Universidade do Minho
Escola de Engenharia

Carolina de Lemos Barros

Development of high-performance recyclable films for food packaging

abril de 2024

Development of high-performance recyclable films for food packaging

Carolina de Lemos Barros

UMinho | 2024

Universidade do Minho
Escola de Engenharia

Carolina de Lemos Barros

Development of high-performance recyclable films for food packaging

Tese de Doutoramento

Ciência e Engenharia de Polímeros e Compósitos

Trabalho efetuado sob a orientação da:

Professora Doutora Ana Vera Alves Machado

Professora Doutora Olga Sousa Carneiro

abril de 2024

DECLARAÇÃO

DIREITOS DE AUTOR E CONDIÇÕES DE UTILIZAÇÃO DO TRABALHO POR TERCEIROS

Este é um trabalho académico que pode ser utilizado por terceiros desde que respeitadas as regras e boas práticas internacionalmente aceites, no que concerne aos direitos de autor e direitos conexos.

Assim, o presente trabalho pode ser utilizado nos termos previstos na licença abaixo indicada.

Caso o utilizador necessite de permissão para poder fazer um uso do trabalho em condições não previstas no licenciamento indicado, deverá contactar o autor, através do RepositóriUM da Universidade do Minho.

Licença concedida aos utilizadores deste trabalho

Atribuição-NãoComercial-SemDerivações
CC BY-NC-ND
https://creativecommons.org/licenses/by-nc-nd/4.0/
DECLARAÇÃO

ACKNOWLEDGMENTS

A nível institucional agradeço o financiamento do Fundo Europeu de Desenvolvimento Regional (FEDER) através do programa "Portugal 2020" e programa Operacional de Lisboa para os projetos em que estive envolvida durante o doutoramento, projeto MobFood, referência POCI-01- 0247-FEDER-024524, e projeto BETTER PLASTIC, referência POCI-01- 0247-FEDER-046091.

Às minhas orientadoras de tese, professora Doutora Ana Vera e professora Doutora Olga Carneiro, por muitas vezes reverem o meu trabalho em fins de semana, feriados e fora de horas de expediente. Por se disponibilizarem a ajudar-me em situações que não o tinham de fazer. Por melhorarem bastante o meu trabalho e por todo o *know-how* que me transmitiram antes e durante o doutoramento. O conhecimento que adquiri no IPC é a base para toda a investigação que desenvolvo hoje.

Agradeço também aos técnicos dos laboratórios do IPC que me ajudaram a trabalhar com os equipamentos de processamento e de caracterização de polímeros.

Aos investigadores do IPC, em especial ao Pedro e Vasco, que tem um conhecimento gigante e força de vontade gigante e que foram meus parceiros quer no processamento quer nas partes mais aborrecidas, como formatações.

Após estes anos de trabalho agradeço ao meu Luís, que esteve e está sempre ao meu lado já desde a minha tese de mestrado, sempre forte e sempre a amparar os meus devaneios. É das pessoas com mais paciência do mundo e sou a mulher mais sortuda por ter este homem ao meu lado.

Aos meus pais, por darem sempre a maior força para atingir os meus objetivos pessoais e profissionais, e acreditarem sempre em mim.

À minha irmã, por ser a pessoa mais carinhosa, dedicada, madura, sensata e inteligente que já conheci, que me ajuda sempre no que pode.

Ao pessoal do PIEP, que sem contar, se tornaram meus amigos e tornam as segundas feiras interessantes e nada aborrecidas e me deram muita força de vontade para acabar esta tese, com a promessa de uma grande jantarada.

À Dricas, à Sónia e à Neiva que têm e sempre tiveram um lugar especial no meu coração, por muito me aturaram ao longo da vida e que só tenho a agradecer por todos os momentos incríveis que passámos.

STATEMENT OF INTEGRITY

I hereby declare having conducted this academic work with integrity. I confirm that I have not used plagiarism or any form of undue use of information or falsification of results along the process leading to its elaboration.

I further declare that I have fully acknowledged the Code of Ethical Conduct of the University of Minho.

RESUMO

Algumas embalagens de plástico para produtos alimentares permitem o aumento do prazo de validade dos alimentos, diminuindo o seu desperdício e tornando-os mais acessíveis a toda a população. Estas embalagens, de um modo geral, combinam diferentes tipos de materiais em filmes coextrudidos ou laminados, permitindo assim melhorar as propriedades estéticas e funcionais (mecânicas e/ou de barreira), mas dificultando a reciclabilidade das mesmas.

Uma estratégia para diminuir a utilização de diferentes materiais numa embalagem sem perda de propriedades poderá ser a incorporação de micro e nanopartículas (nanoargilas (NC), microcristais de celulose (MCC), nanocristais de celulose (CNC), nanopartículas de dióxido de silício (SiO_2)) no filme plástico. Com este objetivo foram realizados dois estudos, um com uma matriz de polietileno de baixa densidade (LDPE) e o outro com matriz de etileno vinil álcool (EVOH), onde foram produzidos diferentes micro e nanocompósitos e correspondentes filmes, procedendo à composição por extrusão e à extrusão de filme tubular, respetivamente. O desempenho destes filmes foi analisado através de uma caracterização abrangente com especial foco nas propriedades barreira e mecânicas. Para além desta análise, foi estudada a incorporação de plástico recuperado de sobras e aparas de produção industrial de filmes multi-material, em filmes de base em LDPE virgem e avaliado o seu comportamento quando sujeito a vários ciclos de reprocessamento (numa tentativa de simulação de reciclagem termomecânica). Estes filmes foram também submetidos a uma caracterização de largo espetro, com foco nas propriedades mecânicas e óticas.

Concisamente, os resultados dos três diferentes estudos reportados neste trabalho revelaram que: a dispersão de NC numa matriz de LDPE e a barreira ao oxigénio do filme resultante melhoram com a incorporação de Polietileno enxertado com anidrido maleico (PE-g-MA); a incorporação de 0, 5 wt.% NC e 1,0 wt.% MCC numa matriz de EVOH diminui os valores de taxa de transmissão ao oxigénio (OTR) sem condicionar a boa visibilidade dos produtos na embalagem; apesar de o LDPE e o EVOH serem materiais incompatíveis, o reprocessamento dos grânulos provenientes de filmes multicamada contendo estes materiais, e a sua mistura com LDPE, não afetou negativamente a produção de filme e as suas propriedades em relação ao LDPE virgem.

No geral, a incorporação de NC e MCC melhora as propriedades barreira do polímero virgem e a incorporação de plástico reciclado (de fontes rastreáveis) numa embalagem alimentar prova ser uma estratégia viável com vista à sustentabilidade.

Palavras-chave: Embalagem alimentar, Filme tubular, Propriedades barreira, Material reciclado

ABSTRACT

The primary goal of plastic packaging for food products is to extend the shelf life of packaged foods, thereby reducing food waste and making this type of product more accessible to the majority of the population. This type of packaging generally combines different types of materials in coextruded or laminated films, thus improving the aesthetic and functional properties (mechanical and/or barrier) of plastic films, but detrimentally affecting their recyclability.

This work aims to explore the incorporation of micro and nanoparticles (nanoclays (NC), cellulose microcrystals (MCC), cellulose nanocrystals (CNC), silicon dioxide nanoparticles (SiO2)) in plastic films as a strategy to reduce the use of different materials in packaging. Therefore, two studies were carried out, one with a low-density polyethylene (LDPE) matrix and another with an ethylene vinyl alcohol (EVOH) matrix, where different micro and nanocomposites and corresponding films were produced, by extrusion compounding and blown film extrusion, respectively. The performance of these films was analyzed through a comprehensive characterization with a special focus on the barrier properties. Additionally, the possibility of incorporating recycled plastic material (from leftovers, second quality and scraps from the industrial production of multi-material films) into films with virgin LDPE base was studied, and its behavior when subjected to several reprocessing cycles (in an attempt to simulate thermomechanical recycling) was assessed. These films were also subjected to a broad-spectrum characterization, with a focus on mechanical and optical properties.

Concisely, the results of the three different studies reported in this work revealed that: NC dispersion in a LDPE matrix improves, and oxygen permeability of the resulting film decreases, with the incorporation of Polyethylene grafted with maleic anhydride (PE-g-MA) compatibilizer; the incorporation of 0.5 wt.% NC and 1.0 wt.% MCC in an EVOH matrix reduces the oxygen transmission rate (OTR) without affecting the visibility of food products in the packaging; furthermore, despite the incompatibility of LDPE and EVOH, reprocessing of granules from multilayer films incorporating these two materials and their blend with LDPE did not have a negative impact on film production or their properties when compared to the corresponding LDPE virgin film.

In general, the incorporation of NC and MCC improves the barrier properties of the virgin polymer and the incorporation of recycled material (from traceable sources) in food packaging showed to be a viable strategy towards sustainability.

Keywords: Food packaging, Blown film, Barrier properties, Recycled material

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABREVIATIONS AND SYMBOLS

Abbreviations

ASTM – American Society for Testing and Materials

ave – Average

BUR – Blow-up ratio

$CaCO_3$ – Calcium carbonate

CNC – Cellulose nanocrystals

CO_2 – carbon dioxide

D – Diameter

d – interlayer distance

DSC – differential scanning calorimetry

D_T – diffuse transmittance

EC – European Commission

EU – European Union

EVOH – ethylene vinyl alcohol

FCM – Food Contact Materials

FDA – Food and Drug Administration

FTIR – Fourier-transform infrared spectroscopy

GRAS – Generally regarded as safe substances

HDPE – High-density polyethylene

ISO – International Organization for Standardization

L/D – Length per Diameter

LDPE – Low density polyethylene

LLDPE – Linear low-density polyethylene

MCC – Cellulose microcrystals

MD – Machine Direction

MFI – Melt Flow Index

MgO – Magnesium oxide

NaOH – Sodium hydroxide

NC – Nanoclays

O_2 – Oxygen

OP – Oxygen permeability

OTR – Oxygen transmission rate

PA – Polyamide

PE – Polyethylene

PET – Polyethylene terephthalate

PLA – Polylactic acid

PP – Polypropylene

PVDC – Polyvinylidene chloride

PVOH – Polyvinyl alcohol

PE-g-MA – Polyethylene grafted with maleic anhydride

RFID – Radio Frequency Identification

rpm – Rotation per minute

sd – standard deviation

SEM – Scanning Electron Microscopy

SiO_2 – silicon dioxide nanoparticles

TD – transverse direction

TGA – Thermogravimetric analysis

T_m – melting temperature;

T_T – total light transmittance

TTI's – temperature indicators

TUR – take-up ratio

WAXD – Wide angle X-Ray diffraction

WVP – Water vapor permeability

WVTR – Water vapour transmission

X_c – crystallinity degree

ΔH_m – melting enthalpy

ZnO – Zinc oxide

Symbols

µl – microlitre

µm – micron

2θ – double theta

Å – Angstrom

c.p.s. – counts per second

cc·mil/100in^2·day·atm – cubic centimetre one thousandth of an inch per one hundred square inches day Standard atmosphere

cm – centimetres

cm^2 – square centimetre

$E_{1\%}$ – Young's modulus at 1% strain

g – grams

g/10 min – gram per ten minutes

g/h·m^2 – grams per hour square meter

h – hours

J/g – Joule per gram

kg – kilogram

kg/h – kilogram per hour

kg/m^3 – kilogram per cubic metre

kV – kilovolt

mA – milliampere

mol% – mole percent

mg – milligrams

mil – one thousandth of an inch

min – minutes

mL/min – millilitre per minute

Ml·cm/Pa·s·cm^2 – megalitre centimetre per Pascal per second per square centimetre

mm – millimetre

mm/min – millimetre per minute

mm^3- cubic millimetres

MPa – mega Pascal

N – Newton

s – second

wt. % – weight percentage

ε_m – strain at maximum stress.

ε_b – strain at break

λ – wave-length

σ_m – maximum stress

σ_y – yield stress

1. INTRODUCTION

The theme "Development of high-performance recyclable films for food packaging" involves a set of research activities carried out mainly at the Institute of Polymers and Composites of the University of Minho, within the scope of the projects BETTER PLASTICS – Plastics in a circular economy and MOBFOOD – Mobilization of Scientific and Technological Knowledge in response to the Challenges of the Agrifood Market. Both projects were created to promote the transition of the Portuguese plastics industry sector towards a circular economy.

This chapter contains a general introduction to the thesis, referring to the contextualization, motivation, research questions, and objectives of this study.

1.1 Motivational Framework

Conventional plastic packaging poses a significant environmental burden stemming from its reliance on non-renewable resources and its decomposition processes, spanning hundreds of years, contributing to the pollution of oceans and landfills, accentuating the urgent need for sustainable alternatives in the packaging industry. Worldwide plastic production has been increasing over the years. In 2021, the packaging sector accounted for 39.1 wt.% of all plastic product production from virgin raw materials in the EU27+3. This represents a slight decrease when compared to the 2019 and 2020 figures, that were 39.6 wt. % and 40.5 wt. %, respectively [1–3]. Regardless of this slight decrease, this sector continues to be dominant in the production of primary plastics and, as a result, also dominant in the production of plastic waste [1–3]. Plastic waste can have three different destinations: recycling, incineration and disposal in landfills [4]. The disposal of packaging in landfills has decreased between the years of 2006 to 2020 from 7.2 to 3.1 Mt, and recycling has increased from 3.9 to 8.2 Mt. Despite this positive trend, the amount of waste sent to landfills is still too high [1]. For these reasons, environmental awareness regarding the use of plastics has grown, with governments and consumers pushing to sustainable alternatives and new regulations around single-use plastics. In this way, companies have increased their adoption of more sustainable measures to reduce their environmental footprint. One approach can be the incorporation of particles into packaging plastic films, to enhance the performance of the packaging while reducing the overall amount of plastic needed. Another approach towards sustainability involves the use of recycled plastic in food packaging to reduce the demand for virgin plastic production, minimizing energy consumption and diverting plastic waste from landfills and oceans.

