Brazil) and glycerol (Dinamica, Brazil).

2.2 Methods

2.2.1 Factorial design

It was used a 3^2 factorial design with replicate in the central point (total of 10 runs), the independent variables were PVA grade and barrel temperature profile of the five heating zones of the extruder, and the coded and real values for all runs are showed in Table 1.

The factorial design were analyzed using the Experimental Design proceeding of Statistica 7.0 (Statsoft, USA) software. The 2-way interaction equation (eq. 1) was used to modeling the responses:

$$y = \beta_0 + \beta_1 x_1 + \beta_{11} x_1^2 + \beta_2 x_2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \beta_{122} x_1 x_2^2 + \beta_{112} x_1^2 x_2 + \beta_{1122} x_1^2 x_2^2 \qquad (1)$$

Where: y is the dependent variable (response), β is the regression coefficient of each term, x_1 is the PVA grade, x_2 is the extrusion temperature profile.

Table 1. Coded and real values for 3^2 factorial design.

	Coded value		Real value	
Formulation	**PVA Grade X_1**	**Temperature Profile X_2**	**PVA Grade* X_1**	**Temperature Profile** X_2**
1	-1	-1	S 203	170 °C
2	-1	0	S 203	190 °C
3	-1	1	S 203	210 °C
4	0	-1	S 523	170 °C
5	0	0	S 523	190 °C
6	0	1	S 523	210 °C
7	1	-1	S 540	170 °C
8	1	0	S 540	190 °C
9	1	1	S 540	210 °C
10	0	0	S 523	190 °C

* **S 203**: Selvol™ 203; **S 523**: Selvol™ 523; **S 540**: Selvol™ 540

** **170 °C**: 90/170/170/170/170 °C; **190 °C**: 90/170/190/190/190 °C; **210 °C**: 90/170/210/210/210 °C

The desirability function, the relationship between predicted responses on one or more dependent variables and the desirability of responses, was determined using the Experimental Design proceeding of Statistica 7.0 (Statsoft, USA) software.

2.2.2 Sheet production

All the formulations were composed by 38 wt% of starch, 27 wt% of PVA and 35 wt% of glycerol. After manual homogenization, the samples were placed in a vacuum oven (model Q819V2, Quimis, Brazil) with a vacuum pressure of 0.085 MPa for 90 minutes at 85 °C to incorporate the glycerol using the methodology adapted from Jang & Lee (2003). After this step, the blends were extruded in a co-rotating twin-screw extruder (model D-20, BGM, Brazil) with a screw diameter of 20 mm (L/D = 35), a screw speed of 100 RPM and a temperature profile according the experimental design based in Table 1. The samples were extruded using a flat die with 0.8 mm height and 320 mm length, coupled with a 3-roll water-cooled calender (AX Plásticos, Brazil) for sheets production.

2.2.3 Mechanical properties

The tensile strength, Young's modulus and elongation at break were analyzed in a texture analyzer (model TA.XT2i, Stable Micro Systems, England) with an initial distance between the grips of 30 mm and a crosshead speed of 0.8 mm.s^{-1}, according to ASTM D882-02 method, with some modifications. Ten samples from each treatment (50 mm in length and 20 mm in width) were conditioned in a desiccator with controlled relative humidity and temperature (53 ± 2% and 23 ± 2 °C respectively) for 72 hours before analysis.

For puncture analysis, ten specimens from each treatment were conditioned as described above, and punctured perpendicularly with a 6.35 mm diameter cylindrical probe at a velocity of 2.0 mm.s^{-1}. The puncture elongation (mm) was characterized as the maximum elongation supported by the sheet. The puncture strength (N/mm) was obtained by dividing the maximum force by the sheet thickness.

2.2.4 Water vapor permeability (WVP)

Water vapor permeability was determined gravimetrically according to the ASTM E96-009 standard. The measurements were performed using a relative humidity gradient of 33 - 64%.

2.2.5 Weight loss in water (WLW)

The WLW analysis was performed according to Olivato et al. (2012), in triplicate and expressed as the percentage of the original mass (Mi) and the final mass (Mf) of the film after immersion in water for 48 hours at 25 °C, according to eq. 2.

$$\mathrm{WLW} = [(\mathrm{M_i} - \mathrm{M_f})/\mathrm{M_i}] \times 100 \qquad (2)$$

2.2.6 Apparent opacity (Op) and color difference (ΔE*)

The Op values of the films were measured according to the method described by Maria et al. (2008), using a colorimeter (BYK Gardner, Germany) with illuminant D65 (daylight) and visual angle of 10°. Opacity (Op) was determined as the ratio of the opacity of the sample over a black standard Op_b and the opacity over a white standard Op_w being represented on an arbitrary scale (0-100%), and the analyses were performed in triplicate according to eq. 3.

$$Op = (Op_b/Op_w) \times 100 \quad (3)$$

The ΔE* values are obtained according Maria et al. (2008) too, based in eq. 4, where: ΔL*, Δa* and Δb* are the differences between the sample measured under the white standard and the white standard alone.

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (4)$$

2.2.7 X-ray diffraction (XRD)

XRD analysis was performed using a diffractometer (Panalytical X´Pert PRO MPD, Netherlands), emitting copper Kα radiation (λ = 1.5418 angstrom). The anode radiation was generated at 40 kV and 50 mA and was monochromatized using a 20 mA current. Diffraction intensity measurements were performed between 2θ = 2° to 60° at room temperature. The relative crystallinity of each film was calculated by dividing the area of the strongest peaks by the total area of the crystalline region (the total area under the curve minus the baseline).

2.2.8 Scanning Electron Microscopy (SEM)

SEM was recorded using a scanning electron microscope (FEI Quanta 200, USA). The films were fractured in liquid nitrogen, attached to aluminum supports and coated with gold (BAL-TEC SCD 050 sputter coater, Leica Microsystems, Germany) (40-50 nm in thickness) at 25 °C and a pressure of 2.105 Torr for 180 seconds. The surface and the fracture surface of the films were analyzed.

2.2.9 Fourier Transform Infrared Spectroscopy (FT-IR)

The samples were dried over anhydrous calcium chloride salt for one week and analyzed in a Fourier transform infrared spectrophotometer (FT-IR) (IR Prestige 21, Shimadzu, Japan) using a horizontal attenuated total reflection (ATR) module operating over the spectral range of 4000 cm^{-1} - 750 cm^{-1}.

2.2.10 Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed using a TGA – 50 (Shimadzu, Japan). The samples were dried over anhydrous calcium chloride salt and analyzed from 25 °C to 600 °C with a 10 $°C.min^{-1}$ heating rate under a nitrogen atmosphere (20 $mL.min^{-1}$).

3. RESULTS AND DISCUSSION

The sheets of all formulation were continuous and visually homogenous, with a medium thickness of 850±191 μm.

All the equations generated by the mathematical model had coefficients of determination (R^2) higher than 0.70, indicating that the models fitted well the experimental data.

3.1 Mechanical properties

The Table 2 presents the factorial design models (Eq. 1) for the mechanical properties of the sheets. The Table 3 presents the experimental data.

Figures 1 and 2 presents the response surface plots.

Table 2. Factorial design models for the mechanical properties of the biodegradable sheets at 53% RH.

Coefficient	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Puncture strength (N/mm)	Puncture elongation (mm)
β_0	1.70	4.75	187	69.3	13.3
β_1	0.21	– 0.44	65	17.0	4.7
β_{11}	0.38	ns	98	6.7	3.2
β_2	ns	– 0.94	97	ns	3.6
β_{22}	ns	– 1.11	33	ns	1.0
β_{12}	0.20	– 0.43	51	11.4	3.3
β_{122}	ns	ns	ns	ns	ns
β_{112}	0.19	ns	70	ns	ns
β_{1122}	ns	ns	22	ns	0.5
R^2	0.81	0.96	0.98	0.83	0.99

$y = \beta_0 + \beta_1 x_1 + \beta_{11} x_1^2 + \beta_2 x_2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \beta_{122} x_1 x_2^2 + \beta_{112} x_1^2 x_2 + \beta_{1122} x_1^2 x_2^2$

y = response; x_1= PVA grade; x_2= extrusion temperature profile; $x_1 x_2$= interaction PVA grade: extrusion temperature profile.

ns =not significant.

The tensile strength of the sheets ranged from 1.0 to 2.6 MPa, and according to the factorial design model the tensile strength were influenced mainly by the PVA grade (Table 2 and Figure 1), and there was a positive interaction between PVA and temperature profile of extrusion. The sheets with the higher tensile strength calculated by the desirability function (2.7 MPa) can be obtained producing them with PVA S523 (coded 0) and temperature profile of 90/170/190/190/190 °C (coded 0), and this value is close to the experimental data (2.5 MPa).

The Young's modulus ranged from 3.0 to 6.9 MPa, and according to the factorial design model the modulus were influenced by both the PVA grade and the temperature profile (Table 2 and Figure 1), and there was a negative interaction between PVA and temperature profile of extrusion. According to the desirability function the sheets produced with lower molecular weight PVA (S203) and lower temperature profile (90/170/170/170/170 °C) has the higher Young's modulus (6.7 MPa).

The elongation at break ranged from 42 to 421%, and according to the factorial design model the elongation were influenced by both the PVA grade and the temperature profile (Table 2 and Figure 1), and there was positive interactions between PVA and temperature profile of extrusion. According to the desirability function the sheets produced with intermediate molecular weight PVA (S503) and higher temperature profile (90/170/210/210/210 °C) has the higher elongation at break calculated by the desirability function (496%).

Table 3. Experimental data for mechanical properties of the sheets.

Formulation	**Tensile strength (MPa)**	**Young's modulus (MPa)**	**Elongation at break (%)**	**Puncture strength (N/mm)**	**Puncture elongation (mm)**
1	1.5±0.2	6.2±0.9	42±5	64±6	5.9±0.3
2	1.0±0.1	3.6±0.2	74±7	41±1	6.8±0.2
3	1.0±0.1	5.8±0.3	49±5	40±3	6.8±0.1
4	1.9±0.2	6.9±0.3	107±43	85±15	11.7±3.0
5	2.0±0.3	3.2±0.2	358±76	82±12	18.7±1.7
6	2.5±0.2	4.3±0.3	418±51	92±7	19.9±0.6
7	1.5±0.1	6.2±0.3	62±10	64±10	7.3±0.7
8	1.5±0.1	3.0±0.2	203±34	70±28	15.4±2.0
9	1.9±0.1	3.6±0.1	310±55	78±12	20.9±1.1
10	2.6±0.2	3.9±0.3	421±51	84±6	21.5±1.0

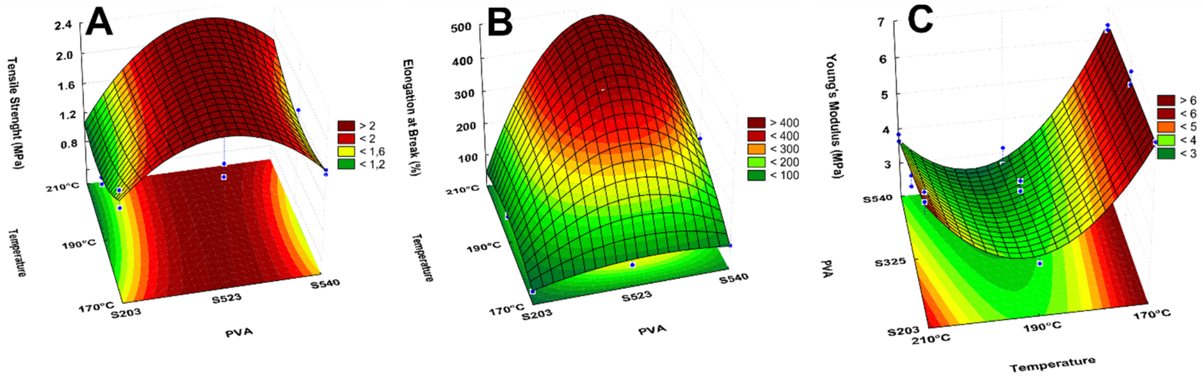

Figure 1. Surface response plot for tensile strength (A), Young's modulus (B), and elongation at break (C) of the biodegradable sheets.

Mao et al. (2002) extruded films of cornstarch (61 wt%), PVA (9 wt%), and glycerol (30 wt%), and the films had tensile strength of 4 MPa and elongation at break of 150% at conditioning humidity of 50%. The PVA used by the authors was similar to S540; and the tensile strength was higher and the elongation was lower than those obtained in our study. These differences can be attributed to the PVA concentration in the films, because according to Zanela et al. (2015a, 2015b) the concentration of PVA was the mainly factor for increasing the tensile strength, elongation at break and Young modulus of cassava starch:PVA biodegradable sheets.

According to Follain et al. (2005) the extrusion forces the PVA molecules to be stretched and aligned in a linear conformation, that promotes a good interaction with starch, and higher temperatures enhance this interaction because the PVA reaches the melting temperature. According to Sin et al. (2010), the neat PVA (fully hydrolyzed and with medium chain size) has a melting temperature of 207 °C, and when plasticized with 40 parts per hundred parts of resin (phr) of glycerol, the melting point reduces to 177 °C. So higher temperatures can melt the PVA completely and the shear forces in extrusion process promoted a better interaction with polymer chains. Thus, these facts explain the tendency of increasing tensile strength and elongation at break of the materials with increasing the extrusion temperature profile.

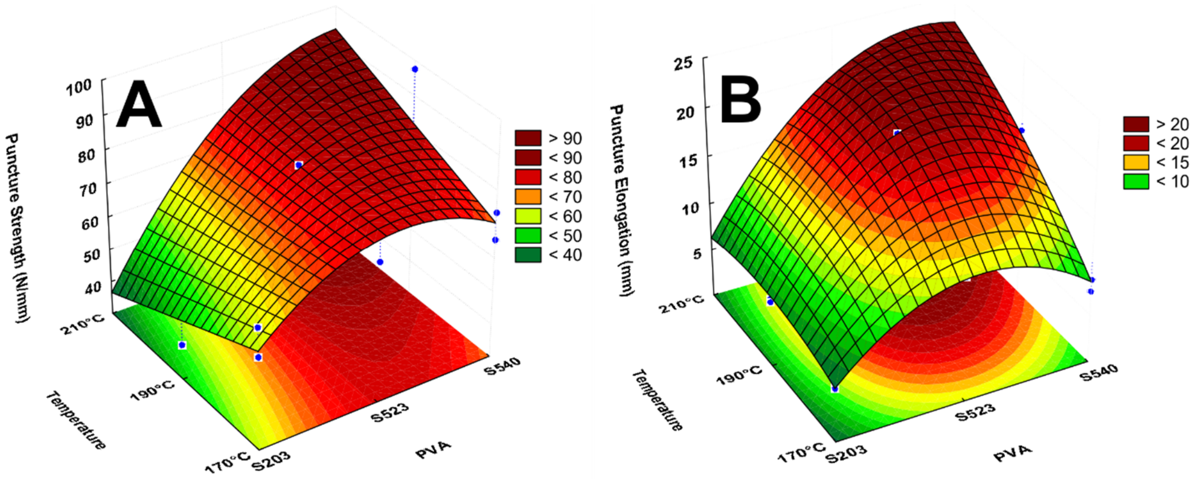

Figure 2. Surface response plot for puncture strength (A) and puncture elongation (B) of the biodegradable sheets.

The puncture strength of the sheets ranged from 40 to 92 N/mm, and according to the factorial design model the puncture strength were influenced mainly by the PVA grade (Table 2 and Figure 2), and there was a positive interaction between PVA and temperature profile of extrusion. The sheets with the higher tensile strength calculated by the desirability function (98 N/mm) can be obtained producing them with PVA S540 (coded 1) and temperature profile of 90/170/210/210/210 °C (coded 1).

The puncture elongation ranged from 5.9 to 21.5 mm, and according to the factorial design model the elongation were influenced by both the PVA grade and the temperature profile (Table 2 and Figure 2), and there was positive interactions between PVA and temperature profile of extrusion. According to the desirability function the sheets produced with higher molecular weight PVA (S540) and higher temperature profile (90/170/210/210/210 °C) has the higher puncture elongation calculated by the desirability function (22.2 mm).

3.2 Water Vapor Permeability (WVP)

The WVP of the sheets ranged from 3.4 to 8.2 $\times 10^{-10}$ $g.m^{-1}.s^{-1}.kPa^{-1}$, and according to the factorial design model the WVP were influenced mainly by the PVA grade (Table 4 and Figure 3), and there was a positive interaction between quadratic terms of PVA and temperature profile of extrusion. The sheets with the lower WVP calculated by the desirability function (3.3 x10^{-10} g.m^{-1}.s^{-1}.kPa^{-1}) can be obtained producing them with PVA S203 (coded -1) and temperature profile of 90/170/210/210/210 °C (coded 1).

Sheets produced with lower molecular weight PVA had lower WVP, probably because the PVA with lower MW can originate a more compact network with starch, that difficult the transport of water molecules through the polymeric matrix. Limpan et al. (2012) had similar results in films produced with fish myofibrillar protein blended with different PVA grades and according to the authors, PVA with higher molecular weight increase the disorder in the amorphous region, promoting an increase in the free volume between the polymer chains.

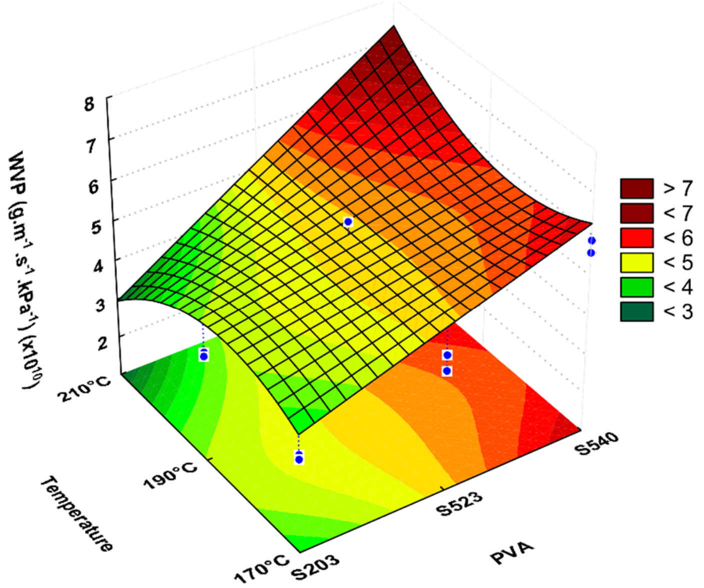

Figure 3. Surface response plot for water vapor permeability of the biodegradable sheets.

Zanela et al. (2015b) obtained WVP values ranging from 3.0 to 8.56 x10^{-10} g.m^{-1}.s^{-1}.kPa^{-1} for cassava starch/PVA (S203) sheets using glycerol as plasticizer and PVA ranging from 7.5 to 22.5 wt%. The authors observed that glycerol was the main factor that promoted an increasing of WVP due to its plasticizer properties. Wang, Ren & Kong (2014) also observed an increase of WVP in casting films of PVA/xylan at higher plasticizer content, because glycerol is a hydrophilic small molecule that allows its inclusion between polymers chains, increasing the free volume and so permitting water mobility through the material.

Table 4. Regression coefficients water vapor permeability, weight loss in water, apparent opacity, and color difference of the biodegradable sheets.

Coefficient	Water vapor permeability ($g.m^{-1}.s^{-1}.kPa^{-1}$) ($x10^{10}$)	Weight loss in water (%)	Apparent opacity (%)	Color difference (ΔE*)
β_0	4.99	47.26	39.11	27.06
β_1	1.32	– 6.06	– 2.93	ns
β_{11}	ns[b]	ns	– 3.51	ns
β_2	ns	ns	2.42	6.94
β_{22}	ns	ns	– 1.57	– 1.00
β_{12}	ns	ns	– 4.37	– 2.89
β_{122}	– 0.51	ns	ns	ns
β_{112}	ns	ns	– 4.50	– 3.82
β_{1122}	0.84	ns	– 1.50	ns
R2	0.72	0.79	0.98	0.94

[a] β_0= great mean; x_1= PVA grade; x_2= extrusion temperature profile; x_1x_2= interaction PVA grade: extrusion temperature profile.
[b] ns =not significant.

3.3 Weight Loss in Water (WLW)

The WLW of the sheets ranged from 36.2 to 55.4 %, and according to the factorial design model the WLW were influenced negatively only by the PVA grade (Table 4).

Limpan et al. (2012) observed the same behavior, but the factor of major influence in solubility of films was the hydrolysis degree of PVA. The surface plot of WLW is shown in Figure 4.

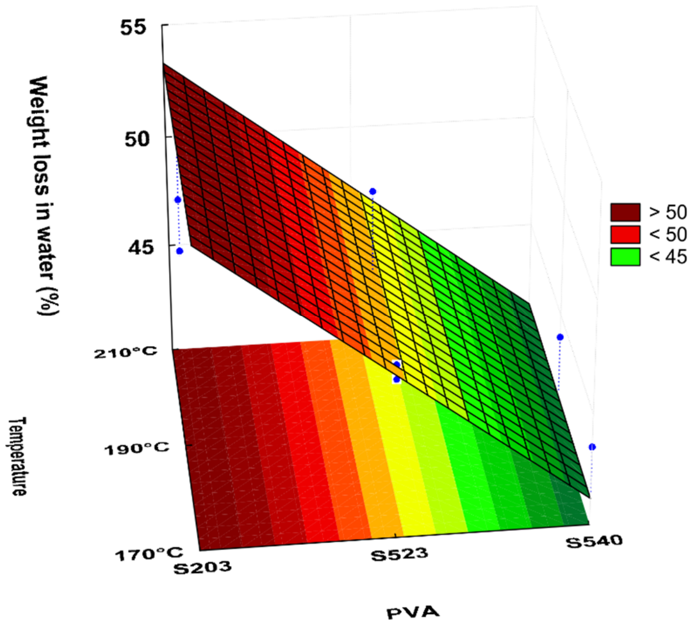

Figure 4. Surface response plot for weight loss in water – WLW of the biodegradable sheets.

