INSTITUTO DE TECNOLOGIA DE ALIMENTOS
Centro de Tecnologia de Embalagem

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EMBALAGENS PLÁSTICAS FLEXÍVEIS PARA PRODUTOS CÁRNEOS COM MAIOR RECICLABILIDADE

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Dissertação apresentada ao Instituto de Tecnologia de Alimentos para obtenção do título de Mestre em Ciência e Tecnologia de Alimentos.

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Este exemplar corresponde à versão final da Dissertação defendida pela aluna Bruna Bonato Turriziani e orientada pela Profa. Dra. Rosa Maria Vercelino Alves

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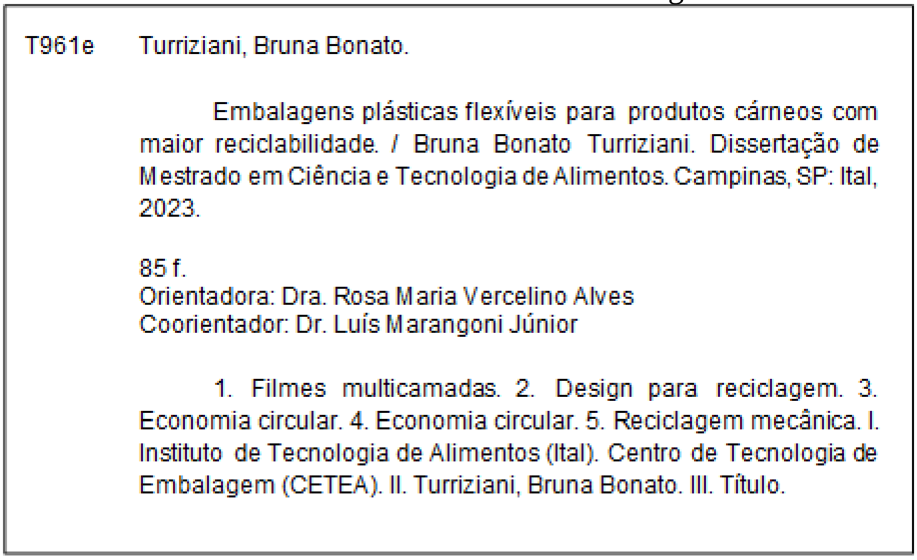

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RESUMO

A sustentabilidade de embalagens plásticas têm sido foco nos últimos anos de empresas produtoras e consumidoras, que vêm buscando a redução do consumo de plástico e/ou substituição por embalagens recicláveis. Os filmes plásticos multicamadas usualmente utilizados no acondicionamento de alimentos, são frequentemente rejeitados nos fluxos de resíduos de reciclagem mecânica, pois não permitem a separação dos diversos polímeros que os compõem. Com isso o emprego de aditivos compatibilizantes para facilitar a miscibilidade dos diferentes polímeros se tornou uma alternativa. Esta pesquisa teve como objetivo explorar o efeito de diferentes concentrações (5-7%) de PCA-MA (aditivo compatibilizante a base de poliolefina com anidrido maleico) nas propriedades, no potencial de migração de dois diferentes materiais de embalagem multicamadas atualmente usados para produtos cárneos: PE/PE/ad/PA/ad/PE/PE e PE/ad/PA/EVOH/PA/ad/PE (PE: polietileno; ad: adesivo; PA: poliamida; EVOH: etileno vinil álcool) e avaliar o potencial de reciclabilidade teórica dos dois filmes multicamadas, utilizando a ferramenta RecyClass, bem como a reciclagem mecânica pós-industrial de filmes sem compatibilizante e com diferentes concentrações de compatibilizante (5-7%). A incorporação de PCA-MA nos filmes multicamadas resultaram na redução do índice de cristalinidade e, consequentemente, uma redução na resistência à tração, resistência à perfuração e barreira ao vapor de água. Os filmes multicamadas apresentaram valores de migração total e migração específica de anidrido maleico abaixo do limite de quantificação dos métodos utilizados para os simulantes de alimentos aquosos e gordurosos. Portanto, estão dentro das especificações da legislação vigente de materiais para contato com alimentos. No geral, embora a incorporação de PCA-MA tenha resultado em alguma perda de propriedades de embalagem, esse aditivo pode ser considerado uma alternativa atraente para facilitar o processo de reciclagem desses materiais complexos. Os filmes multicamadas sem compatibilizante foram classificados pelo RecyClass como materiais não recicláveis. No entanto, o uso do compatibilizante mostrou-se promissor para a reciclagem dessas embalagens. Os espectros de infravermelho mostraram que o copolímero PA-MA-PE foi criado durante a mistura, confirmado pelas imagens de microscopia, onde o compatibilizante proporcionou uma adesão entre a interface da mistura. A temperatura de fusão do PE mostrou-se estável durante o processamento. No entanto, o compatibilizante resultou em mudanças na temperatura de fusão da PA do filme reciclado oriundo da embalagem de PE/PE/ad/PA/ad/PE/PE. Os filmes com compatibilizante apresentaram um aumento significativo no alongamento na ruptura em comparação com os filmes sem compatibilizante. Esses resultados confirmam a forte eficiência da compatibilização PA-MA-PE, sendo uma alternativa para embalagens multicamadas de produtos cárneos a serem reciclados.

Palavras-chave: filmes multicamadas; design para reciclagem; economia circular; reciclagem mecânica.

ABSTRACT

The sustainability of plastic packaging has been a focus in recent years for producing and consumer companies, which have been seeking to reduce plastic consumption and/or replace it with recyclable packaging. The multilayer plastic films usually used in food packaging are often rejected in the mechanical recycling waste streams, as they do not allow the separation of the different polymers that compose them, thus the use of compatibilizing additives to facilitate the miscibility of the different polymers has become an alternative. This research aimed to explore the effect of different concentrations (5-7%) of PCA-MA (compatibilizing additive based on polyolefin with maleic anhydride) on the properties, migration potential of two different multilayer packaging materials currently used for products meat products: PE/PE/ad/PA/ad/PE/PE and PE/ad/PA/EVOH/PA/ad/PE (PE: polyethylene; ad: adhesive; PA: polyamide; EVOH: ethylene vinyl alcohol) and evaluate the theoretical recyclability potential of the two multilayer films, using the RecyClass tool, as well as the post-industrial mechanical recycling of films without compatibilizer and with different concentrations of compatibilizer (5-7%). The incorporation of PCA-MA in the multilayer films resulted in a reduction in the crystallinity index and, consequently, a reduction in tensile strength, puncture resistance and water vapor barrier. The multilayer films presented values of total migration and specific migration of maleic anhydride below the limit of quantification of the methods used for simulants of aqueous and fatty foods. Therefore, they are within the specifications of the current legislation on materials for contact with food. Overall, although the incorporation of PCA-MA has resulted in some loss of packaging properties, this additive can be considered an attractive alternative to facilitate the recycling process of these complex materials. Multilayer films without compatibilizer were classified by RecyClass as non-recyclable materials. However, the use of the compatibilizer has shown to be promising for the recycling of these packages. The infrared spectra showed that the PA-MA-PE copolymer was created during the mixing, confirmed by the microscopy images, where the compatibilizer provided an adhesion between the mixing interface. The melting temperature of PE was stable during processing. However, the compatibilizer resulted in changes in the PA melting temperature of recycled film from PE/PE/ad/PA/ad/PE/PE packaging. Films with compatibilizer showed a significant increase in elongation at break compared to films without compatibilizer. These results confirm the strong efficiency of the PA-MA-PE compatibilization, being an alternative for multilayer packaging of meat products to be recycled.

Key words: multilayer film; design for recycling; circular economy; mechanical recycling

Sumário

INTRODUÇÃO GERAL

A expansão do consumo de alimentos embalados aumentou nas últimas décadas, devido à conveniência, avanços tecnológicos e benefícios trazidos pelas embalagens, tais como informações aos consumidores sobre o conteúdo, validade, condições adequadas de armazenamento, manutenção da segurança alimentar, melhoria da vida de prateleira e redução das perdas e desperdício de alimentos (KAN; MILLER, 2022).

As embalagens plásticas, oriundas de polímeros derivados do petróleo, são amplamente utilizadas no mercado de alimentos, por apresentarem menor custo de produção, maior flexibilidade do material com diferentes combinações de polímeros, propiciar propriedades de barreira a gases, umidade e luz e resistência mecânica. Essas propriedades vão depender da combinação dos materiais utilizados na sua fabricação, diversidade de formato, facilidade e qualidade de impressão (SANTANA, 2019).

As propriedades de barreira de uma embalagem estão relacionadas com a sua capacidade de resistir à absorção ou evaporação de gases e vapores, à passagem da luz e à permeação de gorduras. As propriedades de barreira devem ser definidas para cada produto, dependendo do seu sistema de embalagem, distribuição e durabilidade desejada. Para obter as características de barreira necessárias, é importante combinar diferentes polímeros, pois um único polímero pode não apesentar as propriedades requeridas (TWEDE; GODDARD, 2009) (SARANTÓPOULOS et al., 2017).

As embalagens plásticas flexíveis multicamadas para produtos cárneos, são fabricadas visando aproveitar as melhores propriedades de cada polímero, protegendo o produto de agentes externos, como microrganismos, oxigênio, umidade e irradiação de luz. A poliamida (PA) e/ou o copolímero de etileno e álcool vinílico (EVOH) são utilizados nas camadas intermediárias, devido às suas propriedades de barreira a gases e o polietileno (PE), nas camadas interna e externa, em função da sua barreira ao vapor d’água e das suas excelentes propriedades de selagem. O sistema comumente utilizado para a conservação desse tipo de alimento combina o uso de materiais com propriedades adequadas para proteger o produto e uso de vácuo para diminuir e/ou eliminar o oxigênio do espaço livre em contato com o produto, reduzindo o crescimento de microrganismos aeróbicos (CRIPPA, 2006) (SARANTÓPOULOS; DANTAS, 2014).

No entanto, as embalagens multicamadas, principalmente para produtos cárneos, costumam ser um fator complicador para a indústria de reciclagem, porque os sistemas convencionais de gestão de resíduos não estão adaptados para identificar, classificar e reciclar embalagens multicamadas. As indústrias têm realizado pesquisas visando desenvolver embalagens que facilitem a reciclagem. Um possível método para viabilizar a reciclagem de embalagens multicamadas à base de diferentes polímeros é o uso de aditivos compatibilizantes (LAHTELA; SILWAL; KÄRKI, 2020a). A compatibilização usa produtos químicos para aumentar a estabilidade mecânica das multicamadas e reciclar todas as camadas em um único fluxo sem separação (SOARES et al., 2022b), garantindo que os diferentes polímeros sejam misturados o mais uniformemente possível. O aditivo a base de anidrido maleico (MA) é uma alternativa interessante devido ao seu baixo custo, acessibilidade e ampla aplicabilidade (HORODYTSKA; VALDÉS; FULLANA, 2018).

OBJETIVOS

Objetivo principal

O presente estudo teve por objetivo avaliar diferentes materiais de embalagem para produtos cárneos incorporados de diferentes concentrações de aditivo a base de anidrido maleíco, bem como avaliar a reciclabilidade desses materiais.

Objetivos específicos

- Produzir filmes multicamadas com diferentes concentrações de compatibilizante a base de anidrido maleíco;
- Avaliar o efeito do compatibilizante sobre a cristalinidade, propriedades mecânicas, propriedades de barreira e potencial de migração das embalagens;
- Avaliar a reciclabilidade das embalagens flexíveis multicamadas utilizando a ferramenta RecyClass;
- Reciclar os filmes multicamadas com e sem compatibilizante e caracterizar os materiais obtidos.

CAPÍTULO 1

REVISÃO BIBLIOGRÁFICA

1. Embalagens para produtos cárneos

A embalagem, além de desempenhar funções como proteger o produto e preservar sua qualidade, também influencia a intenção de compra do consumidor. A conservação do alimento é um fator importante, e depende da qualidade da matéria prima, das condições de temperatura e umidade relativa durante a estocagem e comercialização do produto e a embalagem utilizada. A embalagem por sua vez, exerce a função de regular as transferências que podem ocorrer entre o ambiente interno (dentro da embalagem) e as condições de estocagem e manuseio (ambiente externo), ao qual o produto é exposto (MERGEN, 2004) (MCMILLIN, 2017b) (KAN; MILLER, 2022).

O que determina as propriedades de barreira de uma embalagem é sua capacidade de resistência a absorção ou evaporação de gases e vapores, passagem de luz e permeação de gorduras. Essas propriedades de barreira influenciam na estabilidade do produto, como por exemplo, o contato com o oxigênio pode causar rancificação de sua gordura e/ou oxidação de suas vitaminas, afetando as características desejadas do produto e reduzindo sua vida de prateleira. Dessa forma as propriedades de barreira devem ser definidas para cada produto, dependendo do seu sistema de acondicionamento, distribuição e durabilidade desejada (SARANTÓPOULOS et al., 2017).

Para obtenção das características de barreira requeridas, é importante a combinação de diferentes polímeros, visando a obtenção de todas as propriedades, como por exemplo, um polímero com boa propriedade de barreira ao oxigênio pode apresentar baixa barreira ao vapor d’água além de não permitir a termosselabilidade para um fechamento adequado (OLIVEIRA et al., 2006).

Uma vez definida as propriedades necessárias para proteção e acondicionamento do produto, também é importante verificar se os materiais são factíveis para a aplicação, processo de acondicionamento, definindo assim a estrutura da embalagem a ser utilizada (TWEDE; GODDARD, 2009).

A interação entre produto e embalagem envolve vários fatores para apresentar um desempenho adequado nas linhas de produção e durante o transporte e distribuição do produto. Dentre esses fatores tem-se as características físico-químicos e microbiológicos do produto, as condições de armazenamento e distribuição, tipo de acondicionamento na linha de produção e as características da embalagem (espessura, integridade das termosselagens, propriedades de barreira, propriedades mecânicas, etc.).

As propriedades dos materiais plásticos variam dependendo do tipo de material, por exemplo poliolefínico, poliéster, poliamida etc. Assim, a escolha e combinação de materiais visam a obtenção de ampla gama de propriedades como: características de barreira a gases e vapor de água, resistência mecânica, flexibilidade, resistência química, rigidez e termossoldagens integras (SOUSA et al., 2012). Em geral, a permeabilidade de embalagens plásticas depende de muitos fatores, como a natureza do polímero, espessura da camada barreira, pressão e temperatura. Outros atributos estruturais como polaridade, insaturação, cristalinidade, temperatura de transição vítrea e orientação também interferem na permeabilidade a gases do polímero (ROBERTSON, 2010).

Uma das mais importantes interações entre a embalagem e o alimento está ligada a permeabilidade de gases. O oxigênio desempenha um papel crucial no desenvolvimento de muitas reações que afetam a vida útil dos alimentos, favorecendo o crescimento microbiano e causando alterações de cor, oxidação de lipídios e desenvolvimento de odor de ranço.

Outra barreira importante para produtos com alta atividade de água como produtos cárneos é a barreira contra a perda de umidade durante a vida de prateleira, o que requer o uso de embalagens com adequada taxa de permeabilidade ao vapor d’água (SARANTÓPOULOS et al., 2017).