The motivation for developing the research topic stems from the need to develop scientific knowledge in the plastic film sector for the food market, to promote the production of high-performance packaging that retains its value when recycled, in an attempt to reduce plastic waste disposal in landfills. Furthermore, the possibility to incorporate recycled material into this type of packaging will be investigated.

1.2 Objectives

In line with the overarching goal of enhancing sustainability in food packaging, the objectives of this research delve into the improvement of key polymer properties essential for packaging through the incorporation of nanoparticles.

Several studies have been carried out in order to obtain the ideal incorporation rate of nanoparticles into polymeric matrices, to develop methodologies to improve the interaction between the two materials, and to improve the processing techniques for the production of nanocomposites with good dispersion and distribution of these particles [7–10]. However, most of the studies published in this field do not use industrial scale packaging production techniques for producing the test samples. In this way, the typical molecular orientation of films obtained by blown film extrusion, as well as the reduced thicknesses used in films intended for food packaging are not reproduced. Therefore, there is a need for a study to evaluate the properties of different nanocomposites and corresponding films, produced through industrial processing techniques, incorporating different types of nanoparticles and incorporation rates. In this way, the results thus obtained will have direct industrial practical relevance.

Considering the research opportunity, the present study comprises two main research questions:

- How to reduce the number of different materials present in multi-material films in order to facilitate their recycling?
- How to introduce recycled material into a film without affecting its performance?

For the identified research questions, two main objectives were defined:

The first is developing flexible and recyclable nanocomposite films, produced through the blown film extrusion process, with good mechanical, barrier and thermal properties. The quality of these films will allow to draw conclusions about the possibility of incorporating nanoparticles with a view to replace, or reduce, the use of additional functional materials, such as polyethylene terephthalate (PET), polyamide (PA) and ethylene-vinyl-alcohol (EVOH), in low-density polyethylene (LDPE) based multi-material and multilayer packaging.

The second objective is to develop multilayer films with recycled content with similar performance of those produced with virgin polymers. These films will also be produced by blown film extrusion and characterized by different techniques. Reprocessing is also addressed in this study.

1.3 Thesis Outline

This thesis is divided into seven chapters:

1. Thesis Overview - addresses the motivation for developing the research topic, identifies both the research opportunity and the research questions, and presents the main objectives of the present research work.

2. Literature review - provides a bibliographical review of the research carried out in the field of food packaging. The focus is on plastic packaging with nanocomposite films, and films produced with the incorporation of recycled plastic. In any case, the objective is to progress towards sustainability and circular economy. This chapter also addresses the concept of food packaging and presents research carried out in the fields of nanotechnology.

3. LDPE-nanoclay films for food packaging with improved barrier properties - reports a study on the barrier, thermal and mechanical properties of LDPE nanoclays (NC) nanocomposites for food packaging films. The samples were produced by blown film extrusion, in order to reproduce the low thicknesses and molecular orientation characteristic of industrially produced packaging films. The goal of the study is to reduce the amount of plastic for the production of a flexible food packaging while maintaining its properties.

4. Towards mechanical recyclability of high barrier food packaging films through filler incorporation on the EVOH layer - reports a study on the incorporation of various types of particles (cellulose nanocrystals (CNC), cellulose microcrystals (MCC), silicon dioxide nanoparticles (SiO_2) and NC) in an ethylene vinyl alcohol (EVOH) matrix. This research stems from de need to reduce the amount of different materials (EVOH, in this case) in a thin and flexible LDPE packaging, with the aim of facilitating its recycling.

5. Feasibility of incorporating recycled multilayer LDPE/EVOH films into new flexible packaging - describes the research performed to assess the feasibility of incorporating two different recycled plastic materials, from industrial scraps, into extruded flexible films for food packaging. In this study, thermomechanical recycling of the recycled materials was simulated by repeatedly reprocessing them. The recycles essentially consist of LDPE, linear-LDPE (LLDPE) and EVOH. The incorporation of virgin LDPE into the recycled material, via extrusion, was also evaluated in terms of extrusion process stability and blend properties.

6. From multilayer LDPE/EVOH film scraps to new flexible multilayer films - explores the mechanical and optical properties of multilayer films incorporating recycled materials, reported in chapter 5, mimicking the structure of industrial flexible packaging films. The process stability was

analysed upon the incorporation of recycled materials, and a comparative assessment of mechanical and optical properties with virgin polymers was conducted. The aim of the study was to contribute to the development of sustainable packaging solutions.

7. Conclusions - presents the general conclusions of all the work developed and suggestions for future work.

2. LITERATURE REVIEW

2.1 Food packaging

Food packaging is used to wrap food and protect it from contamination and gases from the surrounding environment, odours, dust, temperature, light, microorganisms, humidity and physical damage. This packaging allows food to be preserved for longer, increasing its quality and safety, resulting in a reduction in monetary losses for the industry and a reduction in food waste [9].

Due to the advantages that come from increasing the shelf life of food, several investigations have been carried out in the packaging industry, resulting in the emergence of intelligent and active packaging [9, 10]. Smart packaging provides additional information about the product, monitoring the condition of the food and the environment that surrounds it, such as time and temperature indicators (TTI's), gas indicators, and radio frequency identification (RFID). Active packaging improves food protection by increasing shelf life, or maintaining or improving the condition of food, through the use of antioxidants, antimicrobials, oxygen absorbers, and moisture absorbers [11, 12].

The loss of food quality is directly linked to oxidation and microbial growth processes that result in food deterioration during processes such as production, transport, storage and display [9]. Because food oxidation poses a risk to consumer health, several studies have been developed to produce new active food packaging using substances with antioxidant and antimicrobial properties. The component responsible for providing these properties can be included in a separate packaging, for example desiccant sachets, or incorporated into the packaging material, for example in the plastic film that constitutes the packaging [11]. These films, with the incorporation of new active substances, must be approved and authorized by the U.S. Food and Drug Administration (FDA) and the European Commission (EC). The regulations issued by these organizations aim to limit the admissible migration to food of substances that could be harmful to human health from occurring into food [13].

For example, in the case of meat packaging, the incorporation of active materials, such as antioxidants, delays oxidation increasing the shelf life of these foods. As meat contains different amounts of fat and a high content of unsaturated fatty acids, the deterioration in the quality of this product is directly related to lipid oxidation, which leads to changes in flavour, odour, texture, and

colour. The latter influences the choice decision of the consumer. Lipid oxidation can also be delayed by reducing oxygen in these packages through vacuum or modified atmosphere packaging [14].

Multilayer films with different materials have been widely used in the food industry due to the possibility of combining different properties, such as mechanical properties, barrier properties and good sealing, in a single film [15]. One of the most used materials for the production of blown film is polyethylene (PE), due to its transparency, relative low cost, flexibility, low melting temperature ($T_{m,LDPE}$ = 110 °C; $T_{m,LLDPE}$ = 123 °C), water and vapor barrier, and high elongation at break [16, 17]. Sometimes this material does not offer sufficient mechanical strength, barrier properties or rigidity to meet the packaging requirements of certain products. Consequently, many multilayer films contain materials other than PE, such as PA, PET and EVOH.

PA is used in films for food packaging due to its high mechanical and thermal resistance and low oxygen permeability. Its hygroscopic nature allows the penetration of water molecules and their positioning between carbon chains. Therefore, this material is typically used in an internal layer in order to prevent the passage of water vapor through the packaging to the food [18]. PA undergoes hydrolysis in the presence of moisture during the melting process, leading to a decrease in viscosity due to chain scission [19]. For this reason, this material should be dried before use in thermomechanical processes [20]. There are different types of polyamides (PA6, PA6.6, PA11 and PA12) related to different number of carbon atoms in the starting monomers that form different chemical structures and, consequently, polymers with different properties [21]. In the production of films for food packaging, the most used PA is PA6 (T_m = 223 °C) and PA6.6 (T_m = 265 °C). Although the better flexibility and gloss, and lower moisture sensitivity of PA6.6, PA6 continues to be widely used in film production due to its lower cost.

PET (T_m = 260 °C) is a polymer widely used for film production due to its transparency (when amorphous), higher stiffness when compared to PE or polypropylene (PP), stretchability during processing, and gas-barrier properties against moisture, CO_2 and O_2. Like PA, PET also undergoes hydrolysis, requiring drying before processing at 120 – 180 °C for 6 – 24h to get a moisture content of 0.005 wt.% [22]. Despite the fact that the polymers mentioned have a good oxygen barrier, none of them outperforms EVOH or polyvinyl alcohol (PVOH).

As mentioned, EVOH is a polymer widely used in the film industry due to its excellent oxygen barrier properties. This polymer is characterized by ethylene content, which means that at high ethylene content (48 mol%) processing becomes easier, but oxygen transmission rate (OTR)

increases [23]. In order to balance processability and oxygen barrier, an EVOH with 32 mol% of ethylene is often used in industrial film production. EVOH is always used in a multilayer structure, with adjacent layers typically composed of LDPE or PET, for protection against humidity. This is a requirement, as this polymer loses barrier and mechanical properties when exposed to moisture, due to the presence of hydrophilic OH groups [24]. The use of PVOH in films is not as frequent as that of EVOH since there are very few extrusion film grades available. This polymer is applied as a coating, through aqueous solution and subsequent drying. A PVOH with a higher degree of saponification (99%) presents a greater oxygen barrier, but lower capacity for dissolution in water and adhesion to other polymers such as Polylactic acid (PLA), LDPE, and PP [25]. Aquapak has recently been developing a PVOH base grade under the trade name *hydropol*, for extrusion coating, and blown film extrusion [26]. As this polymer is non-toxic and soluble in water, it can be used to promote recycling methods for packaging with multiple layers, allowing their separation by dissolution of the intermediate layer (PVOH).

Table 2-1 presents a compilation of permeability values, taken from various studies, obtained for different polymers commonly used in the production of films for flexible packaging. Although the results differ considerably among different studies, it is possible to observe some common trends: i) the oxygen permeability (OP) of polymers such as LDPE and PP is always higher than that of polymers such as PET, PA, EVOH and PVOH, and within these, EVOH and PVOH always present much lower OP values than PET and PA; ii) as for water vapor permeability (WVP), LDPE and PP have superior barrier, unlike other polymers. Table 2-2 presents the OTR and WVTR results for common multilayer structures used for food packaging, that take advantage of the combination of barrier properties of the different polymers mentioned in Table 2-1.

Table 2-1 Oxygen and water vapor permeability results of several studies of common polymers used in packaging films [27-30]

Polymer	Oxygen permeability (OP)			Water vapor permeability (WVP)			Reference
	$\times 10^{7}$ (ml·m/m²·day·Pa)	T (°C)	RH (%)	$\times 10^{14}$ (g·m/m²·s·Pa)	T (°C)	RH (%)	
LDPE	44.756	25		6.673 – 8.704	38	100	[31-33] cited by [27]
PP	4.936 - 9.869	23	50	2.321 – 4.642	23	85	
PET	0.098 – 0.494	23	50	5.803 – 22.921	23	85	
PVOH	0.003	23	0	342.652	23	85	
PA	0.010 – 0.098	30	60	5.803 – 114.314	23	65	
	$\times 10^{27}$			$\times 10^{21}$			
LDPE	21500	23	0	1200	38	90	[34] cited by [28]
PP	6750	23	0	726	38	90	
PVOH	0.17 / 900	23	0 / 75	485000	38	90	
EVOH	0.77 / 91	23	0 / 75	17000	38	90	
PA6	52 / 225	23	0 / 75	20600	38	90	
	$\times 10^{-16}$			$\times 10^{-13}$			
LDPE	22503			7			[35] cited by [29]
PET	1012			60			[36] cited by [29]
EVOH	0.915			30			[37] cited by [29]
	$\times 10^{-11}$						
LDPE	2.88						[30]
LLDPE	2.01						
PP	1.71						
PET	0.0592						
PA6	0.0270						

Table 2-2 OTR and WVTR of Multilayer film structure for packaging [38]

Multilayer film for packaging	OTR ($cm^3/m^2 \cdot day$)	WVTR ($g/m^2 \cdot day$)
LDPE/PA/LDPE	86.3 ± 1.46	3.93 ± 0.29
LDPE/EVOH/LDPE	1.01 ± 0.32	4.88 ± 0.13
PET/LDPE/PA/EVOH/PA/LDPE	4.17 ± 0.49	7.04 ± 0.13

The coexistence of different materials in multilayer films makes packaging recycling difficult. As a consequence, they usually end up incinerated or deposited in landfills [4, 39]. To separate the different layers, it is necessary to resort to delamination processes using physical, chemical or mechanical methods. The physical method of delamination involves dissolving layers, as with Tetra Pak's 1996 patented packaging, where water-soluble PVOH is used to separate the different layers of packaging. The chemical method involves the decomposition of layers, as, for example, in the case of a multilayer packaging made up of PET and PE where the PET layer is degraded by sulphuric acid, without affecting the PE, which can be reused. The mechanical method involves mixing all film components without layer separation, typically resulting in a mixture with poor mechanical properties [40, 41].