According to Zanela et al. (2015a), the high WLW can be important for biodegradable sheets, accelerating the biodegradation process when these materials are disposed in aquatic environment for example.

3.4 Apparent Opacity (Op) and Color Difference (ΔE*)

The Op analysis ranged from 29.1 to 55.3 % (Table 5), and according to the factorial design model the Op were influenced negatively by PVA grade and positively by the temperature profile (Table 4 and Figure 5), and there was negative interactions between PVA and temperature profile of extrusion. According to the desirability function the higher Op values (55.4 %) was obtained for sheets produced with lower molecular weight PVA (S203) and higher temperature profile (90/170/210/210/210 °C).

The ΔE* analysis ranged from 17.8 to 39.5 (Table 5), and according to the factorial design model the Op were influenced mainly by the temperature profile (Table 4 and Figure 3). The sheets with the higher ΔE* value calculated by the desirability function (40.7) can be obtained producing them with PVA S203 (coded -1) and temperature profile of 90/170/210/210/210 °C (coded 1).

Table 5. Observed data for water vapor permeability, weight loss in water, apparent opacity and color difference of the biodegradable sheets.

Formulation	**WVP (x10^{10})***	**Weight loss in water (%)**	**Apparent opacity (%)**	**Color difference (ΔE*)**	**Crystallinity Index (%)**
1	3.4±0.1	55.4±0.2	37.2±2.1	17.8±3.4	21.2
2	3.4±0.1	48.7±2.6	45.3±2.6	27.8±2.5	21.4
3	3.5±0.3	53.7±1.2	55.3±1.1	39.5±1.5	21.7
4	4.2±0.3	48.2±1.5	38.1±6.4	24.3±3.6	20.0
5	5.2±0.6	46.8±3.7	33.7±3.7	26.5±2.0	20.6
6	4.5±0.1	46.3±0.5	36.2±5.7	32.9±3.8	20.8
7	5.7±0.2	36.2±9.1	35.0±2.9	22.6±2.8	20.7
8	5.0±0.2	41.0±2.7	37.6±1.2	24.5±3.1	20.4
9	7.9±0.1	42.3±4.4	39.5±1.2	34.1±3.7	21.5
10	8.2±0.1	48.0±3.2	29.1±0.8	23.6±1.6	21.9

* WVP – Water vapor permeability (g.m^{-1}.s^{-1}.kPa^{-1})

The Figure 5 shows the surface plot for apparent opacity and color difference.

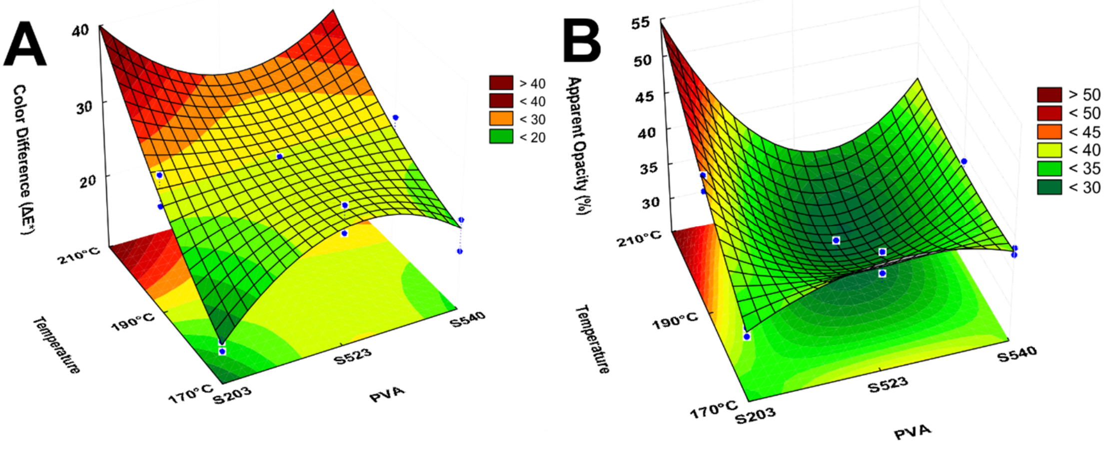

Figure 5. Surface response plot for color difference (A) and apparent opacity (B) of the biodegradable sheets.

Maria et al. (2008) produced casting films with gelatin/PVA/glycerol and they did not find relationship with Op or ΔE* and PVA grade (hydrolysis degree and molecular weight), and the Op and ΔE* values reported were lower than those obtained in our work. This can be explained because films are thinner than sheets, and the casting process leads to more transparent materials than extrusion. Besides that, the high temperatures in extrusion can degrade some compounds and/or induce non-enzymatic reactions, resulting in yellowish sheets that present greater difference when compared to white standard.

3.5 X-Ray diffraction (DRX)

The biodegradables sheets of all formulations presented similar diffractograms (Figure 6), with a sharp peak in 19.9°, and an overlapped peaks in 17.7° and 23.5°, similar to observed by Zanela et al. (2015b), and a diffraction peak in 40.6°. Das et al. (2010) produced starch:PVA film, and they attributed the 19.6° peak to the ordered arrangement of PVA chains in the material, and the 17.7° peak was attributed to plasticized starch, but this peak had little intensity and it was overlapped by 19.9° peak.

According to Moorthy (2002), cassava starch possess diffraction pattern 'A', 'C' or a mixture of them, and three major peaks were observed in 15.3, 17.1 and 23.5°, but these peaks was not clearly observed in our diffractograms and probably they were overlapped by the 19.9° sharp peak.

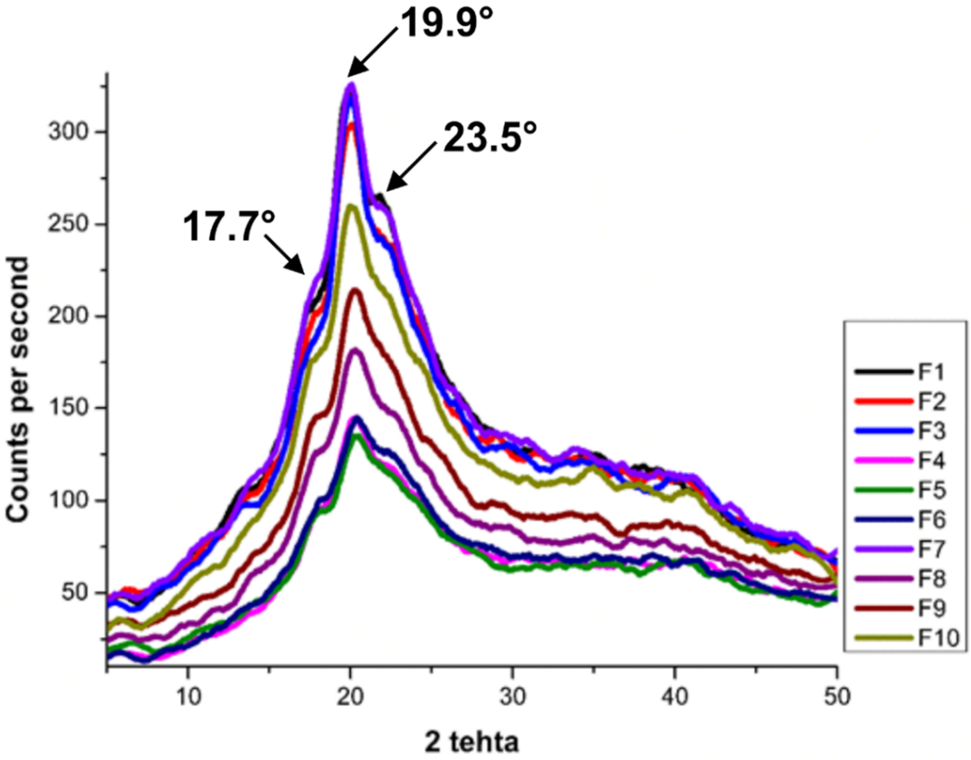

Figure 6. Diffractogram of the biodegradable sheets based in starch:PVA.

The crystallinity index ranges from 20.0 to 21.9% according to Table 5. The starch crystallinity could be originated from the retrogradation of starch after the extrusion process or, according to Li et al. (2014) the crystallinity structure could be due to the native crystallinity that remains after the extrusion, but the crystallinity of the sheets can be attributed mainly to PVA.

3.6 Scanning Electron Microscopy (SEM)

The Figure 7 shows the SEM analysis of the fracture of the biodegradable sheets, and it is possible to observe a smooth surface, without cracks and domains, due to the good compatibility of both polymers. Similar results was observed by Priya et al. (2014) in PVA:cornstarch casting film, and by Maiti, Ray & Mitra (2012), in casting starch:PVA films. It was not possible observe differences in microstructure promoted by temperature or PVA grade used.

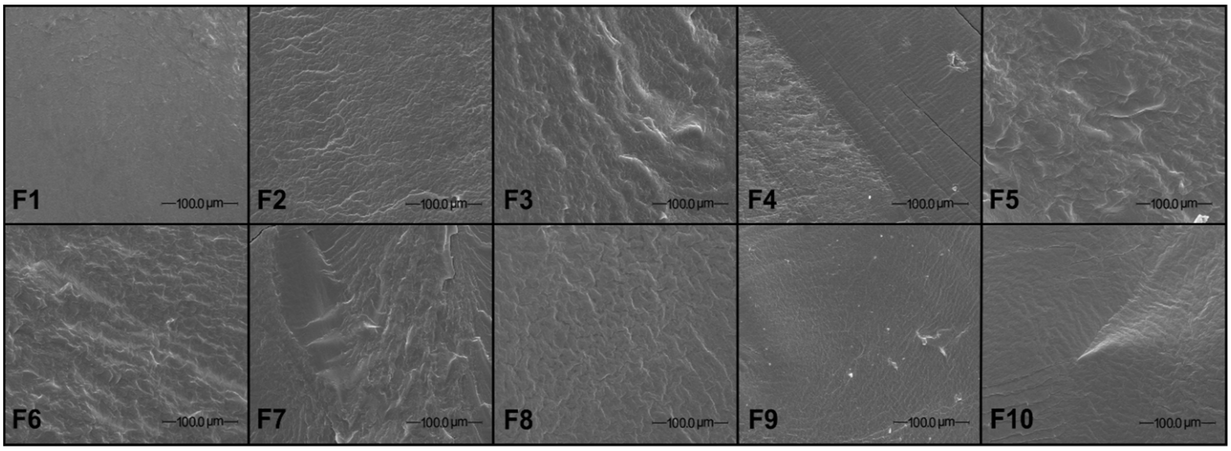

Figure 7. Scanning electron microscopy micrographs of the fracture of the sheets with magnification at 800 x.

3.7 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of the biodegradable sheets are shown in Figure 8, and it is possible to observe that all sheets presented a similar spectra. The region near 3300 cm^{-1} is related to the hydroxyl (O-H) stretching assigned to molecular and intermolecular hydrogen bonding. The vibration region between 3000 – 2800 cm^{-1} is due to the (C-H) stretching, and it is in agreement with observed by Singha & Kapoor (2014), in potato starch:PVA blends produced by casting. According to Mansur et al. (2008), the spectral range between 1750 – 1735 cm^{-1} is assigned to the stretching of C-O and C=O groups present in residual acetate groups of PVA molecules. The band at 1275 cm^{-1} is due to the secondary alcohol present in PVA structure. Similar results was observed by Brandelero et al. (2015), and Imam et al. (2005) in films based in cassava starch:PVA and cornstarch:PVA respectively.

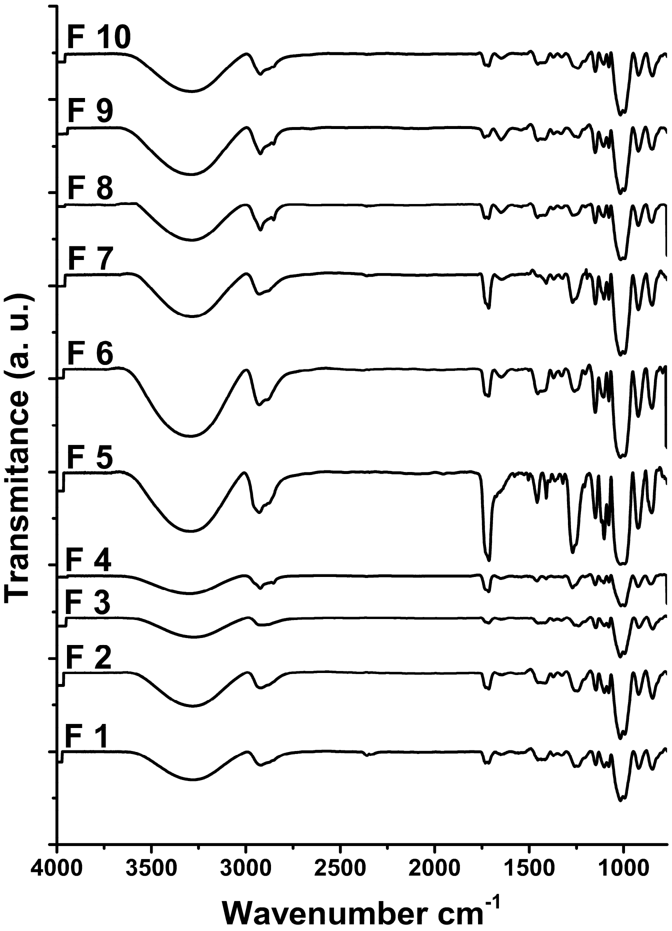

Figure 8. FT-IR analysis of the biodegradable sheets based in starch:PVA.

3.8 Thermogravimetric Analysis (TGA)

The Figure 9 presents the weight loss versus temperature curves of the biodegradable sheets. The weight loss occurred between 150 - 450 °C, and the main weight loss was around 300 °C (61.8 to 53.5%), and these results are similar to those reported by Zanela et al. (2015a).

The DTG curves (Figure 9) show three weight-loss stages, occurring around 250, 320 and 440 °C, respectively. According to Rahman et al (2010), the TG curve of starch:PVA blends plasticized with glycerol can be divided in three phases. The first weight-loss stage is below 200 °C, that involves the vaporization of volatiles substances, for example, water. The second stage occurs between 200 - 500 °C, and is related to boiling of glycerol (290 °C), and severe degradation of main chain, lateral groups, and depolymerization producing small hydrocarbon degradation products, like alkenes, alkanes and aromatics with posterior vaporization of degradation products. The third stage occurs above 500 °C, and corresponds to the carbonization of the organic matter.

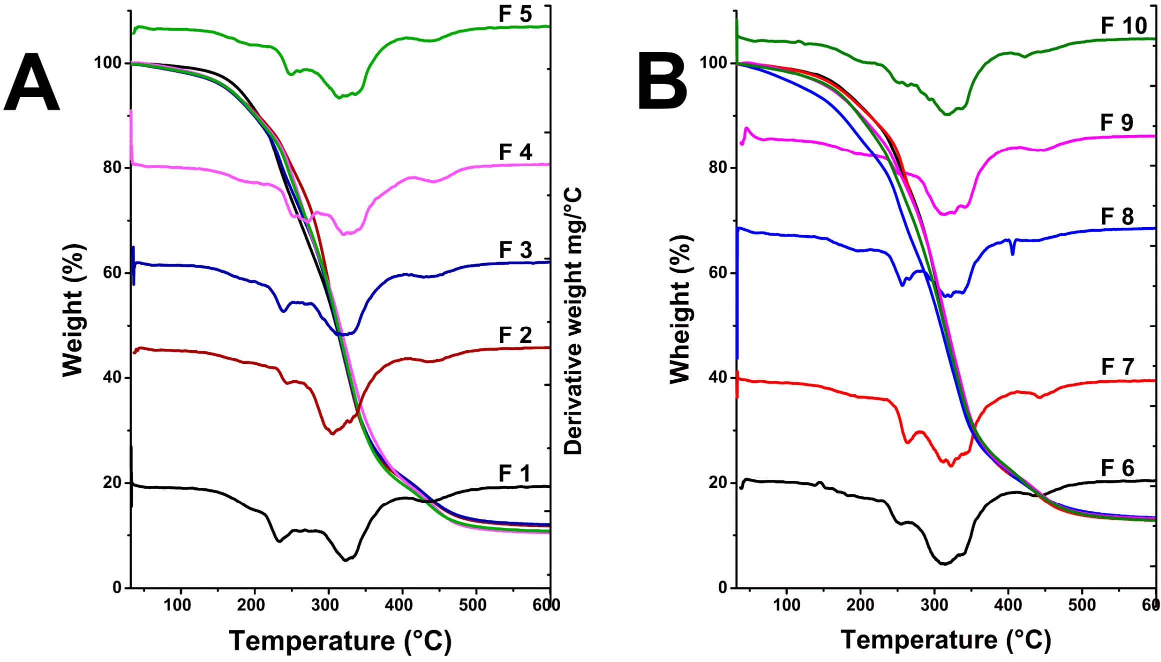

Figure 9. TG and DTG analysis of the biodegradable sheets based in starch:PVA.

According to the TG analysis, neither the PVA grade or the temperature profile of the extruder influenced the thermal behavior of the biodegradable sheets.

4. CONCLUSION

The biodegradable sheets presented good processability, mechanical, thermal, optical, and microstructural properties; indicating that PVA/cassava starch blends has potential for replacement of conventional non-biodegradable polymers.

It was not possible to state a conclusive relationship between PVA molecular weight and the materials properties, but in general, PVA with medium molecular weight and high extrusion temperature profile promote an increasing of mechanical properties of the sheets.

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CAPÍTULO 6 – POLYVINYL ALCOHOL WITH DIFFERENT MOLECULAR WEIGHT AND HYDROLYSIS DEGREE BLENDED WITH STARCH: EFFECT ON THE PROPERTIES OF FLAT-DIE EXTRUDED SHEETS

ABSTRACT: Blends of polyvinyl alcohol - PVA and starch was already studied in order to replace non-biodegradable plastic materials, but there are several PVA grades with different molecular weight - MW and hydrolysis degree - HD, and it was necessary a study to understand how these characteristics affect the properties of the material produced by flat-die extrusion. It was used PVA with different MW and HD: Selvol™ 203 (HD: 88.14 %, viscosity: 4.10 cP); Selvol™ 523 (HD: 87.84 %, viscosity: 24.50 cP), Selvol™ 540 (HD: 88.04 %, viscosity: 49.40 cP), Selvol™ 107 (HD: 98.30%, viscosity: 6.00 cP) and Selvol™ 325 (HD: 98.42 %, viscosity: 31.40 cP), native cassava starch and glycerol as plasticizer. The blends were composed by 40:25:35 wt% of starch, PVA and glycerol respectively, and sheets were produce in a twin-screw extruder. The sheets were characterized by mechanical properties, water vapor permeability, opacity, X-ray difraction, cristalinity index, FT-IR spectra, and microstructure (SEM). The extruded biodegradable sheets produced using PVA/starch/glycerol blends presented adequate processability, handleability and mechanical properties, with uniform appearance. The produced with higher hydrolysis degree PVA were more rigid, and those produced with higher molecular weight PVA were more resistance, but all PVA grades had good compatibility with starch in the extrusion process, therefore the PVA/starch blends are adequate for industrial scale production.

Keywords: biodegradable polymers; mechanical properties, extrusion.

1. INTRODUCTION

It is necessary to replace part of synthetic non-biodegradable plastics material by others eco-friendly polymers due to the environmental concerns (PANAITESCU et al., 2015).

Polyvinyl alcohol – PVA is a synthetic water-soluble biodegradable polymer, and it has excellent gas barrier properties, high strength and flexibility. However it presents some drawbacks, like the high melting point (220~245°C) when compared to other conventional polymers, so it is necessary to reduce the melting point or to protect the PVA from decomposition. The most used methods are the copolymerization, plasticization or polymer blending with for example starch, a renewable and low cost polymer (PRYIA et al., 2014, WANG et al., 2016).

The starch and PVA are both polar polymers, so their blends presents good compatibility, producing materials with excellent properties (SIDDARAMAIAH, RAJ & SOMASHEKAR, 2004). Both PVA and starch molecules have a large number of hydroxyl groups in the chain, and the hydroxyl groups can form either intermolecular hydrogen bonds, allowing a strong interaction between them (SUN et al., 2014).

The PVA presents a large application field in the industry, being widely used in adhesives, films and packaging, paper, textile, ceramics among others, so, PVA possess many different grades, based mainly in its hydrolysis degree – HD and molecular weight – MW (generally expressed in terms of solution viscosity), (SEKISUI, 2015).