Além da barreira a gases e vapor de água, as propriedades mecânicas dos materiais flexíveis normalmente utilizados em embalagens para alimentos cárneos estão associadas ao processo de produção do material, a estrutura química de cada polímero e a composição de blendas. A fabricação do filme, determina a orientação das moléculas, a distribuição da espessura, a ocorrência ou não de defeitos na superfície, junto com isso as propriedades de tração, perfuração, resistência ao impacto, propagação do rasgo. Em geral, nos filmes multicamadas as propriedades dependem de cada material. O acondicionamento de produtos que apresentam vida de prateleira estável em temperatura ambiente, requer uma especificidade de material, combinando resinas que proporcionem barreira a gases e vapor de água adequadas de forma a manter sua qualidade durante a vida de prateleira em condições ambientes (CRIPPA, 2006) (SANTANA, 2019).

O sistema comumente utilizado para conservação de produtos cárneos combina o uso de uma embalagem adequada e o vácuo. A principal função do vácuo é diminuir a quantidade de oxigênio em contato do produto, o que reduz o crescimento de microrganismos aeróbios de alto potencial de deterioração, e que causam alterações de cor, sabor. Além disso o oxigênio também promove reações de oxidação de gorduras como mencionado anteriormente. O acondicionamento à vácuo pode ser realizado em embalagens pré-formadas (sacos), em equipamentos com câmara de vácuo ou em termoformadoras, utilizando materiais em forma de bobinas (SARANTÓPOULOS; DANTAS, 2014).

Uma vez definida as propriedades necessárias para proteção e acondicionamento do produto, avalia-se os materiais factíveis para aplicação, o processo de acondicionamento, construindo assim a embalagem final (TWEDE; GODDARD, 2009). Alguns dos polímeros mais utilizados em embalagens multicamadas para o acondicionamento de produtos cárneos são PE, PA e EVOH.

1.1. ***Polietileno (PE)***

O Polietileno começou a ser produzido em 1933 e é um dos materiais com inúmeras aplicações. É facilmente processado, por possuir uma estrutura simples comparativamente a outros polímeros. Sua obtenção se deve à polimerização do monômero gasoso etileno ($CH_2= CH_2$) em reator sob determinadas condições de temperatura e pressão (Figura 1). A estrutura pode apresentar ramificações ou cadeias laterais, sendo que essas ramificações e o comprimento das cadeias exercem influência nas características do material, podendo apresentar maior cristalinidade e maior densidade (PIATTI; RODRIGUES, 2005).

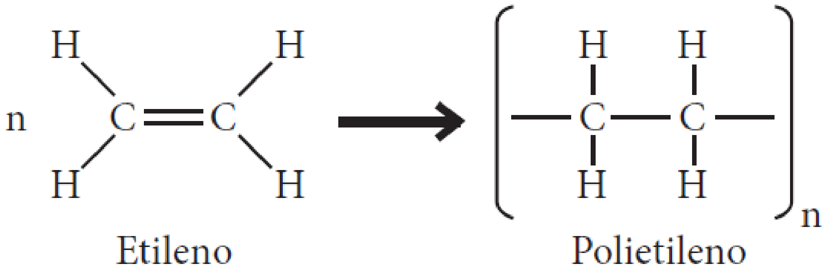


Figura 1. Estrutura química do polietileno.

Fonte: (JORGE, 2013).

O polietileno pode ser classificado conforme a densidade em: PEBD (polietileno de baixa densidade) (0,910 – 0,940 g/cm³), PEBDL (polietileno linear de baixa densidade) (0,910 – 0,925 g/cm³), PEMD (polietileno de média densidade) (0,925 – 0,940 g/cm³) e PEAD (polietileno de alta densidade) (0,940 – 0,970 g/cm³) (CULTER; SELKE, 2016).

O PEBD apresenta moléculas com alto grau de ramificações e é um material flexível, com boa resistência ao impacto, boa processabilidade e estabilidade. É um material barreira ao vapor d’água, porém vapores orgânicos o permeiam com facilidade e não apresenta barreira a gases, sendo assim requer a combinação com outros polímeros quando utilizado para acondicionar produtos susceptíveis à oxidação devido a permeação do oxigênio. Apresenta resistência mecânica e tenacidade a baixas temperaturas e na temperatura ambiente (CULTER; SELKE, 2016; TWEDE; GODDARD, 2009).

O PEBD contém ramificações que determinam o grau de cristalização, sendo um material pouco cristalino em torno de 50-60% e apresentando temperatura de fusão entre 110 a 115°C. Na forma de filmes, o PEBD apresenta boa processabilidade, porém baixa resistência mecânica (COUTINHO; MELLO; MARIA, 2003).

O PEBDL (polietileno linear de baixa densidade) apresenta alta resistência mecânica e maior temperatura de fusão que o PEBD, sendo muito utilizado em blendas com o PEBD na extrusão de filmes de para se obter as características desejadas. As ramificações de cadeia curta influenciam as propriedades físicas do PEBDL, como densidade, dureza, resistência a tração e rigidez. É um termoplástico que apresenta elevada capacidade de selagem a quente e por isso muito utilizado em filmes de uso geral, plástico bolha, sacarias, em revestimentos de fios e cabos (COUTINHO; MELLO; MARIA, 2003; GUERRINI et al., 2004).

A maior densidade e a linearidade das cadeias do polietileno de alta densidade - PEAD fazem com que sua fusão ocorra em temperaturas mais elevadas que o PEBD. Em geral, o PEAD apresenta reatividade química baixa, não sendo solúvel à temperatura ambiente em nenhum solvente. É utilizado em processos de injeção para fabricação de frascos e potes utilizados para acondicionar alimentos, remédios e cosméticos ou em embalagens flexíveis de alimentos desidratados por apresentar baixa permeabilidade ao vapor d’água (COUTINHO; MELLO; MARIA, 2003).

1.2. ***Poliamida (PA)***

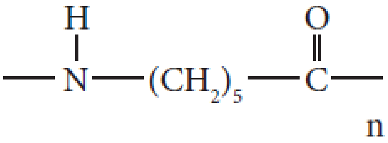
A poliamida (PA) também denominada nylon é um material que apresenta boa resistência química e boas propriedades de barreira a gases, óleos e aromas, porém é um material sensível a umidade e permeável ao vapor d’água, usado comumente em forma de filmes em estruturas multicamadas (SELKE; CULTER, 2016).

Outra característica da poliamida é a alta resistência mecânica (perfuração e impacto), possui boa estabilidade térmica e facilidade de termoformação. Apresenta flexibilidade à baixa temperatura e resiste a bases e a ácidos diluídos. Porém ácidos fortes e agentes oxidantes tendem a reagir com a poliamida (CULTER; SELKE, 2016).

A baixa permeabilidade ao vapor d’agua, a perda de propriedades mecânicas e de barreira causada pela umidificação é uma das maiores deficiências apresentadas pela poliamida, pois o efeito plastificante no polímero, reduzindo a resistência a tração e o módulo de elasticidade, porém com o ganho de umidade ocorre um aumento da resistência ao impacto e a flexibilidade, sendo que as poliamidas 6 e 6.6 são mais afetadas (SARANTOPOULOS; TEIXEIRA, 2017).

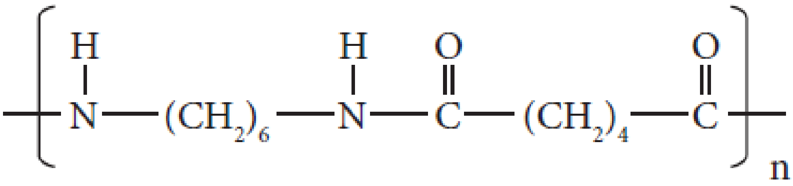
As propriedades da poliamida estão associadas à sua estrutura polimérica dependendo da matéria-prima utilizada e do processo de produção: obtido pela condensação de dois monômeros (diaminas e diácidos), sendo identificado pelo número de átomos de carbono da diamina, seguido pelo número de carbono do diácido. O outro tipo é formado pela condensação de aminoácidos hetero funcionais e a identificação da poliamida é feita por um único número associado ao número total de átomos de carbono no aminoácido.

Dessa forma classifica-se por exemplo como nylon 6 a poliamida constituída de um polímero de e-caprolactama, que contém 6 átomos de carbono (Figura 2). Já o nylon 6.6 é formado pela reação de hexametilenodiamina com ácido adípico, contendo 6 carbonos cada (Figura 3) (SARANTÓPOULOS et al., 2002).



$$-\overset{H}{\overset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}{-}_{n}$$

Figura 2. Polímero Nylon 6 - Fonte: (JORGE, 2013).



$$\left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

Figura 3. Polímero Nylon 66 - Fonte: (LEE; YAM; PIERGIOVANNI, 2008).

Para evitar a absorção de umidade da poliamida (PA) que compromete seus atributos de barreira a gases e resistência mecânica, essas são frequentemente usadas em processos de coextrusão com materiais plásticos como as poliolefinas, que apresentem propriedades combinadas dos materiais, atendendo as diversas condições de desempenho técnico requeridos. Porém, poliamidas e poliolefinas não são miscíveis, dessa forma há necessidade da inclusão de um terceiro componente na mistura, de um adesivo, que tem a função de juntar e acentuar a homogeneidade do material (CRIPPA, 2006) (SELKE; CULTER, 2016).

Em embalagem de alimentos, geralmente as poliamidas são utilizadas na forma de filmes produzidos por extrusão ou coextrusão, em matriz plana ou tipo balão, podendo ser mono ou biorientados, considerando que o processo de orientação uma vantagem na melhoria das propriedades mecânicas e de barreira, sendo os filmes não orientados mais aplicados em processo de termoformação. Os fimes multicamadas contendo nylon são usados para embalar produtos a vácuo como bacon, queijo, mortadela, salsichas e outros produtos processados e em tripas para embutidos cárneos (SARANTÓPOULOS et al., 2002) (GARCIA; SARANTOPOULOS; COLTRO, 2017).

*1.3. **Copolímero de etileno e álcool vinílico (EVOH)***

O EVOH é altamente cristalino, apesar dos grupos etileno e álcool vinílico serem distribuídos aleatoriamente na cadeia. A propriedade mais importante do EVOH é sua excelente barreira ao oxigênio, além de ter alta resistência à permeação de óleos e gorduras e a vapores orgânicos. Os teores de etileno variam de 27 a 48%, são as formulações mais disponíveis comercialmente. À medida que a % molar de etileno diminui, ocorre a diminuição da taxa de transmissão de oxigênio. Conforme observado na Figura 4 pode-se verificar a taxa de permeabilidade ao oxigênio do EVOH em função da variação de umidade relativa. A presença de umidade interfere nas propriedades de barreira a gases do polímero, principalmente em condições acima de 60% (MORRIS, 2017).

O filme de EVOH apresenta alta transparência e brilho, boa resistência mecânica, elasticidade e alta resistência à abrasão. O EVOH é a resina barreira mais estável termicamente, com boa resistência a óleos e ótimas propriedades de barreira à permeação de gases e solventes (YEH; CHEN; TSAI, 2006).

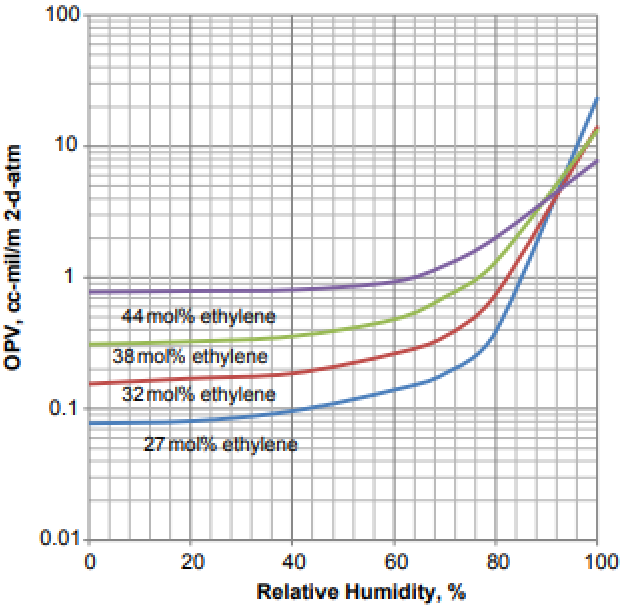


Figura 4: Taxa de transmissão de oxigênio do EVOH em função da umidade relativa. Fonte: (MORRIS, 2017).

O EVOH é usado principalmente em estruturas coextrusadas com o emprego em embalagens flexíveis. Devido a sua alta cristalinidade pode apresentar dificuldades no processo de termoformar ou orientar, porém as tecnologias como extrusão e coextrusão são utilizados para minimizar essas deficiências, incluindo a combinação com poliolefinas e poliamida (GARCIA; SARANTOPOULOS; COLTRO, 2017; MORRIS, 2017)

Em embalagens termoprocessáveis, o uso das poliolefinas como barreira à umidade para proteção do EVOH pode não ser suficiente dependendo das necessidades do produto que será acondicionado, sendo necessário incorporar uma camada de adesivo entre o EVOH e a poliolefina, que funcionará como um dessecante, absorvendo a umidade que porventura permeie, preservando suas propriedades mecânicas e de barreira. Quando se trata de um processo de co-extrusão entre o EVOH e a poliamida, não é necessária a aplicação da camada de adesivo, pois os materiais são compatíveis química e termicamente (SARANTÓPOULOS et al., 2002).

2. Responsabilidade ambiental e reciclagem de materiais plásticos multicamadas

Atualmente, o desenvolvimento de embalagens além de cumprir as propriedades de proteção o produto, deve levar em consideração as interações ao longo do ciclo de vida, com o intuito de minimizar os impactos ambientais do sistema embalagem produto (KARASKI et al., 2016).

Nos últimos anos, a sustentabilidade de embalagens plásticas tem sido uma preocupação das empresas produtoras e consumidoras, que tem buscado a redução do consumo de plástico e/ou substituição por embalagens recicláveis, reutilizáveis ou compostáveis. No caso de embalagens multicamadas há um agravante na reciclagem, uma vez que as camadas não podem ser separadas (PAUER et al., 2020a).

Além disso, embalagens plásticas coextrusadas flexíveis são consideradas resíduos de baixo valor comercial e o retorno desse material para o ciclo de reutilização é logisticamente inviável. Os filmes são frequentemente rejeitados nos fluxos de resíduos de reciclagem devido à sua leveza e diversidade de polímeros, além de que os filmes multicamadas não permitem a separação dos diversos polímeros que os compõem. Porém, se reciclados, podem evitar o consumo desnecessário de energia e ser benéficos ao meio ambiente, substituindo, em alguns casos, o uso de resina virgem, resultando em uma redução na quantidade de resíduos gerados (BARLOW; MORGAN, 2013)(KAISER et al., 2018a).

As embalagens multicamadas usualmente utilizadas no acondicionamento de alimentos, são compostas por diferentes polímeros que desempenham diferentes funções, sendo utilizadas nas camadas centrais a Poliamida (PA) e/ou o copolímero de etileno e álcool vinílico (EVOH), pelas propriedades de barreira a gases e o polietileno (PE), nas camadas internas e externas, pelas propriedades de resistência mecânica, termossoldagem e barreira ao vapor d’água (JÖNKKÄRI et al., 2020) (MORENO; SARON, 2019).