Nanocomposites are a promising class of multiphase materials that have been introduced in the food industry and have the potential to reduce the number of different polymers that comprise a multilayer film. The incorporation of nanoparticles in a polymeric matrix improves the mechanical, barrier and thermal properties of the packaging, due to their reduced particle size, which allows an increase in the polymeric matrix-nanoparticle contact area, giving the nanocomposite unique properties [15].

Incorporating recycled content into packaging is also a sustainable measure for recovering post-consumer packaging. European reports show that from 2018 to 2021 post-consumer recycled content in new packaging went from 4.6 to 8.5 wt.% [3].

The production of eco-friendly packaging is still a challenge for the food industry due to the difficulty in combining this with the current demanding packaging requirements. To achieve this goal, this industry must inevitably continue to invest in research and development in the coming years [9].

2.2 Production of multilayer films

The production of plastic films for the development of flexible food packaging is normally carried out using the blown film extrusion technique. This processing technique allows the production of films with some biaxial orientation and low thickness, being widely used to produce food packaging. In this process, the material is melted and homogenized in an extruder (generally, single screw), or several, in the case of multi-material solutions (coextrusion). The melt is pumped to the extrusion head which ends in an annular shaped die, through which compressed air is blown to increase the diameter of the extruded bubble. In this way, molecular orientation is induced in the circumferential direction of the bubble, while simultaneously reducing its thickness. The blow-up ratio (BUR) characterizes the degree of bubble inflation, being the ratio of the diameters of the bubble and of the die. The longitudinal orientation is induced through the stretching promoted by the pulling unit, which also promotes a reduction in the film thickness. In this case, the take-up ratio (TUR) quantifies the bubble stretching, being the ratio of the linear velocity of the pulling rolls and the linear extrusion velocity. The combined effect of these two ratios results in an oriented and anisotropic film. For this reason, it is imperative that its properties are measured in both machine direction (MD) and transverse direction (TD), shown in Figure 2-1 [42, 43].

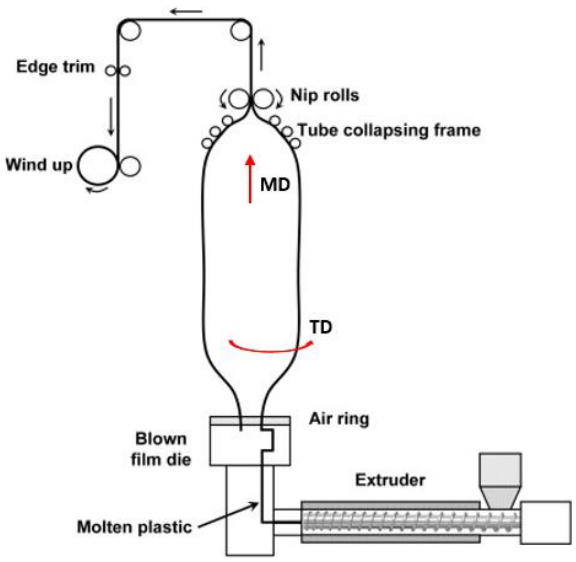


Figure 2-1 Blown film extrusion [43].

The molten plastic is cooled at the die exit through forced air convection around its perimeter [42]. Polyethylene, namely LDPE, LLDPE and High-density polyethylene (HDPE), is the most common polymer used in this extrusion technique [16, 43]. To guarantee the stability of the process, uniform temperature, suitable polymers (ideally with low melt flow rates and high

extensional viscosity or melt strength), high control of the cooling air flow and temperature, and high control of the inflated air flow are required. Bubble stability is crucial for producing films with constant thickness and width throughout the process [44].

Blown film co-extrusion is a method that allows the production of multilayer films. This process involves the use of several extruders (at least, one per material) that feed a single extrusion head. The materials are fed to independent flow channels, one for each of the layers, which join a short distance upstream of the die exit. In this way, a single film composed by several individual layers is produced. This method is widely used in the food packaging film industry, which is highly demanding, particularly with regard to mechanical, barrier and thermal properties, where specific requirements for food packaging are impossible to satisfy with a single material [45]. In Figures 2-2 and 2-3 it is possible to observe the two configurations available for films production with a stackable flat plate blown film die. This die was specifically developed for the current research, in cooperation with a Portuguese company (Periplast). The ABA configuration produces a film with only two materials but three layers, using a single extruder to pump material into the two outer layers of the extrusion head; the ABC configuration allows the production of three-layer films, using three different materials.

Figure 2-2 Schematic of the extruder's layout corresponding to the ABA film configuration

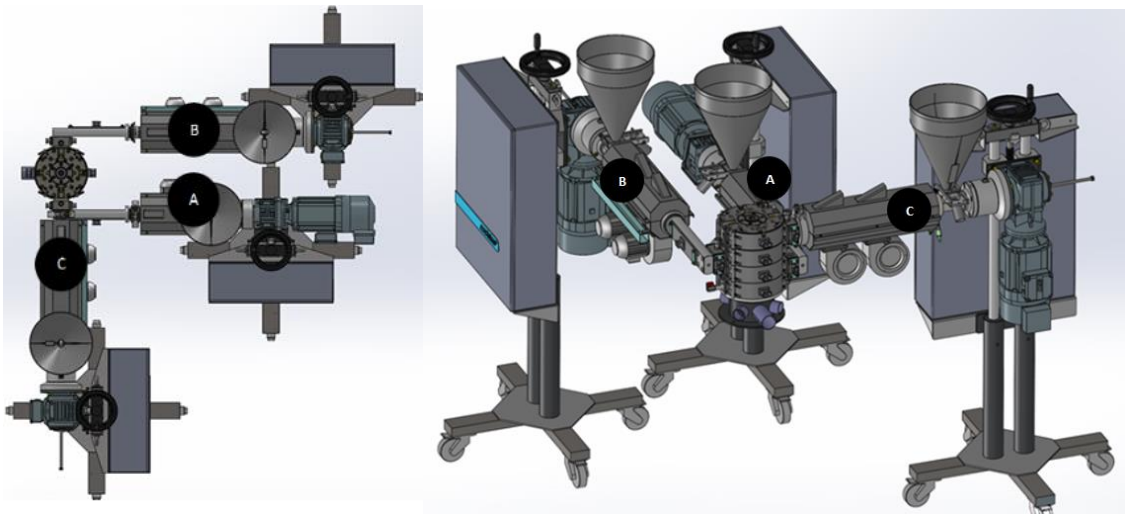


Figure 2-3 Schematic of the extruder's layout corresponding to the ABC film configuration

In industrial film production, blown film extrusion lines usually comprise 4 to 9 extruders, and the inflated bubble can reach a height of 15 meters, or more, to produce multilayer films with an end thickness of 50 to 200 μm. A line with 4 extruders typically produces a film with 7 layers and symmetrical structure (ABCDCBA), which can have a combination of up to 4 different polymers, with layer C typically being an adhesive required to join incompatible polymers from layers B (e.g., LDPE) and D (e.g., EVOH) [44].

In some cases, multilayer films are not exclusively produced by blown film co-extrusion. In fact, lamination techniques can also be used to join films produced by blown film extrusion, LDPE or PP, and cast film extrusion, as is the case with PET. Due to its inherent low melt viscosity and poor melt strength, PET is not a suitable material for blown film extrusion [46]. Normally, this material is laminated with other films, which adds another step in the packaging production. This drawback does not prevent producers from using PET as it provides excellent properties to food packaging, as already mentioned.

Since processes such as co-extrusion and film lamination make it difficult, or even impossible, to recycle each of the materials present in packaging, the development of new solutions for reducing the number or the number of different materials present in a packaging becomes urgent.

2.3 LDPE and EVOH nanocomposites for food packaging

Polymeric nanocomposites are solid composites consisting of a continuous polymeric base phase and one or more dispersed phases at the nanometric scale. The materials present in the

dispersed phase are on the nanometric scale when their size with one, two or three external dimensions, comprises dimensions of approximately 1 nm to 100 nm. Nanoplates have one nanometric dimension, nanofibers have two and nanoparticles have three [47]. According to the literature, polymeric nanocomposites with a good dispersion and distribution of nanoparticles, exhibit better thermal, mechanical, barrier and optical properties when compared to the base polymer and to composites produced with microscale particles, even with the incorporation of low percentages of nanoparticles [48–50].

The amount, by weight, of nanomaterials incorporated into nanocomposites is generally less than 10 %, unlike conventional composites where the incorporation of micromaterials can reach 50 % of the total composite weight [51]. The enormous difference in size between microparticles and nanoparticles confers drastic changes in the physical properties of these composite materials. Since the ratio between surface area and volume is inversely proportional to the diameter of the particle, the smaller the diameter, the greater the ratio between surface area and volume, increasing the interaction between the particle surface and the matrix [52, 53]. The use of nanoparticles instead of microparticles results in an increase of approximately three orders of magnitude in the ratio between surface area and volume [53].

The incorporation of low weight percentages of nanomaterials into a polymeric matrix can improve the properties of the virgin polymer without affecting its processing [50]. For the nanomaterials being effective, they must be well dispersed and distributed into the polymer matrix. Poor dispersion and distribution can lead to the formation of aggregates, which can act as defects. Due to the strong bonds existing between the particles that form the aggregate, such as covalent ones, the surface area in contact with the matrix is significantly lower than the sum of the area of each nanoparticle [54]. Good dispersion promotes the required increase in the contact area between the nanomaterial and the polymer matrix [50]. The distribution of the nanomaterial in the matrix is related to the homogeneity of the nanocomposite, while dispersion is associated with the level of agglomeration [54].

Several studies can be found on the incorporation of nanoparticles into LDPE or EVOH matrices, with the aim of improving the properties of these polymers for use in food packaging [55–57].

Due to their low water vapor permeability, polyolefins are often used in packaging for the food industry. As these materials have a hydrophobic nature, their interaction with the surface of hydrophilic nanomaterials is weak, which presents a major difficulty in the production of

nanocomposites by melt mixing (extrusion). This weak interaction does not allow the destruction of nanoparticles aggregates and agglomerates, despite the high shear forces applied to the molten material during processing [58]. On the other hand, the production of EVOH nanocomposites requires the use of lower amounts of compatibilizers, as the matrix is made up of polar segments, vinyl alcohol, and non-polar segments, ethylene [16, 59-61]. For example, in the case of cellulose nanoparticles, the hydrophilicity of the EVOH vinyl alcohol promotes the compatibility by the formation of hydrogen bridges with the -OH groups of these nanoparticles [61].

The use of chemical or physical methods can improve the quality of the dispersion in the nanocomposite. Chemical treatment of the nanoparticles surface can improve nanoparticle-matrix compatibility, thus promoting better dispersion of the nanoparticles [49]. Surface treatment can be carried out through chemical corrosion (treatment with NaOH), chemical grafting, treatment with UV radiation, and corona discharge, among others. The most commonly used methods include treatment with silane agents and grafting maleic anhydride onto the surface of a thermoplastic [62]. Polyethylene grafted with maleic anhydride, PE-g-MA, is a compatibilizer widely used to improve the interaction between the polar surface of the nanomaterial and the non-polar surface of the matrix [63]. Physical methods can also improve the dispersion of nanomaterials in the matrix through ultrasound vibrations and mechanical methods such as extrusion processing [49].

To improve the properties of plastic films, various nanoparticles have been studied. SiO_2 nanoparticles, NC, CNC and calcium carbonate ($CaCO_3$) nanoparticles, among others, are currently used in packaging to improve antimicrobial activity, improve mechanical properties, reduce oxygen and water vapor permeability and, in certain cases, reduce the price of the raw material [64–66]. These nanoparticles, with the exception of CNC and $CaCO_3$, are approved by the European Union in regulation (EU) no. 10/2011, as being safe for food applications [67]. Although cellulose and $CaCO_3$ have been approved by the FDA as generally regarded as safe substances (GRAS), and by the EU as approved for use in plastic as Food Contact Materials (FCM), their nanoforms are not, due to different chemical characteristics such as particle size, crystalline structures, shape and surface charge [68].

2.3.1 SiO_2 nanocomposites

Nano-SiO_2 particles can be used in flexible food packaging to improve barrier, antimicrobial and mechanical properties. SiO_2, as talc, are widely used as anti-blocking additives in LDPE and

PP matrices [69]. These particles roughen the film surface, preventing adhesion between two plastic films in contact. This facilitates the opening of supermarket fruit bags, or unwinding plastic film reels, for example. To promote the interaction between the matrix and silica, the nano-SiO_2 surface can be modified through chemical or physical methods [70]. Tests carried out on LLDPE nanocomposite films with nano-SiO_2, with and without surface treatment with vinyltrimethoxysilane, show that the LLDPE nanocomposite with 1 wt.% nano-SiO_2 with surface treatment shows an increase in tensile strength and Young's modulus when compared to pure LLDPE and to LLDPE with 1 wt.% nano-SiO_2 without surface treatment [71]. In addition to this surface treatment, maleic anhydride can also be used as a compatibilizer agent between the silica and the polymer matrix [72]. Also, the study by Ji Hun Jang et. al. (2019) found that incorporating 5 wt.% UV-treated SiO_2 into an EVOH matrix improved the WVTR of this polymer from 4.72×10^{-2} to 1.55×10^{-2} g/m²·day [73]. It was found that incorporating amounts of nano-SiO_2 greater than 2 wt.% into the EVOH matrix does not significantly increase the tensile strength, but the moisture permeability decreases considerably with the incorporation of 5 wt.% nano-SiO_2 [60].