Due to the wide range of PVA grades, the properties of biodegradable materials depend on the PVA grade, and there are several studies on the relationship of PVA molecular weight and hydrolysis degree on the materials properties, but it was not clearly established the relationship between them. For example, Maria et al. (2008) did not obtain a direct relationship between five PVA grades with different HD in mechanical properties of biodegradable casting films based on PVA and pigskin gelatin.

Chai, Chow & Chen (2012) produced hot-pressing films with cornstarch and PVA with two different molecular weight, and they observed that increasing the starch concentration (0-40 wt%) the tensile strength and elongation at break of the materials were reduced. The films produced with the higher MW PVA presented higher tensile strength and elongation at break compared with those with lower MW PVA, independent of starch concentration present in the blend.

Abd El-Kader et al. (2002) produced PVA casting films with four different MW (no further information of hydrolysis degree), and they observed a tendency to reduced Young's modulus and tensile strength with increasing MW. The opposite behavior was observed by Limpan et al. (2012), in biodegradable films of fish myofibrillar protein and PVA with different MW and HD. According to the authors, the higher MW increased tensile strength and elongation at break, and high HD increased the rigidity of the films.

The aim of this work was to study the influence of PVA molecular weight and degree of hydrolysis on flat-die extruded sheets produced with PVA and cassava starch blends.

2. EXPERIMENTAL

2.1 Materials

The PVA was supplied by Sekisui Chemical (Japan) with different hydrolysis degree – HD and molecular weight – MW (based on their viscosity in 4% aqueous solution). Three partially hydrolyzed: Selvol™ 203 (HD: 88.14 %, viscosity: 4.10 cP); Selvol™ 523 (HD: 87.84 %, viscosity: 24.50 cP) and Selvol™ 540 (HD: 88.04 %, viscosity: 49.40 cP), and two PVA fully hydrolyzed: Selvol™ 107 (HD: 98.30%, viscosity: 6.00 cP) and Selvol™ 325 (HD: 98.42 %, viscosity: 31.40 cP). Native cassava starch supplied by Indemil (Brazil) and glycerol supplied by Dinamica (Brazil).

2.2 Methods

2.2.1 Sheet production

The five formulations were composed by 40 wt% of starch, 25 wt% of PVA and 35 wt% of glycerol. After manual homogenization, the samples were placed in a vacuum oven (model Q819V2, Quimis, Brazil) with a vacuum pressure of 0.085 MPa for 90 minutes at 85 °C to incorporate the glycerol using a method adapted from Jang & Lee (2003). After this step, the polymer blends were extruded in a single-screw extruder (model EL-25, BGM, Brazil), 25 mm screw diameter (L/D = 28). The screw speed was set at 30 RPM, and the temperature profile was set at 90/180/200/190 °C from feeder to die zone. It was used a six-hole cylindrical matrix (2 mm) for pellets production.

The pellets were extruded in a co-rotating twin-screw extruder (model D-20, BGM, Brazil) with a screw diameter of 20 mm and L/D ratio of 35, screw speed was set at 110 RPM and a temperature profile was set at 90/160/190/190/190 °C from feeder to flat die matrix. The samples were extruded using a flat die with a 0.8 mm aperture and 320 mm length, coupled with a 3-roll water-cooled calender (AX Plásticos, Brazil) for sheets production.

2.2.2 Mechanical properties

The tensile strength, Young's modulus and elongation at break were analyzed according to the ASTM D882-02 method, with some modifications, using a texture analyzer (model TA.XT2i, Stable Micro Systems, England) with an initial distance between the grips of 30 mm and a crosshead speed of 0.8 $mm.s^{-1}$. Ten samples from each blend were cut (50 mm in length and 20 mm in width) and conditioned in a desiccator with controlled relative humidity and temperature (53±2% and 23±2 °C respectively) for 72 hours before analysis.

For puncture analysis, ten replicates from each treatment were conditioned as described above and punctured perpendicularly with a 6.35 mm diameter cylindrical probe at a velocity of 2.0 $mm.s^{-1}$. The puncture elongation (mm) was characterized how the maximum elongation supported by the sheet. The puncture strength (N/mm) were calculated dividing the maximum force by the sheet thickness.

2.2.3 Water vapor permeability (WVP)

The water vapor permeability was determined according to the ASTM E96-009 standard (gravimetrically). The measurements were performed using a relative humidity gradient of 33 - 64%.

2.2.4 Apparent opacity (Op) and Color difference (ΔE*)

The Op and ΔE* was determined according to the method described by Maria et al. (2008).

The Op values were measured using a colorimeter (BYK Gardner, Germany) with illuminant D65 (daylight) and a visual angle of 10°. Opacity (Op) was calculated as the ratio of the opacity of the sample over a black standard Op_b and the opacity over a white standard Op_w (0-100%), and the analyses were performed in triplicate according to eq. 1.

$Op = (Op_b/Op_w) \times 100$ (1)

The ΔE* are obtained based in eq. 2, where: ΔL*, Δa* and Δb* are the differences between the sample measured under the white standard and the white standard alone.

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (2)$$

2.2.5 X-ray diffraction (XRD)

The XRD analysis was performed using a diffractometer (Panalytical X´Pert PRO MPD, Netherlands), emitting copper Kα radiation (λ = 1.5418 angstrom). The anode radiation was generated at 40 kV and 50 mA and was monochromatized using a 20 mA current. Diffraction intensity measurements were performed between 2θ = 5° to 50° at room temperature. The relative crystallinity of each film was calculated by dividing the area of the strongest peaks by the total area of the crystalline region (the total area under the curve minus the baseline).

2.2.6 Scanning Electron Microscopy (SEM)

The SEM was recorded using a scanning electron microscope (FEI Quanta 200, USA). The films were fractured in liquid nitrogen, attached to aluminum supports and coated with gold (BAL-TEC SCD 050 sputter coater, Leica Microsystems, Germany) (40-50 nm in thickness) at 25 °C and a pressure of 2.105 Torr for 180 seconds. The fracture surface of the films were analyzed.

2.2.7 Fourier Transform Infrared Spectroscopy (FT-IR)

The sheets were dried over anhydrous calcium chloride salt for one week and analyzed in a Fourier transform infrared spectrophotometer (FT-IR) (IR Prestige 21, Shimadzu, Japan) using a horizontal attenuated total reflection (ATR) module operating over the spectral range of 4000 cm^{-1} - 750 cm^{-1}.

2.2.8 Thermogravimetric analysis (TGA)

The thermogravimetric analysis was performed using a TGA – 50 (Shimadzu, Japan). The samples were dried over anhydrous calcium chloride salt and analyzed from 25 °C to 600 °C with a 10 $°C.min^{-1}$ heating rate under a nitrogen atmosphere (20 $mL.min^{-1}$).

2.3 Statistical Analysis

The data were analyzed using STATISTICA 7.0 (Statsoft, USA), performing analysis of variance (ANOVA) and Tukey's test at a 5% significance level ($p<0.05$).

3. RESULTS AND DISCUSSION

All the formulated sheets produced by flat-die extrusion process were continuous and visually homogenous, presenting a good processability and with a medium thickness of 525±126 µm.

3.1 Mechanical properties

The mechanical properties of the sheets are presented in Table 1, and it is possible to observe that the higher the molecular weight of the PVA the higher the tensile strength of the sheets. The sheets produced with PVA S540 and S325 had the higher tensile strength values, followed by S523 with intermediate MW and finally S107 and S203 with the lower MW and tensile strength values. The same tendency was observed for elongation at break, with PVA S325, S540 and S523 presenting higher values than PVA S107 and S203, and the sheets produced with high HD PVA had the higher Young's modulus. Thus, is possible observe that higher MW promotes an increasing in mechanical properties, but specifically for Young's modulus the HD presents a major influence.

Table 1. Mechanical and puncture properties of the extruded biodegradable sheets.

PVA	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Puncture strength (N/mm)	Puncture elongation (mm)
S325	6.99±0.98^{a}	16.19±1.77^{a}	642±30^{a}	95.08±12.62^{a}	17.44±1.04^{b}
S107	1.54±0.13^{c}	8.03±0.60^{b}	175±40^{b}	52.61±2.37^{b}	8.81±0.84^{c}
S540	7.50±1.58^{a}	5.88±1.81^{c}	598±112^{a}	91.61±4.64^{a}	20.83±1.12^{a}
S523	4.49±0.48^{b}	4.52±0.35^{cd}	569±35^{a}	49.94±3.89^{bc}	19.71±0.52^{a}
S203	0.95±0.06^{c}	3.51±0.39^{d}	102±23^{b}	34.53±1.42^{c}	8.59±0.61^{c}

$^{a,\ b\ c,\ d}$ values with the same letter at the same column are not different statistically ($p<0.05$).

Chen et al. (2008) produced casting films with pea starch/PVA blends plasticized with 20 wt% of glycerol, and starch/PVA proportion of 40/60 (w/w). The PVA characteristics was similar to Selvol S523, and the films had tensile strength and elongation at break of approximately 15 MPa and 350% respectively, higher than those obtained in present work (4.49 MPa and 569% respectively). The difference can be attributed to the higher concentration of PVA and the lower concentration of glycerol used by the authors. According to them, the starch impair the mechanical properties when compared to pure PVA films, and because of the glycerol plasticizing effect the tensile strength decrease and the elongation at break increase.

Ke & Sun (2003) produced materials by injection mold using cornstarch/PLA/PVA blends with different MW, and the PVA concentration was 30 wt% of total weight of the others polymers (starch/PLA 1/1 w/w). The authors observed that with higher MW PVA in the tertiary blends, the tensile strength decreased, and according to them, the PVA-starch interaction weakened with higher MW PVA, reducing the mechanical properties of the materials.

Similar values was observed by Zanela et al. (2015a) for cassava starch/PVA (S523)/glycerol (40/30/30 wt%) extruded sheets; the tensile strength, Young modulus and elongation at break were 4.8 MPa, 6.2 MPa and 543% respectively.

The behavior of both puncture strength and elongation of the sheets as function of PVA grade was similar to the tensile strength. The sheets produced with PVA S325 and S540 showed the higher puncture strength values, and for puncture elongation the sheets produced with PVA S540 and S523 presented the higher values. Therefore, the discussion for mechanical properties is also valid for puncture tests.

Zanela et al. (2015b), using a mixture design for production of extruded sheets using different proportion of cassava starch, PVA (S203) and glycerol obtained values for puncture elongation that ranged from 5.64 to 10.13 mm, similar to those observed in present work (8.59 mm) for this PVA grade.

3.2 Water vapor permeability (WVP)

The WVP of the sheets are presented in Table 2, and there were no difference among them, with an average value of 3.24 x10^{-10} g.m^{-1}.s^{-1}.kPa^{-1}, probably because both PVA and starch are hydrophilic polymer.

Table 2. Water Vapor Permeability, apparent opacity, color difference and crystallinity index of the extruded biodegradable sheets.

PVA	**Water vapor permeability (g.m^{-1}.s^{-1}.kPa^{-1}) (x10^{-10})**	**Apparent opacity (%)**	**Color difference (ΔE*)**	**Crystallinity Index**
S325	3.1±0.4^{ns}	43±7^{a}	33±4^{a}	23.2
S107	3.4±0.6	44±^{a}	34±2^{a}	24.1
S540	3.0±0.6	29±2^{bc}	31±4^{ab}	24.4
S523	3.7±0.4	24±1^{c}	26±2^{bc}	23.8
S203	3.1±0.4	37±5^{ab}	21±1^{c}	24.7

$^{a,\ b\ c}$ values with the same letter at the same column are not different statistically ($p<0.05$).
^{ns} not significant.

Limpan et al. (2012) produced casting films of fish myofibrillar protein and PVA with different MW and HD. They observed that for PVA with the same HD, higher MW increased the WVP of the films, and according to the authors, it was due to the disorder degree in the amorphous region that increased the free volume between polymeric chains, creating channels to water permeation. They also observed that for the PVA with the same MW, a higher HD increased the WVP of the films.

3.3 Apparent opacity (Op) and Color difference (ΔE*)

For both Op and ΔE*, it was observed statistical differences between the sheets, but the MW or HD did not show clear influence on the results (Table 2). For Op, all sheets was translucent, and sheets S325, S107 and S203 presented the higher values, and S523 and S540 were the more transparent sheets. For ΔE*, the sheets S325, S107 and S540 presented the higher values, demonstrating a greater difference when compared to white standard, because these sheets were yellowish, instead of S203 and S523 that were more whitish, consequently presented less difference with the white standard.

Maria et al. (2008) produced pigskin gelatin/PVA casting films with different MW and HD PVAs, and they obtained Op and ΔE* values lower than ours, and they did not find correlation of MW and HD with Op and ΔE*. These lower values can be attributed to the lower thickness and the casting production process that leads a different form of molecular organization. According to Follain et al. (2005), casting process promotes a long time of repose, that permit a macromolecular reorganization, favoring the self-organization between the polymer chains, and the extrusion promotes a stretching of polymer chains in a linear orientation. These differences can explain the mechanical and optical differences between the materials produce by casting and by extrusion. Abd El-kader et al. (2002) determined the optical properties of pure PVA casting films with different MW and they observed no absorption bands in the visible region of spectra, since the films were transparent.

3.4 X-ray diffraction (XRD)

Figure 1 presents the diffractograms for the sheets, and it is possible to observe a similar pattern between them, with a sharp diffraction peak at 20.0°, and two overlapped peaks at approximately 17.8° and 21.9°, and mainly in sheets S325, S107 and S523, a broad and weak diffraction peak at 40.4°. The crystallinity indexes presented little variation, and ranged from 23.2 to 24.7% (Table 2).

Jayasekara et al. (2004) also observed a peak at 20° in casting films containing 60/20/20 wt% of wheat starch, PVA and glycerol, respectively, and a crystallinity index of 24%, similar to those obtained in this work.

Zanela et al. (2015b) obtained crystallinity indexes ranging from 17.2 to 20.5% for extruded sheets of cassava starch/PVA (S203)/glycerol, lower than to those obtained in this work (Table 2).

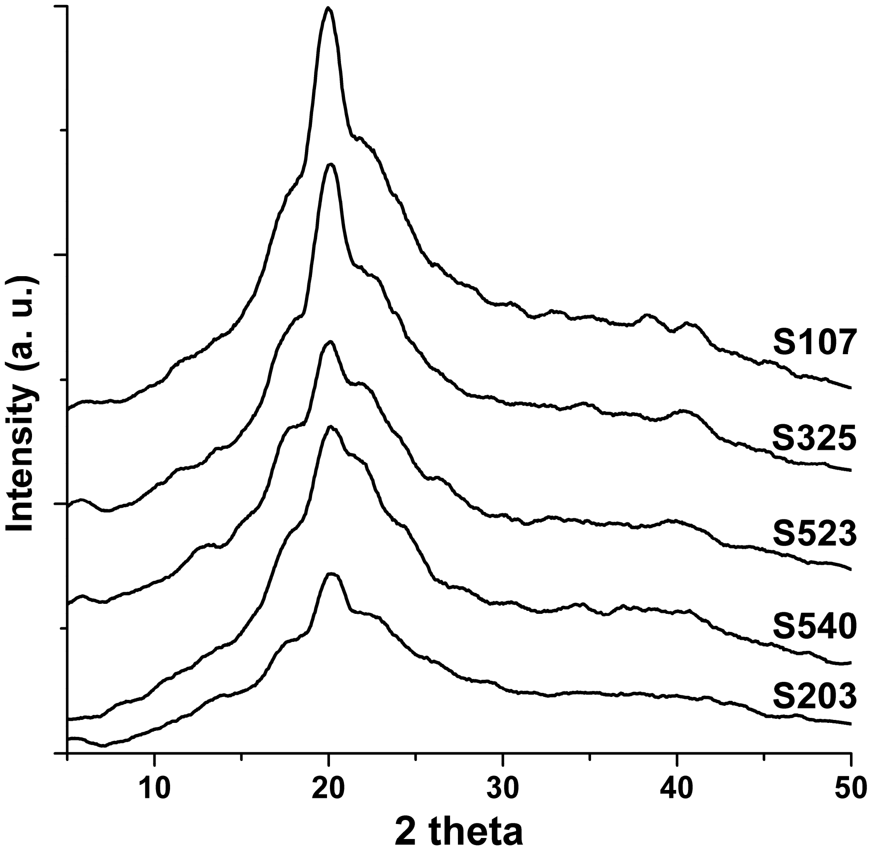

Figure 1. Diffractograms of the extruded biodegradable sheets.

Das et al. (2010) obtained similar results to those shown in Figure 1, for casting films of starch/PVA/glycerol. They observed a peak in 19.6° that was attributed to the ordered arrangement of PVA molecules, as well as the 40° diffraction peak. The peaks near 17 and 22° was attributed to the gelatinized starch, and the PVA was the component that contributed most to the crystallinity of the material.

3.5 Scanning Electron Microscopy (SEM)

The Figure 2 presents the fracture micrographs of the sheets, and all formulations presented smooth surfaces, no visible cracks or domains. The sheets S523 and S540 presented some agglomerations, probably of non-gelatinized starch, but without compromising the integrity of the material. Thus, there was a good compatibility between the blend components (starch, PVA and glycerol), as observed by many authors, like Zanela et al. (2015a), Khan et al. (2006), and Wang et al. (2008).

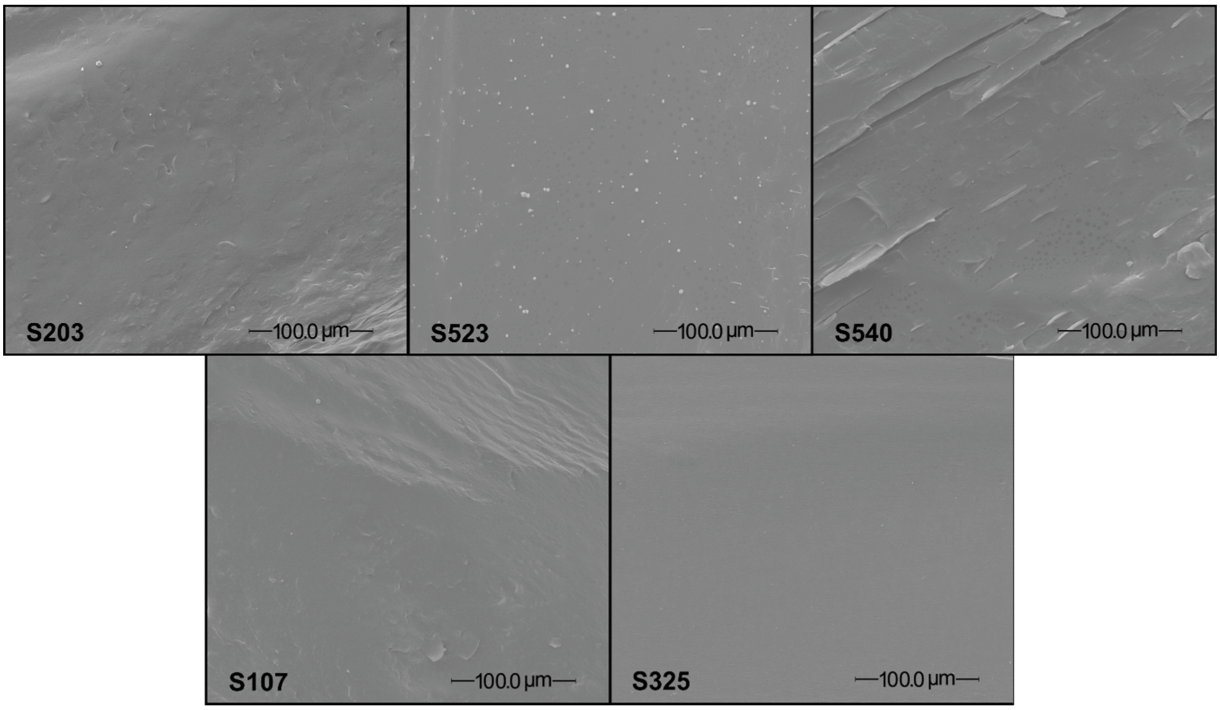

Figure 2. Scanning electron microscopy micrographs of the fracture surfaces with magnification at 800X of the extruded biodegradable sheets.

3.6 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of the biodegradable sheets are presented in Figure 3, and all sheets had similar spectra, due to the presence of many functional groups in common in the structure of PVA, starch and glycerol, resulting in similar spectra. There is a broad absorption band near 3300 cm^{-1}, that is assigned to the stretching of hydroxyl groups (OH) from inter and intramolecular hydrogen bonds (Mansur et al., 2008). The band between 3000 – 2840 cm^{-1} is due to the alkyl groups (C-H), and 1750 - 1735 cm^{-}

^{1} is due to the (C=O) stretching promoted by residual acetate groups present in PVA partially hydrolyzed molecule (Jayasekara et al., 2004), and because of that this band is more intense in films produced with partially hydrolyzed PVA (S203, S523 and S540).