O processo mais comum da reciclagem de resíduos plásticos é o emprego da reciclagem mecânica (reciclagem secundária), comumente utilizado para filmes monomaterial. Este processo normalmente inclui a coleta, classificação, lavagem e trituração do material. As etapas podem ocorrer em uma ordem diferente, dependendo da origem e da composição dos resíduos. Na reciclagem mecânica ocorre a conversão de descartes plásticos em grânulos que podem ser utilizados na produção de outros produtos plásticos, com exceção de embalagens para alimentos, devido a questões de contaminação e de legislação de materiais para contato com alimentos. Uma exceção é o PET PCR que passa por um processo especial de descontaminação, tendendo a ser usado no seguimento de garrafas para refrigerantes (RAGAERT; DELVA; VAN GEEM, 2017a).

Neste sentido, as indústrias estão trabalhando no *design* de embalagens, a fim de facilitar a reciclagem de materiais multicamadas e com isso o uso de aditivos compatibilizantes vem sendo empregado, para facilitar a miscibilidade dos diferentes polímeros empregados (LAHTELA; SILWAL; KÄRKI, 2020a). O aditivo é adicionado à mistura para aumentar a união entre os diferentes polímeros, apresentado na figura 5 e minimizar a aglomeração ou separação de fases durante o processo de reciclagem. Esses aditivos aumentam a estabilidade mecânica das multicamadas e reciclam todas as camadas em um único fluxo (HORODYTSKA; VALDÉS; FULLANA, 2018b).

Os compatibilizantes são geralmente compostos por uma estrutura em blocos, escolhidos de acordo com a mistura polimérica. O anidrido maleico (MA) é uma alternativa interessante, devido ao seu baixo custo, acessibilidade e ampla aplicabilidade em relação aos demais compatibilizantes. MA é reativo para grupos hidroxila e amina, forma ligações covalentes e pontes de hidrogênio que podem resultar em um aumento das propriedades mecânicas do material após a reciclagem (MULAKKAL et al., 2021). Assim, aditivos compatibilzantes a base de anidrido maleíco são uma alternativa interessante para tornar embalagens multicamadas destinadas a mercado de produtos cárneos mais recicláveis.

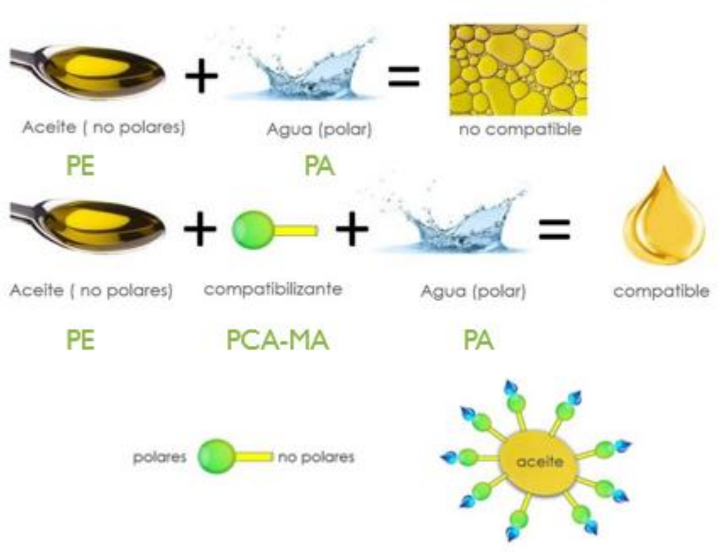


Figura 5: Esquematização processo de compatibilização (MEXPOLIMEROS, 2022).

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CAPÍTULO 2

Effect of maleic anhydride-based compatibilizer incorporation on the properties of multilayer packaging films for meat products

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Abstract: This research aimed to explore the effect of different concentrations (5-7%) of PCA-MA (polyolefin compatibilizer additive with maleic anhydride) on the properties and migration potential of two different multilayer packaging materials currently used for meat products: PE/PE/ad/PA/ad/PE/PE and PE/ad/PA/EVOH/PA/ad/PE (PE: polyethylene; ad: adhesive; PA: polyamide; EVOH: ethylene vinyl alcohol). The incorporation of PCA-MA resulted in the reduction of the crystallinity index and consequently, a reduction in tensile strength and puncture resistance was experienced. Additionally, a loss of water vapor barrier was observed, and the overall and specific migrations of maleic anhydride to the aqueous and fatty food simulants were below the quantification limit of the methods used. Therefore, they are within the specifications of the current legislation of food contact materials. Overall, although PCA-MA incorporation resulted in some loss of packaging properties, this additive can be considered an attractive alternative to facilitate the recycling process of these complex materials.

Keywords: design for recycling; flexible packaging; polyamide; ethylene vinyl alcohol; polyethylene.

1. Introduction

Plastic packaging is essential for food applications and is used for various purposes, such as containing, protecting and communicating [1, 2]. In many applications, plastic packaging is composed of different polymers and combined in multiple layers to meet the desired properties in the packaging of each type of product. Within the food category, in most cases meats, in natura or processed, are packed in multilayer plastic packaging. Some common polymers for meat products include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), ethylene vinyl alcohol (EVOH), and polyamide (PA) [3]. The technology behind meat packaging is responsible for the product's safety, and also for its shelf life. Furthermore, as the global meat consumption is constantly increasing, and its production requires huge amounts of inputs, such as packaging, the optimization of these materials are extremely relevant to ensure higher sustainability [4].

The heterogeneity related to multilayer packaging, especially for meat products, remains a complicating factor for the recycling industry [1, 5]. Conventional waste management systems are not adapted to identify, sort and recycle multilayer packaging, and these factors are critical to the efficiency of recycling steps with high quality end products. Due to its low recyclability, most multilayer packaging is usually incinerated or landfilled, running counter to efforts towards a circular economy [1, 6, 7].

In this sense, innovative technologies have been implemented to make these packaging recyclables. Industries are strongly working on packaging design to facilitate its recyclability. Design strategies include maximizing recyclable components in structures, eliminating non-recyclable materials, and reducing complexity, among other efforts [8]. However, it is not always possible to change the complexity of the structures without losing properties, which makes the recyclability of these materials unfeasible, since many polymers are not ideally miscible and, therefore, tend to separate into phases, forming a heterogeneous mixture [9]. In general, the incompatibility of mixtures of different polymers such as PE, PA and/or EVOH results in unstable morphology and consequently poor mechanical properties mainly due to their different polarities. Thus, to circumvent these problems, films with compatibilizing agents can result in good mechanical properties to the mixed film, mainly as a result of the increase in interfacial adhesion between these polymers [10–13]. Therefore, compatibility can enable the recycling of multilayer packaging based on different polymers in a single flow without separation [1].

Compatibilizer additives are added to the mixture to enhance the interactions between the different polymers and minimize agglomeration during the recycling process [9, 10]. They are typically composed of a block structure, chosen according to the polymer blend [14], and can be incorporated directly into the multilayer/multi-material structure, which would result in recyclable packaging [1]. Some compatibilizer additives frequently used to make different polymers recyclable are glycidyl methacrylate (GMA), acrylic acid (AA), and maleic anhydride (MA) [7]. The use of maleic anhydride (MA) as a compatibilizer represents an interesting alternative, due to its accessibility, and miscibility with most polymers used in the production of multilayer packaging. MA is reactive towards hydroxyl and amine groups, forming covalent and/or hydrogen bonds, resulting in enhancement of properties after recycling [8].

The incorporation of MA compatibilizing additives during the recycling process in multilayer packaging has been reported in the literature. PP/PET/SiOx films compatibilized with polypropylene grafted with maleic anhydride [15]. The results showed that the incorporation of 5% of compatibilizers results in control of the microstructure and interface properties, considerably improving the mechanical properties of the recycled material, leading to applications with high added value. Another research investigated PET/PE films compatibilized with a glycidyl methacrylate (E-GMA) or PE-g-MA [16]. Recycled blends made from compatibilized multilayer film waste showed acceptable physical-mechanical performance. However, the highlighted studies incorporated compatibilizing additives during the recycling process, which may result in a cost to the recycler and even lead to non-recycling of these packages. Thus, the incorporation of a compatibilizing additive directly into the multilayer structure is an alternative that can solve the problem of waste composed of multi-materials, especially when they are recycled in PE or PP fluxes. Therefore, although these compatibilizer additives result in a recyclable multilayer-material, their direct incorporation can influence the primary packaging itself. A complete elucidation of these influences is indispensable, since besides interfering with the material performance, the possibility of migration of the additive can comprise a limiting factor for its wide commercial use.

As described earlier, multilayer films based on PE, PA and/or EVOH are widely used in the meat product market. However, packaging based on PA 6/66 and PE presents difficulties in the recycling chain due to the incompatibility of these materials [17]. On the other hand, PE packages with an EVOH layer are recyclable when EVOH is present in concentrations below 5%. However, above this limit compatibility is low as it can result in increased yellowing of the material, net increase in haze and gels and stains, as well as frequent bubble breakage, which makes the material not compatible with recycling [18]. However, these materials can be technically recyclable under specific conditions in which the compatibility of the structure is ensured with binding layers based on PE-g-MA (polyethylene grafted with maleic anhydride) [17]. Therefore, due to the incompatibility of these three polymers, films based on PE/PA and PE/PA/EVOH were selected for this research.

Therefore, the aim of this research was to investigate the incorporation of different concentrations of maleic anhydride-based compatibilizer additive (PCA-MA) on the properties of two different multilayer packaging materials intended for the meat products market. The films were characterized in terms of their crystallinity, mechanical, barrier properties, and also overall and specific migration of maleic anhydride. This work offers an unprecedented source of information on the most relevant properties of materials for the mentioned application, serving as a basis for the widespread use of PCA-MA in multilayer packaging materials.

2. Material and methods

2.1. Materials

For the production of multilayer packaging films, the following materials were used: LDPE: low density polyethylene (LDPE 219M, Dow, Argentina); LLDPE: linear low-density polyethylene (LLDPE 8051G, Dow, Argentina); ad: adhesive (Bynel 41E1352, Dow, USA); PA 6/66: polyamide (Ultramid C40L, BASF, Germany); PCA-MA: polyolefin compatibilizer additive with maleic anhydride (Retain™ 3000, Dow, USA); EVOH: ethylene vinyl alcohol (F171B, Kuraray, USA). The adhesive resin - Bynel 41E1352 is composed of maleic anhydride modified LLDPE. This material is commonly used in blown and cast film coextrusion processes as a ready-to-use bonding layer for adhesion to a variety of materials including EVOH, PA and PE [19]. The compatibilizer resin - Retain™ 3000 is based on polyolefin compatibilizer additive with maleic anhydride (PCA-MA) and is designed to compatibilization between polar (PA and EVOH) and non-polar (PE) polymeric components commonly found in recycle streams, such as a PE continuous matrix [20].

For the preparation of the aqueous and fatty food simulant, ethanol (≥99.9%, Merck, Germany) and deionized water (Millipore Milli-Q Direct) were used. Maleic acid (99 % purity, Sigma Aldrich, USA) and citraconic acid (99.7 % purity, Sigma Aldrich, USA), as internal standards, were used for the analysis of maleic anhydride. Additionally, ethanol grade HPLC (99.9% purity, PanReac, Spain), acetonitrile (99.9% purity, Merck, Germany) and orthophosphoric acid (85.6 %, Merck, Germany) were also utilized in the migration analysis. Buffer solution used were for calibration of mobile phase: buffer pH 4 (±0.02 uncertainty, Supelco, Merck, Germany) and pH 7 (±0.02 uncertainty, Merck, Germany).

2.2. Production of films by coextrusion

In this study, multilayer films, with two different compositions, were produced intended for meat products packaging. The samples were classified into Film A and Film B, where Film A is composed of PE/PE/ad/PA/ad/PE/PE and Film B is composed of PE/ad/PA/EVOH/PA/ad/PE. Two different concentrations of polyolefin compatibilizer additive with maleic anhydride (5% and 7%) were added to each structure. Table 1 illustrates the nomenclature, composition, and thickness for the different samples. The films were prepared by coextrusion using a pilot balloon extrusion line (Coex Extruder Dr Collin, model BL180/400, Germany) capable of producing films with up to 7 layers and a maximum width of 380 mm. The films were extruded at an average temperature range of 206-234 °C at 60 rpm. The final films prepared by the blowing process were 310 mm wide and about 100 ± 5 μm thick.

Table 1. Composition of the multilayer flexible packaging samples for meat products.

Packaging material	**Sample nomenclature**	**Film composition**	**Partial thickness (µm)**	**Total thickness (µm)**
Film A	Control	LDPE(85%)+LLDPE(15%)/LDPE(85%)+LLDPE(15%)/ad/PA/ad/ LDPE(85%)+LLDPE(15%)/ LDPE(85%)+LLDPE(15%)	15/15/5/27/7/16/19	104
	5% compatibilizer	LDPE(85%)+LLDPE(15%)/LDPE(67%)+LLDPE(15%)+**PCA-MA**(18%)/ad/PA/ad/LDPE(67%)+LLDPE(15%)+**PCA-MA**(18%)/ LDPE(85%)+LLDPE(15%)	14/19/7/24/7/12/13	96
	7% compatibilizer	LDPE(85%)+LLDPE(15%)/LDPE(60%)+LLDPE(15%)+**PCA-MA**(25%)/ad/PA/ad/LDPE(60%)+LLDPE(15%)+**PCA-MA**(25%)/ LDPE(85%)+LLDPE(15%)	15/21/7/25/5/14/15	102
Film B	Control	LDPE(85%)+LLDPE(15%)/ad/PA/EVOH/PA/ad/LDPE(85%)+LLDPE(15%)	15/7/11/4/11/12/40	100
	5% compatibilizer	LDPE(85%)+LLDPE(15%)/ad/PA/EVOH/PA/ad/ LDPE(72%)+LLDPE(15%)+**PCA-MA**(13%)	16/7/9/6/12/12/40	102
	7% compatibilizer	LDPE(85%)+LLDPE(15%)/ad/PA/EVOH/PA/ad/ LDPE(64%)+LLDPE(15%)+**PCA-MA**(19%)	16/7/9/8/11/12/42	105

Film A: PE/PE/ad/PA/ad/PE/PE; Film B: PE/ad/PA/EVOH/PA/ad/PE; LDPE: low density polyethylene; LLDPE: linear low-density polyethylene; ad: adhesive; PA: polyamide; PCA-MA: polyolefin compatibilizer additive with maleic anhydride; EVOH: ethylene vinyl alcohol.

2.3. Characterization of the films

2.3.1. X-ray diffraction (XRD)

An X-ray analyzer (X'Pert-MPD, Philips, Almelo, Netherlands) was employed for crystallinity evaluation. The XRD measurements of multilayer packaging films were operated with Cu Kα radiation ($\lambda = 1.54$ Å) at a scan rate of 0.033°/s (step = 0.04° and time per step = 1.2 s), with the accelerated voltage of 40 kV and the applied current of 40 mA, varying from 5 to 30°. The global crystallinity index (CI) of the films was estimated through the ratio between the area under the peaks (crystalline regions) and the total area (crystalline and amorphous regions).