2.3.2 NC nanocomposites

NC are silico-aluminate layers in the form of stacked platelets that can be bound by Van der Waals forces, for kaolite and montmorillonite NC cases, or by potassium ions, for the ilite NC case [74]. NC nanocomposites have attracted interest in the academic and industrial communities due to their superior mechanical, thermal and barrier properties when compared to pure polymer or micro-composites. Despite the advantages associated with NC, it is quite difficult to obtain nanocomposites with an ideal surface for adhesion between nanoparticles and non-polar polymers, as is the case of the PE matrix [64]. Poor dispersion and distribution of nanoparticles in the matrix can compromise the large surface area of the nanoparticles, leading to the appearance of defects and consequent limitation of the nanocomposite properties [75]. To obtain a nanocomposite with well-dispersed NC, the polymer needs to penetrate the stacked platelets in order to increase the interlayer distance, allowing for NC exfoliation. This penetration only occurs when the polymer and NC are compatible. To improve this interaction, the surface of the clay layers can be organic modified to make them more organophilic, improving their compatibility with organic thermoplastics [76]. This modification can be done with quaternary alkylammonium salts, the most used organic modifier [77]. The use of organoclays in the polymer matrix enhances clay

dispersibility and allows superior mechanical, thermal and barrier properties with low NC incorporation [64, 78]. Several studies also proved that the use of a polyolefin modified with maleic anhydride as a compatibilizer improves the dispersion of NC, improving the tensile strength of nanocomposite films and reducing their oxygen permeability [79, 80]. To promote excellent dispersion and distribution, these two solutions can be combined.

Investigations carried out on the effect of NC on the properties of LDPE nanocomposites show that the incorporation of 1 to 7 wt.% is sufficient to reduce the permeability to O_2 and to increase the tensile strength of the films [79]. Several papers address the production of masterbatch with a high percentage of NC for later dilution in the base polymer during processing by blown film extrusion, reducing the time and costs of producing the raw material for these films [81, 82]. It is also verified that the increase in wt.% of compatibilizer, PE-g-MA, improves the dispersion of NC in the LDPE-based nanocomposite [79]. When NC are incorporated into an EVOH matrix, a decrease in permeability to O_2 and water vapor, and an increase in glass transition temperature (T_g), melting temperature (T_m), and percentage of crystallinity (X_m) is observed [59, 83–85]. Although increasing the incorporation rate of NC in the EVOH matrix improves the permeability and thermal stability of the nanocomposite, above 5 % it reduces the film transparency, which is an important characteristic in food packaging [57].

2.3.3 CNC and MCC composites

Bio-based cellulose nanomaterials, such as CNC and cellulose nanofibrils, have been widely studied as desirable and sustainable reinforcements for nanocomposite materials, due to their high mechanical performance [86]. CNC dispersion, like that of nanoparticles previously discussed, is a challenge [87]. Several studies confirm that dispersion can be improved through the use of a compatibilizer [65, 88]. Nanocomposites com with only 1 wt.% CNC, and 1.7 wt.% PE-g-MA as compatibilizer, show higher tensile strength and elastic modulus when compared to the base polymer and nanocomposites with CNC without compatibilizer. This combination is also advantageous for reducing water vapor permeability [65, 88].

The same was proven in EVOH based nanocomposites, where the incorporation of 1 wt.% of NCC allows to obtain a 71 % decrease in the water vapor transmission rate and an increase in T_g, T_m, X_m, and mechanical properties in relation to the pure EVOH film [89].

Recent investigations compare EVOH composites produced with MCC and NCC and evaluate the effect of the shear forces, during the production of the composites by extrusion, on the distribution of micro and nanoparticles. EVOH micro-composites with 5 and 15 wt.% MCC prepared with a high shear rate screw configuration show better mechanical and thermal properties than those produced with a lower shear rate screw configuration [61]. The properties of the micro-composite with 5 wt.% MCC are similar to those of that with the same NCC incorporation rate [61]. Therefore, the incorporation of MCC into a polymeric matrix can be a low-cost alternative to the use of NCC.

2.3.4 Other nanocomposites

In addition to SiO_2, the incorporation of metal oxides, such as zinc oxide (ZnO) and magnesium oxide (MgO), have been studied, due to their potential in packaging materials, as they act as antibacterial agents and UV radiation blockers [66, 90]. ZnO nanoparticles exhibit low toxicity, good antibacterial and antioxidant activity, and UV absorption capacity. Several studies present good results in relation to antibacterial activity, showing a decrease in bacterial activity with increasing incorporation rates in nanocomposites with HDPE, LDPE or PA matrices [91, 92].

MgO is a crystalline mineral that can be economically produced on a large scale. Given that MgO nanoparticles have good barrier properties, antimicrobial activity, are low in cost, and improve the mechanical performance of the polymeric matrix film, it is reasonable to conclude that their inclusion in the development of new packaging films should be considered [66]. Despite the investigations carried out to study MgO nanoparticles, there is still little information available about their use in plastic films for food packaging.

Although ZnO and MgO particles are referred to in regulation No. (EU) 10/2011 as substances used as additive or polymer production aid as FCM, their nanoform is not suitable for incorporation as an additive in polymers. However, these particles can still be submitted for approval, regarding the EU commission guidelines.

Luo, Wang, Jiang and Xu (2015) presented a study on the effect of calcium carbonate nanoparticles ($CaCO_3$) dispersed in a LDPE matrix on the quality and browning of freshly cut Chinese yams. The results were very positive as the LDPE packaging with nano-$CaCO_3$ was effective in slowing down the total bacterial, yeast and mold count, inhibiting ethylene production, and delaying the reduction of titratable acid and ascorbic acid in fresh-cut yam, during storage at 10°C.

These results showed a delay in the browning of the food, increasing the shelf life of Chinese yams by two days [93].

Despite the advantages of the aforementioned nanoparticles, their dispersion in a polymer matrix presents a challenge. As already mentioned, maleic anhydride grafted onto the surface of the thermoplastic is a compatibilizer frequently used to address this issue [62].

2.4 Incorporation of recycled plastic in new products

In addition to the incorporation of nanoparticles as a strategy to reduce the number of different materials used in the production of a packaging film, with a view to improve its recyclability, the incorporation of recycled plastics plays an important role in reducing the consumption of virgin polymers from non-renewable sources, thus also contributing to the sustainability of packaging. The incorporation of nanoparticles and the utilization of recycled plastic in food packaging are different but complementary approaches to a circular economy, where materials are reused, recycled, and repurposed, creating a more sustainable and closed-loop system.

The use of plastic packaging waste through recycling allows for a reduction in the negative effects of plastic waste on the environment, or for the negative effects of its incineration. To this end, several studies have been carried out to evaluate the properties of plastic films incorporating different percentages of recycled material, in order to ensure that the quality of packaging for the food industry is maintained. In Chytiri, et. al. (2005) study, the introduction of different percentages of recycled material (50% and 100%) in the inner layer (corresponding to 50 wt.% of the multilayer structure) of a five-layer LDPE and LLDPE film did not change the mechanical properties of the film. This study concludes that LDPE scrap may be used in multilayer structures as a middle-buried layer without any significant decline on the mechanical, thermal and permeation properties [94].

Komorowsha et al. (2018) compared the mechanical properties of films made from recycled LDPE/LLDPE blends from post-consumer waste, with LDPE and LLDPE virgin polymers. The waste collected was mainly from packaging films (bags, wraps, stretch film) and agricultural films. The recycled films showed very promising results, with some samples obtaining significantly higher strength and elongation at break values when compared to virgin polymers. Another important result of this study is the fact that these recycled materials showed good processing properties liable to produce thin films [95].

Several studies also refer to the use of maleic anhydride compatibilizer, typically in percentages of 5 and 7 wt.%, to improve the adhesion between incompatible polymers when recycling post-industrial packaging waste from multilayer films [96, 97].

In an attempt to evaluate the effects of thermomechanical recycling, several studies have been conducted on the reprocessing, by extrusion, of various polymers and composites, evaluating the properties along the number of reprocessing cycles [98, 99]. Despite the lack of studies on the repeated reprocessing of recycled materials containing different polymers, studies on this strategy can be beneficial for the industry and environment. This will enable the recovery of leftovers and scraps from industrial films. However, it will be necessary to determine the maximum number of processing cycles without loss of properties.

2.5 Conclusions

The literature review presented confirms the potential of innovation in this area, by replacing the currently used non-recyclable packaging in the market with more sustainable alternatives. This can be achieved either through the incorporation of nanoparticles or the use of recycled materials in food packaging. However, these strategies present concerns regarding food safety. To mitigate these concerns, it is necessary that investigations carried out in the area of food contact materials meet the requirements regulated by the FDA and EU Commission. While studies may yield innovative results, their practical applicability hinges on compliance with these regulations. Scientific knowledge should, therefore, facilitate the advancement of the industry.

In addition to regulatory considerations, studies involving the production of prototypes with non-industrial techniques, while promising, may not be suitable for industrial scale-up. There are a huge number of variables associated with the different industrial processes and the characteristics of each material are different according to the processing technique used. Therefore, studies must seek to produce and test samples under similar conditions to those used in industrial processes.

Even taking into account regulations and the industrial process, it is necessary to adjust processing parameters, nanocomposite formulations, percentage of recycled material and the multilayer structure in order to obtain a homogeneous product with innovative characteristics.

Regarding recycled materials, the studies mentioned demonstrate that there is a huge potential for using recycled material without necessarily damaging the properties of the films when compared to the virgin raw materials (LDPE, LLDPE). Few studies refer to the reprocessing of

recycled materials, making it necessary to study the possibility of recycling multilayer/multi-material flexible films and their continued reincorporation into the production system without significant loss of properties.

Therefore, research concerning the incorporation and dispersion of nanoparticles in polymeric matrices and the use of recycled plastic films, as a total or partial constituent of multilayer films, is still relevant.

2.6 References

[1] Plastics Europe, "Plastics – the Facts 2020 An analysis of European plastics production, demand and waste data," Accessed March 15, 2022. [Online]. Available: https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts-2020

[2] Plastics Europe, "Plastics - the Facts 2021 An analysis of European plastics production, demand and waste data," Accessed February 14, 2022, 2021.

[3] Plastics Europe, "Plastics - the Facts 2022," 2022. Accessed: Sep. 28, 2023. [Online]. Available: https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/

[4] R. Geyer, J. R. Jambeck, and K. L. Law, "Production, use, and fate of all plastics ever made," Sci Adv, vol. 3, no. 7, pp. 25–29, 2017, doi: 10.1126/sciadv.1700782.

[5] P. Dhar, U. Bhardwaj, A. Kumar, and V. Katiyar, "Cellulose nanocrystals: A potential nanofiller for food packaging applications," ACS Symposium Series, vol. 1162, pp. 197–239, 2014, doi: 10.1021/bk-2014-1162.ch017.

[6] A. Kausar, "A review of high performance polymer nanocomposites for packaging applications in electronics and food industries," Journal of Plastic Film and Sheeting, vol. 36, no. 1, pp. 94–112, 2020, doi: 10.1177/8756087919849459.

[7] R. Sharma, S. M. Jafari, and S. Sharma, "Antimicrobial bio-nanocomposites and their potential applications in food packaging," Food Control, vol. 112, no. January, p. 107086, 2020, doi: 10.1016/j.foodcont.2020.107086.

[8] M. Tanahashi, "Development of Fabrication Methods of Filler/Polymer Nanocomposites: With Focus on Simple Melt-Compounding Based Approach without Surface Modification of Nanofillers," Materials, vol. 3, pp. 1593–1619, 2010, doi: doi:10.3390/ma3031593.

[9] J. W. Han, L. Ruiz-Garcia, J. P. Qian, and X. T. Yang, "Food Packaging: A Comprehensive Review and Future Trends," Compr Rev Food Sci Food Saf, vol. 17, no. 4, pp. 860–877, 2018, doi: 10.1111/1541-4337.12343.

[10] T. Janjarasskul and P. Suppakul, “Active and intelligent packaging: The indication of quality and safety,” Crit Rev Food Sci Nutr, vol. 58, no. 5, pp. 808–831, 2018, doi: 10.1080/10408398.2016.1225278.

[11] Comissão Europeia, “Regulamento (CE) N. o 450/2009 da Comissão de 29 de Maio de 2009 relativo aos materiais e objectos activos e inteligentes destinados a entrar em contacto com os alimentos,” 2009.

[12] E. Young, M. Mirosa, and P. Bremer, “A systematic review of consumer perceptions of smart packaging technologies for food,” Front Sustain Food Syst, vol. 4, pp. 1–20, 2020, doi: 10.3389/fsufs.2020.00063.

[13] EFSA, “Active and intelligent packaging substances,” Acedido Maio 13, 2021. [Online]. Available: https://www.efsa.europa.eu/en/topics/topic/active-and-intelligent-packaging-substances

[14] R. Domínguez et al., “Active packaging films with natural antioxidants to be used in meat industry: A review,” Food Research International, vol. 113, pp. 93–101, 2018, doi: 10.1016/j.foodres.2018.06.073.

[15] H. Almasi, M. J. Oskouie, and A. Saleh, “A review on techniques utilized for design of controlled release food active packaging,” Crit Rev Food Sci Nutr, pp. 1–21, 2020, doi: 10.1080/10408398.2020.1783199.