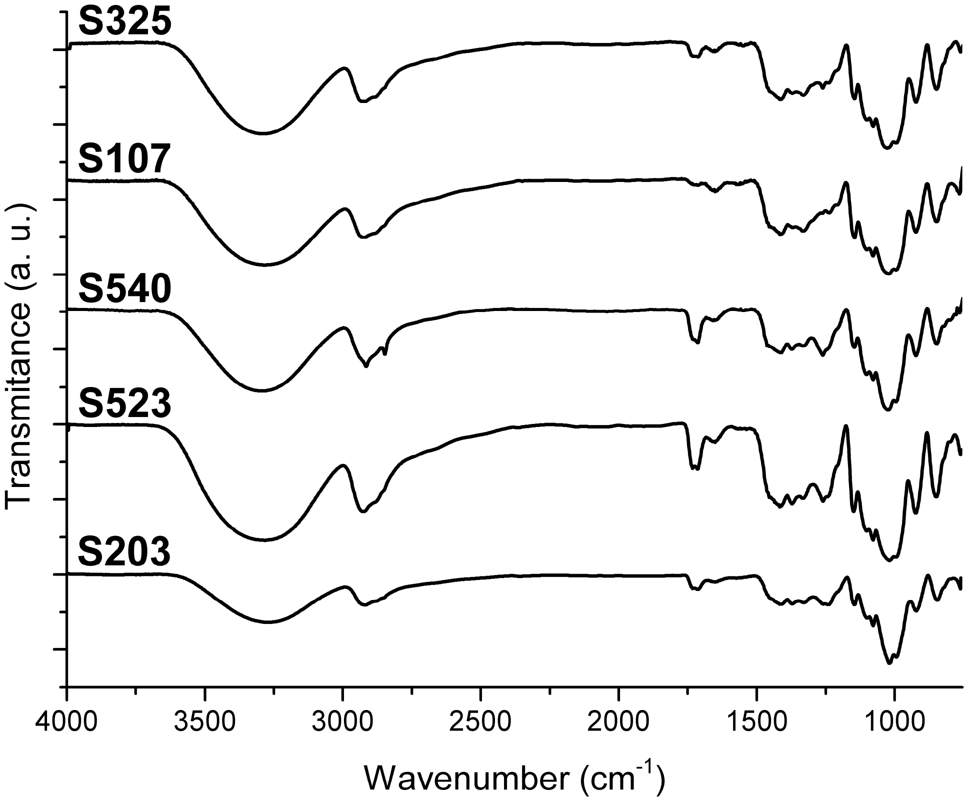

Figure 3. Fourier Transform Infrared Spectroscopy of extruded biodegradable sheets.

The peaks observed at 1024 and 860 cm^{-1} are due to the stretching vibration of C-O and C-C-O of the glucose ring present in starch structure, and there was a slight shift in blended materials, also observed by Cano et al. (2015).

Several researchers obtained similar spectra, like Das et al. (2010), Zanela et al. (2015a), and Sun et al. (2014), with few differences in the absorption bands. According to Das et al (2010), the weakness, disappearance or shift of the bands in spectra can be result from different kinds of interactions between the blend components.

3.7 Thermogravimetric analysis (TGA)

The TG and DTG curves of the biodegradable sheets are presented in Figure 4. All curves are similar, with three weight-loss stages, in approximately 230, 320 and 440 °C, that agree with observed by Aydin & Ilberg (2016) and Cano et al. (2015). According to the authors, the first stage is related to the bounded water and volatile disintegrated products; the second stage is related to the dehydration, chain scission and decomposition of the PVA, and in our case also due to the glycerol (boiling point of 290 °C), and this stage represented the main decomposition. The third stage corresponds to carbonization of the organic matter.

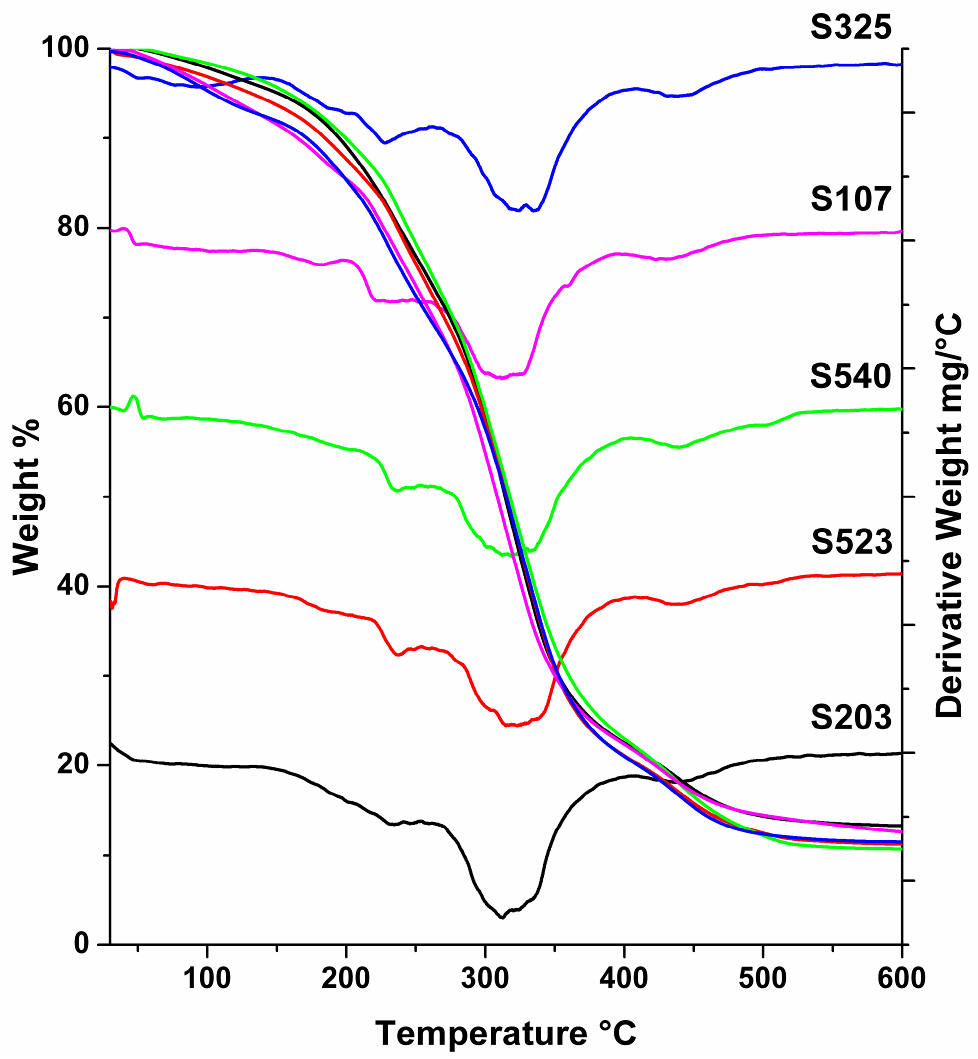

Figure 4. Thermogravimetric analysis of extruded biodegradable sheets.

The weight-loss stages are presented in Table 3, and the PVA with high HD presented higher weight loss at lower temperatures when compared to partially hydrolyzed PVA, but above 300 °C the residual weight becomes similar for all samples. It was not possible to observe differences between the MW with relation to the thermal behavior of the blends.

Table 3. Weight-loss temperature of the extruded biodegradable sheets.

PVA	Temperature at 10% weight loss	Residual weight percentage (%)			
		200 °C	300 °C	400 °C	500 °C
S325	171.6	85.4	57.6	21.0	12.4
S107	164.9	85.4	54.8	22.4	14.4
S540	199.6	89.9	59.8	23.0	12.2
S523	184.6	87.7	58.4	21.1	12.5
S203	194.8	89.1	58.8	22.5	14.3

Ray et al. (2009) observed that the main degradation peak shifted up, and presented lower intensity in PVA/starch blends when compared to pure components, and the degradation curves were similar to those presented in Figure 4. According to the authors, the H bonds formed between the polymers increased the thermal stability of the material. The same behavior was observed by Sin et al. (2013) and Sin et al. (2011) in PVA/cassava starch films; the starch improved the PVA thermal resistance due to the cyclic hemiacetal structure of the starch.

According to the results PVA and starch are compatible, resulting in a material with better thermal properties than the pure components.

4. CONCLUSION

The extruded biodegradable sheets produced using PVA/starch/glycerol blends presented adequate processability, handleability and mechanical properties, with uniform appearance. Increasing the hydrolysis degree of PVA promotes more rigid materials, while with increasing of the molecular weight of PVA promotes more resistant materials, but all PVA grades had good compatibility with starch in the extrusion process, therefore the PVA/starch blends are adequate for industrial scale production.

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CAPÍTULO 7 – EFFECT OF MODIFIED CASSAVA STARCHES ON THE PROPERTIES OF BIODEGRADABLE SHEETS OF POLYVINYL ALCOHOL AND STARCH

ABSTRACT: The aim of this work was to study the effect of modified cassava starches and PVA grade on the properties of biodegradables sheets produce with starch / PVA blends by extrusion-calendering process; using native starch, distarch phosphate, acetylated distarch phosphate, acetylated distarch adipate or oxidized starch; PVA with hydrolysis degrees (HD) of 88% or 98%, and glycerol as plasticizer. The ten formulations (5 starch types x 2 PVA grades) contained 40 wt% of starch, 25 wt% of PVA and 35 wt% of glycerol. The mechanical, optical, and microstructural properties and water vapor permeability of the sheets were investigated. The produced sheets presented tensile strength, Young's modulus and elongation at break that ranged from 6.8 to 1.0 MPa; 16.2 to 3.2 MPa and 443 to 130% respectively. Sheet produced with higher HD PVA had better mechanical properties, independent of starch type. Materials produced with all starch types presented similar response for the same PVA, except those with oxidized starch, that had the poorer mechanical properties. All the sheets were visually homogeneous, presented good processability, and consequently adequate for extrusion processing. The sheets produced with higher HD (98%) PVA had better mechanical properties, were more opaque, and with a higher crystallinity than those produced with lower HD PVA (88%), probably because the higher HD PVA has more hydroxyl groups than the lower that leads to a better interaction with the starch.

Keywords: biodegradable polymers; mechanical properties, extrusion.

1. INTRODUCTION

The large amount of plastic used nowadays in packaging industry have increased the interest to replace conventional non-biodegradable plastics by fully biodegradable materials, reducing the negative impact on the environment caused by the wastes of conventional plastics resins (Abassi, 2012; Arruda et al., 2015).

Nowadays there are several biodegradable synthetic polymers available in the market that present different properties and that can be used for replacement of conventional plastics resins, but they are costly compared to conventional plastics.

Another alternative for biodegradable materials production is the use of renewable and biodegradable biopolymers available in large amounts and with a low cost, such as starch.

The starch has been studied for production of biodegradable materials on both forms, pure or in blends with biodegradable polymers. However, the use of pure starch presents some drawbacks, mainly due to the poor mechanical properties and high absorption of water, leading to weakening of mechanical properties of material in high relative humidity ambient (Rodriguez et al., 2010; Zhang et al., 2007).

There are two approaches to overcome the starch issues, one method is to blend starch with another biodegradable polymer; and the mechanical, and water properties are dependent on the proportion of each component of the blend and on the nature of each polymer. Another form is to modify the starch, like replacing hydroxyl hydrophilic groups by other hydrophobic groups, such as esterification or etherification (Zhang et al., 2007).

The polyvinyl alcohol – PVA presents a broad range of applications in industry, and it can be used for blend with starch to produce biodegradable materials. PVA is the only known carbon-carbon backbone polymer that is fully biodegradable, and the presence of hydroxyl groups in backbone produces inter and intramolecular hydrogen bonds, promoting high tensile strength, and good chemical resistance and gas barrier properties. Biodegradable materials can be produce with PVA by casting or extrusion-melting processes; the latter is more interesting for large-scale production of packaging materials (Alexy & Ka, 2002; Dorigato & Pegoretti, 2012).

Nowadays it is available a wide range of modified starches, and they are used in food and non-food industry. Starch can be modified by chemical, physical, or enzymatic processes, or combining them, to change their functionality.

The chemical modification involves the incorporation of functional groups in starch molecule, without affecting the morphology of the granule, and the usual methods are acetylation, hydroxypropylation, cross-linking, and oxidation. (Raina et al., 2006; Luchese et al., 2015; Alcázar-Alay & Meireles, 2015; Singh, Kaur & McCarthy, 2007, López, Zaritzky & García, 2010).

The aim of this work was to study the effect of modified starch type and PVA grade on the properties of biodegradables sheets produce with starch/PVA blends by extrusion-calendering process. The mechanical, optical, and microstructural properties and water vapor permeability of the sheets were investigated.

2. EXPERIMENTAL

2.1 Materials

There were used five types of cassava starches supplied by Agrícola Horizonte (Brazil): native starch – NS, distarch phosphate – SP, acetylated distarch phosphate – ASP, acetylated distarch adipate – ASA and oxidized starch – OS. There were used two grades of PVA supplied by Sekisui Chemical (Japan), with different hydrolysis degree – HD and molecular weight – MW (based on their viscosity in 4% aqueous solution): Selvol™ 540 – S540 (HD: 88%, viscosity: 49 cP) and Selvol™ 325 – S325 (HD: 98%, viscosity: 31 cP). The glycerol was supplied by Dinamica (Brazil).

2.2 Methods

2.2.1 Sheet production

The ten formulations (5 starch types x 2 PVA grades) contained 40 wt% of starch, 25 wt% of PVA and 35 wt% of glycerol. After manual homogenization, the samples were placed in a vacuum oven (model Q819V2, Quimis, Brazil) with a vacuum pressure of 0.085 MPa for 90 minutes at 85 °C to incorporate the glycerol using the adapted method from Jang & Lee (2003). The blends were firstly extruded in a single-screw extruder (model EL-25, BGM, Brazil), with a screw diameter of 25mm and L/D ratio of 28. Screw speed was set at 30 RPM, temperature profile was set at 90/165/175/165 °C from feeder to die zone, and it was used a six-hole cylindrical die (2 mm) for pellets production.

After pelletization, the blends were extruded in a co-rotating twin-screw extruder (model D-20, BGM, Brazil) with a screw diameter of 20 mm and L/D ratio of 35, and the screw speed was set at 110 RPM and the temperature profile used was set at 90/160/190/190/190 °C from feeder to flat die. The samples were extruded using a flat die with a 0.8 mm aperture and 320 mm length, coupled with a 3-roll water-cooled calender (AX Plásticos, Brazil) for sheets production.

The sampled was identified by the acronym composed by the starch type followed by the PVA type, e.g. NS-S325: sheet using native starch (NS) and PVA Selvol™ 325.

2.2.2 Mechanical properties

The tensile strength, Young's modulus and elongation at break were analyzed according to the ASTM D882-02 method, with some modifications, using a universal testing machine (model DL 2000, EMIC, Brazil) with an initial distance between the grips of 40 mm and a crosshead speed of 0.8 $mm.s^{-1}$. Ten samples from each blend was cut (80 mm in length and 25 mm in width) and conditioned at 53±2% RH and 23±2 °C for 72 hours before analysis.

2.2.3 Water vapor permeability

The water vapor permeability (WVP) analysis was determined according to the ASTM E96-009 standard (gravimetrically). The measurements were performed in triplicate, using a relative humidity gradient of 33 - 64% RH.

2.2.4 Weight loss in water

The analysis of weight loss in water (WLW) was performed as described by Olivato et al. (2012) The weight loss in water measurements were performed in triplicate and expressed as the percentage of the original mass (M_i) and the final mass (M_f) of the film after immersion in water for 48 hours at 25 °C, according to eq. 1.

$$\mathrm{WLW} = [(\mathrm{M_i} - \mathrm{M_f})/\mathrm{M_i}] \times 100 \quad (1)$$

2.2.5 Apparent Opacity and Color Difference

The apparent opacity (Op) and Color difference (ΔE*) was determined according to the method described by Maria et al. (2008).

The Op values were measured using a colorimeter (BYK Gardner, Germany) with the illuminant D65 (daylight) and a visual angle of 10°. The Op was determined as the ratio of the opacity of the sample over a black standard (Op_b) and the opacity over a white standard (Op_w) being represented on an arbitrary scale (0-100%), and the analyses were performed in triplicate according to eq. 2.

$$Op = (Op_b/Op_w) \times 100 \tag{2}$$

The ΔE* are obtained based in eq. 3, where: ΔL*, Δa* and Δb* are the differences between the sample measured under the white standard and the white standard alone.

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \tag{3}$$

2.2.6 X-ray diffraction (XRD)

The X-ray diffraction (XRD) analysis was performed using a diffractometer (Panalytical X´Pert PRO MPD, Netherlands), emitting copper Kα radiation (λ = 1.5418 angstrom). The anode radiation was generated at 40 kV and 50 mA and was monochromatized using a 20 mA current. Diffraction intensity measurements were performed between 2θ = 5° to 50° at room temperature. The relative crystallinity of each sheet was calculated by dividing the area of the peaks by the total area of the crystalline region (the total area under the curve minus the baseline).

2.2.7 Scanning Electron Microscopy

The micrographs of the biodegradable sheets were recorded using a scanning electron microscope (SEM) (FEI Quanta 200, USA). The sheets were fractured in liquid nitrogen, attached to aluminum supports and coated with gold (BAL-

TEC SCD 050 sputter coater, Leica Microsystems, Germany) (40-50 nm in thickness) at 25 °C and a pressure of 2.105 Torr for 180 seconds. The fracture surface of the sheets were analyzed.

2.2.8 Fourier Transform Infrared Spectroscopy (FT-IR)

The sheets were dried over anhydrous calcium chloride salt for seven days and analyzed in a Fourier transform infrared spectrophotometer (FT-IR) (IRPrestige 21, Shimadzu, Japan) using a horizontal attenuated total reflection module (ATR) operating over the spectral range of 4000 cm^{-1} - 750 cm^{-1}. It was used the Standard Normal Variate Transformation - SNV of the spectra to reduce the effect of particle size, light scattering and multi-collinearity, improving the interpretation, according to established by Barnes, Dhanoa & Lister (1989).

2.3 Statistical Analysis

The data were analyzed using STATISTICA 7.0 (Statsoft, USA), performing analysis of variance (ANOVA) and Tukey’s test at a 5% significance level ($p<0.05$).

3. RESULTS AND DISCUSSION

The biodegradable sheets produced by extrusion-calendering process were continuous, visually homogenous and with good handleability, with a medium thickness of 580±167 µm, and the blends had good processability.

3.1 Mechanical properties

The mechanical properties of the biodegradable sheets are presented in Figure 1, and according to the results, both the starch type and the PVA grade influenced the mechanical properties.

The sheets produced with PVA S325 (high hydrolysis degree – HD -

98%) had higher tensile strength, Young's modulus and elongation at break than those produced with PVA S540 (88% HD), comparing the blends with the same starch type, and similar results were observed in sheets described in Chapter 6. Limpan et al. (2012) observed the same behavior in casting films produced with fish myofibrillar proteins/PVA blends, in which films with higher HD PVA had better mechanical properties compared to films produced with lower HD PVA. According to the authors, the higher HD PVA presents more hydroxyl groups in their structure that favors the formation of hydrogen bonds between starch and PVA molecules leading to stronger interactions and consequently improving the mechanical properties.

In general, for the same PVA grade, the sheets produced with oxidize starch (OS) had the lower tensile strength and elongation at break compared with the others starches. According to Sánchez-Rivera et al. (2005) the large cleavage of the starch chains during the oxidation process reduces their molecular weight, and it probably decreases the mechanical properties of the materials produced with this type of starch.

The materials produced with starches SP, ASP and ASA did not showed differences between them, probably because the modifications did not caused sufficient structural and chemical alterations to affect differentially the interaction PVA-starch.

Yun et al. (2008) produced casting films with native and modified cornstarch (distarch phosphate) blended with PVA and plasticized with glycerol, and they observed that the films with modified starch had higher tensile strength and elongation at break than those produced with native starch.

Lee et al. (2007) produce casting films with native or modified cornstarch (distarch phosphate) and PVA (1:1 wt%), plasticized with glycerol (30 wt%), and the tensile strength ranged from 25 to 10 MPa, and the elongation ranged from 110 to 90% for modified and native starch, respectively, a similar behavior of the materials produced with PVA S540.