2.3.2. Mechanical properties

For the mechanical properties' tests, 25 mm wide samples were used, with them being cut in precision equipment to avoid burrs. The samples were conditioned for a minimum period of 48 h at 23 ± 2 °C and 50 ± 5% RH before testing. The tests were performed under the same temperature and relative humidity conditions. All tests were performed with ten repetitions.

2.3.2.1. Tensile strength

Tensile strength was determined using a universal testing machine (Instron, 5565-E2, USA) [21], operating with cell load 5 kN. Test speed was 500 mm min^{-1} and with initial grip separation of 50 mm in the machine direction (MD) and transverse direction (TD).

2.3.2.2. Puncture resistance

Puncture resistance was determined using a universal testing machine (Instron, 5565-E2, USA), with a load cell of 5 kN operating in compression, using a 3.2 mm metal tip at a constant speed of 25 mm min^{-1} [22].

2.3.3. Water vapor transmission rate (WVTR)

The water vapor transmission rate (WVTR) was determined in an equipment with infrared sensor, PERMATRAN (MOCON, USA) [23]. The effective permeation area of each specimen was 50 cm^2. The test was performed at 38 °C and 90% RH, with three repetitions.

2.3.4. Oxygen transmission rate (OTR)

The oxygen transmission rate was determined in an OXTRAN equipment (MOCON, USA) [24]. The external side of the sample was placed in contact with the permeant gas (100% O_2), and the permeation area was 50 cm^2. The reading was corrected for 1 atm permeant gas partial pressure gradient. The test was performed at 23 ºC and 75 ± 2% RH, with four repetitions.

2.3.5. Overall migration

The packages were evaluated for overall migration to food simulant A (non-acidic aqueous food simulant, pH > 4.5: distilled water), and simulant D (fatty food simulant: 95% ethanol solution (v/v) in distilled water), as described by the National Health Surveillance Agency Brazil (Anvisa), Resolution nº 51/10, for meat products [25]. The overall migration tests were carried out in accordance with the standards [26–28]. The films were contacted with simulants A and D at 40 °C for 10 days in an oven (BD400, Binder). Then, the plastic film was removed from the contact, and the simulant was evaporated on the hot plate (TE-038, Tecnal); the migrated residue was quantified by gravimetric method, using an analytical balance (Sartorius, model MSV225S, Germany) with a resolution of 0.01 mg. The tests were performed with three repetitions.

2.3.6. Specific migration of maleic anhydride additive

The packages were evaluated for specific migration of maleic anhydride, expressed as maleic acid, for food simulant A (non-acidic aqueous food simulant, pH > 4.5: distilled water) and simulant D (fatty food simulant: solution of 95% (v/v) ethanol in distilled water), as described by the Anvisa Resolution No. 51/10 [25], for meat products. Specific maleic anhydride migration tests were performed according to standards [29, 30], with mobile phase modification using 0.1% orthophosphoric acid at pH 2.2. The films were contacted with simulants A and D at 40 °C for 10 days in an oven (BD400, Binder). Then the plastic film was removed from the contact, and the simulant was added with citraconic acid, obtaining a final concentration of 30 mg kg^{-1}, filtered through a 0.45 µm membrane, and quantified by liquid chromatography coupled to DAD (diode array detector) at a HP 1100 and 1200 Series of Agilent Technologies, operating of column Licrospher RP18 endcapped (250 mm × 4 mmm × 5 µm) from Agilent Technologies. The used temperature was 25 ºC, mobile phase: 92% (v/v) water with 0.1% orthophosforic acid: 8% (v/v) acetonitrile, injection volume 20 µL, isocratic mode. The flow rate was 1.5 mL min^{-1}, wave length was 220 nm, and stop time was 7 min. Each three specimen of the sample and of the blank was injected in duplicate. The blank was not in contact with the sample. Was a control as area and retention time was injected in duplicate the concentration of 3 mg kg^{-1} of maleic acid with 30 mg kg^{-1} of internal standard.

2.4. Statistical analysis

The results were statistically evaluated by analysis of variance (ANOVA). Comparisons among mean values were determined by Tukey's tests ($p < 0.05$). The results were expressed as the mean ± standard deviation.

3. Results and discussion

3.1. X-ray diffraction (XRD)

Figure 1 presents the XRD patterns for Film A and Film B. The main polyethylene diffraction peaks, at $2\theta = 21.5$ and 24°, may correspond to the (110) and the (200) crystal planes of its orthorhombic unit cell [31, 32]. Researches have shown that LLDPE and LDPE are miscible blends at low LDPE contents, becoming immiscible at higher LDPE proportions [33–35], which is the case of the present study. Based on SAXS patterns, Ree et al. proposed that when LDPE/LLDPE blends are cooled from the molten state, LLDPE crystallizes first and forms volume-filling spherulites, then a secondary crystallization of LDPE within the spherulites of LLDPE occurs [36].

Overall, Figure 1 indicates the XRD profiles undergone minimal changes in the relative areas of the main identified peaks. Global crystallinity indices (CI) values of both films ranged from 24.3 to 28.3% (**Table 2**). Yamaguchi and Abe demonstrated the CI increased with increasing the LDPE content in the LLDPE/LDPE blends, reaching approximately 45% at higher proportions of LDPE [37]. On the other hand, Ree et al. obtained CIs between 15 and 20% during the crystallization of a blend composed of equal amounts of LLDPE and LDPE [36]. The incorporation of the PCA-MA in these layers apparently provided a tendency to slightly reduce the CI for both film A and film B. However, for this sample, the incorporation of different proportions of PCA-MA resulted in a similar effect on CI.

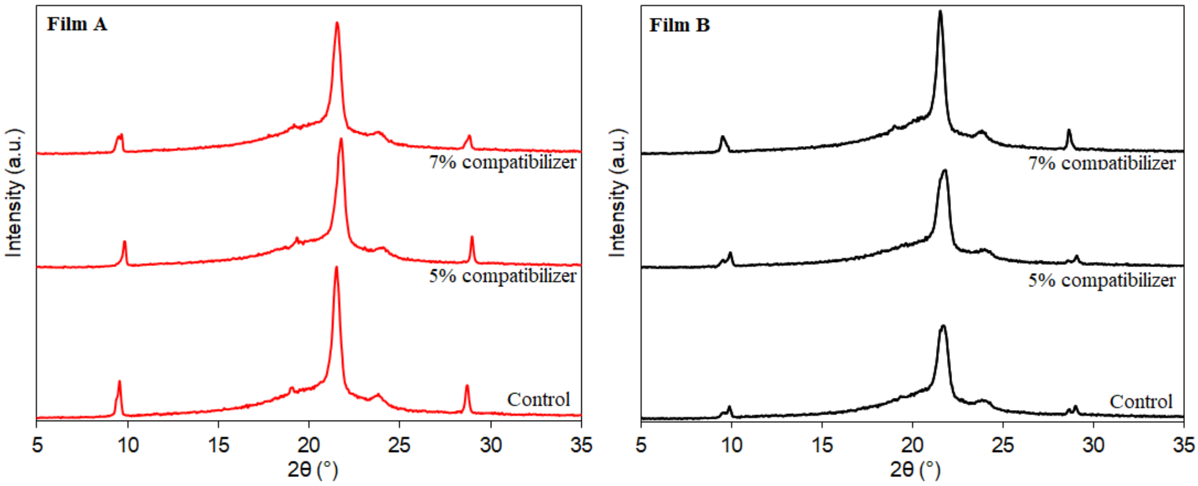

Figure 1. XRD of multilayer packaging films with different compatibilizer concentrations.

Table 2. Crystallinity index (%) of the packaging films

Film A	**CI (%)**	**Film B**	**CI (%)**
Control	27.6	Control	28.3
5% compatibilizer	25.8	5% compatibilizer	26.7
7% compatibilizer	24.3	7% compatibilizer	26.6

3.2. Tensile strength

The results of tensile strength (TS), elongation at break (EB) and modulus of elasticity (ME) in the machine direction (MD) and in the transverse direction (TD) are shown in **Figure 2**. The incorporation of PCA-MA compatibilizer to Film A and Film B significantly reduced the TS of both films in both directions (MD and TD). The results for Film A, in MD and TD, ranged from 36.8 to 26.5 MPa, and from 31.5 to 26.7 MPa, respectively. For Film B, TS ranged from 32.8 to 28.2 MPa in MD, and from 28.7 to 24.9 in TD, as shown in Figure 2 **(a)** and **(b)**. These results may be based on the hypotheses described in the works carried out by Sallem-Idrissi et al. [38, 39] where it says that in the presence of compatibilizer (PCA-MA) and adhesive, the deformation tends to increase simultaneously in the different layers of the films, so the fracture possibly initiated in the PA layer is transmitted to the other layers in a cohesive way, that is, due to the strong adhesion. Thus, the PE layer in the multilayer films therefore breaks with much lower stress when compared to the control films, irrespective of the thickness of the PE layer.

EB of all samples were above 400%, which were typical values found in the literature for films with PE, PA and EVOH [40–42]. The incorporation of the compatibilizer did not significantly influence the EB of Film B in MD and TD, and for Film A only in TD (**Figure 2 (c)** and **(d)**). However, when 5% and 7% of compatibilizer were incorporated, there was a significant reduction of 14.7% and 12.1%, respectively, in the EB of Film A in MD. A similar reduction in EB as a function of maleic anhydride concentration was also observed for PE/PA blends [43]. A possible explanation for this behavior is that the fracture initiated in the PA layer can be transmitted to the other PE layers in a cohesive way, resulting in a reduction of EB

[38], as previously described. However, interestingly this behavior was observed only in the MD of Film A.

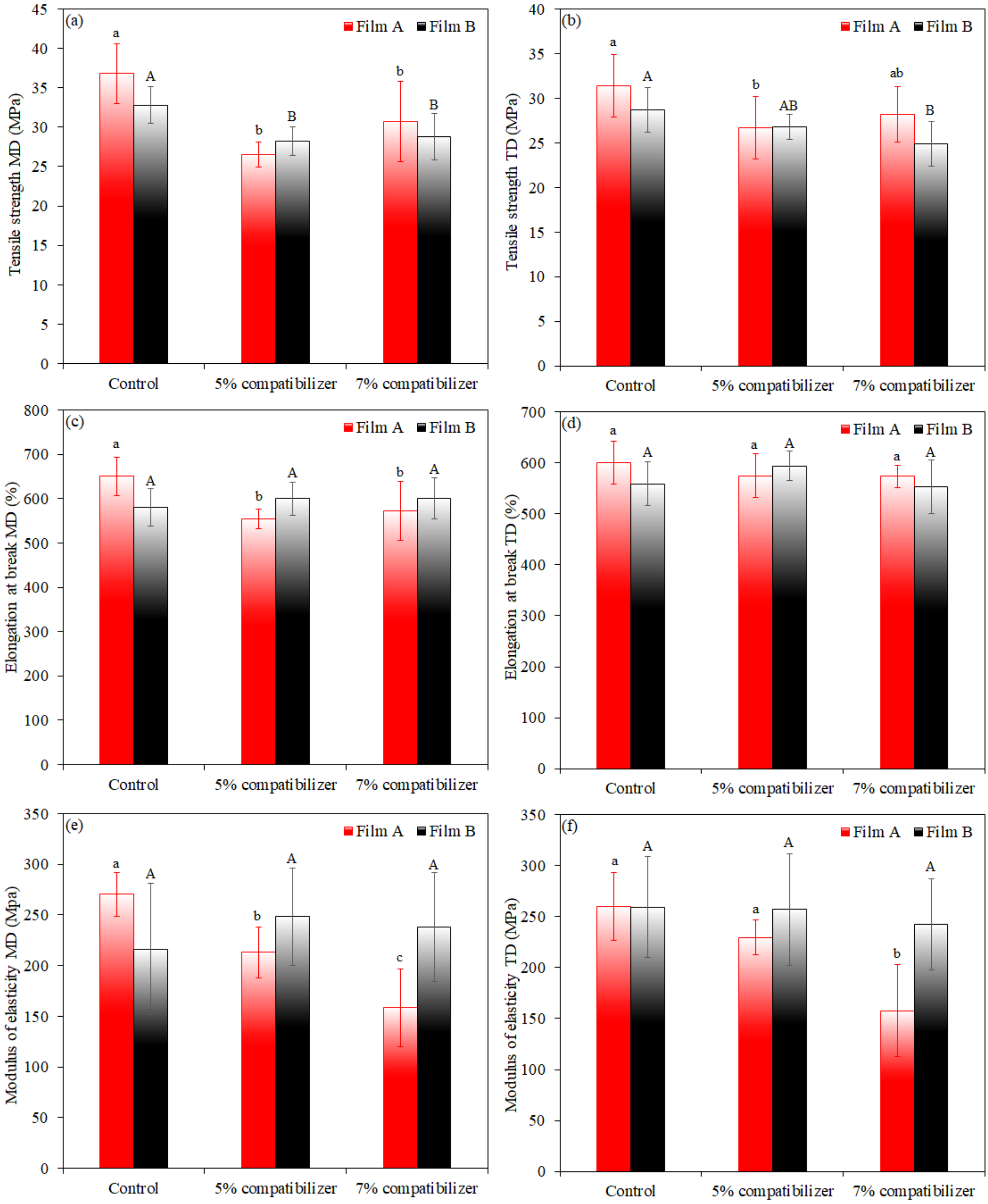

Figure 2. Tensile strength in MD (a), tensile strength in TD (b), elongation at break in MD (c), elongation at break in TD (d), modulus of elasticity in MD (e), and modulus

of elasticity in TD (f) of multilayer packaging films with different compatibilizer concentrations.

The ME results of Film B did not show a significant difference between the different samples in the two directions of the material, regardless of the concentration of compatibilizer used (**Figure 2 (e)** and **(f)**). The maintenance of the EB and ME values of Film B can be attributed to the presence of EVOH, which is a high ME polymer, and the result of its presence in the multilayer structure tends to maintain the ME and also the elastic properties of the final product [44]. However, for Film A, the compatibilizer significantly reduced the ME considering the test in both directions. This reduction is attributed to the more pronounced reduction in the crystallinity index of Film A, that is, the presence of PCA-MA made the material less rigid, mainly due to the greater amount of LLDPE in relation to Film B [45].

Finally, these small reductions in mechanical properties are probably caused by the intrinsic properties of PCA-MA, in addition to the correlation with the observed reductions in the crystallinity index, mentioned above. Similar behavior was also observed in the literature for polypropylene [46].

3.3. Puncture resistance

Puncture resistance is an important quality parameter for packaged products with spikes and bones, such as meat products. The puncture resistance and elongation at puncture results are shown in **Figures 3 (a)** and **(b)**, respectively. The control Film A had a puncture resistance of 23.8 N and elongation at puncture of 17.8 mm. These values are higher than those of the Film B (puncture resistance: 20.4 N; elongation at puncture: 15.4 mm). The higher value presented in Film A in relation to Film B can be attributed to the higher thickness of the polyamide layer. This polymer is widely used for meat products packaging because of its mechanical performance [41, 47].