[16] J. R. Wagner, “Blown Film, Cast Film, and Lamination Processes.,” in Multilayer Flexible Packaging: Second Edition, Elsevier Inc., 2016, pp. 137–145. doi: 10.1016/B978-0-323-37100-1.00010-7.

[17] C. Coben and E. Sancaktar, “Use of Pyrolyzed Soybean Hulls as Fillers in Polypropylene and Linear Low Density Polyethylene,” Sustainable Chemistry, vol. 2, no. 4, pp. 622–644, Nov. 2021, doi: 10.3390/suschem2040035.

[18] M. Y. Kondo et al., “Recent advances in the use of Polyamide-based materials for the automotive industry,” Polímeros, vol. 32, no. 2, 2022, doi: 10.1590/0104-1428.20220042.

[19] V. Venoor, J. H. Park, D. O. Kazmer, and M. J. Sobkowicz, “Understanding the Effect of Water in Polyamides: A Review,” Polymer Reviews, vol. 61, no. 3. Taylor and Francis Ltd., pp. 598–645, 2021. doi: 10.1080/15583724.2020.1855196.

[20] Q. Deshoulles, M. le Gall, C. Dreanno, M. Arhant, D. Priour, and P. Y. le Gac, “Modelling pure polyamide 6 hydrolysis: Influence of water content in the amorphous phase,” Polym Degrad Stab, vol. 183, Jan. 2021, doi: 10.1016/j.polymdegradstab.2020.109435.

[21] K. singh Randhawa, “Hygroscopic behaviour analysis of biocompatible PA6 and PA6 composites containing oxide and nitride compounds of boron,” Ceram Int, vol. 48, no. 19, pp. 29340–29348, Oct. 2022, doi: 10.1016/j.ceramint.2022.05.370.

[22] R. Nisticò, “Polyethylene terephthalate (PET) in the packaging industry,” Polym Test, vol. 90, p. 106707, Oct. 2020, doi: 10.1016/j.polymertesting.2020.106707.

[23] B. A. Morris, “Commonly Used Resins and Substrates in Flexible Packaging,” in The Science and Technology of Flexible Packaging, Elsevier, 2017, pp. 69–119. doi: 10.1016/B978-0-323-24273-8.00004-6.

[24] A. Emblem, “Plastics properties for packaging materials,” in Packaging Technology, Elsevier, 2012, pp. 287–309. doi: 10.1533/9780857095701.2.287.

[25] Axel Pilgrim, Michael Frank, and Robert W. Fuss, “WO2008037764A1 - Use of water-soluble polyvinyl alcohol as an adhesive for plastic labels,” 2008 Accessed: Oct. 01, 2023. [Online]. Available: https://patents.google.com/patent/WO2008037764A1/en

[26] Aquapak, “About Hydropol.” Accessed: Oct. 01, 2023. [Online]. Available: https://www.aquapakpolymers.com/hydropol/

[27] L. Bastarrachea, S. Dhawan, and S. S. Sablani, “Engineering Properties of Polymeric-Based Antimicrobial Films for Food Packaging: A Review,” Food Engineering Reviews, vol. 3, no. 2, pp. 79–93, Jun. 2011, doi: 10.1007/s12393-011-9034-8.

[28] J.-M. Lagarón, “Multifunctional and nanoreinforced polymers for food packaging,” in Multifunctional and Nanoreinforced Polymers for Food Packaging, Elsevier, 2011, pp. 1–28. doi: 10.1533/9780857092786.1.

[29] M. Elhamnia, G. H. Motlagh, and S. H. Jafari, “Improved barrier properties of biodegradable <scp>PBAT</scp> films for packaging applications using <scp>EVOH</scp> : Morphology, permeability, biodegradation, and mechanical properties,” J Appl Polym Sci, vol. 140, no. 20, May 2023, doi: 10.1002/app.53855.

[30] F. Guisheng, L. Incarnate, L. Di Maio, and D. Acierno, “Discussion about the use of relative values of permeabilities between two gases for high molecular weight polymers,” 1995.

[31] O. Piringer, “Permeation of gases, water vapor and volatile organic compounds,” in Plastic Packaging Materials for Food, Wiley, 2000, pp. 239–285. doi: 10.1002/9783527613281.ch09.

[32] Liesl K. Massey, Film Properties of Plastics and Elastomers, 2nd edn. Norwich: Plastic design library, 2004.

[33] J. Lange and Y. Wyser, “Recent innovations in barrier technologies for plastic packaging?a review,” Packaging Technology and Science, vol. 16, no. 4, pp. 149–158, Jul. 2003, doi: 10.1002/pts.621.

[34] Plastics Design Library, Permeability and Other Film Properties of Plastics and Elastomers PDL Handbook Series. New York, 1995.

[35] Giannakas, Salmas, Leontiou, Tsimogiannis, Oreopoulou, and Braouhli, “Novel LDPE/Chitosan Rosemary and Melissa Extract Nanostructured Active Packaging Films,” Nanomaterials, vol. 9, no. 8, p. 1105, Aug. 2019, doi: 10.3390/nano9081105.

[36] F. Wu, M. Misra, and A. K. Mohanty, “Challenges and new opportunities on barrier performance of biodegradable polymers for sustainable packaging,” Prog Polym Sci, vol. 117, 2021, doi: 10.1016/j.progpolymsci.2021.101395.

[37] L. Kurarry Co., “EVAL TM Technical Brochure.” Accessed: Oct. 02, 2023. [Online]. Available: https://evalevoh.com/en/about-eval/brochures.aspx

[38] L. Marangoni Júnior, R. M. V. Alves, C. Q. Moreira, M. Cristianini, M. Padula, and C. A. R. Anjos, “High-pressure processing effects on the barrier properties of flexible packaging materials,” J Food Process Preserv, vol. 44, no. 11, Nov. 2020, doi: 10.1111/jfpp.14865.

[39] K. Kaiser, M. Schmid, and M. Schlummer, “Recycling of Polymer-Based Multilayer Packaging: A Review,” Recycling, vol. 3, no. 1, p. 1, Dec. 2017, doi: 10.3390/recycling3010001.

[40] T. Anukiruthika, P. Sethupathy, A. Wilson, K. Kashampur, J. A. Moses, and C. Anandharamakrishnan, “Multilayer packaging: Advances in preparation techniques and emerging food applications,” Compr Rev Food Sci Food Saf, vol. 19, no. 3, pp. 1156–1186, 2020, doi: 10.1111/1541-4337.12556.

[41] K. Kaiser, M. Schmid, and M. Schlummer, “Recycling of polymer-based multilayer packaging: A review,” Recycling, vol. 3, no. 1, 2017, doi: 10.3390/recycling3010001.

[42] L. W. McKeen, “Production of Films, Containers, and Membranes,” in Permeability Properties of Plastics and Elastomers (Fourth Edition), S. Holt, Ed., Matthew Deans, 2017, pp. 41–60. doi: 10.1016/b978-0-323-50859-9.00003-8.

[43] J.Vlachopoulos, R. Castillo, N. Polychronopoulos, and S. Tanifuji, “ Blown Film Dies,” in Design of Extrusion Forming Tools, O. S. Carneiro and M. Nobrega, Eds., London, 2012, pp. 141–168.

[44] J. R. Wagner, E. M. Mount, and H. F. Giles, “Blown Film,” in Extrusion, Elsevier, 2014, pp. 539–549. doi: 10.1016/B978-1-4377-3481-2.00046-6.

[45] M. Hyvärinen, R. Jabeen, and T. Kärki, “The modelling of extrusion processes for polymers-A review,” Polymers (Basel), vol. 12, no. 6, 2020, doi: 10.3390/polym12061306.

[46] M. Härth and A. Dörnhöfer, “Film Blowing of Linear and Long-Chain Branched Poly(ethylene terephthalate),” Polymers (Basel), vol. 12, no. 7, p. 1605, Jul. 2020, doi: 10.3390/polym12071605.

[47] International Organization for Standardization (ISO), “ISO/TS 80004-4 Nanotechnologies — Vocabulary — Part 4: Nanostructured materials,” Acedido maio 13, 2021. Accessed: May 14, 2021. [Online]. Available: https://www.iso.org/obp/ui/fr/#iso:std:iso:ts:80004:-4:ed-1:v1:en

[48] M. Alexandre and P. Dubois, “Polymer-layered silicate nanocomposites: preparation , properties and uses of a new class of materials,” Materials Science and Engineering, Reports: A Review Journal, vol. 28, pp. 1–63, 2000.

[49] K. Müller et al., “Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields,” Nanomaterials, vol. 7, no. 74, p. 47, 2017, doi: 10.3390/nano7040074.

[50] A. D. de Oliveira and C. A. G. Beatrice, “Polymer Nanocomposites with Different Types of Nanofiller,” in Nanocomposites - Recent Evolutions, 2018, pp. 103–128. doi: 10.5772/intechopen.81329.

[51] I. Pleşa, P. V. Noţingher, S. Schlögl, C. Sumereder, and M. Muhr, “Properties of polymer composites used in high-voltage applications,” Polymers (Basel), vol. 8, no. 173, p. 63, 2016, doi: 10.3390/polym8050173.

[52] A. B. Asha and R. Narain, “Nanomaterials properties,” in Polymer Science and Nanotechnology, Edmonton: Elsevier Inc., 2020, pp. 343–359. doi: 10.1016/B978-0-12-816806-6.00015-7.

[53] F. Hussain, M. Hojjati, M. Okamoto, and R. E. Gorga, “Review article: Polymer-matrix nanocomposites, processing, manufacturing, and application: An overview,” J Compos Mater, vol. 40, no. 17, pp. 1511–1575, 2006, doi: 10.1177/0021998306067321.

[54] International Organization for Standardization (ISO), “ISO/TS 80004-2:2015(en) Nanotechnologies — Vocabulary — Part 2: Nano-objects,” Acedido maio 13, 2021. [Online]. Available: https://www.iso.org/obp/ui/#iso:std:iso:ts:80004:-2:ed-1:v1:en

[55] M. Nuruddin, J. Hamlin, C. M. Clarkson, A. J. Howarter, C. R. Szczepanski, and J. P. Youngblood, “Processing and Characterization of Food-Grade Plasticizer-Compatibilized Cellulose

Nanocrystals and Ethylene Vinyl Alcohol Copolymer Nanocomposites," Applied Polymer Materials, vol. 3, no. 10, pp. 5000–5011, 2021, doi: https://doi.org/10.1021/acsapm.1c00756.

[56] S. Seethamraju, P. C. Ramamurthy, and G. Madras, "Flexible poly(vinyl alcohol-co-ethylene)/modified MMT moisture barrier composite for encapsulating organic devices," The Royal Society of Chemistry, vol. 3, pp. 12831–12838, 2013.

[57] S. W. Kim and S. H. Cha, "Thermal, Mechanical, and Gas Barrier Properties of Ethylene–Vinyl Alcohol Copolymer-Based Nanocomposites for Food Packaging Films: Effects of Nanoclay Loading," Applied Polymer Science, p. 8, 2013.

[58] F. R. Passador, D. R. Travain, E. H. Backes, A. C. R. Filho, and L. A. Pessan, "Nanocompósitos de Blendas HDPE / LLDPE e OMMT – Parte II : Avaliação das Propriedades Térmica , Óticas e de Transporte a Gases," Polímeros, vol. 23, no. 6, pp. 748–757, 2013.

[59] M. Rahnama, A. Oromiehie, S. Ahmadi, and I. Ghasemi, "Effect of different blend compositions on properties of low-density polyethylene/ethylene vinyl alcohol/clay toward high oxygen barrier nanocomposite films," Polymer Science - Series A, vol. 59, no. 4, pp. 533–542, 2017, doi: 10.1134/S0965545X1704006X.

[60] Y. Liu, Y. Liu, and S. Wei, "Processing technologies of EVOH/nano-SiO2 high-barrier packaging composites," 17th IAPRI World Conference on Packaging 2010, pp. 269–274, 2010.

[61] G. Graninger, S. Kumar, G. Garrett, and B. G. Falzon, "Effect of shear forces on dispersion-related properties of microcrystalline cellulose-reinforced EVOH composites for advanced applications," Compos Part A Appl Sci Manuf, vol. 139, no. August, p. 106103, 2020, doi: 10.1016/j.compositesa.2020.106103.

[62] T. Nanda, K. Singh, D. Shelly, and R. Mehta, "Advancements in multi-scale filler reinforced epoxy nanocomposites for improved impact strength: A review," Critical Reviews in Solid State and Materials Sciences, p. 49, 2020, doi: 10.1080/10408436.2020.1777934.

[63] A. Mengual, D. Juárez, R. Balart, and S. Ferrándiz, "PE-g-MA, PP-g-MA and SEBS-g-MA compatibilizers used in material blends," Procedia Manuf, vol. 13, pp. 321–326, 2017, doi: 10.1016/j.promfg.2017.09.083.

[64] A. Durmus, M. Woo, A. Kasgoz, C. Macosko, and M. Tsapatsis, "Intercalated linear low density polyethylene (LLDPE)/ clay nanocomposites prepared with oxidized polyethylene as a new type compatibilizer : Structural , mechanical and barrier properties," Eur Polym J, vol. 43, pp. 3737–3749, 2007, doi: 10.1016/j.eurpolymj.2007.06.019.

[65] A. Kaboorani, N. Gray, Y. Hamzeh, A. Abdulkhani, and Y. Shirmohammadli, "Tailoring the low-density polyethylene - thermoplastic starch composites using cellulose nanocrystals and compatibilizer," Polym Test, vol. 93, p. 11, 2020, doi: 10.1016/j.polymertesting.2020.107007.