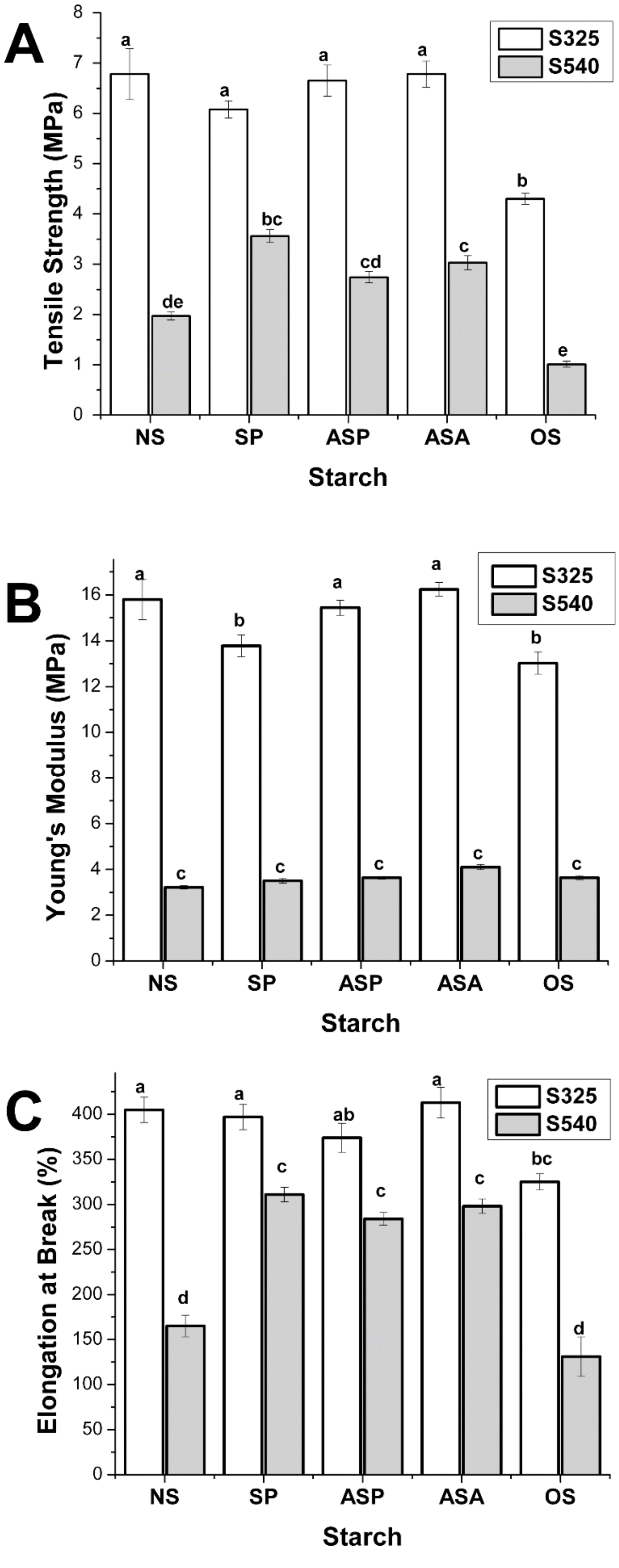

Figure 1. Mechanical properties of the biodegradable sheets: tensile strength (a), Young's modulus (b) and elongation at break (c). Native starch (NS), distarch phosphate (SP), acetylated distarch phosphate (ASP), acetylated distarch adipate (ASA) and oxidized starch (OS).

Wang et al. (2015) produced films by blown extrusion using hydroxypropyl distarch phosphate or native starch blended with PVA and plasticized with glycerol. The starch:PVA ratios ranged from 100:0 to 80:20, and the tensile strength ranged from 2.1 to 4.0 and from 1.9 to 2.8 MPa for modified and native starch respectively, and the elongation at break ranged from 75 to 150% and from 40 to 70% for modified and native starch respectively, lower than those observed in Figure 1. According to the authors, the differences can be explained by the internal structure differences in starch molecules that can produces different intra- or intermolecular interactions with the PVA during the extrusion process. Zhang et al. (2009) produced films with cornstarch with different degree of oxidation, and the tensile strength and the elongation at break of the films decreased with increasing the degree of oxidation. The poor mechanical properties of the materials produced with the starch with higher degree of oxidation were due to the breaking of the hydrogen bonds and the low molecular weight of these starches.

3.2 Water vapor permeability (WVP)

The WVP of the sheets are presented in Table 1, and it is possible to observe that the sheets produced with PVA S540 had the lowest WVP values, independent of starch type, indicating that PVA grade is the main factor that leads to reduction of WVP. On the other hand, the sheets produced with PVA S325 and SP, ASP and OS starch had the higher values of WVP, and differed from the NS and ASA starches.

Limpan et al. (2012), in PVA casting films, observed that for PVA with the same molecular weight, higher HD promotes an increasing of the WVP, similar to observed in this work. According to Limpan et al (2010), matrix with lower polarities are more resistant to water transference through it, and as the HD is directly related with the hydroxyl content in the PVA molecule, materials produced with higher HD PVA have higher polarity, and consequently are more permeable to water.

Table 1. Water vapor permeability, weight loss in water, apparent opacity, color difference and crystallinity index of the extruded biodegradable sheets.

Starch	PVA	Water vapor permeability ($g.m^{-1}.s^{-1}.kPa^{-1}$) ($x10^{-10}$)	Weight loss in water (%)	Apparent opacity (%)	Color difference (ΔE*)	Crystallinity Index (%)
NS	S325	3.2 ± 0.1^{ab}	38 ± 2^{b}	30 ± 1^{abc}	24 ± 1^{bc}	24.7
	S540	2.8 ± 0.1^{a}	38 ± 4^{b}	25 ± 1^{bcd}	16 ± 2^{d}	24.9
SP	S325	3.9 ± 0.2^{d}	36 ± 1^{b}	31 ± 1^{ab}	21 ± 1^{cd}	25.0
	S540	3.2 ± 0.1^{ab}	39 ± 3^{b}	28 ± 3^{abc}	19 ± 2^{cd}	23.8
ASP	S325	3.6 ± 0.1^{bcd}	38 ± 1^{b}	31 ± 1^{ab}	23 ± 1^{bcd}	27.0
	S540	3.0 ± 0.1^{a}	38 ± 2^{b}	28 ± 1^{abc}	20 ± 1^{cd}	23.8
ASA	S325	3.2 ± 0.1^{abc}	41 ± 1^{ab}	32 ± 1^{a}	19 ± 1^{cd}	25.4
	S540	2.8 ± 0.1^{a}	45 ± 1^{ab}	29 ± 2^{abc}	18 ± 1^{cd}	24.7
OS	S325	3.7 ± 0.1^{cd}	52 ± 3^{a}	24 ± 1^{cd}	32 ± 2^{a}	29.4
	S540	2.9 ± 0.1^{a}	39 ± 4^{b}	20 ± 1^{d}	28 ± 1^{ab}	25.8

$^{a,\ b\ c,\ d}$ values with the same letter at the same column are not different statistically ($p<0.05$).

Gao et al. (2012) produced films by blown extrusion with hydroxypropyl distarch phosphate plasticized with glycerol (35 wt%), with WVP of 6.3 $x10^{-10}$ $g.m^{-1}.s^{-1}.kPa^{-1}$, higher than the obtained in present work for all starch grades, indicating that PVA reduced the WVP of starch biodegradable materials. Similar results was obtained by Wang et al. (2015), in blown films with the same starch type and five starch:PVA ratios that ranged from 80:20 to 100:0 and the WVP ranged from 3 to 6 $x10^{-10}$ $g.m^{-1}.s^{-1}.kPa^{-1}$, higher than those obtained in present work. According to the authors, increasing the PVA content the WVP was reduced, due to the good interaction of starch and PVA chains that reduced the number of free hydroxyl groups to interact with water molecules, so reducing the WVP. This fact was also observed by Zanela et al. (2015b) for starch:PVA sheets, in which the WVP was reduced with increasing of PVA content.

3.3 Weight loss in water

According to the weight loss in water (WLW) analysis (Table 1), the sheets ASA-S325 and ASA-S540 and OS-S325 had the higher solubility, 41, 45 and 52%, respectively. The higher values of WLW of sheets produced with ASA (acetylated distarch adipate) are due the fact that this modification promotes an increasing in solubility, viscosity and a reduction in gelatinization temperature of the starch (Gonzáles & Pérez, 2002; Mali & Grossmann, 2001).

The high WLW of sheets produced with oxidized starch (OS) can be attributed to the low MW of starch after the oxidation process that increases its solubility. Luchese et al. (2015) reported increasing solubility of the films that range from 18.7 to 68.9 for native and oxidized starch films, respectively.

Lee et al. (2007) reported that the higher the glycerol content (30 – 40 wt%) the higher the solubility of native starch films (56 - 60%, respectively), and of modified cornstarch (32 - 36%, respectively). This behavior was due to the high hydrophilicity and solubility of glycerol, and in our work, due to the high glycerol content in the sheets (35 wt%), it was expected a high solubility, but in general the solubility was lower than those observed by these authors.

3.4 Apparent opacity and Color difference

The OS and NS-540 sheets had the lower apparent opacity (Op), for both PVA grades (Table 1), being more translucent than the others sheets, and had the higher color difference (ΔE*) (Table 1) compared to the white standard. In general, sheets with PVA S540 had lower ΔE* values, it means that these sheets presented a whitish color, close to the white standard.

According to López, García & Zaritzky (2008), in modified corn starch films, the opacity increased with increasing the glycerol amount (0 - 5%). Zanela et al. (2015a) observed the same behavior, for sheets produced with cassava starch, PVA and glycerol, and the opacity ranged from 24 to 43%, close to those obtained in present work.

3.5 X-ray diffraction (XRD)

The Figure 2 presents the diffractograms of the sheets, and it is possible to observe a broad peak near 20°, for both PVA used, but only in S325 sheets it is possible to observe a peak overlapped near 23°, in S540 sheets probably this peak presents a lower intensity being completely overlapped by the main peak at 20°. The crystalline index ranged from 23.8 to 29.4% (Table 1), and the S325 sheets presented higher crystallinity than S540 for the same starch grade. According to Tang & Alavi (2011), partially hydrolyzed PVA, as S540, have residuals acetate groups in their structures, that reduce their crystallinity due to a steric impediment, and the fully hydrolyzed PVA have hydroxyl groups that due to their small volume favors the ordering of the chains, and increasing the crystallinity. The more crystalline sheets were obtained when it was used the OS starch combined with PVA S325, probably due to the lower MW of this starch, that permit a better ordering of the chains, so increasing the crystallinity of the sheet.

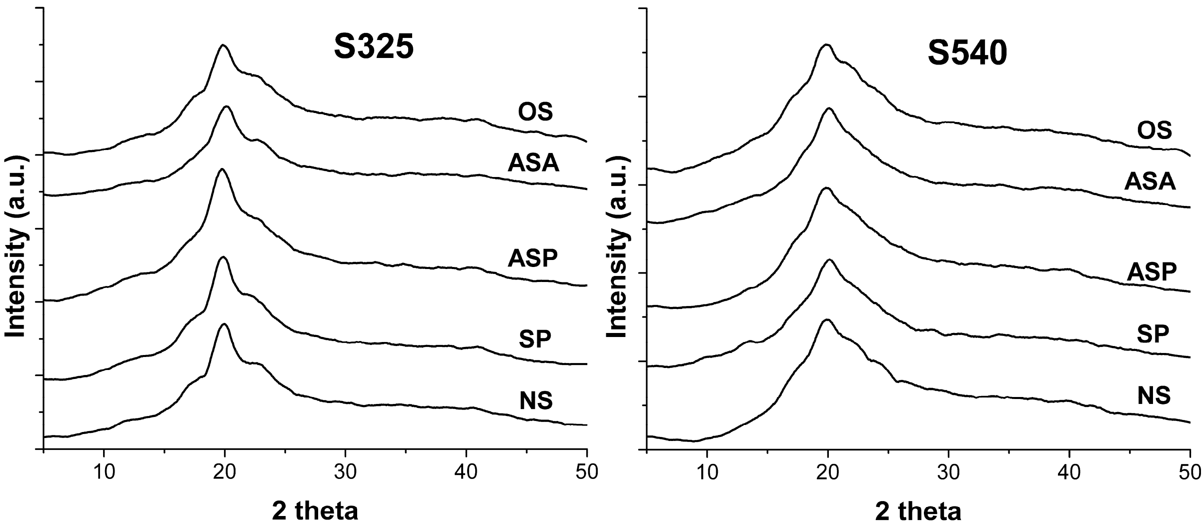

Figure 2. Diffractograms of the extruded biodegradable sheets based in modified starch with PVA S325 and S540.

Wang et al. (2015), in hydroxypropyl distarch phosphate/PVA films obtained similar diffraction pattern, with a main diffraction peak at 20° that was assigned as PVA, and the 23° peak was due to the starch structure, and it is consistent with the results obtained in our work.

The type of modified starch did not change the diffraction profile, indicating that the modification occurs mainly in the amorphous regions of starch granules (Qiu, Hu & Peng, 2013).

3.6 Scanning Electron Microscopy (SEM)

The Figure 3 presents the micrographs of the fracture surface of the sheets, and all the sheets presented a relatively smooth surface, without pores, cracks, domains, or phase separation, indicating good compatibility between all types of starch and both PVA grades (S325 and S540).

Chai, Chow & Chen (2012), in hot-pressed materials of fully hydrolyzed PVA with different MW and modified cornstarch (distarch phosphate), observed similar surfaces, without phase separation. Zanela et al. (2015b) obtained similar results in sheets of PVA/native cassava starch.

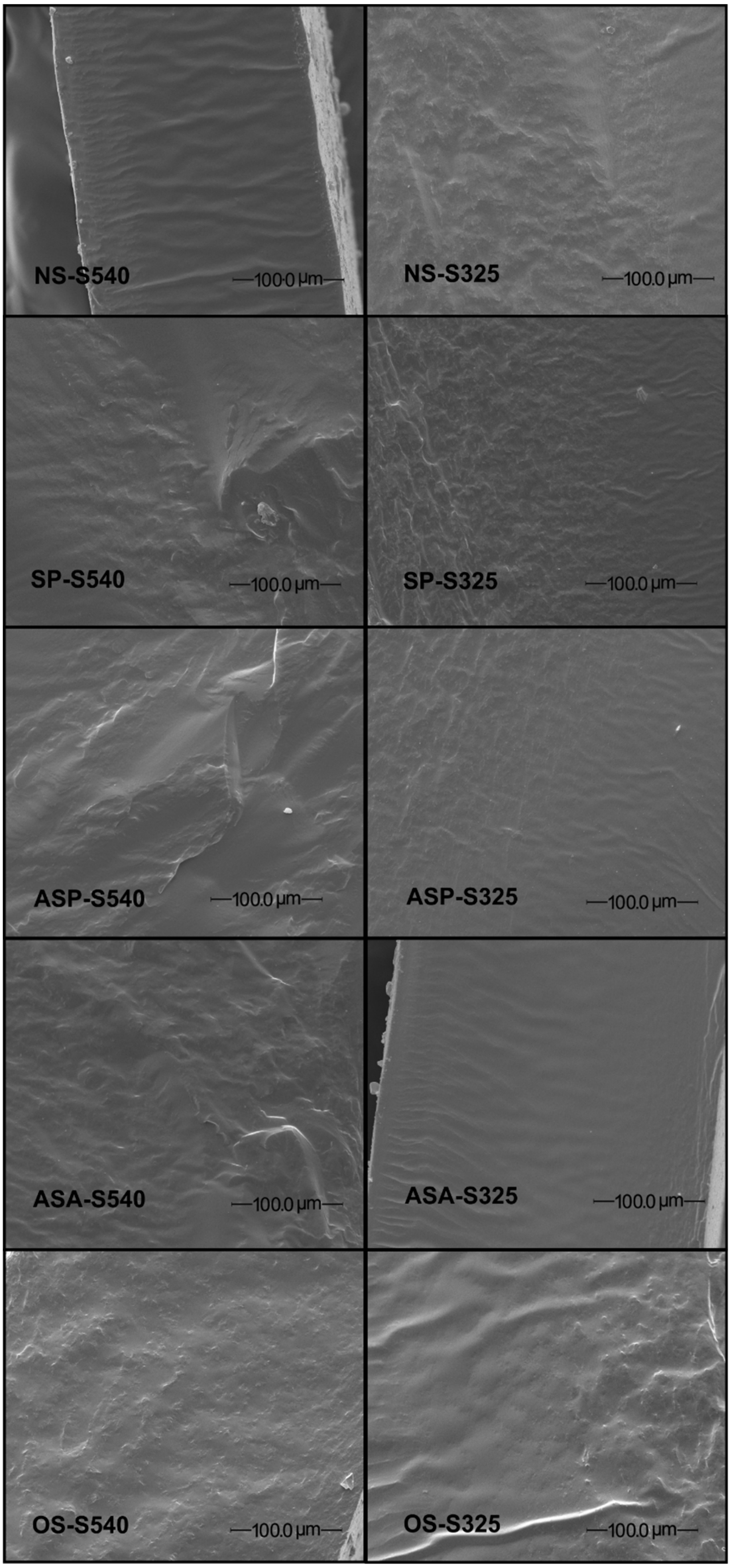

Figure 3. Scanning electron microscopy micrographs of the fracture surfaces of the extruded biodegradable sheets (magnification at 800X).

3.7 Fourier Transform Infrared Spectroscopy (FT-IR)

The Figure 4 presents the FT-IR analysis of the sheets, and all the spectra were similar, with a large absorption band near 3300 cm^{-1} attributed to the stretching of hydroxyls groups present in the three components of the sheets (starch, PVA and glycerol) (Zanela et al., 2015b; Qiu, Hu & Peng, 2013).

The sheets produced with acetylated distarch phosphate (ASP) and acetylated distarch adipate (ASA) blended with S325 had absorption bands at 1730 cm^{-1} and 1245cm^{-1}. These bands are attributed to the stretching of the C=O and C-O bonds respectively, due to the acetil groups presents in ASP and ASA, respectively (Demiate et al., 2000; Fringant et al., 1996). All the sheets produced with PVA S540 had these bands due to the acetate residual groups present in partially hydrolyzed PVA molecule (Zanela et al., 2015a; Tudorachi et al., 2000).

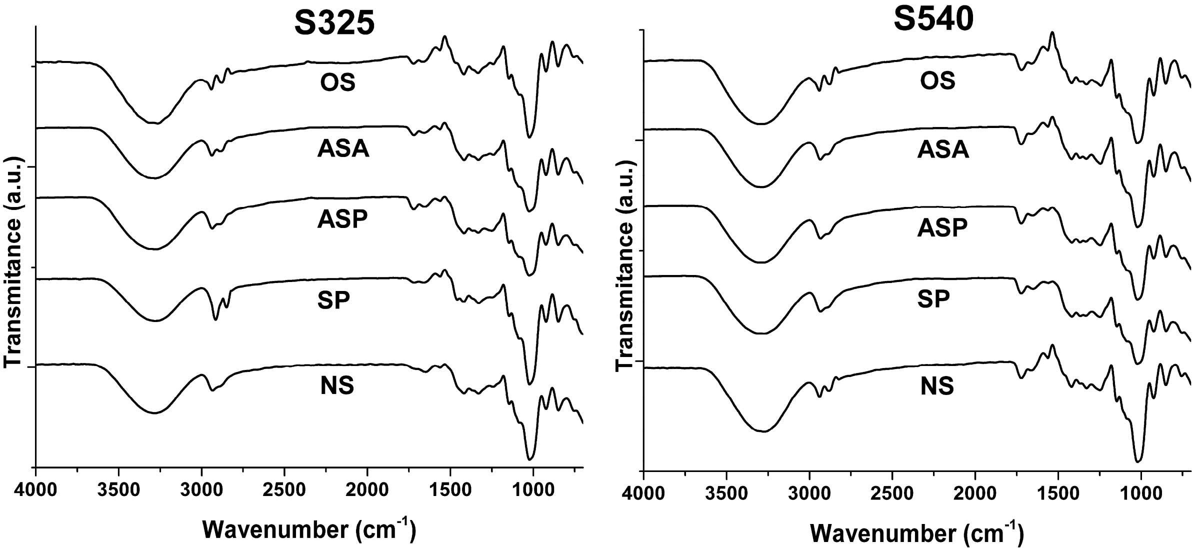

Figure 4. Fourier Transform Infrared Spectroscopy of extruded biodegradable sheets based in modified starch with PVA S325 and S540.

4. CONCLUSION

The native and the modified starches blended with PVA with different hydrolysis degrees (HD) were able to produce sheets by extrusion-calendering process with good mechanical, optical, barrier, and microstructural properties, evidencing the good compatibility between starch and PVA, regardless of the type or grade of them.

The sheets produced with higher HD PVA (98%) had better mechanical properties, and with higher crystallinity than those produced with lower HD PVA (88%), probably because the higher HD PVA has more hydroxyl groups than the lower that leads to a better interaction with the starch. The modified starches did not change the properties of the sheets that justify their use, as compared with native starch.

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CAPÍTULO 8 – BIODEGRADABLE BLENDS OF POLYVINYL ALCOHOL AND CATIONIC STARCHES

ABSTRACT: The aim of this work was to study the effect of cationic cassava starch with different degrees of substitution on the properties of biodegradable sheets produced with cassava starch and PVA by extrusion-calendering process. It was used four cassava starches, one native and three cationic starches with different degrees of substitution (0.019; 0.027 and 0.033 mol/mol), and two PVA grades, one partially hydrolyzed (S540 - hydrolyze degree = 88%) and one fully hydrolyzed (S325 - hydrolyze degree = 98%) and glycerol as plasticizer. All sheets were visually homogeneous, with a good processability and handleability. By the SEM analysis, it was observed a good compatibility between the polymers, without presence of pores or cracks, all the sheets had a semi-crystalline pattern, and the sheets produced with PVA S325 had the higher crystallinity. The biodegradable sheets of native or cationic starch / PVA blends produced by extrusion-calendering process presented good mechanical, optical, barrier, and microstructural properties indicating a good compatibility between them, and the blends are appropriate for thermoplastic extrusion process. Apparently the materials produced with cationic starch have better properties than native starch, and the sheets produced with S325 (high hydrolyze degree) presented better characteristics than those produced with S540, mainly the mechanical properties.

Keywords: biodegradable polymers; mechanical properties, extrusion.

1. INTRODUCTION

The synthetic plastics are widely used in our daily life and they causes serious environmental problems when disposed in environment, so in the recent years the research for biodegradable materials has increased as an alternative for petroleum-based plastics (YUN & YOON, 2010).