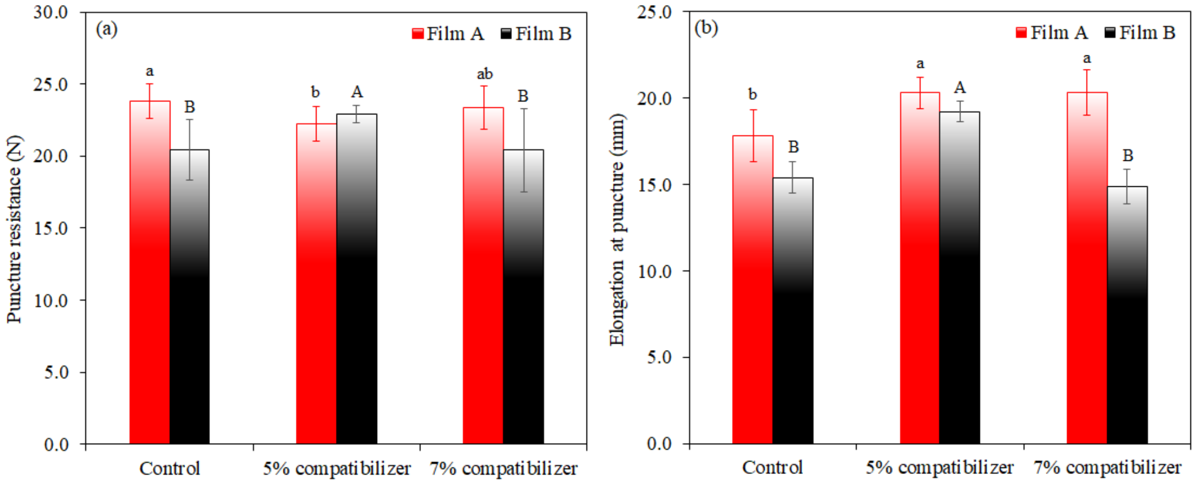

Figure 3. Puncture resistance (a) and elongation at puncture (b) of multilayer packaging films with different compatibilizer concentrations.

The incorporation of PCA-MA resulted in a slight and significant reduction in puncture resistance and an increase in elongation at puncture of Film A. These results are similar to those found for polypropylene added with maleic anhydride [46]. However, this behavior seems to be more related to the different thicknesses between the samples, since Film A with 5% compatibilizer had a lower total thickness compared to the control **(Table 1)**. Added to this, the lower thickness of the PA layer tends to reduce the occurrence of high local plastic deformations that usually trigger early rupture of the PA, and consequently results in a better stretching capacity of the PA6 layer in multilayer films [39]. This behavior was observed for Film A with compatibilizer, since the thickness of the PA layer is lower than the control film. On the other hand, for Film B with 5% compatibilizer, the values of puncture resistance and elongation at puncture were slightly and significantly higher than the other samples. This result may be associated with small variations in the thickness of the different layers and the intrinsic properties of the compatibilizing layer. Finally, it is important to highlight that the changes in puncture performance are within the acceptable range by the industry, which is 25% [48].

3.4. WVTR and OTR

The results of water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) are shown in **Figures 4 (a)** and **(b)**, respectively. The WVTR of control Film A was 4.93 ± 0.32 g m^{-1} day^{-1}, and 3.58 ± 0.11 g m^{-1} day^{-1} for control Film B. The addition of the compatibilizer additive at different concentrations (5% and 7%) resulted in a significant loss of water vapor barrier compared to the control. An increase in WVTR between 16.6% and 17.2% for Film A, and between 14.5% and 27.9% for Film B was observed. These results may be correlated with the decrease in the crystallinity index, as shown in **Table 2**.

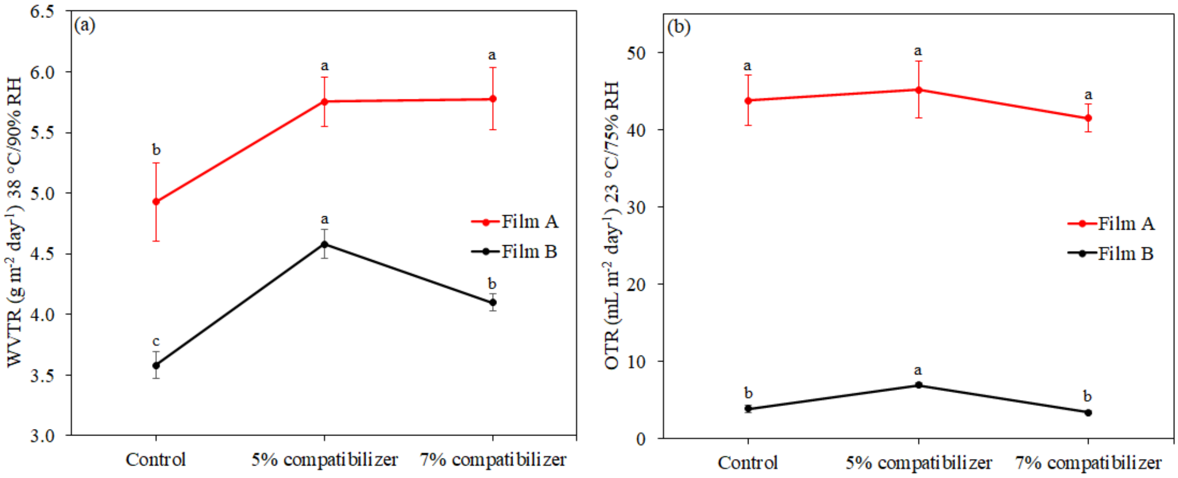

Figure 4. WVTR (a) and OTR (b) of multilayer packaging films with different compatibilizer concentrations.

Moreover, the hydrophilic groups of the compatibilizer may result in improved interaction with water molecules, consequently increasing water vapor permeation [46]. A similar increase in WVTR was found for LLDPE/PA/LLDPE-MA films [49]. As observed in the literature, PE-g-MA presents a superior water vapor permeability when compared to a pure polyolefin [43], naturally conferring a loss of water barrier to the films that are added with this compatibilizing agent.

Regarding OTR, the results for control Films A and B were 43.84 ± 3.25 and 3.88 ± 0.48 mL m^{-2} day^{-1}, respectively. The lower OTR of Film B is attributed to the combined presence of PA and EVOH layers in the packaging. EVOH and PA are widely used to confer elevated oxygen barrier to multilayer packaging. Due to the hydrophilic nature of these polymers, they are generally applied as an intermediate layer between at least two layers of a hydrophobic material (inner and outer layer), such as polyethylene (PE) or polypropylene (PP) [41]. The incorporation of the compatibilizer additive did not result in significant changes in the OTR of Film A. However, a small increase in the OTR of Film B was observed with the incorporation of 5% of the compatibilizer. A small reduction in the oxygen barrier was also observed for PE/EVOH films compatibilized with LDPE-g-MA, and was attributed to a possible modification of the film morphology [50].

3.5. Overall migration and specific migration of maleic anhydride additive

Packaging is composed of substances that can migrate to food, affecting the level of toxicity of the products. These substances include low molecular weight compounds, such as residual solvents and monomers, additives, among others. Therefore, migration must be controlled to ensure compliance of a food contact material [51, 52]. The specific limits for migration of monomers and additives are regulated by government bodies such as the Resolution of the Collegiate Board of Directors - RDC No. 56/2012 and RDC No. 326/2019, of the Anvisa [53, 54], and Regulation No. 10/2011, of the European Union [55]. These regulations have a maximum maleic anhydride migration limit of 30 mg kg^{-1} of food simulant. In addition to the specific migration, Anvisa Resolution No. 589/21 [56], and Regulation EU No. 10/2011 [55] established 10 mg dm^{-2} and the limit of overall migration from materials for contact with food (FCMs).

The results of overall and specific migration of maleic anhydride, expressed in maleic acid, from Films A and B in contact with aqueous (distilled water) and fatty (95% ethanol v/v) food simulants evaluated after conditioning at 40 °C and 10 days are shown in **Table 3**. All results of total migration and specific migration of maleic anhydride were below the quantification limit of the methods used. Therefore, the migration to aqueous and fatty food simulants (95% ethanol) of all samples comply with Anvisa Resolutions No. 589/21, No. 56/2012 and No. 326/2019 [53, 54, 56] and EU Regulation No. 10/2011 [55], as they were below the limits established in the aforementioned legislation. In this sense, it is understood that the incorporation of the concentrations of PCA-MA reported in this present study did not influence the total migration and the specific migration of maleic anhydride, being a positive result in the application of these packages for contact with food.

Table 3. Results of overall migration and specific migration of maleic anhydride, expressed as maleic acid, from the multilayer packaging films with different compatibilizer concentrations.

Material	**Sample nomenclature**	**Overall migration (mg dm^{-2})**		**Specific migration of maleic anhydride additive (mg kg^{-1})**	
		Food simulants		**Food simulants**	
		Aqueous (distilled water)	**Fatty (95% v/v ethanol)**	**Aqueous (distilled water)**	**Fatty (95% v/v ethanol)**
Film A	Control	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾
	5% compatibilizer	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾
	7% compatibilizer	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾
Film B	Control	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾
	5% compatibilizer	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾
	7% compatibilizer	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾	≤ 3.0⁽¹⁾

Film A: PE/PE/ad/PA/ad/PE/PE; Film B: PE/ad/PA/EVOH/PA/ad/PE. The results are expressed as mean of three repetitions.

(1) Limit of quantification.

4. Conclusions

Flexible multilayer films with different concentrations of PCA-MA (polyolefin compatibilizer additive with maleic anhydride) have been successfully produced. The incorporation of PCA-MA provided a to slightly reduce the crystallinity index of the films, which may be also correlated with the reductions in tensile strength and puncture resistance. Additionally, an increase in the water vapor transmission rate was observed after the incorporation of PCA-MA, being related with the presence of hydrophilic groups of the compatibilizer and also the reduction in crystallinity. The oxygen transmission rate was little influenced by the compatibilizer. The results of total migration and specific migration of maleic anhydride were below the quantification limit of the methods used, in compliance with Brazilian and European Union legislation. Overall, although the incorporation of PCA-MA has resulted in some loss of property, it does not render the material unsuitable for use as food packaging. In addition, this technology is a promising alternative to enable that flexible multi-material PE, PA and EVOH-based packaging are recyclable. Future studies are suggested covering the recycling of the materials produced here, to expand the knowledge about flexible multilayer packaging with PCA-MA, as well as to understand the properties of the materials obtained by the recycling process.

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CAPÍTULO 3

Mechanical recycling of multilayer flexible packaging employing maleic anhydride as compatibilizer

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Abstract: Mechanical recycling is an important alternative to reduce the amount of fossil resources needed to produce plastic materials. This research evaluated the theoretical recyclability of two multilayer films for meat products packages, composed of PE/PE/ad/PA/ad/PE/PE (Film A) and PE/ad/PA/EVOH/PA/ad/PE (Film B), using the RecyClass tool. Then, an extrusion was carried out as post-industrial recycling step. Recycled films were prepared without compatibilizer and with different concentrations (5–7%) of a commercial compatibilizer based on maleic anhydride (MA), and were evaluated according to their chemical, thermal, morphological, and mechanical properties. Films without compatibilizer were classified as non-recyclable using the RecyClass. However, the use of compatibilizer proved to be promising for the recycling of these packages. The infrared spectra showed that the PA-MA-PE copolymer was obtained during the mixing, confirmed by the microscopy images, where the compatibilizer provided an adhesion between the mixing interfaces. The melting temperature of PE proved to be stable during processing. However, the compatibilizer addition resulted in changes in the PA melting temperature in Film A. Films with compatibilizer showed a significant increase in elongation at break compared to films without it. These results confirm the strong efficiency of PA-MA-PE compatibilization, which is an alternative for recycling multilayer packaging of meat products.

Keywords: *design for recycling; circular economy; mechanical recycling; polyamide; polyethylene; ethylene vinyl alcohol*

1. Introduction

The demand for flexible plastic packaging for food applications continues to grow significantly due to its excellent functional performance, including serving as a barrier to oxygen and water vapor [1,2], which significantly reduces food waste by increasing shelf life [3]. In most cases, plastic packaging for meat products is produced by combining polymers, each with its own specific functionality. The most common polymers for meat are polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC), ethylene vinyl alcohol (EVOH), and polyamide (PA) [4]. Multilayer packaging for vacuum-sealed meat are usually composed of PE, PA, and/or EVOH [5]. EVOH and PA are packaging materials commonly used in multilayer packaging due to their high oxygen barrier properties and good mechanical performance. However, these polymers are very sensitive to water due to their hydrophilic nature [6–8]. Thus, in most applications, EVOH and PA are used in multilayer structures, usually between two layers of a hydrophobic material (inner and outer layer), such as PE, reducing water vapor permeation [9].

The heterogeneity of these multilayer materials can prevent recycling, since they hinder identification in waste management systems and cause incompatibility between the different polymers during mechanical recycling [1,10,11]. Therefore, the aspects surrounding multilayer packaging materials have become a major challenge for the circular economy [11,12].

Regarding recyclability, EVOH is compatible with PE recycling flow when present in small quantities (≤ 5%), a situation common in most flexible food packaging containing EVOH. Low concentrations of EVOH hardly impact the quality of recycled materials [13,14]. On the other hand, PA becomes a limiting factor for the recyclability of these packages, since PE and PA are immiscible and incompatible [15]. When the multilayer packaging structure of PE and PA has less than 15% PA and with up to 10% PE-g-MAH (maleic anhydride grafted polyethylene) in the structure, the package can be recycled in PE lines [16,17]. However, in most cases the amount of PA is greater than 15% and the multilayer materials do not contain PE-g-MAH incorporated into their structure, which makes recycling these packages impossible.

Recycling plastics in circulation is essential to prevent increased accidental or intentional release of polymeric materials into the environment and thus reduce environmental pollution [10]. To increase the recycling rate of packaging, research on multilayer plastics have been rising interest from industry and scientific community [1]. In this sense, the design of the packaging should be focused on facilitating the recycling of materials, which includes maximizing recyclable components in structures, eliminating non-recyclable materials, reducing complexity, among other efforts [18,19].

If the design challenges are not overcome, mixed polymer currents, although prevalent in mechanical recycling, will continue to result in weakened materials due to the immiscibility of the phases of the different polymers [10]. Phase separation into blends results in poor mechanical properties due to ineffective tensile transfer across phase boundaries. The tensile transfer across the boundaries can be improved by increasing the number of interactions between phases [10,18]. The use of compatibilizer additives is one of the methods to recycle immiscible multilayer materials. Improved compatibility of polymer mixtures would increase the value of the recycled product due to better processability, plant flexibility, product adaptation, and improved mixed recycled performance [10]. Thus, copolymer compatibilizers are used to assist in the mixing of polymers of different chemical polarities.

Compatibilizer additives are typically composed of a block structure, chosen according to the polymer mixture [20]. Some common compatibilizers include styrene grafted with maleic anhydride or different polyolefins grafted with maleic anhydride [10,21,22]. Using maleic anhydride (MA) as a compatibilizer is an interesting alternative, due to its accessibility and miscibility with most polymers used in the production of multilayer packaging. MA is an additive reactive to hydroxyl and amine groups, forming covalent and/or hydrogen bonds, resulting in improved properties after recycling [18].