[66] C. Swaroop and M. Shukla, "Nano-magnesium oxide reinforced polylactic acid biofilms for food packaging applications," Int J Biol Macromol, vol. 113, pp. 729–736, 2018, doi: 10.1016/j.ijbiomac.2018.02.156.

[67] Comissão Europeia, "Regulamento (UE) N.o 10/2011 da Comissão de 14 de janeiro de 2011 relativo aos materiais e objectos de matéria plástica destinados a entrar em contacto com os alimentos," 2011.

[68] S. Huang, X. Liu, C. Chang, and Y. Wang, "Recent developments and prospective food-related applications of cellulose nanocrystals: a review," Cellulose, vol. 27, no. 6, pp. 2991–3011, 2020, doi: 10.1007/s10570-020-02984-3.

[69] J. Markarian, "Slip and antiblock additives: surface medication for film and sheet," Plastics, Additives and Compounding, vol. 9, no. 6, pp. 32–35, Nov. 2007, doi: 10.1016/S1464-391X(07)70156-3.

[70] M. Conradi, "Nanosilica-reinforced polymer composites," Materiali in Tehnologije, vol. 47, no. 3, pp. 285–293, 2013.

[71] S. Thanakkasaranee, A. Pradittham, D. Atong, and C. Pechyen, "Effect of nano-silica loading on barrier and mechanical properties of food packaging based LLDPE film," Adv Mat Res, vol. 488–489, pp. 919–922, 2012, doi: 10.4028/www.scientific.net/AMR.488-489.919.

[72] L. J. Silva, J. C. Campos Rubio, T. H. Panzera, and P. H. R. Borges, "The effect of silica microparticles and maleic anhydride on the physic-Mechanical properties of epoxy matrix phase," Science and Engineering of Composite Materials, vol. 20, no. 3, pp. 203–208, 2013, doi: 10.1515/secm-2012-0088.

[73] J. H. Jang et al., "A Novel Approach for the Development of Moisture Encapsulation Poly(vinyl alcohol- co -ethylene) for Perovskite Solar Cells," ACS Omega, vol. 4, no. 5, pp. 9211–9218, May 2019, doi: 10.1021/acsomega.9b00350.

[74] X. Chen and Y. Peng, "Managing clay minerals in froth flotation—A critical review," Mineral Processing and Extractive Metallurgy Review, vol. 39, no. 5, pp. 289–307, 2018, doi: 10.1080/08827508.2018.1433175.

[75] L. S. Schadler, "Polymer-based and Polymer-filled Nanocomposites," in Nanocomposite Science and Technology, 2003, pp. 77–144. doi: https://doi.org/10.1002/3527602127.ch2.

[76] N. Bumbudsanpharoke and S. Ko, “Nanoclays in Food and Beverage Packaging,” J Nanomater, p. 13, 2019, doi: https://doi.org/10.1155/2019/8927167.

[77] S. Joshi, “Can nanotechnology improve the sustainability of biobased products? The case of layered silicate biopolymer nanocomposites,” J Ind Ecol, vol. 12, no. 3, pp. 474–489, 2008, doi: 10.1111/j.1530-9290.2008.00039.x.

[78] S. C. Carroccio, P. Scarfato, E. Bruno, P. Aprea, N. T. Dintcheva, and G. Filippone, “Impact of nanoparticles on the environmental sustainability of polymer nanocomposites based on bioplastics or recycled plastics – A review of life-cycle assessment studies,” J Clean Prod, vol. 335, no. December 2021, 2022, doi: 10.1016/j.jclepro.2021.130322.

[79] S. Arunvisut, S. Phummanee, and A. Somwangthanaroj, “Effect of Clay on Mechanical and Gas Barrier Properties of Blown Film LDPE/Clay Nanocomposites,” J Appl Polym Sci, vol. 106, no. 4, pp. 2210–2217, 2007, doi: 10.1002/app.26839.

[80] K. Majeed, A. Hassan, and A. A. Bakar, “Influence of maleic anhydride-grafted polyethylene compatibiliser on the tensile, oxygen barrier and thermal properties of rice husk and nanoclay-filled low-density polyethylene composite films,” Journal of Plastic Film and Sheeting, vol. 30, no. 2, pp. 120–140, 2014, doi: 10.1177/8756087913494083.

[81] N. Bumbudsanpharoke, W. Lee, J. C. Choi, S. J. Park, M. Kim, and S. Ko, “Influence of montmorillonite nanoclay content on the optical, thermal, mechanical, and barrier properties of low-density polyethylene,” Clays Clay Miner, vol. 65, no. 6, pp. 387–397, 2017, doi: 10.1346/CCMN.2017.064071.

[82] S. I. Hong and J. W. Rhim, “Preparation and properties of melt-intercalated linear low density polyethylene/clay nanocomposite films prepared by blow extrusion,” LWT - Food Science and Technology, vol. 48, no. 1, pp. 43–51, 2012, doi: 10.1016/j.lwt.2012.03.009.

[83] L. Cabedo, E. Giménez, J. M. Lagaron, R. Gavara, and J. J. Saura, “Development of EVOH-kaolinite nanocomposites,” Polymer (Guildf), vol. 45, no. 15, pp. 5233–5238, 2004, doi: 10.1016/j.polymer.2004.05.018.

[84] S. W. Kim and S. H. Cha, “Thermal, Mechanical, and Gas Barrier Properties of Ethylene–Vinyl Alcohol Copolymer-Based Nanocomposites for Food Packaging Films: Effects of Nanoclay Loading,” Applied Polymer Science, p. 8, 2013.

[85] S. Seethamraju, P. C. Ramamurthy, and G. Madras, “Flexible poly(vinyl alcohol-co-ethylene)/modified MMT moisture barrier composite for encapsulating organic devices,” The Royal Society of Chemistry, vol. 3, pp. 12831–12838, 2013.

[86] A. Dufresne, “Cellulose nanomaterials as green nanoreinforcements for polymer nanocomposites,” Philosophical Transactions of the Royal Society A, vol. 376, no. 20170040, 2018, doi: 10.1098/rsta.2017.0040.

[87] A. Menezes, G. Siqueira, A. A. S. Curvelo, and A. Dufresne, “Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites,” Polymer (Guildf), vol. 50, no. 19, pp. 4552–4563, 2009, doi: 10.1016/j.polymer.2009.07.038.

[88] N. Gray, Y. Hamzeh, A. Kaboorani, and A. Abdulkhani, “Influence of cellulose nanocrystal on strength and properties of low density polyethylene and thermoplastic starch composites,” Ind Crops Prod, vol. 115, pp. 298–305, 2018, doi: 10.1016/j.indcrop.2018.02.017.

[89] M. Nuruddin, J. Hamlin, C. M. Clarkson, J. A. Howarter, C. R. Szczepanski, and J. P. Youngblood, “Processing and Characterization of Food-Grade Plasticizer-Compatibilized Cellulose Nanocrystals and Ethylene Vinyl Alcohol Copolymer Nanocomposites,” ACS Appl Polym Mater, vol. 3, no. 10, pp. 5000–5011, 2021, doi: 10.1021/acsapm.1c00756.

[90] A. Marra, C. Silvestre, D. Duraccio, and S. Cimmino, “Polylactic acid/zinc oxide biocomposite films for food packaging application,” Int J Biol Macromol, vol. 88, pp. 254–262, 2016, doi: 10.1016/j.ijbiomac.2016.03.039.

[91] G. Droval et al., “Thermal and rheological characterization of antibacterial nanocomposites: Poly (amide) 6 and low-density poly(ethylene) filled with zinc oxide,” Journal of Thermoplastic Composite Materials, vol. 27, no. 2, pp. 268–284, 2014, doi: 10.1177/0892705712445037.

[92] G. Pavoski et al., “Antimicrobial High-Density Polyethylene (HDPE)/ZnO Nanocomposites Obtained by in situ Polymerization,” J Braz Chem Soc, vol. 31, no. 8, pp. 1566–1574, 2020, doi: 10.21577/0103-5053.20200042.

[93] Z. Luo, Y. Wang, L. Jiang, and X. Xu, “Effect of nano-CaCO3-LDPE packaging on quality and browning of fresh-cut yam,” LWT - Food Science and Technology, vol. 60, pp. 1155–1161, 2015, doi: 10.1016/j.lwt.2014.09.021.

[94] S. Chytiri, A. E. Goulas, K. A. Riganakos, and M. G. Kontominas, “Thermal, mechanical and permeation properties of gamma-irradiated multilayer food packaging films containing a buried layer of recycled low-density polyethylene,” Radiation Physics and Chemistry, vol. 75, no. 3, pp. 416–423, 2006, doi: 10.1016/j.radphyschem.2005.07.005.

[95] D. Czarnecka-Komorowska, K. Wiszumirska, and T. Garbacz, “FILMS LDPE/LLDPE MADE FROM POST - CONSUMER PLASTICS: PROCESSING, STRUCTURE, MECHANICAL PROPERTIES,”

Advances in Science and Technology Research Journal, vol. 12, no. 3, pp. 134–142, Sep. 2018, doi: 10.12913/22998624/92205.

[96] Bruna Bonato Turriziani, Roniérik Pioli Vieira, Luís Marangoni Júnior, and Rosa Maria Vercelino Alves, "Mechanical Recycling of Multilayer Flexible Packaging Employing Maleic Anhydride as Compatibilizer," J Polym Environ, Sep. 2023, doi: https://doi.org/10.1007/s10924-023-03057-9.

[97] Gabriel Abreu Uehara, Marcos Pini França, and Sebastiao Vicente Canevarolo Junior, "Recycling assessment of multilayer flexible packaging films using design of experiments," Polímeros , vol. 25, no. 4, 2015, doi: https://doi.org/10.1590/0104-1428.1965.

[98] C. Bascucci et al., "Investigating thermomechanical recycling of poly(ethylene terephthalate) containing phosphorus flame retardants," Polym Degrad Stab, vol. 195, p. 109783, Jan. 2022, doi: 10.1016/j.polymdegradstab.2021.109783.

[99] Dylan Jubinville, Elnaz Esmizadeh, Costas Tzoganakis, and Tizazu Mekonnen, "Thermo-mechanical recycling of polypropylene for the facile and scalable fabrication of highly loaded wood plastic composites," Compos B Eng, vol. 219, no. 15, Aug. 2021, doi: https://doi.org/10.1016/j.compositesb.2021.108873.

3. LDPE-NANOCLAY FILMS FOR FOOD PACKAGING WITH IMPROVED BARRIER PROPERTIES

Abstract

This study focuses on the development of LDPE matrix nanocomposite films for food packaging industry and aims at improving LDPE oxygen barrier properties while maintaining other relevant characteristics, such as processability, easy post-processing, optical and mechanical properties.

LDPE nanocomposites, with 1 and 2.5 wt.% nanoclay (NC) and also compatibilized with 5 wt.% polyethylene grafted with maleic anhydride (PE-g-MA), were prepared and used to produce blown films. The nanocomposites were characterized in terms of their morphology, thermal, rheological, mechanical, barrier and optical properties, through scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), rheological measurements, tensile tests, water vapor transmission, oxygen permeability tests and spectrophotometry. The results demonstrated good NC dispersion in the polymer matrix and decreased oxygen permeability in the compatibilized nanocomposite films. All the other properties did not significantly change when compared to neat LDPE.

Overall, the film properties were improved with the added NC and PE-g-MA and, have potential for food packaging.

Keywords: LDPE nanocomposites, Nanoclay, Compatibilizer, Permeability, Blown-film, Food packaging

This chapter is based on the article: **Barros, C.,** Miranda, S., Castro, O., Carneiro, O. S., & Machado, A. v. (2023). LDPE-Nanoclay films for food packaging with improved barrier properties. Journal of Plastic Film and Sheeting. SAGE Publications Ltd. https://doi.org/10.1177/87560879221151190

3.1 Introduction

Adding fillers in a polymer matrix is a common process, in the plastics industry, that improves properties, such as, mechanical, gas barrier, antimicrobial and, in some cases, reduce raw material costs [1, 2].

Polymeric nanocomposites consist of a continuous polymer-based phase and one or more phases dispersed at the nanoscale [3]. According to the literature, these systems exhibit better performance when compared to micro-composites and neat polymer, even at low nanoparticle concentrations [2, 4]. The size difference between micro and nanoparticles results in drastic changes in the material properties. Since the surface area to volume ratio is inversely proportional to the particle diameter, the smaller the diameter, the greater the surface area to volume ratio, increasing the interaction between the particle surface and the matrix [5-7]. To take advantage of the improved properties resulting from this increased interaction, a good nanoparticle dispersion and distribution in the polymeric matrix is mandatory. However, it is quite difficult to obtain nanocomposites with a good NC dispersion in non-polar polymers, such as polyolefins [8-12].

Polyolefins are widely used in flexible food packaging due to their low moisture permeability, among other features. Since they have a hydrophobic nature, their interaction with the organically modified clay is weak. Therefore, the desired intercalation and/or exfoliation of the clay lamellas, despite the high shear forces applied during melt mixing process used to produce the nanocomposite, is not always achieved [13]. Adding compatibilizers improves the interface between polymer matrix and nanoparticle surface, enhancing nanoparticles dispersion [14]. PE-g-MA has been widely used to improve the interaction between the nanomaterial polar surface and the nonpolar matrix [15].