Nowadays several polymers can be used for replacement of conventional plastics, like the polyvinyl alcohol - PVA a polymer with a high technological potential because it is a melt processable polymer that possess excellent optical and physical properties. It is used in a wide range of industrial fields; however, PVA is relatively expensive when compared to conventional non-biodegradable polymers (TANG & ALAVI, 2011). Therefore, blending PVA with other biodegradable polymer such as starch can reduce the costs, and allowing the new blend to be cost-competitive compared to the conventional polymers.

Starch can presents some limitations for its use in native form, so to improve some specific properties there are physical, chemical or enzymatic methods to produce modified starches. Cationic starches are widely used in numerous industrial applications in food or non-food industry, including as thickening agent in foods, or in paper and textile industry for example. Cationic starch is usually produced through etherification reaction of starch with compounds containing tertiary or quaternary ammonium salts (CHAISAWANG & SUPHANTHARIKA, 2005; ALCÁZAR-ALAY & MEIRELES, 2015).

Usually the cationic starches present degrees of substitution - DS lower than 0.2. The process can be made by dry or wet route; usually the physical and chemical properties and the morphology of starch are changed after the cationization, mainly in higher DS values (ASHOGBON & AKINTAYO, 2014; ZHANG et al. 2007).

Chivrac et al. (2010) and Chivrac et al. (2008) produced cationic starch-based nano-biocomposites using sepiolite and montmorillonite, and according to the authors, the use of cationic starch favors the exfoliation process of the sepiolite and montmorillonite nanoclays because the cationic starch has the adequate polarity, promoting a better clay exfoliation process.

Starch of different sources and PVA was already used in blends with relative success, like pea starch (CANO et al., 2015), cornstarch (YAN et al., 2015), potato starch (SINGHA & KAPOOR, 2014), and cassava starch (RAHMAN et al., 2010, ZANELA et al., 2015a).

The aim of this work was to study the effect of cationic cassava starch with different degrees of substitution on the properties of biodegradable sheets produced with cassava starch and PVA by extrusion-calendering process.

2. EXPERIMENTAL

2.1 Materials

There were used four cassava starch supplied by Agricola Horizonte Ltda. (Brazil): one native starch – NS and three cationic cassava starch with different degree of substitution (DS), CS19 (DS = 0.019 mol/mol), CS27 (DS = 0.027 mol/mol) and CS33 (DS = 0.033 mol/mol). There were used PVA supplied by Sekisui Chemical (Japan), with different hydrolysis degree – HD and molecular weight – MW (based on their viscosity in 4% aqueous solution): Selvol™ 540 – S540 (HD: 88%, viscosity: 49 cP) and Selvol™ 325 – S325 (HD: 98%, viscosity: 31 cP). The glycerol was supplied by Dinamica (Brazil).

2.2 Methods

2.2.1 Sheet production

The eight formulations were composed by 40 wt% of starch, 25 wt% of PVA and 35 wt% of glycerol. After manual homogenization, the samples were placed in a vacuum oven (model Q819V2, Quimis, Brazil) with a vacuum pressure of 0.085 MPa for 90 minutes at 85 °C to incorporate the glycerol using a method adapted from Jang & Lee (2003). After this step, the polymer blends were firstly extruded in a single-screw extruder (model EL-25, BGM, Brazil), with a screw diameter of 25mm and a L/D ratio of 28. Screw speed used was set in 30 RPM, temperature profile used was set in: 90/180/200/190 °C from feeder to die zone, was used a six-hole cylindrical matrix (2 mm) for pellets production.

After pelletization, the blends were extruded in a co-rotating twin-screw extruder (model D-20, BGM, Brazil) with a screw diameter of 20 mm and L/D ratio of 35, screw speed was set in 110 RPM and a temperature profile used was set in: 90/160/190/190/190 °C from feeder to flat die matrix. The samples were extruded using a flat die with 0.8 mm aperture and 320 mm length, coupled with a 3-roll water-cooled calender (AX Plásticos, Brazil) for sheets production.

The sampled was identified by the acronym composed by the starch type followed by the PVA type, e.g. CS19-S540: sheet using cationic cassava starch with DS of 0,019 mol/mol (C19) and PVA Selvol™ 540.

2.2.2 Mechanical properties

The tensile strength, Young's modulus and elongation at break were analyzed according to the ASTM D882-02 method, with some modifications, using an universal testing machine with a load cell of 5 kN (model DL2000, EMIC, Brazil) with an initial distance between the grips of 40mm and a crosshead speed of 0.8 $mm.s^{-1}$. Ten samples from each blend was cut (80 mm in length and 25 mm in width) and conditioned at 53±2% RH and 23±2 °C for 72 hours before analysis.

2.2.3 Water vapor permeability (WVP)

The water vapor permeability (WVP) analysis was determined according to the ASTM E96-009 standard (gravimetrically). The measurements were performed in triplicate, using a relative humidity gradient of 33 - 64% RH.

2.2.4 Weight loss in water (WLW)

The analysis of weight loss in water (WLW) was performed as described by Olivato et al. (2012) The weight loss in water measurements were performed in triplicate and expressed as the percentage of the original mass (M_i) and the final mass (M_f) of the film after immersion in water for 48 hours at 25 °C, according to eq. 1.

$$\mathrm{WLW} = [(\mathrm{M_i} - \mathrm{M_f})/\mathrm{M_i}] \times 100 \qquad (1)$$

2.2.5 Apparent opacity and Color difference

The apparent opacity (Op) and Color difference (ΔE*) was determined according to the method described by Maria et al. (2008).

The Op values were measured using a colorimeter (BYK Gardner, Germany) with the illuminant D65 (daylight) and a visual angle of 10°. The Op was determined as the ratio of the opacity of the sample over a black standard (Op_b) and the opacity over a white standard (Op_w) being represented on an arbitrary scale (0-100%), and the analyses were performed in triplicate according to eq. 2.

$$Op = (Op_b/Op_w) \times 100 \qquad (2)$$

The ΔE* are obtained based in eq. 3, where: ΔL*, Δa* and Δb* are the differences between the sample measured under the white standard and the white standard alone.

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \qquad (3)$$

2.2.6 X-ray diffraction (XRD)

The X-ray diffraction (XRD) analysis was performed using a diffractometer (Panalytical X´Pert PRO MPD, Netherlands), emitting copper Kα radiation (λ = 1.5418 angstrom). The anode radiation was generated at 40 kV and 50 mA and was monochromatized using a 20 mA current. Diffraction intensity measurements were performed between 2θ = 5° to 50° at room temperature. The relative crystallinity of each film was calculated by dividing the area of the peaks by the total area under the curve of the crystalline region plus amorphous region (the total area under the curve minus the baseline).

2.2.7 Scanning Electron Microscopy (SEM)

The micrographs of the biodegradable sheets were recorded using a scanning electron microscope (SEM) (FEI Quanta 200, USA). The sheets were fractured in liquid nitrogen, attached to aluminum supports and coated with gold (BAL-TEC SCD 050 sputter coater, Leica Microsystems, Germany) (40-50 nm in thickness) at 25 °C and a pressure of 2.105 Torr for 180 seconds. The fracture surfaces of the sheets were analyzed.

2.2.8 Fourier Transform Infrared Spectroscopy (FT-IR)

The sheets were dried over anhydrous calcium chloride salt for one week and analyzed in a Fourier transform infrared spectrophotometer (FT-IR) (IRPrestige 21, Shimadzu, Japan) using a horizontal attenuated total reflection (ATR) module operating over the spectral range of 4000 cm^{-1} - 750 cm^{-1}. It was used the Standard Normal Variate Transformation - SNV of the spectrums to reduce the effect of particle size, light scattering and multicollinearity, improving the interpretation of spectra, according to established by Barnes, Dhanoa & Lister (1989).

2.3 Statistical Analysis

The data were analysed using STATISTICA 7.0 (Statsoft, USA), performing analysis of variance (ANOVA) and Tukey's test at a 5% significance level ($p<0.05$).

3. RESULTS AND DISCUSSION

The biodegradable sheets produced by extrusion-calendering showed good processability, handleability, and they were visually homogeneous and continuous, with an average thickness of 543±156 µm.

3.1 Mechanical properties

The results of the mechanical properties of the biodegradable sheets are shown in Figure 1. The sheets produced with PVA with higher hydrolysis degree (S325 - HD = 98%) had the higher values for mechanical properties when compared to the sheets produced with PVA with the lower HD (S540 – HD = 88%) and the same type of starches.

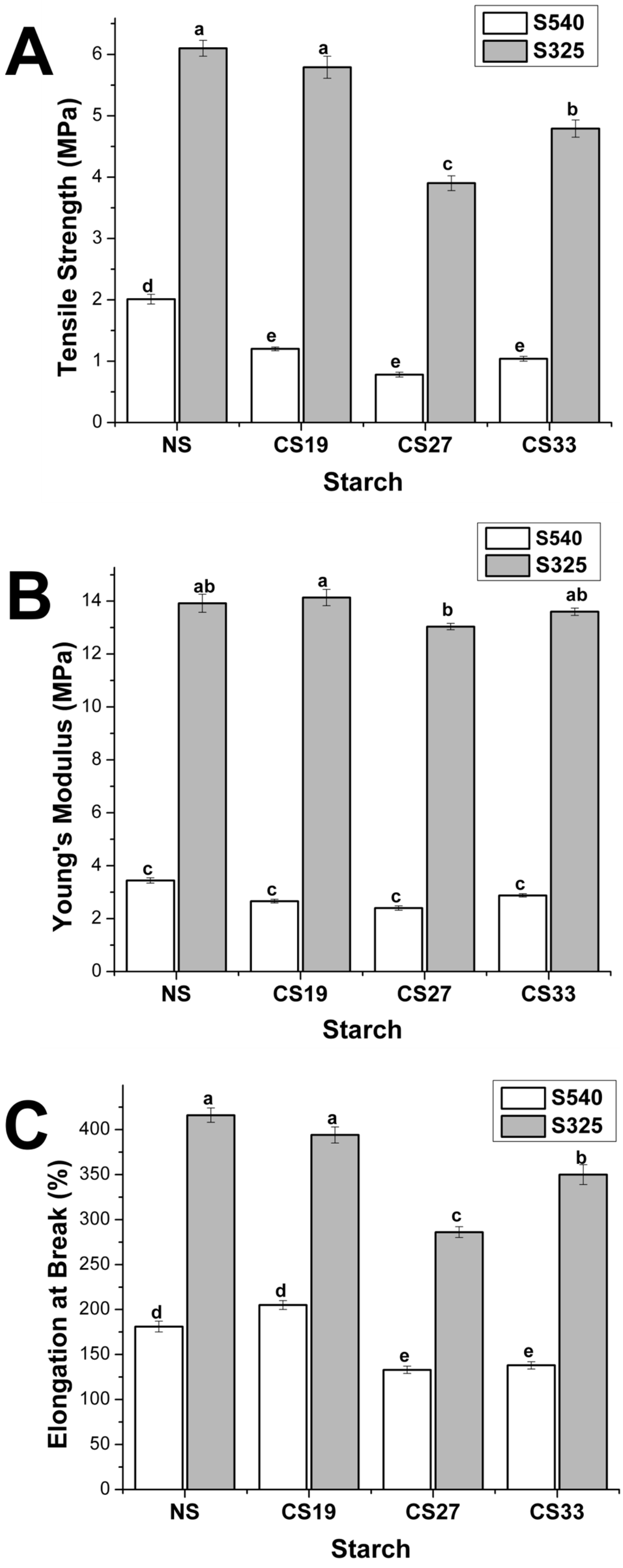

Figure 1. Mechanical properties of the biodegradable sheets produced: tensile strength (a), Young's modulus (b) and elongation at break (c).

Limpan et al. (2012) observed the same behavior in casting films produced with fish myofibrillar proteins/PVA blends, in which films with higher HD PVA had better mechanical properties compared to films produced with lower HD PVA. According to the authors, the higher HD PVA presents more hydroxyl groups in their structure that favors the formation of hydrogen bonds between starch and PVA molecules leading to stronger interactions and consequently more rigid structures.

Comparing the tensile strength (TS) of the sheets produced with PVA S325, those produced with native starch (NS) and with cationic cassava starch with the lower degree of substitution (CS19 DS=0.019 mol/mol) presented the higher tensile strengths (TS = 5.79±0.18 and 6.10±0.13, respectively) (Figure 1A), followed by CS33 and CS27. For the sheets produced with PVA S540, the higher TS were observed for those produced with native starch (NS) (TS = 2.01±0.08), and there were no difference between the cationic starches (TS = 1.20±0.03; 0.78±0.04 and 1.04±0.04 for CS19; CS27 and CS33, respectively).

The Young's modulus (YM) (Figure 1B) of the sheets presented the higher differences between the PVA grades, with values about four times higher for sheets produced with PVA S325 (YM = 13.92±0.34; 14.14±0.31; 13.04±0.37 and 13.60±0.28 for NS; CS19; CS27 and CS33, respectively) compared to PVA S540 (YM = 3.44±0.10; 2.66±0.07; 2.40±0.08 and 2.88±0.06 for NS; CS19; CS27 and CS33, respectively). For the sheets produced with PVA S325, those produced with starch CS19 had the higher Young's modulus and with CS27 the lowest. For the sheets produced with PVA S540, there were no differences between the starches.

The elongation at break (EB) of the sheets (Figure 1C) presented a wide variation, with values upper to 400% and lower than 150%, and the sheets produced with PVA S325 had the higher EBs, mainly with native starch (EB = 416±8) and with cationic cassava starch with the lower degree of substitution (CS19) (EB = 394±9). Comparing the sheets produced with PVA S540, those produced with native starch and CS19 had higher EB than those produced with CS27 and CS33.

Wang et al. (2015) produced blow films by extrusion with cationic starch and PVA fully hydrolyzed, and starch:PVA ratio ranging from 100:0 to 80:20 wt%. The authors reported that increasing of PVA content the tensile strength increase and the values ranges from 2 to 3 MPa, lower than those obtained in present work for the high HD PVA (S325). The same behavior was observed for elongation at break, that the values ranged from 50 to 75%, lower than those observed in present work for both types of starch, probably because of the lower level of PVA when compared to our work; the concentration of plasticizer was not informed by the authors.

The sheets produced with PVA with higher HD (S325) had mechanical properties similar to sheets described in Chapter 7 (modified starches and the same PVA grades), but the sheets produced with PVA S540 (lower HD) had inferior mechanical properties than those in Chapter 7, probably because the PVA S325 presents better interaction with cationic starch when compared to PVA S540. According to Briscoe, Luckmam & Zhu (1999) the residual acetate groups in the partially hydrolyzed PVA has a hydrophobic nature, that leads to a weakening of the hydrogen bonds intra and intermolecular of the polymers, reducing the mechanical properties of the sheets.

3.2 Water vapor permeability (WVP)

The Table 1 presents the WVP of the biodegradable sheets, and they ranged from 2.7 to 3.8 $x10^{-10}$ $g.m^{-1}.s^{-1}.kPa^{-1}$. These values were similar to those reported by Zanela et al. (2015a) that produced sheets of PVA, native cassava starch and glycerol using a mixture design, and they had values that ranged from 2.1 to 4.7 $x10^{-10}$ $g.m^{-1}.s^{-1}.kPa^{-1}$.

Wang et al. (2015), in blown films of cationic starch and PVA, had higher WVP, that ranged from 4.5 to 7.0 $x10^{-10}$ $g.m^{-1}.s^{-1}.kPa^{-1}$, for PVA content that ranged from 0 to 20%. According to the author these variations were due to structural modifications of the polymeric network and interaction between the hydroxyl groups of both polymers, because the water vapor permeation depend on both diffusivity and solubility of water in the polymeric matrix.

Table 1. Water Vapor Permeability, apparent opacity, color difference, and crystallinity index of the extruded biodegradable sheets.

Starch	**PVA**	**Water vapor permeability (g.m^{-1}.s^{-1}.kPa^{-1}) (x10^{-10})**	**Weight loss in water (%)**	**Apparent opacity (%)**	**Color difference (ΔE*)**	**Crystallinity Index (%)**
NS	**S540**	2.8 ± 0.1^{ab}	37 ± 1^{bc}	24 ± 2^{cd}	18 ± 2^{b}	25.6
	S325	3.2 ± 0.1^{abc}	42 ± 1^{abc}	31 ± 1^{b}	23 ± 1^{ab}	25.3
CS19	**S540**	3.4 ± 0.1^{cd}	44 ± 3^{abc}	29 ± 1^{bc}	20 ± 1^{b}	22.5
	S325	3.6 ± 0.1^{cd}	47 ± 2^{ab}	38 ± 1^{a}	28 ± 2^{a}	24.8
CS27	**S540**	3.3 ± 0.1^{bcd}	41 ± 3^{abc}	22 ± 1^{d}	12 ± 1^{c}	24.6
	S325	3.8 ± 0.2^{d}	52 ± 1^{a}	27 ± 1^{bcd}	20 ± 1^{b}	26.5
CS33	**S540**	3.3 ± 0.1^{bcd}	34 ± 3^{c}	28 ± 1^{bc}	22 ± 1^{b}	21.9
	S325	2.7 ± 0.1^{a}	48 ± 1^{a}	27 ± 2^{bcd}	18 ± 1^{bc}	25.9

$^{a, b c, d}$ values with the same letter at the same column are not different statistically ($p<0.05$).

Apparently, neither the cationization of the starch nor the PVA grade had major influence on the WVP of the sheets, probably because the blend components (starch, PVA and glycerol) are hydrophilic.

3.3 Weight loss in water

The biodegradable sheets produced with PVA S540 (HD = 88%) had usually lower weight loss in water (WLW) than those with PVA S325 (HD = 98%) (Table 1), and ranged from 34 to 52%, characterizing these materials as soluble in water because as previously discussed the blend components (starch, PVA and glycerol) are hydrophilic. However, these WLW are lower than those reported by Zanela et al. (2015a), that obtained values ranging from 54 to 75% for native starch/PVA, but they used a PVA with lower molecular weight than those used in this work. According to SEKISUI (2016), the increasing of molecular weight promotes a decreasing of the water solubility of the PVA, that can explain this differences obtained. The lower WLW (34%) was close to the WLW reported by Soares et al. (2013) for sheets produced with native cassava starch, poly (lactic acid) and glycerol (0.3 g of glycerol/g of starch) (starch:PLA 70:30 wt%), that obtained WLW of 35.2 despite the PLA be less hydrophilic than PVA.

3.4 Apparent opacity (Op) and Color difference (ΔE*)

The color of the packaging is an important factor for the consumer acceptance, furthermore the color changes in a sheet can be better described using a color function such as the ΔE* (TAQI, MUTIHAC & STAMATIN, 2014).

The apparent opacity (Op) of the sheets ranged from 22 to 38% (Table 1), and the biodegradable sheets CS19-S325 had the higher Op and the sheets NS-S540, CS27-S540, CS27-S325 and CS33-S325 had the lower Op, and consequently they were the more translucent sheets.

For ΔE* analysis (Table 1), the sheets NS-S325 and CS19-S325 presents the higher ΔE* values, indicating that these sheets had the highest color difference when compared to white standard. These films were more yellowish, on the other hand, the sheets CS27-S540 and CS33-S325 had the lower ΔE*, because of the higher transparency of these sheets (lower Op).

Both the PVA grade and the type of starch influenced the opacity and the color of the biodegradable sheets but it was not possible to correlate these components with the Op and ΔE*.

3.5 X-ray diffraction (XRD)

The X-ray diffractograms of the sheets were similar, and, the crystallinity index (Table 1) had a low variation and ranged from 21.9 to 26.5%. In general, the sheets produced with PVA S325 (HD = 98%) were more crystalline than those with PVA S540 (HD = 88%). According to Tang & Alavi (2011) fully hydrolyzed PVA have more hydroxyl groups in their structure than the partially hydrolyzed ones that possess some residual acetate groups, making it difficult the formation of ordered zones in the polymeric structure due a steric impediment that results in a lower crystallinity index.

The diffractograms of the sheets produced with PVA S325 show a peak near 20° and two another peaks partially overlapped at 23 and 17.9, while for PVA S540 sheets, it is possible to observe a broad peak near 20°, and probably the 23 and 17.9° peak is completely overlapped by the more intense peak at 20°. Zanela et al. (2015b) obtained similar results for native cassava starch/PVA extruded sheets, and also Dass et al. (2010).

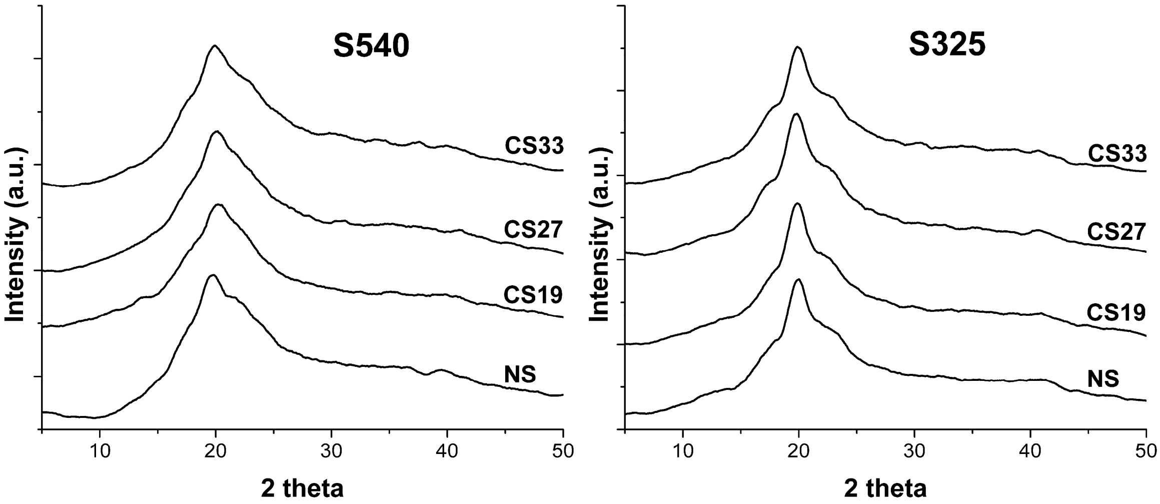

Figure 2. Diffractograms of the extruded biodegradable sheets.