A promising compatible additive is Retain™ polymer modifier based on maleic anhydride (PCA-MA: polyolefin compatibilizer additive with maleic anhydride), which is an alternative to recycling post-industrial barrier films without compromising performance or aesthetics. Based on an ultra-low reactive viscosity, the compatibilizer allows barrier films containing PE, PA, and EVOH to be dispersed more evenly in a polyolefin matrix [23]. In this sense, the compatibilizer additive takes multilayer flexible plastic packaging to another level, since it can be incorporated directly into the packaging material, making it recyclable in PE lines.

Therefore, based on the problem of recyclability of multilayer flexible packaging for meat based on PE, PA, and/or EVOH, this study aimed to evaluate the theoretical recyclability of two multilayer films, PE/PE/ad/PA/ad/PE/PE (Film A) and PE/ad/PA/EVOH/PA/ad/PE (Film B) by using the RecyClass tool. The studied films were also evaluated after mechanical recycling, comparing the films without compatibilizer and those containing different concentrations of compatibilizer (Retain^{TM}), incorporated into the films, that is, the post-industrial material already contained compatibilizer in its structure. Thus, since the compatibilizer is already incorporated into the film, the recycler does not need to add it during the recycling process, that is, the recycler would have no additional costs. Finally, the recycled films produced were evaluated for their chemical, thermal, morphological, and mechanical characteristics. The main innovation of this research was to evaluate the recycling of complex multilayer flexible packaging with a compatibilizer additive based on maleic anhydride directly incorporated into its structure.

2. Material and methods

2.1. Materials

To produce 100% recycled films, multilayer films with two compositions were used, namely: PE/PE/ad/PA/ad/PE/PE (Film A) and PE/ad/PA/EVOH/PA/ad/PE (Film B), composed of different concentrations of polyolefin compatibilizer additive with maleic anhydride (0% ‘control’, 5%, and 7%) as shown in **Table 1**. Also, a virgin PE film was used for comparison purposes.

The specifications of the polymeric resins that make up the multilayer films are, LDPE: low-density polyethylene (LDPE 219M, Dow, Argentina); LLDPE: linear low-density polyethylene (LLDPE 8051G, Dow, Argentina); ad: adhesive (Bynel 41E1352, Dow, USA); PA: polyamide (Ultramid C40L, BASF, Germany); PCA-MA: polyolefin compatibilizer additive with maleic anhydride (Retain 3000, Dow, USA); EVOH: ethylene vinyl alcohol (F171B, Kuraray, USA).

Table 1. Composition of samples of flexible multilayer packaging for meat products used to produce recycled films.

Packaging material	**Sample nomenclature**	**Film composition (Partial thickness - μm)**
Film A	Control	LDPE(85%)+LLDPE(15%)/LDPE(85%)+LLDPE(15%)/ad/PA/ad/LDPE(85%)+LLDPE(15%)/LDPE(85%)+LLDPE(15%)(15/15/5/27/7/16/19)
	5% compatibilizer	LDPE(85%)+LLDPE(15%)/LDPE(67%)+LLDPE(15%)+**PCA-MA**(18%)/ad/PA/ad/LDPE(67%)+LLDPE(15%)+**PCA-MA**(18%)/LDPE(85%)+LLDPE(15%) (14/19/7/24/7/12/13)
	7% compatibilizer	LDPE(85%)+LLDPE(15%)/LDPE(60%)+LLDPE(15%)+**PCA-MA**(25%)/ad/PA/ad/LDPE(60%)+LLDPE(15%)+**PCA-MA**(25%)/LDPE(85%)+LLDPE(15%) (15/21/7/25/5/14/15)
Film B	Control	LDPE(85%)+LLDPE(15%)/ad/PA/EVOH/PA/ad/LDPE(85%)+LLDPE(15%) (15/7/11/4/11/12/40)
	5% compatibilizer	LDPE(85%)+LLDPE(15%)/ad/PA/EVOH/PA/ad/LDPE(72%)+LLDPE(15%)+**PCA-MA**(13%) (16/7/9/6/12/12/40)
	7% compatibilizer	LDPE(85%)+LLDPE(15%)/ad/PA/EVOH/PA/ad/LDPE(64%)+LLDPE(15%)+**PCA-MA**(19%) (16/7/9/8/11/12/42)

Film A: PE/PE/ad/PA/ad/PE/PE; Film B: PE/ad/PA/EVOH/PA/ad/PE; LDPE: low-density polyethylene; LLDPE: linear low-density polyethylene; ad: adhesive; PA:

polyamide; PCA-MA: polyolefin compatibilizer additive with maleic anhydride; EVOH: ethylene vinyl alcohol.

2.2. Recyclability assessment

Films recyclability was evaluated using a free online tool, RecyClass v.1.11.1 [17]. In this methodology, information on the composition of the packaging material is provided and incompatibilities that affect the recycling efficiency are verified. After completing the online questionnaire, the package is classified with a class system from A to F, as shown in **Table 2**.

Table 2. Recyclability classification according to RecyClass [17].

Class	Description
A	The package does not pose any recyclability issues and it can potentially feed a closed-loop scheme to be used in the same application.
B	The package has minor design issues that caused its downgrading, but it can still potentially feed a closed-loop scheme.
C	The package has some recyclability issues that affect the quality of its final recyclate, but still allowing cascade-open loop schemes, or issues that lead to material losses during recycling, resulting in this case to possible closed-loop schemes
D	The package has some significant design issues that highly affect its recyclability, leading to low-value applications for the recyclate.
E	The package has major design issues that put in jeopardy its recyclability.
F	The package is not recyclable either because of fundamental design issues or a lack of specific waste stream widely present in the EU. If the package obtains this class in one of the question areas, then the analysis is completed.

Class A represents the best recyclability of a package, whereas class B, C, D, and E represent increasingly lower recyclability. Finally, class F represents packages that *are not recyclable and can only be incinerated. ‘+’ class bonus is obtained for the use of post-consumer recycled material.*

2.3. Production of recycled films

Approximately 50 kg of each film with and without compatibilizer were ground separately in dimensions from 10 to 20 mm in a Grinder Wortex Model GSG 300/800 (Campinas, Brazil) to produce the films with 100% recycled material. Then, the ground materials were washed, repelletized, dried, and homogenized in a pilot plant. Finally, the films were produced using a balloon extruder (Coex Extruder Dr Collin, model BL180/400, Germany). The temperature profile (°C) of the heating zones was 190/220/230/235/235/235. The average extrusion speed was 43 rpm. The final films prepared by the blowing process were 310 mm wide and about 50 ± 3 μm thick. Recycled films were called Film A 100% recycled – control; Film A 100% recycled – 5% compatibilizer; Film A 100% recycled – 7% compatibilizer; Film B 100% recycled – control; Film B 100% recycled – 5% compatibilizer; Film B 100% recycled – 7% compatibilizer. A commercial virgin PE film was also used for comparison and was named PE – 100% virgin resin. Then, all films were characterized regarding their chemical, thermal, morphological, and mechanical properties.

2.4. Characterization of recycled films

2.4.1. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR analyses were recorded using a Spectrum 100 spectrometer (PerkinElmer, Waltham, MA, USA). All samples were analyzed using the attenuated total reflectance (ATR) mode (zinc selenide crystal), using the Perkin Elmer Spectrum software version 10.4.00, at 4000–650 cm^{-1}, with resolution of 4 cm^{-1}, scans: 4 [24,25]. Three spectra were recorded at different locations on the film for each sample to estimate the average of the film inhomogeneous potential and measurement variability.

2.4.2. Differential scanning calorimetry (DSC)

The thermal properties of the films were measured by DSC using a calorimeter (TA Instruments – DSC 250, New Castle, USA), at a 10 °C/min heating rate, ranging 40–300 °C and the determinations were carried out under a dry nitrogen purge. The sample weight was approximately 5 mg. The melting temperature (T_m) was estimated based on the DSC thermograms [26]. The results were the mean of three replicates.

2.4.3. X-ray diffractometry (XRD)

An X-ray analyzer (X'Pert-MPD, Philips, Almelo, Netherlands) was employed for crystallinity evaluation. The XRD measurements of multilayer packaging films were operated with Cu Kα radiation (λ = 1.54 Å) at a scan rate of 0.033°/s (step = 0.04° and time per step = 1.2 s), with the accelerated voltage of 40 kV and the applied current of 40 mA, varying from 10 to 30°. The overall crystallinity of the films was estimated by the ratio between the area under the peaks (crystalline regions) and the total area (crystalline and amorphous regions).

2.4.4. Scanning electron microscopy (FEG-SEM)

The microstructure of the films was examined through Field Emission Gun (FEG) Scanning Electron Microscopy (SEM) (Quattro S, TermoFisher Scientific, Brno, Czech Republic) with Energy Dispersive X-ray Detector (ANAX-60P-B, Thermo Scientific UltraDry, Brno, Czech Republic) at a 5 kV voltage and a 14-pA current. The samples were immersed in liquid nitrogen for fracture until they naturally broke (around 1 min) and fixed in a metallic support and coated with gold (K450, Emitech, Kent, United Kingdom). The thickness of the gold layer was estimated at 200 Å. SEM images were analyzed at 1000× magnification (film surface and cross-section).

2.4.5. Thickness

Thickness measurements were taken at five different locations of each sample, using a digital micrometer with a resolution of 0.1 µm (Mitutoyo Co., Kawasaki-Shi, Japan) [27].

2.4.6. Mechanical Properties

For the mechanical properties' tests, 25 mm wide samples were used, with them being cut in precision equipment to avoid burrs. The samples were conditioned for a minimum period of 48 h at 23 ± 2 °C and 50 ± 5% RH before testing. The tests were performed under the same temperature and relative humidity conditions. Tensile strength was determined using a universal testing machine (Instron, 5565-E2, USA), operating with cell load of 5 kN. Test speed was 500 mm min^{-1} and with initial grip separation of 50 mm in the machine direction (MD) and transverse direction (TD) [28]. Puncture resistance was determined using a universal testing machine, with a load cell of 5 kN operating in compression, using a 3.2 mm metal tip at a constant speed of 25 mm min^{-1} [29]. All tests were performed with ten repetitions.

2.5. Statistical analyses

Results were expressed as mean ± standard deviation and statistically evaluated by analysis of variance (ANOVA). Comparisons between mean values were determined by Tukey's tests ($p < 0.05$).

3. Results and discussion

3.1. Recyclability of films by RecyClass

After evaluating the recyclability of the virgin PE film, the packaging was classified as “A” by the RecyClass tool, i.e., the packaging does not present any recyclability problem and can potentially feed a closed-circuit scheme to be used in the same application. For Film A and B with and without compatibilizer, both materials presented classification F, i.e., the packaging is not recyclable due to fundamental design issues or the lack of a specific waste stream. The result is based on the combination of polymers of the polyolefins and non-polyolefins class in the packaging structure, i.e., it contains more than 15% PA in the structure compared with the amount of PE, thus it cannot follow the PE recycling line. These results are compatible with those found in the literature for films containing PE and PA [30]. In a hypothetical situation, excluding the PA from Film B, a PE film with a limit of up to 5% EVOH can be classified as class B, where the packaging is recyclable with some minor recyclability problems, since producing a secondary granule from this material is possible at first; however, with some reduction in final quality. Thus, these results show that the main factor for the F classification of the studied films is the presence of PA [17].

In this sense, to improve the recyclability of multilayer packaging containing PA, it is necessary to work on the design of the composition of these packages in order to facilitate the recycling of materials. Design for recycling includes maximizing recyclable components in structures, eliminating non-recyclable materials, reducing complexity, among other efforts [18]. One possible method to enable multilayer packaging recycling based on different polymers, such as those studied here, is the use of compatibilizer additives. Thus, to make the studied packages recyclable, the results of this research show the influence of the maleic anhydride-based compatibilizer on Films A and B after mechanical recycling and a comparison with a virgin PE film.

3.2. Characterization of recycled films

3.2.1. FT-IR analysis

The FT-IR was used to identify the functional groups of the virgin PE film and recycled films, as shown in **Figure 1(a)**. The characteristic peaks of polyethylene are observed in the 100% virgin PE resin film, corresponding to asymmetric and symmetric C–H stretching vibrations in CH_2 at the absorption peaks of 2915 cm^{-1} and 2849 cm^{-1}, respectively. The peak at 1646 cm^{-1} can be attributed to the presence of C–C stretching vibration. The peak at 1471 cm^{-1} is attributed to C–H deformation vibrations in CH_2, the peak at 1369 cm^{-1} is attributed to flexion in CH_3, and the peak at 717 cm^{-1} is due to C–C equilibrium vibrations in CH_2 [31–33].

Regarding recycled films, both Film A and B, with or without compatibilizer, had the PE peaks, since this is the major polymer in the composition of the films. Additionally, some of these peaks are found in the other materials that make up the recycled films, resulting in an overlap of these peaks. However, the peak at approximately 1640 cm^{-1} was more intense, due to the C=O stretching of the PA amide group present in recycled films [34] compared with the film with virgin PE resin. The other peaks can be attributed mainly to PA spectra, since it is the second material in greater quantity in the recycled films. In this sense, the bands around 3300 -3302 cm^{-1}, 1639-1640 cm^{-1}, and 1544 cm^{-1} are associated with N–H stretch vibrations, where they represent amide A (N–H stretching by hydrogen bond), amide I (C=O stretching) and amide II (N–H bond and C–N stretching), respectively [35,36].

Finally, the characteristic peak of maleic anhydride appeared at 1790 and 1710 cm^{-1}, corresponding to anhydride-type carbonyls and acid-type carbonyls, respectively. However, films with the PCA-MA compatibilizer did not show these peaks, only the peaks similar to recycled films without compatibilizer. The disappearance of the characteristic peak of the compatibilizer is an indicative of the reaction between NH groups, from PA, with PCA-MA anhydride moieties. The occurrence of these types of reactions demonstrates that the PA-MA-PE copolymer is created during mixing [37,38]. Also, the non-emergence of any different group in the films with compatibilizer occurs by the degradation of the MA group grafted to –COOH during the fusion process. Thus, the reaction of the PA, the PE alkyl group, and the maleic anhydride form a PA-MA-PE copolymer [39]. This formation is proven by the presence of a functional group overlaid of C–H and N–H [35].