Despite the good properties associated to PE in food packaging industry, such as flexibility, transparency and good sealing properties, it has poor oxygen barrier properties [16, 17], which might be overcome using NC. With the added NC, permeability is significantly affected due to the tortuous path imposed by the NC arrangement in the matrix to gas diffusion [18].

Therefore, since NC are authorized by the European Union in Commission Regulation (EU) No. 10/2011, as safe for food applications this study aims to improve the LDPE film barrier properties for food packaging applications. For this purpose, adding NC at 1 and 2.5 wt.%, with and without a compatibilizer (PE-g-MA), in a LDPE matrix affected the film performance for food packaging. The NC morphology and dispersion were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD), thermal properties were characterized by differential scanning

calorimetry (DSC), and processability was assessed through melt flow index (MFI). The barrier, mechanical and optical film properties were measured through oxygen permeability, tensile and turbidity tests, respectively. To assess the film performance in post-processing operations such as heat sealing and printing, sealing and contact angles tests were carried out. The characterization protocol evaluated not only the new films adequacy for food packaging, but also their viability to be produced in an industrial environment without significantly modifying the processing conditions.

3.2 Experimental

3.2.1 Materials

ExxonMobil LD 159 AC a low density polyethylene, extrusion blown film grade (density = 924 kg/m3, MFI = 1.2 g/10 min and melt temperature = 110 °C) was used as matrix, Dow Inc. FUSABOND E226 a PE-g-MA compatibilizer (MFI = 1.75 g/10 min, melting temperature = 120 °C), was selected. Laviosa Mineral Solutions SpA Dellite 67 G, montmorillonite modified with quaternary ammonium salt and purified was the NC used.

3.2.2 Preparation of LDPE Based Nanocomposites

Before compounding, the NC was dried for 8 h at 80 °C in a forced convection oven. Table 3-1 shows the NC additions with/without PE-g-MA. They were prepared in a Coperion ZSK 26 co-rotating twin-screw extruder. The screw configuration used five distinct mixing zones consisting of disks staggered at 30, 45 and 90° separated by conveying zones. The processing conditions were: barrel temperature =190 °C, screws speed = 250 rpm and throughput = 10 kg/h.

Table 3-1 Sample codes and LDPE/NC/PE-g-MA nanocomposite formulations.

Sample code	LDPE (wt.%)	NC (wt.%)	PE-g-MA (wt.%)
NanoC(1.0)	99.0	1.0	0
NanoC(2.5)	97.5	2.5	0
NanoC(1.0)MA	94.0	1.0	5.0
NanoC(2.5)MA	92.5	2.5	5.0

3.2.3 Blown Film Extrusion

The nanocomposite pellets were dried at 60 °C for 4 hours before the blown film extrusion process, carried out in a laboratorial Periplast single-screw extruder (D=25 mm and L/D=25) coupled to an extrusion head with a 50 mm diameter annular die and 1.25 mm gap. The extruder temperature profile was set at 175 °C - 180 °C - 180 °C, and the three heating zones of the extrusion head were set at 190 °C. A blow-up 2.5 ratio (BUR) and a 8.5 take-up ratio (TUR) were used in the film production. These are typical ratios used in industry. The final film thickness was between 50 and 60 μm.

These processing conditions were maintained for all the nanocomposites tested.

3.2.4 Structural and Thermo-rheological Characterization

3.2.4.1 Morphology

Scanning Electron Microscopy (SEM) - SEM analysis was carried out on film samples fractured in liquid nitrogen coated with gold in a Nano SEM - FEI Nova 200 equipment.

X-Ray Diffraction (XRD) - XRD measurements were carried out, on film samples, at room temperature, 23 ± 2 °C, using a diffractometer (i.e., Bruker D8 Discover) equipped with a CuKα generator (λ = 1.5404 Å) at 40 kV and 40 mA, in a 2θ range from 2° to 10° with a step of 0.01° with a counting time of 1 second per step. The NC interlayer distance, d, was calculated using Bragg's law [19].

3.2.4.2 Barrier, Mechanical and Optical Properties

Oxygen Permeability - The oxygen permeability tests were carried out on a Gas Diffusion Permeameter (DP-100A) from Porous Materials, Inc, using the pressure increase method. The 4 cm diameter film samples were subjected to a 101,325 kPa (1 atm) pressure, at 23 ± 2 °C for 3 hours. Three specimens were used for each film sample. Before the tests, samples were stored at a temperature of 23 ± 2 °C.

Water Vapor Transmission (WVT) -The WVT tests were performed according to the desiccant method from ASTM E96/E96M -10. The samples with 8 cm diameter were sealed to the open mouth of a test cup, containing calcium chloride pre-dried at 200 °C. The samples were placed inside a desiccator at 23 ± 2 °C and weighed every 24 hours for a period of 25 days to

determine the water vapor transmission through the sample to the desiccant. The WVT was the slope obtained by curve fitting the weight change over time via linear regression.

Tensile Tests - The tensile tests were carried out in a universal mechanical testing machine, Shimadzu AG-X, with a 1kN load cell, at 23 ± 2 °C, at 50 mm/min. Following ISO 527-3 standard, for each sample, 5 film specimens of type 2 (160 x 25mm) taken from the transverse (TD) and the machine (MD) directions.

Optical Properties - The turbidity was determined in a XL-211 Hazegard System transmittance meter, according to ASTM D1003-00. This system measures the total light transmittance, T_T, and the percentage of diffuse transmittance, D_T. Six specimens from each sample were tested.

3.2.4.3 Thermal and Rheological Properties

Differential Scanning Calorimetry (DSC) - The nanocomposite granules (or part of a granule) (4-5 mg) were placed in aluminium crucibles with pierced lid under nitrogen flow rate = 50 ml/min on a DSC Netzsch equipment, the procedure was repeated twice for each sample. As recommended in ISO 11357-1 each sample was subjected to two heating-cooling cycles. The samples were heated at 10 °C/min, from 30 °C to 200 °C, held at this temperature for 1 minute, then cooled to 30 °C, at a cooling rate of 20 °C/min, and then re-heated to 200 °C with a heating rate of 10 °C/min. The melting temperature (T_m) and melting enthalpy (ΔH_m), were obtained from the second heating. The crystallinity degree (X_c) was calculated using ΔH_m^0, the 293 J/g melting enthalpy for 100% crystalline PE [20, 21].

Melt Flow Index (MFI) - Before this test, the pellets were dried at 60 °C for 4 hours. The test was carried out in a MFI Daventest, at 190 °C and using 2.16 kg weight, according to ISO 1133-1.

3.2.4.4 Post-processing

Heat sealing tests and contact angle measurements were carried out to check the possibility of maintaining the usual conditions in post-processing operations, i.e., film sealing and printing (through the film surface wettability by a liquid [22]).

Heat sealing - Films were heat sealed at 351 kPa, for 1 s, using a Labthink, model PARAM HST-H3 to obtain the minimum sealing temperatures.

For the tensile test, to measure the maximum sealing force of a 15 mm long weld, the films were again sealed under the same conditions, at 130 °C for all samples. For each sample, five specimens were collected from the MD an TD direction sealed, and then tested on a LF-Plus testing machine, from Lloyd Instruments, with a 50 N load cell, at 100 mm/min.

Contact Angles - The contact angle measurements were carried out in a Contact Angle System OCA equipment using distilled water on the film samples at 23 ± 2 °C, in accordance with ASTM D7334-08. Distilled water (3 µl) was deposited on the films at 2 µl/s, using a syringe. The contact angle was measured immediately after the water drop was placed on the film surface. A total of thirty contact angles per sample were measured.

3.3 Results and Discussion

3.3.1 Film Production

The SEM micrographs in Figure 3-1 demonstrate that the nanocomposites exhibit different NC dispersion when the PE-g-MA at 5 wt.% is added. Comparing NanoC(1.0) and NanoC(1.0)MA, i.e., with the same NC amount without and with PE-g-MA, it is clearly visible that NanoC(1.0)MA presents a better dispersion. Similar observation can be made for NanoC(2.5) and NanoC(2.5)MA. Similar observations were made by Majeed et al. [19].

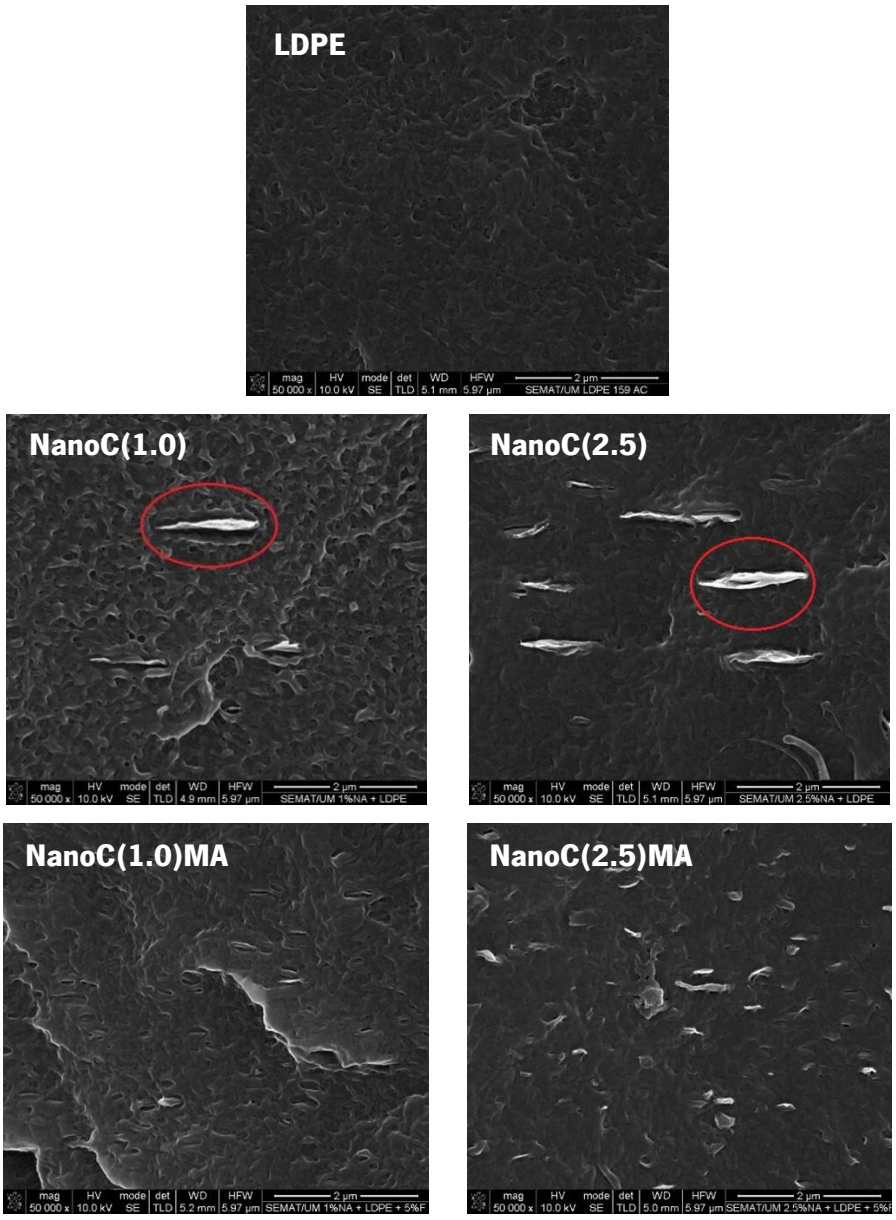


Figure 3-1 SEM micrographs of LDPE and nanocomposite films

Figure 3-2 shows the XRD patterns for the NC, and the four LDPE/nanocomposite samples. They demonstrate that NC presents two diffraction peaks corresponding to interlayer distance d_{001} =34.21 Å and d_{002} =18.32 Å, Table 3-2. In samples NanoC(1.0)MA and NanoC(2.5)MA the peak at d_{001} is not observed. This can be an indication of higher intercalation or even exfoliation of NC platelets due to the added 5 wt.% PE-g-MA. Also the peak at d_{002} shifted to lower angles indicating an increase of the d spaces (NanoC(1.0)MA: 23.79 Å; NanoC(2.5)MA: 23.05 Å). NanoC(1.0) and NanoC(2.5) clearly show two diffraction peaks, both d_{001} and d_{002}, that shifted to lower angles, Table and Figure 3-2. The shift of the peak d_{002} to lower 2θ and the low intensity of the peak at d_{001} in compatibilized nanocomposites, suggest an increase in

interlayer distance promoted by the diffusion of the PE-g-MA chains into the NC galleries, this was also observed by Majeed et al. [19].