Wang et al. (2015), obtained similar diffractograms for films of PVA/cationic starch produced by blown extrusion. The diffraction pattern of native and cationic starches (Figure 2) were similar, and according to Qiu, Hu & Peng (2013), it indicates that the modification occurred mainly in the amorphous regions of the starch granules, and the cationization of the starch did not influence the re-crystallization of the polymers after the extrusion process.

3.6 Scanning Electron Microscopy (SEM)

According to the SEM analysis (Figure 3), the surface of the sheets are smooth, without cracks or pores, evidencing the good compatibility of the polymers, because both PVA and starch are hydrophilic, with large amounts of hydroxyl groups in their structures, favoring the interaction between them via hydrogen bonds. That is in accordance with Zanela et al. (2015b) for cassava starch/PVA extruded sheets and with Luo et al. (2012) for cornstarch/PVA plasticized with glycerol.

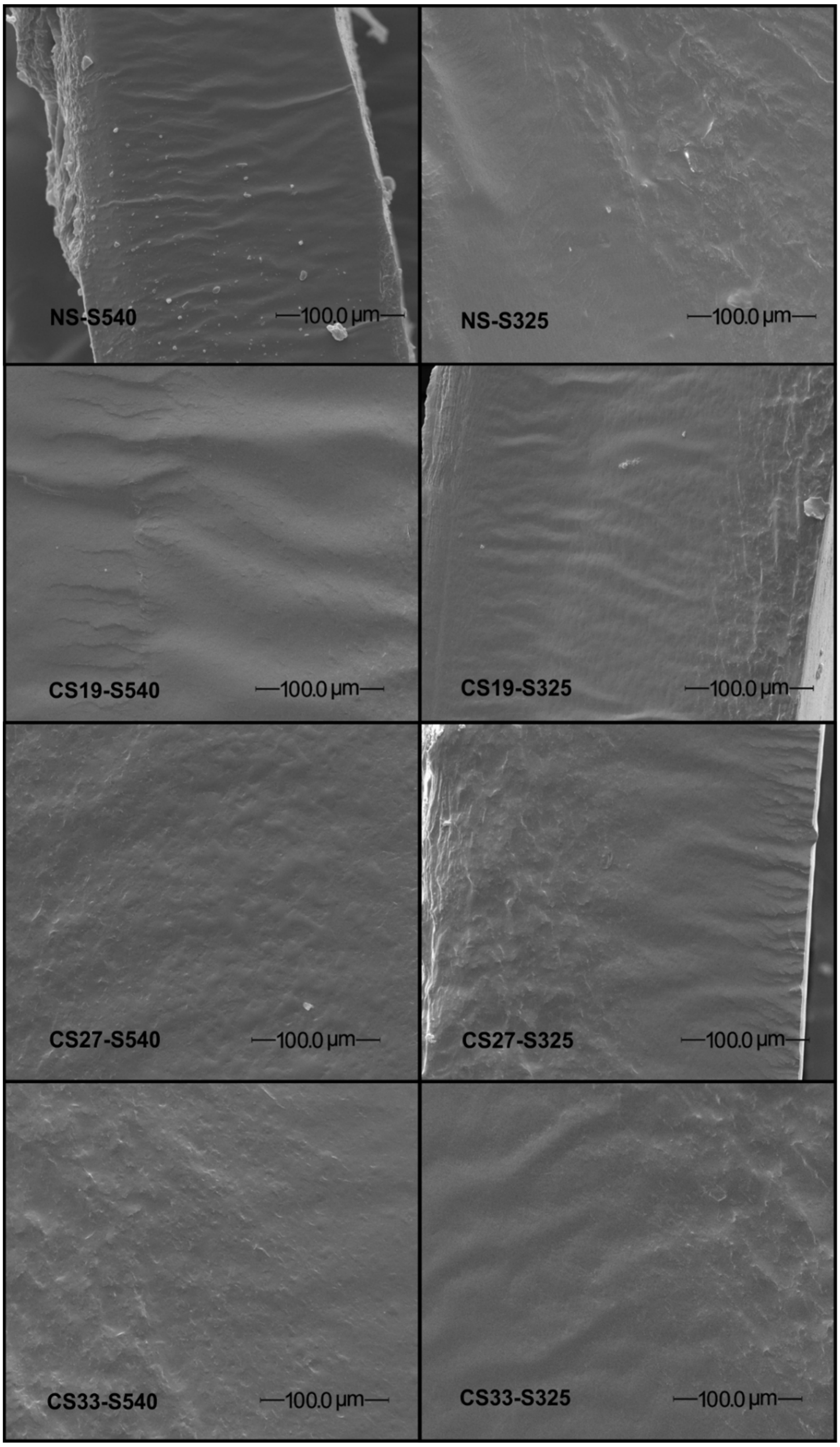

Figure 3. Scanning electron microscopy – SEM micrographs of the fracture surfaces of the extruded biodegradable sheets (magnification at 800X).

On the other hand, Wang et al (2015) observed granules of starch partially melted in cationic starch/PVA blown films, but the authors reported that the production of the films were continuous; indicating as well obtained in present work a good compatibility between the polymers.

3.7 Fourier Transform Infrared Spectroscopy (FT-IR)

The Figure 4 presents the FT-IR analysis of the sheets, and all the spectra were similar, with a large absorption band near 3300 cm^{-1} attributed to the stretching of hydroxyls groups present in the three components of the sheets (starch, PVA and glycerol) (Zanela et al., 2015b; Qiu, Hu & Peng, 2013).

All the sheets produced with PVA S540 present absorption bands at 1730 cm^{-1} and 1245 cm^{-1}, attributed to the stretching of C=O and C-O bonds respectively, due to the acetate residual groups present in partially hydrolyzed PVA molecule (Zanela et al., 2015a; Tudorachi et al., 2000), as previously discussed in Chapter 7.

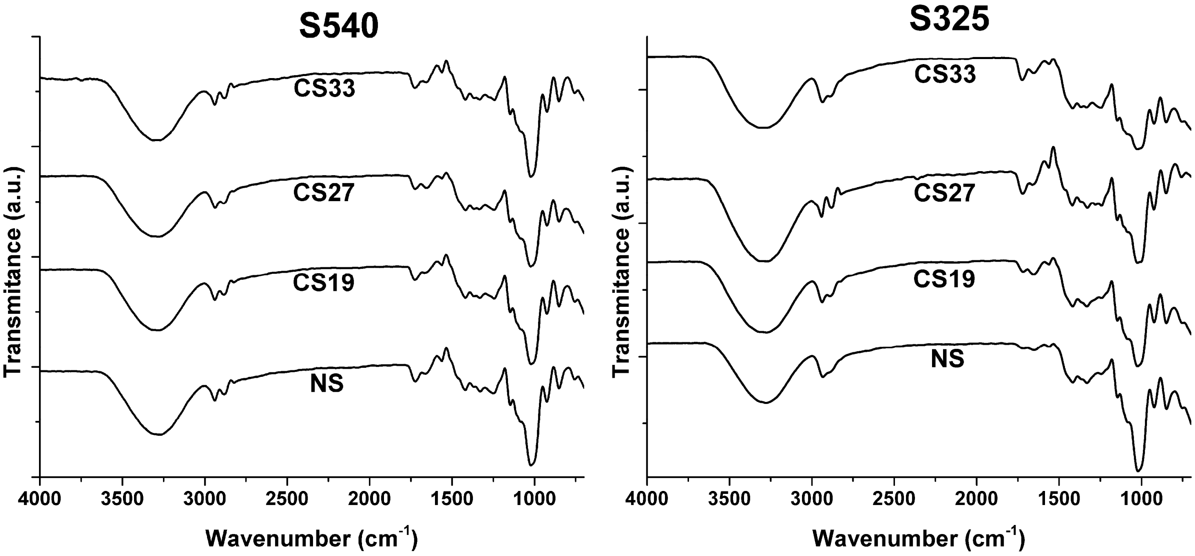

Figure 4. Fourier Transform Infrared Spectroscopy – FTIR of extruded biodegradable sheets.

Sin et al (2010) studied the hydrogen bonds interactions in native cassava starch/fully hydrolyzed PVA, experimentally and through computational modeling, and the authors observed that starch/ PVA binding is favorable and stable, indicating a good compatibility between them.

4. CONCLUSION

The biodegradable sheets of native or cationic starch / PVA blends produced by extrusion-calendering process presented good mechanical, optical, barrier, and microstructural properties indicating a good compatibility between them, and the blends are appropriate for thermoplastic extrusion process. There were no evidence that the materials produced with cationic starch has better properties than native starch.

The sheets produced with PVA with higher hydrolyze degree (S325 HD = 98%) presented better characteristics than those produced with PVA with lower HD (S540 HD = 88%), mainly the mechanical properties.

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CAPÍTULO 9 – OAT FIBER AS REINFORCEMENT FOR POLYVINYL ALCOHOL - PVA / STARCH MATERIALS PRODUCED BY INJECTION MOLDING

ABSTRACT: The use of low-cost natural fibers is an interesting alternative to both improve the mechanical properties and reduce the cost of biodegradable materials, maintaining their biodegradability. The aim of this work was to study oat fibers as reinforcer or filler in starch/PVA biodegradable materials produced by injection mold, using native and cationic cassava starches. The formulations were composed by 45 wt% of starch+fiber, 25 wt% of PVA and 30 wt% of glycerol, the oat fiber was added in proportions of 0; 2.5; 5.0; 7.5 and 10.0 wt%, and two types of cassava starches (native and cationic), totalizing ten formulations. All materials had good processability, with adequate mechanical properties, and the tensile strength, Young's modulus and elongation at break ranged from 5.5 to 4.7 MPa, 12.4 to 7.1 MPa and 260 to 180% respectively, and higher oat fibers concentration lead to more rigid materials, and medium fibers levels lead to more elastic materials. The type of starch (native or cationic) did not influenced the biodegradable materials properties, unlike the fiber that modified mainly the color and the weight loss in water of the materials. The oat fiber presented a good dispersion and compatibility with the polymeric matrix of native or cationic cassava starch and PVA but the fiber did not reinforced the material adequately, probably because the oat fibers acted more like a filler than as a reinforcer. The use of oat fiber is interesting from a commercial point of view to produce biodegradable materials by injection mold; the oat fibers act as a filler reducing the material costs because these fibers are low-cost by-product of the oat industry.

Keywords: biodegradable polymers; mechanical properties, composites.

1. INTRODUCTION

Starch is a low cost, renewable and the second most abundant biopolymer in nature after the cellulose, and thermoplastic starch is a promising and well-known material to replace petroleum-based non-biodegradable plastics, but it presents some drawbacks as high hydrophilicity and poor mechanical properties (DUANMU et al., 2010). To overcome these drawbacks it is possible to blend starch with another biodegradable polymer with better properties, as polyvinyl alcohol (PVA), because it is a polar polymer that presents good compatibility with the starch

(CHIELLINI et al., 2009).

Another way to improve the mechanical properties of starch-based materials is the addition of natural fibers because it maintains the renewable and biodegradable characteristic of the material, and most natural fibers is considered industrial waste and / or has low added value.

Due the limitations for use in native form, the starch can suffer some chemical modifications to improve some specific properties, like the cationic starch, that possess numerous industrial applications in food or non-food industry, being much used in paper industry due the interaction with the anionic charges of cellulose (ALCÁZAR-ALAY & MEIRELES, 2015; CHAISAWANG & SUPHANTHARIKA, 2005). Therefore, the use of cationic starch in natural cellulosic-based fibers can improve the interaction between the starch and the fibers, improving the mechanical properties of the material.

The main advantages of the use of natural fibers include low density, low-cost, and biodegradability, and some natural fibers have resistance similar to conventional fibers such as glass fiber. However, natural fibers presents some drawbacks, like incompatibility with hydrophobic matrix, tendency to aggregate that can reduce the application of these fibers. (LI, TABIL & PANIGRAHI, 2007; SAHEB et al., 1999).

The oat fiber is a by-product of the production of oat products such as oat flour or flakes for example, and it is extracted from the outer layers of the oat grain, this fiber possess a low commercial and nutritive value, being used mainly as energetic font (burning) in industrial boilers. However, this material can be used as reinforcement of biodegradable materials produced by injection molding.

The aim of this work was to study oat fibers as reinforcer or filler in starch/PVA biodegradable materials produced by injection mold, using native and cationic cassava starches.

2. EXPERIMENTAL

2.1 Materials

There were used two cassava starches supplied by Agricola Horizonte (Brazil): one native starch – NS and one cationic starch – CS with a degree of substitution of 0.033 mol/mol. There was used PVA supplied by Sekisui chemical (Japan), with commercial name of Selvol™ 325, having a hydrolysis degree of 98.42 % and a molecular weight (based on their viscosity in 4% aqueous solution) of 41.40 cP, and glycerol supplied by Dinamica (Brazil). The micronized oat fiber was supplied by SL Alimentos (Brazil), with size lower than 200 µm, and 79.9% (dry basis) of total fiber, which 3.5% is lignin.

2.2 Methods

2.2.1 Materials processing

The formulations were composed by 45 wt% of starch+fiber, 25 wt% of PVA and 30 wt% of glycerol, the oat fiber was added in proportions of 0; 2.5; 5.0; 7.5 and 10.0 wt%, and two types of starches (NS and CS), totalizing ten formulations. After manual homogenization, the samples were placed in a vacuum oven (model Q819V2, Quimis, Brazil) with a vacuum pressure of 0.085 MPa for 90 minutes at 85 °C to incorporate the glycerol using a method adapted from Jang & Lee (2003). After this step, the polymer blends were firstly extruded in a single-screw extruder (model EL-25, BGM, Brazil), with a screw diameter of 25 mm and L/D ratio of 28. The screw speed was set at 25 RPM, temperature profile was set at: 90/165/175/165 °C from feeder to die zone, using a six-hole cylindrical die (2 mm) for pellets production.

After pelletization, the blends were processed in a lab-scale injection molding machine AX16 III (AX-Plasticos, Brazil), with a temperature profile of 160/195/185 °C from feeder to injection nozzle, the mold was maintained at 20 °C, the material was molded in a dog bone shape (test specimen type 4), according to ASTM D638 (2003).

2.2.2 Mechanical properties

The tensile strength, Young's modulus and elongation at break were analyzed according to ASTM D638-03 method, with some modifications, using a universal testing machine (model DL2000, EMIC, Brazil) and a 5 kN load cell, with an initial distance between the grips of 40mm and a crosshead speed of 0.8 mm.s^{-1}. Ten specimens from each blend were conditioned in a desiccator with controlled relative humidity and temperature (53±2 % and 23±2 °C respectively) for one week before analysis.

2.2.3 Weight loss in water

The analysis of weight loss in water (WLW) was performed as described by Olivato et al. (2012) The weight loss in water measurements were performed in triplicate and expressed as the percentage of the original mass (M_i) and the final mass (M_f) of the film after immersion in water for 48 hours at 25 °C, according to eq. 1.

$$\mathrm{WLW} = [(\mathrm{M_i} - \mathrm{M_f})/\mathrm{M_i}] \times 100 \qquad (1)$$

2.2.4 Color evaluation

The color of the specimens was determined using a colorimeter BYK-Gardner (Germany), using an illuminant D65 (daylight) and a visual angle of 10°. The specimens were placed on a white standard plate, and the CIE coordinates L* a* b* was recorded of five specimen for each treatment.

2.2.5 Scanning Electron Microscopy

The micrographs of the biodegradable materials were recorded using a scanning electron microscope (FEI Quanta 200, USA). The specimens were fractured in liquid nitrogen, attached to aluminum supports and coated with gold (BAL-TEC SCD 050 sputter coater, Leica Microsystems, Germany) (40-50 nm in thickness) at 25 °C and a pressure of 2.105 Torr for 180 seconds. The fracture surface of the specimen were analyzed.

2.2.6 Fourier Transform Infrared Spectroscopy (FT-IR)

The specimens were dried over anhydrous calcium chloride salt for one week and analyzed in a Fourier transform infrared spectrophotometer (FT-IR) (IRPrestige 21, Shimadzu, Japan) using a horizontal attenuated total reflection (ATR) module operating over the spectral range of 4000 cm^{-1} - 750 cm^{-1}. Was used the Standard Normal Variate Transformation - SNV of the spectrums, for reduce the effect of particle size and light scattering and multicollinearity, improving the interpretation of spectra, according to established by Barnes, Dhanoa & Lister (1989).

2.3 Statistical Analysis

The data were analyzed using STATISTICA 7.0 (Statsoft, USA), performing analysis of variance (ANOVA) and Tukey’s test at a 5% significance level ($p<0.05$).

3. RESULTS AND DISCUSSION

The starch/PVA/fiber/glycerol composites had good processability on both extrusion (to produce the pellets) and injection molding processes, and the injected materials were visually homogeneous and without cracks or air bubbles. The incorporation of oat fiber promoted a browning of the materials, despite the starch, native or cationic.

3.1 Mechanical properties

In Figure 1 is presented the mechanical properties of the biodegradable materials produced by injection molding. The materials coded as NS-0, CS-0, NS-2.5 and NS-5.0 had the higher tensile strengths (Fig. 1A), but the tensile strength ranged from 4.7 to 5.5 MPa for all samples, a relatively small variation.

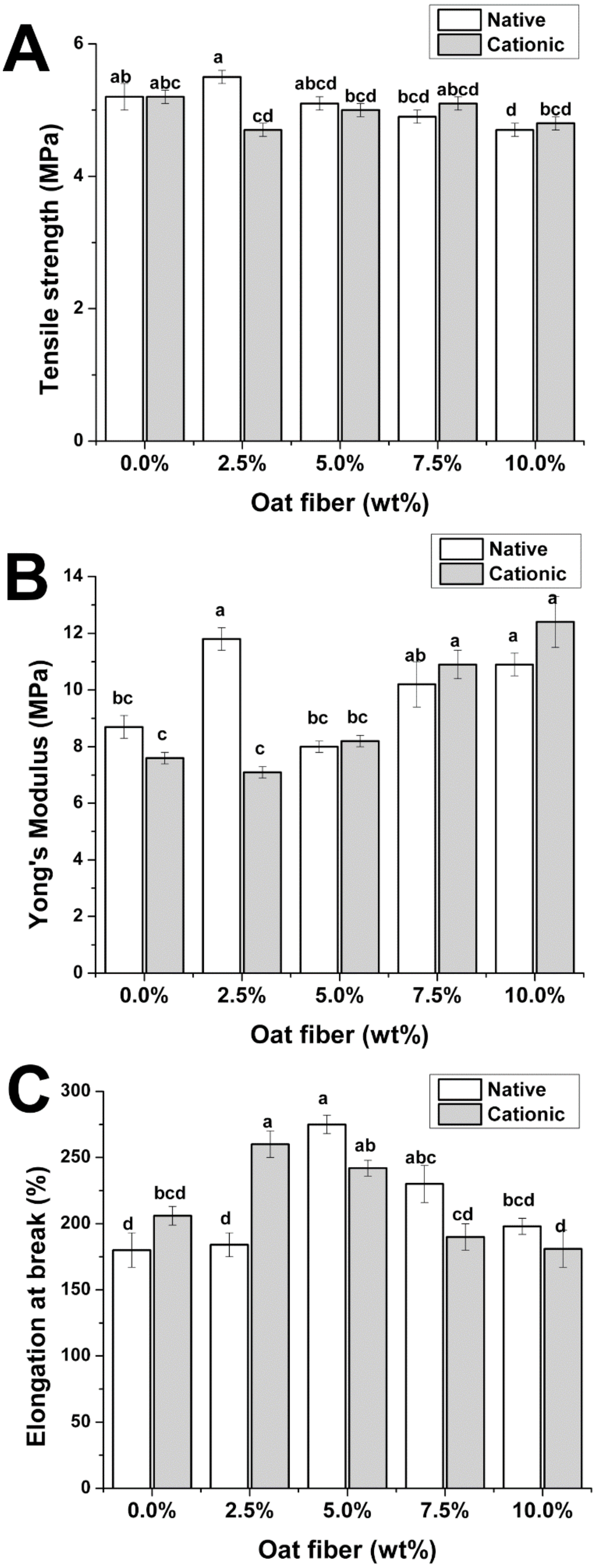

Figure 1. Mechanical properties of biodegradable material of starch, PVA and oat fiber produced by injection mold.

The elongation at break of the biodegradable materials ranged from 180 to 260%, and materials containing intermediate levels of fiber had the higher elongations values (CS-2.5, NS-5.0, CS-5.0 and NS-7.5).