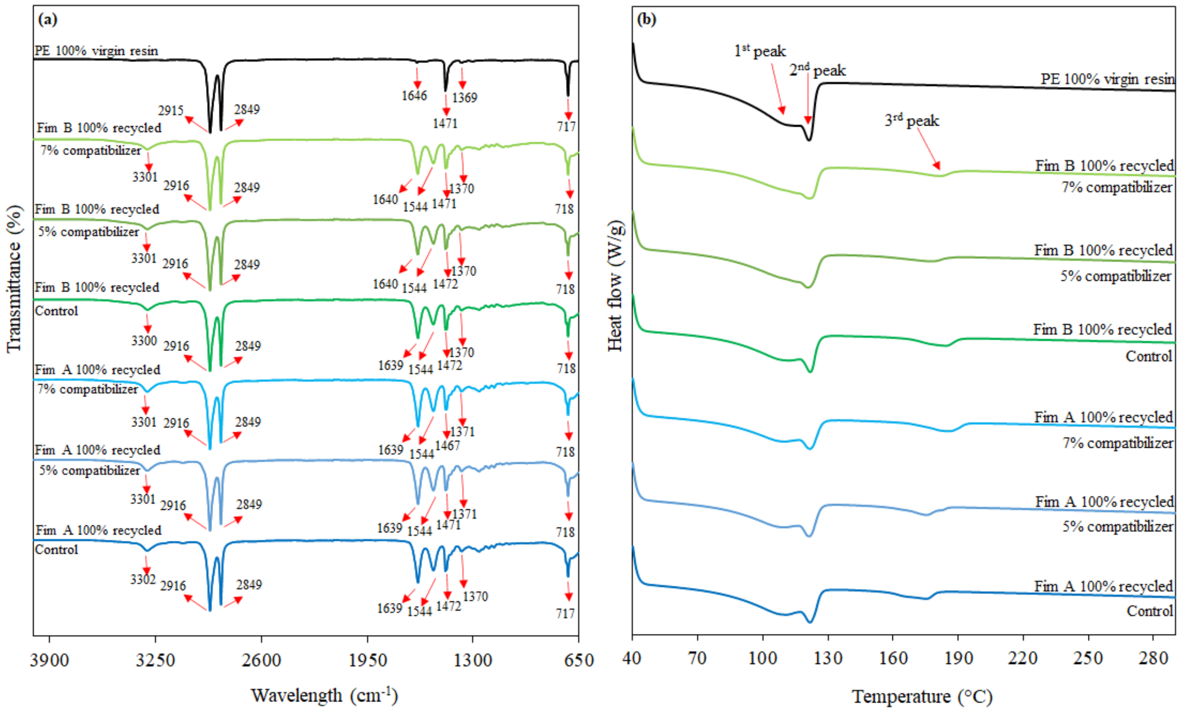

Figure 1. Fourier-transform infrared spectroscopy (a) and differential scanning calorimetry (b) of the different recycled films. Film A: PE/PE/ad/PA/ad/PE/PE and Film B: PE/ad/PA/EVOH/PA/ad/PE.

3.2.2. DSC analysis

The thermal characteristics of virgin PE film and recycled films were evaluated by DSC. **Figure 1(b)** shows the thermal profile of the different samples, and **Table 3** shows the melting temperatures (T_m).

The DSC curves of the different films presented two PE peaks, corresponding to LDPE (1st peak), LLDPE (2nd peak). The T_m values of the 1st peak were between 110.0 ± 1.3 and 113.9 ± 0.2 °C and for the 2nd peak between 120.9 ± 0.3 and 122.4 ± 0.8 °C. These ranges are similar to those found in the literature for LDPE and LLDPE blends [40]. The PE peaks of recycled films (Film A and Film B) with compatibilizer did not show significant difference in T_m compared with films without compatibilizer. Also, these peaks were similar to the peaks found for PE film with virgin resin, demonstrating that PE thermal stability was not affected by the compatibilizer addition and the recycling process. Regarding the 3rd peak, it represents the T_m of PA for Film A and possibly of PA and EVOH for Film B. The T_m

of the 3rd peak ranged between 175.4 ± 0.4 and 184.1 ± 2.2 °C, these values are within the thresholds found in previous studies with PA and EVOH films [9,33]. Film B showed no significant difference in T_m between samples with and without compatibilizer. On the other hand, Film A with 7% compatibilizer presented a significantly higher T_m than the Film A without compatibilizer and with 5% compatibilizer. This increase in T_m may be related to excess maleic anhydride, which may result in nucleation by PE for PA crystals, thus resulting in a higher melting point of PA [41].

Table 3. DSC results of different recycled packaging materials with different compatibilizer concentrations.

Packaging Material	**Sample**	**PE**		**PA and/or EVOH**
		T_m (°C) 1st peak	**T_m (°C) 2nd peak**	**T_m (°C) 3rd peak**
Film A – 100% recycled (PE/PE/ad/PA/ad/PE/PE)	Control	110.5 ± 0.3^{ab}	121.8 ± 0.1^{a}	175.4 ± 0.4^{b}
	5% compatibilizer	110.0 ± 1.3^{b}	121.7 ± 0.7^{a}	175.5 ± 0.6^{b}
	7% compatibilizer	110.7 ± 1.7^{ab}	122.4 ± 0.8^{a}	184.1 ± 2.2^{a}
Film B – 100% recycled (PE/ad/PA/EVOH/PA/ad/PE)	Control	112.8 ± 1.1^{ab}	121.7 ± 0.3^{a}	181.7 ± 3.8^{ac}
	5% compatibilizer	113.9 ± 0.2^{a}	120.9 ± 0.3^{a}	177.7 ± 0.2^{bc}
	7% compatibilizer	113.8 ± 2.5^{ab}	121.9 ± 0.9^{a}	181.2 ± 0.6^{ac}
PE – 100% virgin resin	PE	111.2 ± 0.8^{ab}	121.3 ± 0.1^{a}	-

PE: polyethylene, ad: adhesive, PA: polyamide, EVOH: ethylene vinyl alcohol, T_m: melting temperature.

Values referring to the mean of three repetitions ± standard deviation.

^{a,b,c} *means followed by the same letter in the column do not differ at the 95% confidence level ($p < 0.05$).*

3.2.3. XRD analysis

Since the crystalline structure affects the mechanical properties, a possible change in the crystallinity of the polymer matrix resulting from the mixture of recycled films with and without compatibilizer becomes fundamental for this research. **Figure 2** shows the XRD patterns for the PE Film with virgin resin and for Film A and B with and without compatibilizer. The main diffraction peak of polyethylene is observed at 2θ = 21.5° and a slight peak is observed at 2θ = 24.0°. These peaks correspond to the crystalline planes (110) and (200) of their orthorhombic unit cell, indicating crystalline phase [42,43]. These diffraction peaks are characteristic of PE, differing in magnitude of area in different crystallinities [44,45]. For recycled films with and without compatibilizer, the peak at 2θ = 21.5° is also observed, in addition to a slight expansion of the magnitude of the peak by 2θ = 24.0°. This behavior occurs mainly due to the presence of PA in these materials [46].

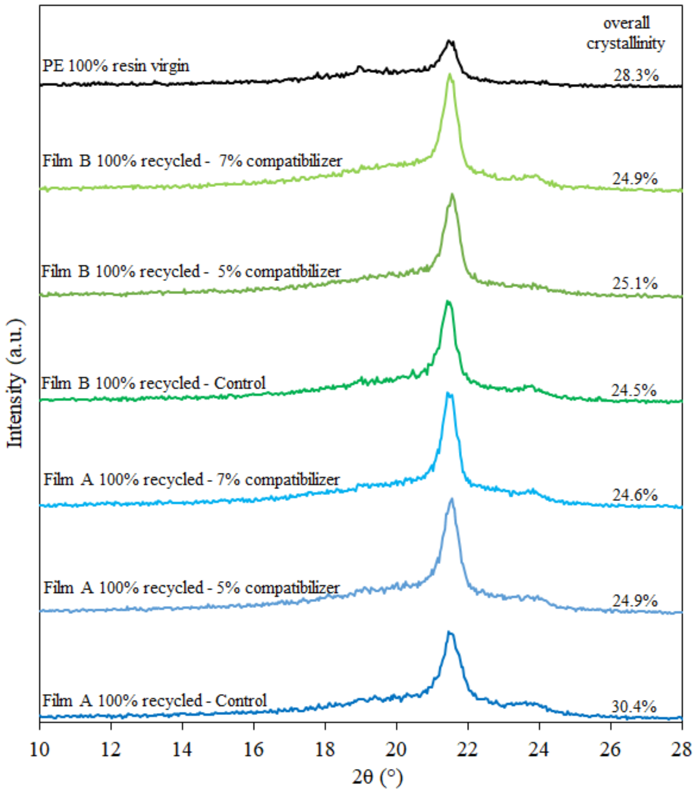

Figure 2. X-ray diffraction patterns of the different recycled films. Film A: PE/PE/ad/PA/ad/PE/PE and Film B: PE/ad/PA/EVOH/PA/ad/PE.

The overall crystalline value for the virgin PE film sample was 28.3%, similar to that found for the LDPE/LLDPE film [45]. In the recycled materials of Films A and B, the overall crystallinity was 30.4% and 24.5%, respectively. These values are very close to those found for the PE film with virgin resin, mainly due to the higher proportion of PE in films compared with other materials that compose them. For Film B with the different concentrations of compatibilizer, the values of crystallinity were very close to those of the film without compatibilizer. However, for Film A, the crystallinity of the films with compatibilizer slightly decreased. The data from Film A indicate the addition of the PCA-MA compatibilizer decreases the overall crystallinity, indicating that the PA-MA-PE mixture provided better miscibility. This behavior is in accordance with was observed for PP-MA-PA mixtures [36].

3.2.4. *Morphology of recycled films*

Figure 3 shows the surface morphologies and cross-section of virgin PE film. The film features an essentially smooth and homogeneous surface as well as a quite cohesive cross section. These characteristics are mainly observed due to the mixing and processing of two compatible materials LDPE and LLDPE with very similar fusion behaviors, as shown in **Table 3**. Similar characteristics for LDPE and LDPE blends are often reported [47,48].

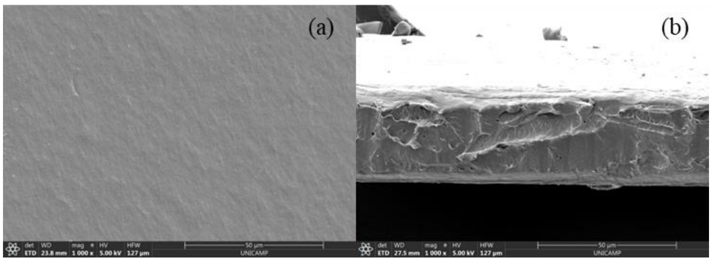

Figure 3. Images of scanning electron microscopy of the surface (a) and cross-section (b) of the PE film 100% virgin resin.

Mixing PA with PE leads to an immiscible biphasic system. The polyolefinic compatibilizer additive with maleic anhydride (PCA-MA) serves as a precursor for reactive compatibilization. In this sense, the groups of maleic anhydride with polyolefin are expected react promptly with the amine terminal group(s) of PA and PE mixtures, since the two are miscible, resulting in a stabilized PA-MA-PE mixture. **Figure 4** shows the SEM surface and cross-sectional micrographs of Films A and B with and without compatibilizer.

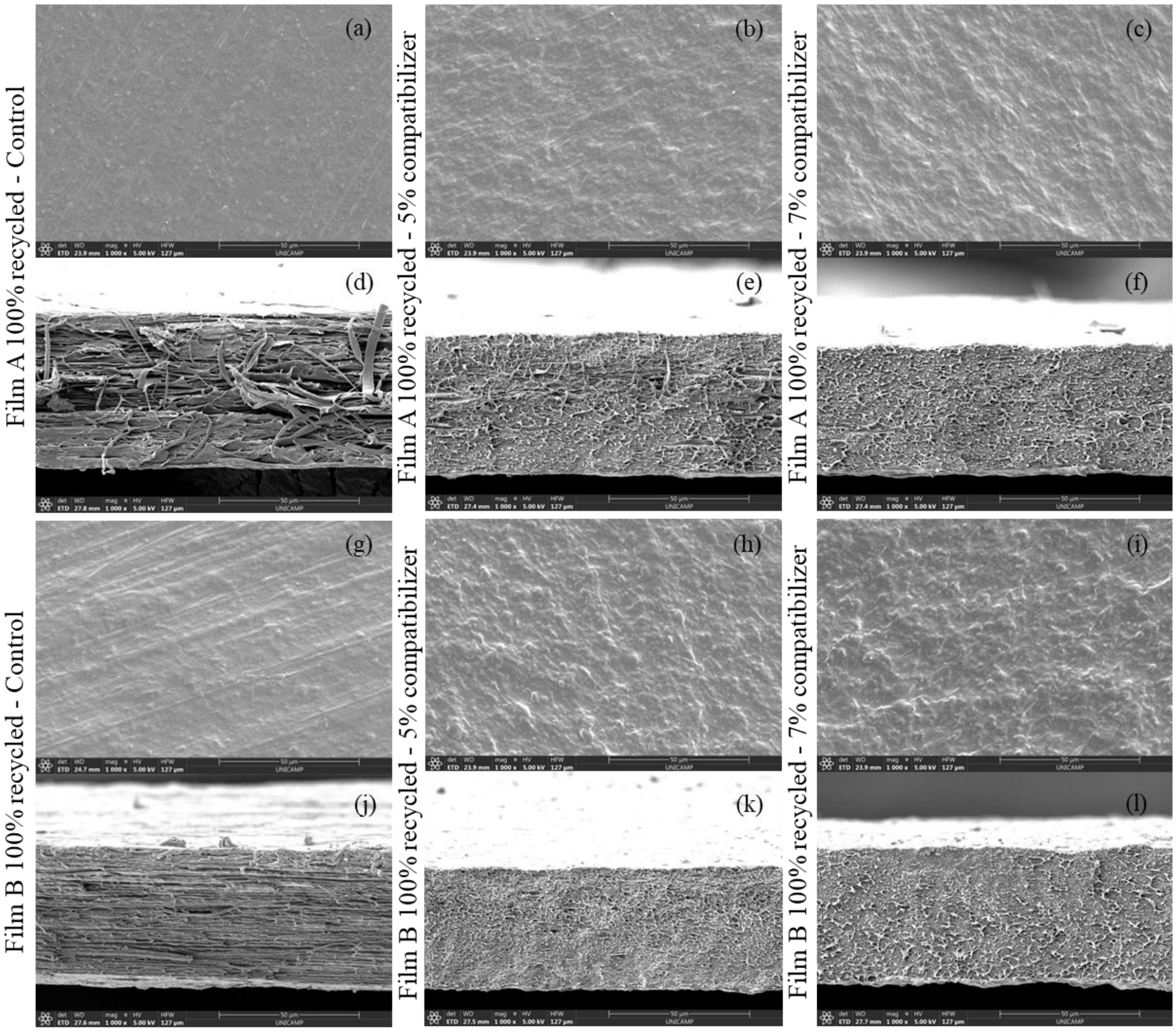

Figure 4. Images of scanning electron microscopy of the surface (a, b, c, g, h, and i) and cross-section (d, e, f, j, k, and l) of the different recycled films. Film A: PE/PE/ad/PA/ad/PE/PE and Film B: PE/ad/PA/EVOH/PA/ad/PE.

The morphology of the surface of the films without compatibilizer was non-uniform and rough (**Figures 4a,g**). In general, immiscible mixtures of PE and PA without compatibilizer present low interfacial adhesion and weak dispersion. The films with compatibilizer were also rough; however with a characteristic of network formation (**Figures 4b,c,h,i**), caused by the compatibilization of the PE and PA phases. The rougher surfaces of films with compatibilizer is an indication that the compatibilization between the different polymers occurred successfully, since the PCA-MA presents rougher and more irregular particles, as described by [49].

The SEM micrographs of the cross-sectional section of films without compatibilizer (**Figures 4d,j**) show macromolecules in elongated formats and in the same direction, which may indicate a poor adhesion between the different polymers, especially between PE and PA, which are immiscible. The literature showed similar behavior for PE/PA blend [50]. In particular, evaluating the interfacial modification and dispersion of the phases in the presence of compatibilizers is possible. For films with 5% compatibilizer (**Figures 4e,k**) and 7% compatibilizer (**Figures 4f,l**) macromolecules showed smaller and more homogeneous typical domain sizes compared with those found for films without compatibilizer, as expected by the decrease in surface tension [51,52]. Also, they were shown to be in network format, which can be attributed to the positive effect of the compatibilizer on the miscibility between the PE and PA macromolecules. Thus, the compatibilizer may be located at the interface between the PA and the PE, providing better support between them during fusion mixing [49,53].

3.2.5. Thickness and mechanical properties

The recycled films produced presented thickness values between 47.2 to 52.2 μm and are within the 50 ± 3 μm processing variation. Comparatively, a virgin PE commercial film of 34.8 μm was also evaluated (**Table 4**).

Table 4. Total thickness of the different recycled films

Packaging Material	Sample	Thickness (μm)

Fim A – 100% recycled (PE/PE/ad/PA/ad/PE/PE)	Control	52.0 ± 2.3
	5% compatibilizer	49.0 ± 3.2
	7% compatibilizer	51.6 ± 1.5
Film B – 100% recycled (PE/ad/PA/EVOH/PA/ad/PE)	Control	51.8 ± 1.1
	5% compatibilizer	47.2 ± 1.6
	7% compatibilizer	52.2 ± 1.3
PE – 100% virgin resin	PE	34.8 ± 1.5

Values referring to the mean of five repetitions ± standard deviation.

Figure 5 shows the effect of the compatibilizer on tensile strength (TS) and elongation at break (EB) of the samples in the machine direction (MD) and in the transverse direction (TD). The results show that adding the compatibilizer reduced the TS in the MD of the films compared with the films without compatibilizer. However, the TS values of the films with the compatibilizer are close to those of the virgin PE film. Moreover, the different concentrations of compatibilizer did not show significant difference between themselves in the values of TS in MD, both for Film A and B. On the other hand, in the TD the effect of the compatibilizer on TS was the inverse, with an improvement of TS with the incorporation of the compatibilizer. For Film B, the different concentrations of compatibilizer had the same effect on TS in the TD. However, for Film A, the incorporation of 5% of compatibilizer resulted in higher TS compared with the control film and the film with higher concentration of compatibilizer. Also, note that the TS of the films with 5% compatibilizer was significantly equal to the TS of the virgin PE film.

In general, the compatibilizer was expected to improve TS in both directions, since this property tends to increase as the miscibility of PE and PA increases, since it results from the better interfacial adhesion caused by the formation of the PA-MA-PE copolymer [54]. However, this behavior was only observed in the TD. Given this inconsistency of TS in the MD of the films, this reduction can be attributed to possible modifications in the continuous phase of the matrix with the incorporation of compatibilizer. Similar results were found in the literature for blends of HDPE/PA6 compatible with maleic anhydride [55].

Regarding EB, in the MD the values were significantly equal for all samples. However, in the TD the incorporation of compatibilizer resulted in a significant increase in EB compared with films without compatibilizer, going from 10.8% to 646.9% for Film A and from 8.0% to 608.0% for Film B. The EB increase in the presence of compatibilizer can be interpreted by the elastomeric nature of the compatibilizer [35]. Moreover, as discussed earlier, the compatibilizer resulted in a better interfacial adhesion between PE and PA and consequently increased the EB of the films, corroborating the SEM results presented. Finally, the results of the mechanical tests confirm the strong efficiency of PA-MA-PE compatibilization.

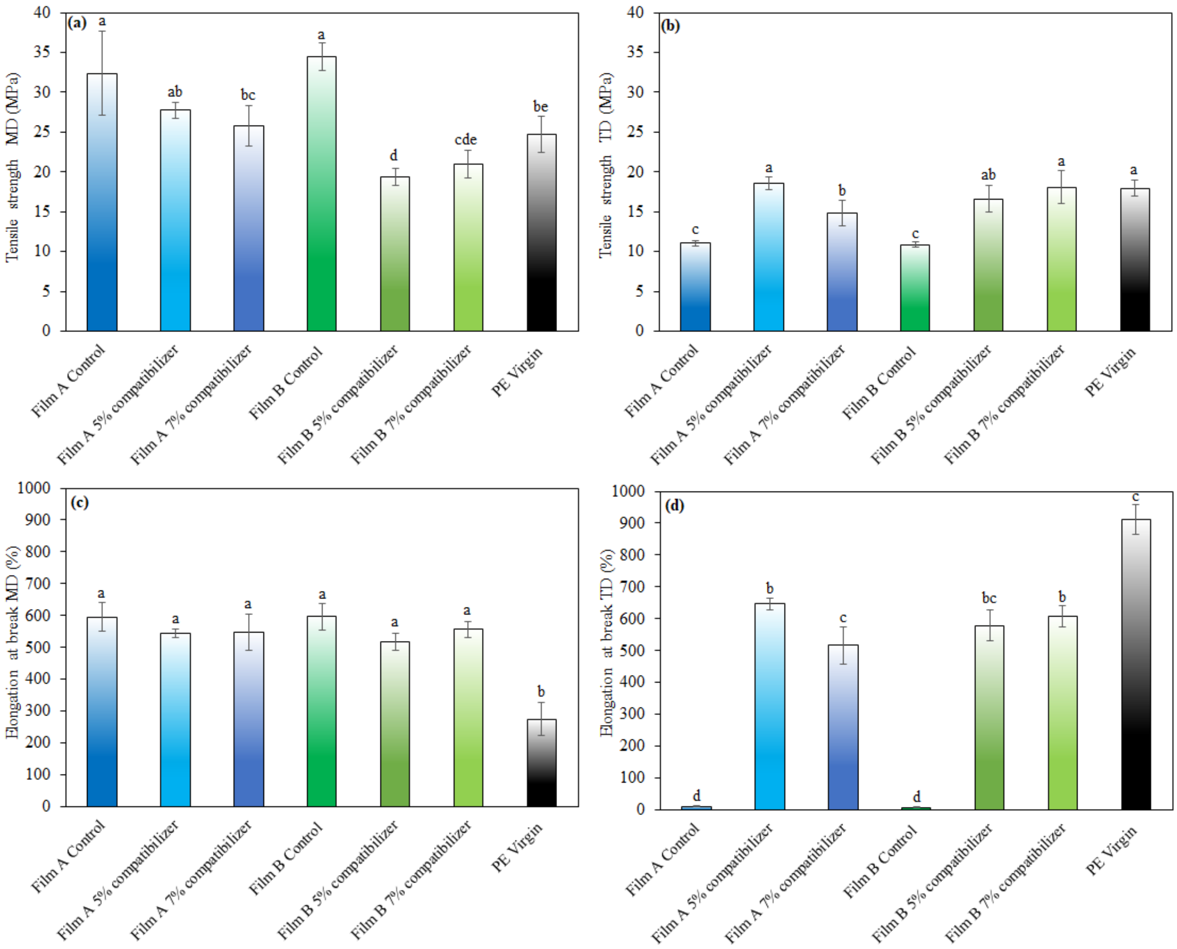

Figure 5. Tensile strength in MD (a), tensile strength in TD (b), elongation at break in MD (c), and elongation at break in TD (d) of the different recycled films. Film A: PE/PE/ad/PA/ad/PE/PE and Film B: PE/ad/PA/EVOH/PA/ad/PE.

Figures 6(a) and 6(b) show the results of puncture resistance and elongation at puncture. Film A without compatibilizer showed a higher puncture resistance (9.33 N) than Film B without compatibilizer (6.11 N). The higher value of Film A compared with Film B can be attributed to the greater amount of PA in the film, since this polymer is responsible for providing better mechanical performance [9,56]. The puncture resistance of Film A is significantly reduced in recycled films with compatibilizer. On the other hand, for Film B, the puncture resistance was significantly higher compared with the control. Regarding elongation at puncture, the values of Film A with and without compatibilizer are significantly equal; however, for Film B with compatibilizer the elongation at puncture was higher compared with the control. These results show the same approach presented for TS and EB. The compatibilized films also show values of puncture resistance and elongation at puncture similar to those of the virgin PE film. Note that changes in puncturing performance are within the industry acceptable range, which is 25% [57]

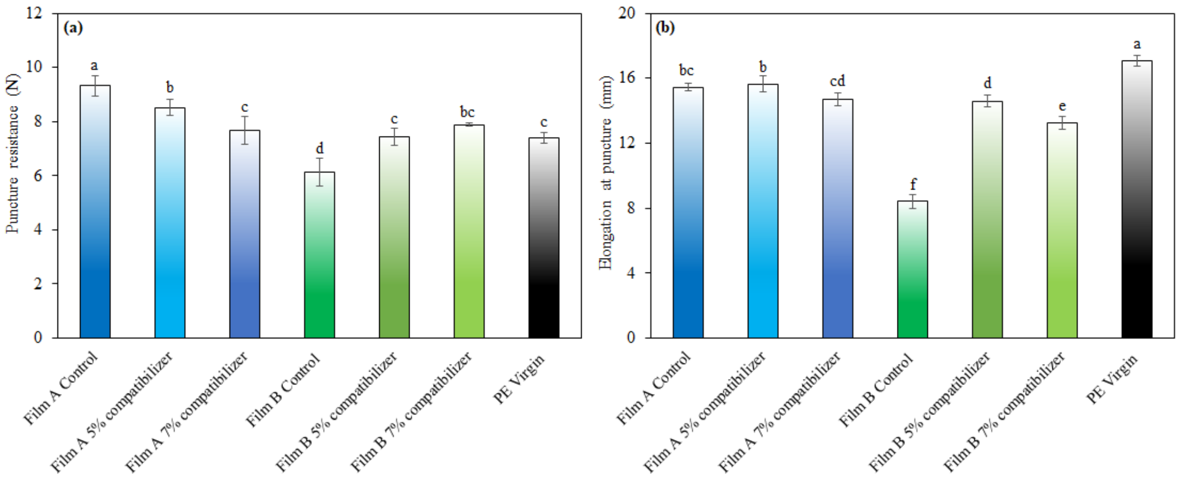

Figure 6. Puncture resistance (a) and elongation at puncture (b) of the different recycled films. Film A: PE/PE/ad/PA/ad/PE/PE and Film B: PE/ad/PA/EVOH/PA/ad/PE.

4. Conclusions

Flexible multilayer packaging based on polyethylene (PE) and polyamide (PA) shows enormous challenges for recycling. However, when these packages present a compatibilizer based on maleic anhydride (MA) in their structure, they can be recycled. Two films (Film A: PE/PE/ad/PA/ad/PE/PE and Film B: PE/ad/PA/EVOH/PA/ad/PE) with different concentrations of compatibilizer (5% and 7%) were recycled via extrusion, and infrared spectra showed that the PA-MA-PE copolymer was created during mixing. The PE fusion temperature was stable at processing. However, the greater amount of compatibilizer changed the melting temperature of the PA of Film A. The overall crystallinity of Film A with compatibilizer was lower than the film without compatibilizer, indicating that the PA-MA-PE mixture was miscible, which was confirmed by the SEM images that demonstrate that the compatibilizer provided a better support between the interface of the mixture. Consequently, incorporating a compatibilizer significantly increased stretching in the rupture compared with the films without compatibilizer. These results confirm the strong efficiency of PA-MA-PE compatibilization, which is an alternative to make multilayer packaging of meat products recyclable.

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

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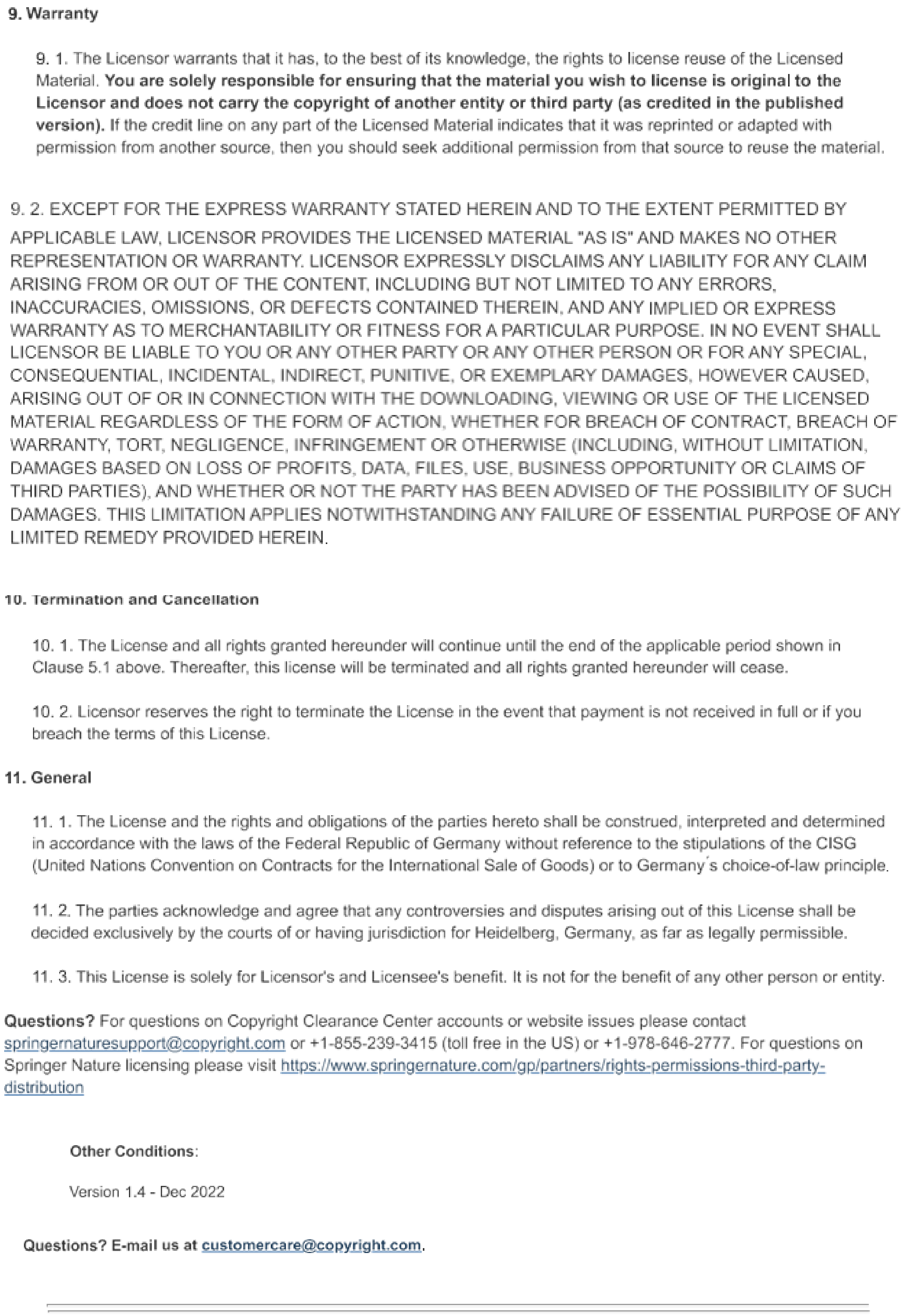

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