The Young Modulus of the biodegradable materials ranged from 7.1 to 12.4 MPa (Fig. 1B), and the formulations NS-2.5, NS-7.5, CS-7.5, NS-10.0 and CS-10.0 presented the higher Young's modulus, demonstrating that the incorporation of oat fibers increases the rigidity of the biodegradable materials.

In general, the materials produced with 2.5 and 5.0 wt% of fibers presented better mechanical properties for both types of starch, but the percentage of improvement for tensile strength compared to non-reinforced materials was relatively low (5.4 and 1.9%, for native and cationic starch, respectively), probably because the oat fibers acted more like a filler than as a reinforcer.

According to Ku et al. (2011) and Saheb & Jog (1999), many factors influence the performance of natural fiber as composites reinforcement, such as volume fraction of the fibers, aspect ratio (fiber length divided by its diameter), fiber-matrix adhesion, stress transfer interface, and orientation. Moreover, the tensile strength is more dependent on the polymeric matrix properties, and the Young's modulus is more dependent on the fiber properties.

Ma, Yu and Kennedy (2005) produced cylindrical strands of corn starch and winceyette fibers plasticized with urea and formamide by extrusion, and the authors observed reduction of the elongation at break and increasing of the tensile strength and Young modulus with increasing the fiber content.

Cinelli, Chiellini & Imam (2008) produced thermoformed laminates with PVA/starch/glycerol and fiber from orange and apple pomace and sugarcane bagasse, and the authors observed a wide variation of the mechanical properties depending on the fiber source, and the laminates produced with fibers of apple pomace and sugarcane bagasse had the higher values. According to the authors, this variation was due to the fiber shape and composition.

Besides the fiber characteristics, the production process is directly related with the material properties as reported by Chiellini et al. (2001), that used the same fillers cited before but produced the films by casting method. The results were significantly different, and the orange pomace presented a superior response for mechanical properties.

Torres, Arroyo & Goméz (2007) produced by compression molding materials with starch and fibers of sisal, jute and cabuya at concentrations ranging from 2.5 to 12.5 wt%, and the authors reported that the mechanical properties was improved with the increasing of fiber content, and the better mechanical properties was obtained with 10 wt% of sisal fiber.

3.2 Weight loss in water

The Figure 2 present the weight loss in water (WLW) of the biodegradable materials, and the values ranged from 39.3 to 34.3%, i.e., a relative small variation. Apparently, the inclusion of fiber increased the WLW compared with materials without fiber, but the fiber content (2.5 to 10%) did not influenced the WLW, unlike the reported by Kaisangsri, Kerdchoechuen & Laohakunjit (2012), in starch based foams with addition of Kraft fibers, that observed a slight decreasing of water solubility index with the increasing of fibers content.

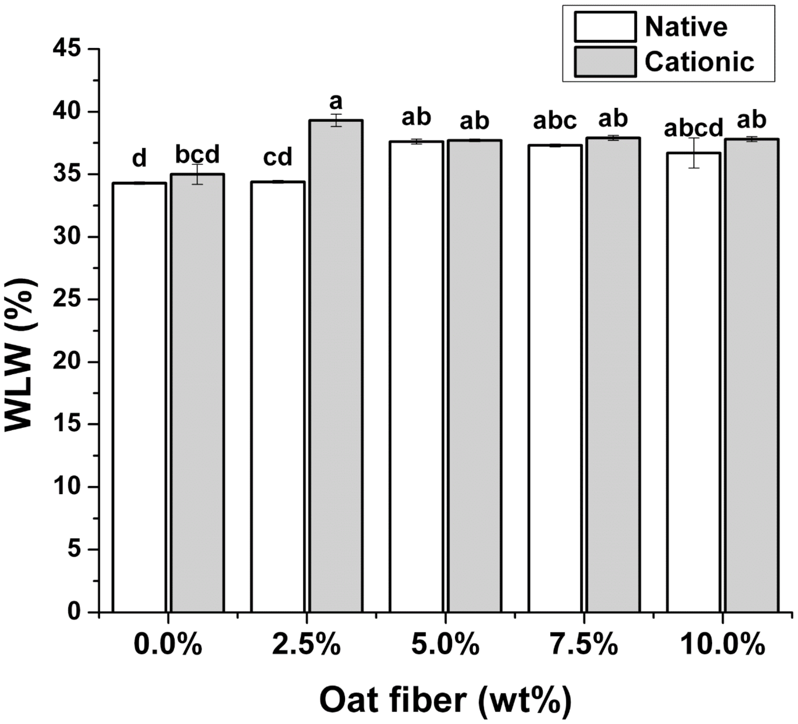

Figure 2. Weight loss in water of biodegradable material of starch, PVA and oat fiber produced by injection mold.

The WLW of the materials without fiber (34.3 and 35.0% for native and cationic starch, respectively) are lower than those reported in Chapter 8 for extruded sheets of native and cationic cassava starches, 42 and 48% respectively. Probably the injection molding process lead to lower soluble materials, and the oat fiber addition did not promoted alterations in this parameter,

3.3 Color evaluation

The lightness (L*) of the biodegradable materials ranged from 53.9 to 17.3 (Figure 3A). The materials produced without fiber (CS-0 and NS-0) had the higher L*, i.e., these materials was more translucent than the materials with fiber, and the higher the fiber content the lower the L*, until 7.5% of fiber. There were no difference between the materials with 7.5% and 10%.

The color component a* (red/green) ranged from +24.2 to +4.6 (Fig. 3B), that indicates a reddish coloration, and the specimens produced without fiber presented the lower values, so the fiber promoted a more reddish color but the increase of the values of a* were not proportional to the fiber content.

The component b* (yellow/blue) of the biodegradable materials ranged from +30.5 to +17.3 (Figure 1C), and the positive values indicates a yellowish color, and the formulations NS-0.0 and NS-2.5 presented the higher values.

In general, higher fiber content produced materials more brownish, due to the color of the pure oat fibers, and the materials without fiber were more translucent and yellowish, agreeing with the results of Zanela et al. (2015a) for extruded sheets of cassava starch and PVA.

Kaisangsri, Kerdchoechuen & Laohakunjit (2012) produced biodegradable foams of starch and Kraft fibers, and the authors also observed an increasing in parameters L, a* and b* with increasing the fiber content. Stevens, Klamczynski & Glenn (2010) produced biodegradable foams of cornstarch and lignin, and they observed the browning of the material containing fibers.

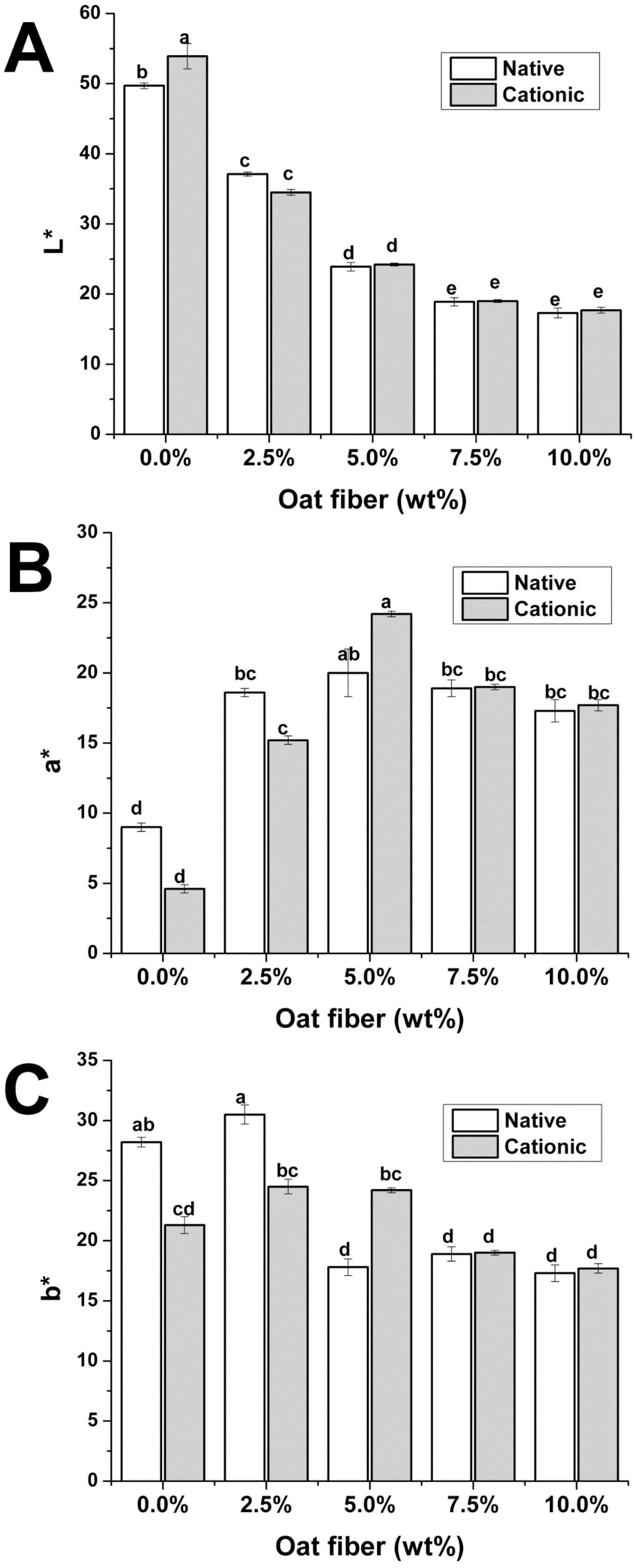

Figure 3. CIE Lab color parameters of biodegradable material of starch, PVA and oat fiber produced by injection mold.

3.4 Scanning Electron Microscopy (SEM)

The Figure 4 presents the micrographs obtained on a scanning electron microscope of the oat fibers used to produce the biodegradable materials. It is possible to observe a rough surface and irregular shapes and sizes, due to the lignin and hemicellulose that cement the fibers together, similar to those observed in wheat straw fibers by Panthapulakkal, Zereshkian & Sain (2006).

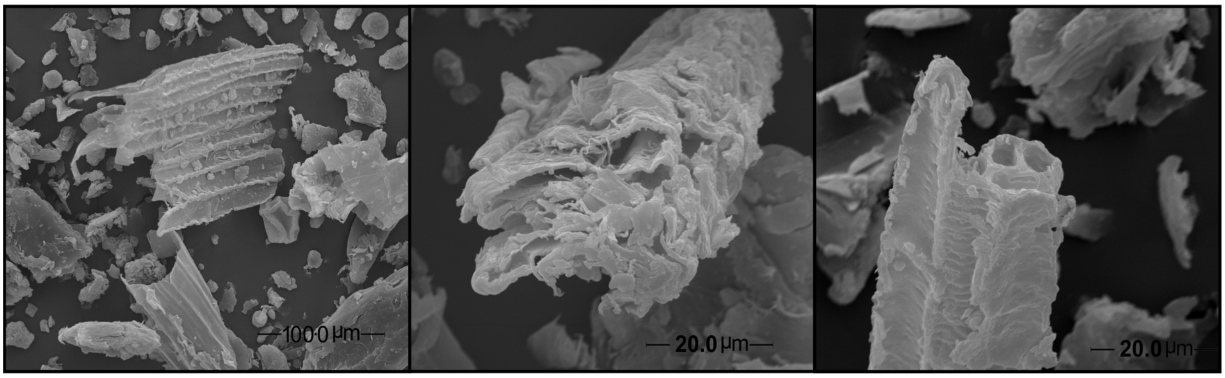

Figure 4. Micrographs of oat fibers.

The Figure 5 presents the SEM micrographs of the biodegradable materials, and the samples without oat fiber (NS-0 and CS-0) have a smooth surface, without pores or cracks, similar to those observed by Zanela et al. (2015a), Zanela et al. (2015b) and Jayasekara et al. (2003) in materials of PVA/starch, demonstrating the good compatibility between both polymers.

The fracture surfaces of the materials containing fibers are smooth and it is possible to observe a good adhesion of fibers within the polymer matrix. Gironès et al. (2012) also observed, in thermo-pressed material of cornstarch, sisal and hemp fibers, a good adhesion of the fiber within the starch matrix. Berthet et al. (2015) produced wheat straw fibers/ PHBV composites, and the authors observed in some formulations the presence of holes in the interface between the fiber and the polymer matrix, due to an inherent hydrophobicity of PHBV and hydrophilicity of the fiber.

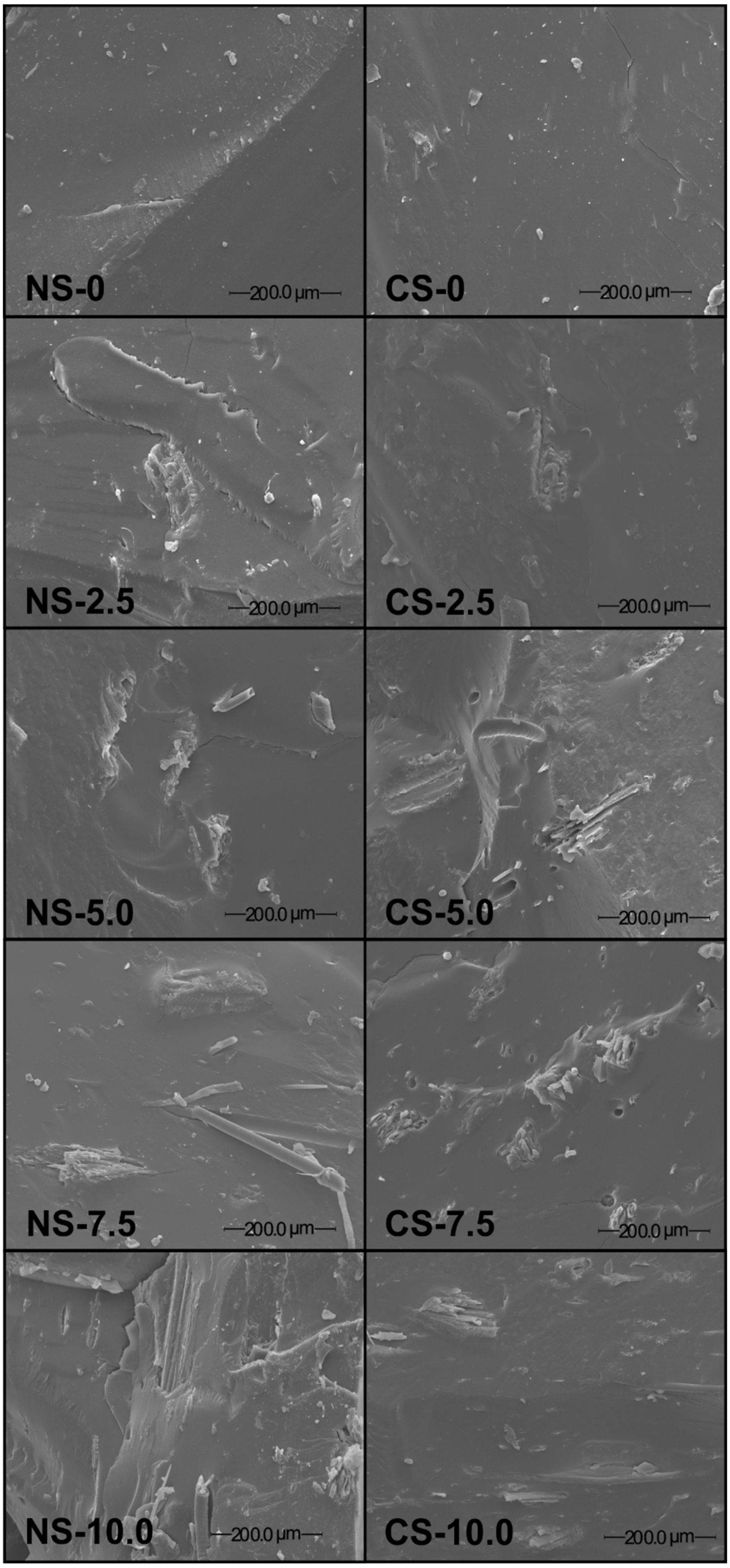

Figure 5. SEM micrographs of biodegradable material of starch, PVA and oat fiber produced by injection mold (magnification at 800X).

3.5 Fourier Transform Infrared Spectroscopy (FT-IR)

In Figure 6 is presented the FT-IR spectra of the biodegradable material of starch, PVA and oat fiber produced by injection mold.

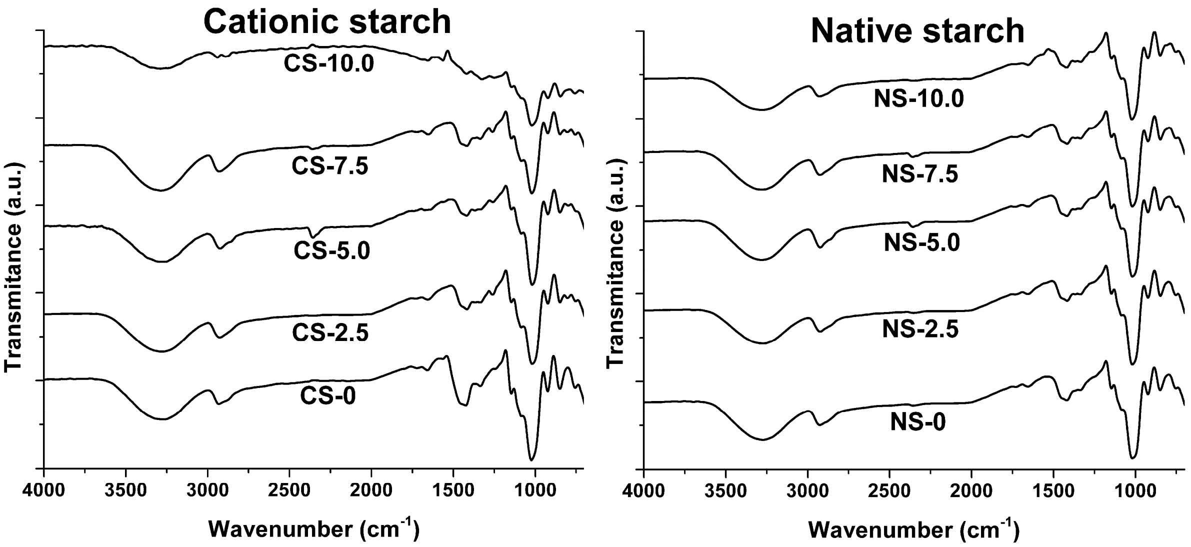

Figure 6. FT-IR analysis of biodegradable material of starch, PVA and oat fiber produced by injection mold.

The materials spectra are very similar between them, with a broad absorption band at 3300 cm^{-1} due the hydrogen bonds between the hydroxyl groups, and absorptions peaks at 2920, 1430 and 1020 cm^{-1} attributed to CH2, CC and CO stretching, respectively. These spectra are similar with those reported by Imam et al. (2005) for casting films of PVA, cornstarch and orange pomace fibers; Pryia et al. (2014) for casting films of PVA, cornstarch and cellulosic fibers; Zanela et al. (2015a,b) for cassava starch/ PVA sheets; as well the spectra reported in Chapters 5, 6, 7 and 8.

4. CONCLUSION

The oat fiber presented a good dispersion and compatibility with the polymeric matrix of native or cationic cassava starch and PVA but the fiber did not reinforced the material adequately, probably because the oat fibers acted more like a filler than as a reinforcer.

The use of oat fiber is interesting from a commercial point of view to produce biodegradable materials by injection mold; the oat fibers act as a filler reducing the material costs because these fibers are low-cost by-product of the oat industry.

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CONCLUSÃO GERAL

Através da realização desse trabalho foi possível observar que o amido e o poli (álcool vinílico) possuem uma boa compatibilidade, pois os materiais biodegradáveis produzidos foram homogêneos, apresentaram boa processabilidade e manuseabilidade, sendo possível seu processamento por técnicas convencionais de processamento de polímeros como a extrusão e a injeção.

Materiais produzidos com PVA de tamanho de cadeia maiores apresentam maior resistência a tração, enquanto que materiais com PVA de grau de hidrólise maiores apresentam maior rigidez. Dentre os tipos de PVA testados, o PVA com maior tamanho de cadeia dentre os totalmente hidrolisados (S 325), foi o que apresentou, de forma geral, as melhores propriedades mecânicas, tendo maior potencial para aplicação industrial.

O uso de amidos modificados de mandioca (fosfato de di-amido; fosfato de di-amido acetilado; adipato de di-amido acetilado; amido oxidado e amidos catiônicos com diferentes graus de substituição) em blendas com o PVA, nas condições testadas no presente trabalho, apresentaram resultados semelhantes ou inferiores aos materiais produzidos com o amido nativo, não sendo assim, viável e justificável seu uso devido a seu maior custo em comparação aos amidos nativos.

O emprego de fibras de aveia em compósitos de amido nativo ou catiônico e PVA produzidos por injeção não atuaram como um reforço, atuando principalmente como uma carga inerte. O uso de fibras de aveia em compósitos biodegradáveis pode ser comercialmente interessante, pois promove uma redução dos custos de produção devido ao fato de ser um material de baixo custo, além do fato de manter os compósitos produzidos totalmente biodegradáveis.

Os materiais produzidos apresentaram caraterísticas adequadas para seu uso como substitutos de polímeros petroquímicos convencionais em aplicações específicas, sendo uma opção interessante do ponto de vista ambiental, e apresentando potencial comercial.