Table 3-2 Diffraction peaks and interlayer distance

	d_{001}		d_{002}	
	Å	2θ	Å	2θ
NC	34.21	2.58	18.32	4.82
NanoC(1.0)	38.71	2.28	22.81	3.87
NanoC(2.5)	34.61	2.55	22.99	3.84
NanoC(1.0)MA	-	-	23.79	3.71
NanoC(2.5)MA	-	-	23.05	3.83

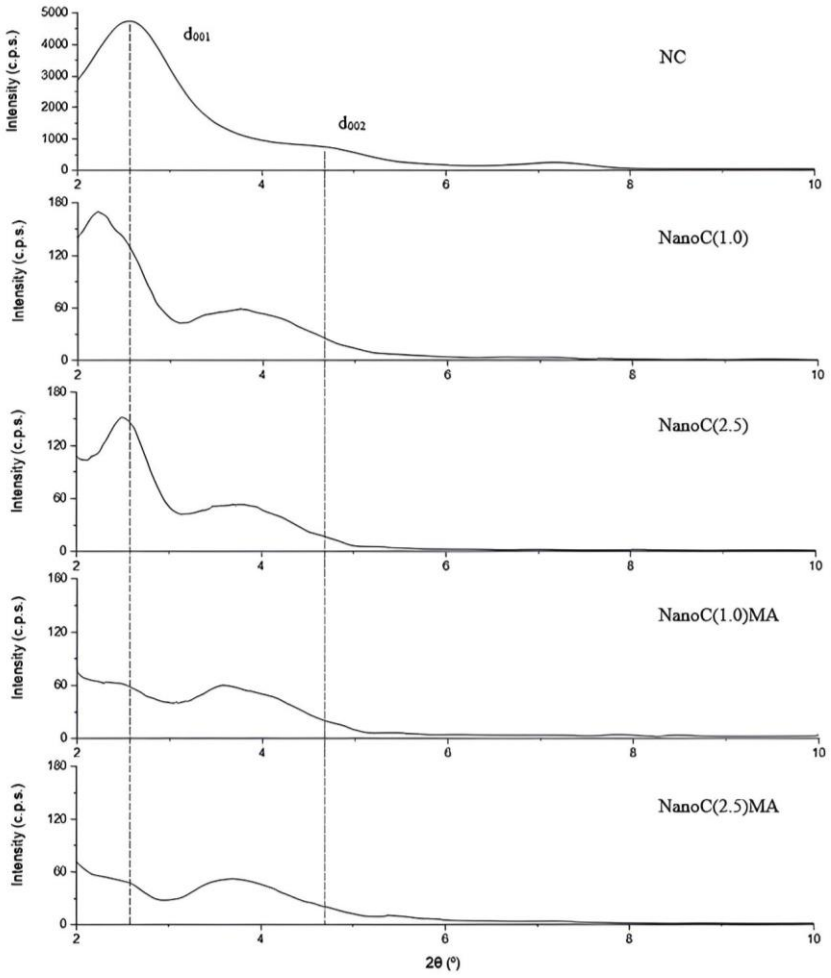


Figure 3-2 XRD patterns of NC and nanocomposites.

3.3.2 Film Properties

Table 3-3 presents the film barrier properties to oxygen and water vapour. For

convenience the oxygen permeability is also presented in common US units. The data shows that the added NC lowers the film oxygen permeability, particularly when compatibilizer is added. This can be due to the NC platelets in the matrix that creates a tortuous path for gas permeation [10, 23]. Regarding the percentage of NC used, in NanoC(1.0) the permeability decreases 11.9% with the incorporation of 1 wt.% of NC, but in NanoC(2.5) the permeability only decreases 6.3% contrary to what is seen in compatibilized samples. This difference may be promoted by the poor dispersion of NC in the polymeric matrix, probably to the formation of aggregates as it was noticed by SEM. Film samples NanoC(1.0)MA and NanoC(2.5)MA, the effect of the incorporation of NC is much more effective, increasing with the rate of incorporation, and promoting a decrease in oxygen permeability of 45.5 % for NanoC(2.5)MA, when compared to LDPE.

The WVT results demonstrate, in some way, a similar trend to the previous, but in this case, while the incorporation of NC without compatibilizer deteriorates the property, it improves when compatibilizer is used. The sample with the best WVT result was NanoC(1.0)MA, which has the lowest wt.% of NC, with a WVT of 4.91×10^{-2} g/(h·m^2), i.e., a reduction of around 14 % relative to LDPE. The increase of WVT in NanoC(2.5)MA sample, compared to NanoC(1.0)MA, can be associated to the agglomerates, as observed by SEM, where it can be seen that although the incorporation of PE-g-MA helps to promote the dispersion of NC, it is not sufficient.

Table 3-3 Oxygen permeability and WVT results of the films produced.

Sample	**Oxygen Permeability**				**WVT**
	Ml · cm/ Pa · s · cm^2		cc · mil/ 100in^2 · day · atm		g/h·m^2 x 10^2
	ave	sd	ave	sd	ave, sd
LDPE	3.19×10^{-13}	9.59×10^{-15}	709	22	6.70 ± 0.63
NanoC(1.0)	2.81×10^{-13}	9.01×10^{-15}	625	20	7.87 ± 1.97
NanoC(2.5)	2.99×10^{-13}	1.26×10^{-14}	665	28	7.20 ± 1.84
NanoC(1.0)MA	1.86×10^{-13}	5.21×10^{-15}	416	12	4.91 ± 0.74
NanoC(2.5)MA	1.74×10^{-13}	1.69×10^{-14}	387	38	5.79 ± 0.87

Table 3-4 and Figure 3-3 show the tensile tests results in MD and TD. The nanocomposites with PE-g-MA have the highest strength and modulus, especially NanoC(2.5)MA, which has the best results despite not being very different from NanoC(1.0)MA. Figure 3-3 indicates that for the same amount of PE-g-MA, the modulus increases as the NC content increases.

According to the data provided the reinforcing capability of the NC only increases when the compatibilizer is added, which follows the literature results that shows that two incompatible systems have poor mechanical properties due to poor interfacial adhesion between the different components [19, 24].

Table 3-4 Results of the films tensile tests: σ_y - yield stress; $E_{1\%}$ - Young's modulus at 1% strain; σ_m - maximum stress; ε_m - strain at maximum stress.

Sample		σ_y MPa ave, sd	$E_{1\%}$ Mpa ave, sd	σ_m MPa ave, sd	ε_m %
LDPE	MD	6.6 ± 0.3	208 ± 13.6	9.2 ± 0.6	278
	TD	6.5 ± 0.5	220 ± 15.1	>9.5 ± 0.5	>401
NanoC(1.0)	MD	6.3 ± 0.5	177 ± 18.0	8.0 ± 0.8	133
	TD	6.0 ± 0.7	209 ± 19.0	6.9 ± 0.6	89
NanoC(2.5)	MD	6.8 ± 0.6	202 ± 22.0	8.5 ± 0.8	136
	TD	6.3 ± 0.6	239 ± 26.0	7.5 ± 0.7	123
NanoC(1.0)MA	MD	8.7 ± 0.7	274 ± 31.0	11.9 ± 1.1	309
	TD	9.1 ± 0.7	279 ± 42.0	9.7 ± 1.0	222
NanoC(2.5)MA	MD	9.7 ± 0.4	333 ± 18.0	12.5 ± 0.8	263
	TD	9.2 ± 0.4	381 ± 31.0	>10.2 ± 1.1	>296

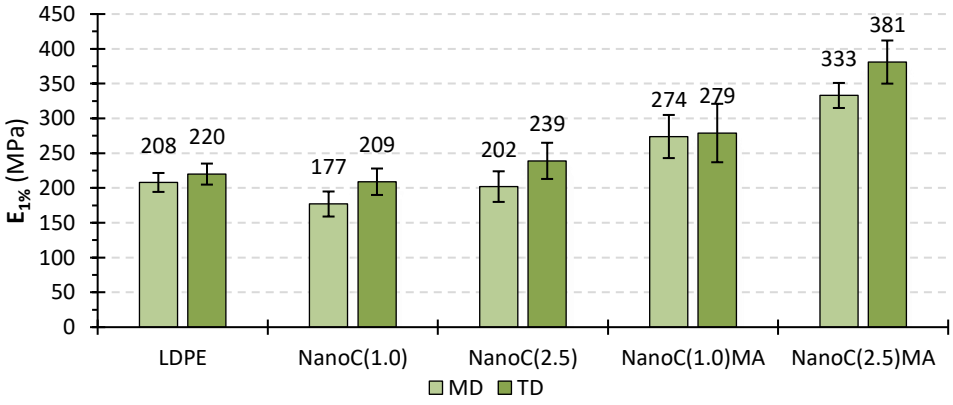


Figure 3-3 Young's modulus values for LDPE and nanocomposite films.

Table 3-5 presents the total light transmittance, T_T, the percentage of diffuse transmittance, D_T and turbidity. They indicate that while T_T does not vary between LDPE and

nanocomposite films, D_T and turbidity increase with the added NC. The turbidity for films with and without PE-g-MA at 1 wt.% NC is the same.

Table 3-5 T_T, D_T and turbidity values of LDPE and nanocomposite films.

Sample	T_T(%) AVE, SD	D_T (%) AVE, SD	Turbidity (%) AVE, SD
LDPE	92.8 ± 0.1	6.2 ± 0.1	6.7 ± 0.1
NanoC(1.0)	92.3 ± 0.1	9.6 ± 0.5	10.4 ± 0.5
NanoC(2.5)	92.2 ± 0.4	14.0 ± 0.2	15.2 ± 0.2
NanoC(1.0)MA	92.5 ± 0.1	9.7 ± 0.3	10.4 ± 0.4
NanoC(2.5)MA	92.3 ± 0.4	10.3 ± 0.4	11.2 ± 0.5

Figure 3-4 presents the turbidity as a bar chart. It shows that NanoC(2.5), which has 2.5 wt.% of NC, is the nanocomposite with the lowest transparency. This can probably be associated to the existence of NC agglomerates, resulting from the low compatibility between NC and LDPE. This result also explains the permeability results obtained for this sample.

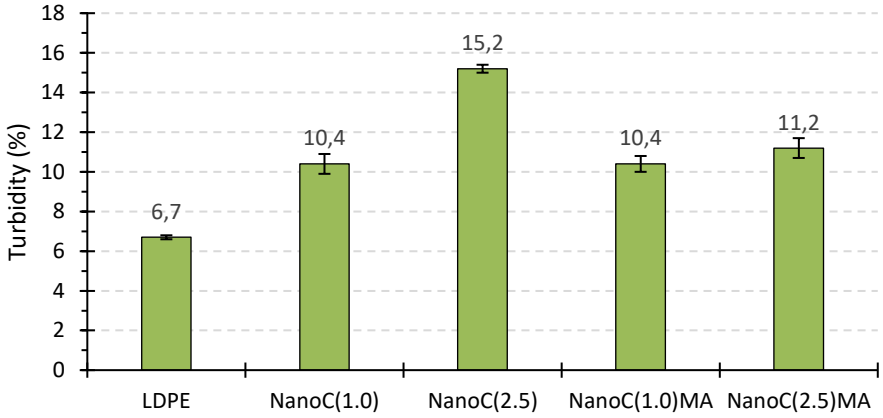


Figure 3-4 Turbidity of LDPE and the nanocomposite films.

Figure 3-5 shows the LDPE film and NanoC(2.5) photographed when placed over some text. Although NanoC(2.5) has higher turbidity, the film transparency is not sufficiently affected to prevent reading the text positioned under the films. The colour with NC is slightly brown, the brownish colour can only be noticeable when several films overlap. The film transparency for the food packaging industry is very important to capture consumer interest and, fortunately, was kept at a reasonable level.

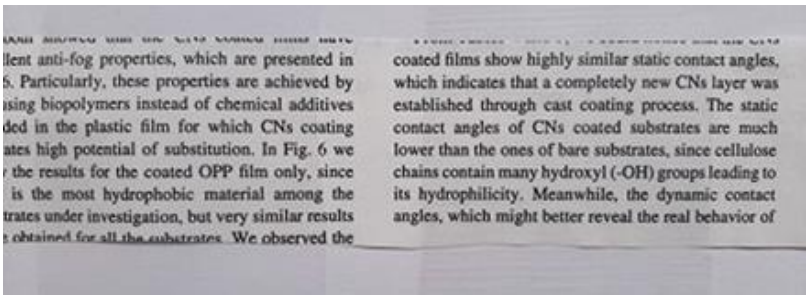


Figure 3-5 Transparency of the LDPE film (on the left) and NanoC(2.5)(on the right).

3.3.3 Film Extrusion and Post-processing

Taking into account the measurement error of about 10%, the average values of DSC results depicted in Table 3-6 show that the LDPE and nanocomposite's melting temperature $\mathrm{T_m}$ and the crystallinity $\mathrm{X_c}$, are very similar for all the samples, revealing that the added NC does not affect the matrix melting temperature. Therefore, for processing proposes the set extrusion temperature can be maintained. This fact, together with the similar values of crystallinity, is also an indication that the sealing conditions of the nanocomposite films can be similar to those used for LDPE films.

Table 3-6 DSC results for LDPE and nanocomposites: T_m - melting temperature; ΔH_m - melting enthalpy; X_c - crystallinity degree.

Sample	$\boldsymbol{T_m}$ **C°**	$\boldsymbol{\Delta H_m}$ **J/g**	$\boldsymbol{X_c}$ **%**
LDPE	111.2	119.5	40.8
NanoC(1.0)	110.9	111.4	38.0
NanoC(2.5)	111.0	109.9	37.1
NanoC(1.0)MA	111.6	106.6	36.4
NanoC(2.5)MA	111.3	115.7	39.4

MFI values (Figure 3-6) decrease with the added compatibilizer, i.e., these samples exhibit higher shear viscosity (at least at the low shear rate values corresponding to the MFI test), indicating that the NC are effectively reinforcing the melt. SEM results also indicate higher intercalation/exfoliation when PE-g-MA was added. The same was noticed by Pedroso and Rosa study [25]. Without compatibilizer, the added NC does not affect the MFI, revealing a low interaction (compatibility) between NC and the LDPE matrix.

The increase in apparent viscosity of the compatibilized nanocomposites had a positive impact on film extrusion, since it is also expected to impact the melt strength, increasing the bubble stability, facilitating the extrusion process.

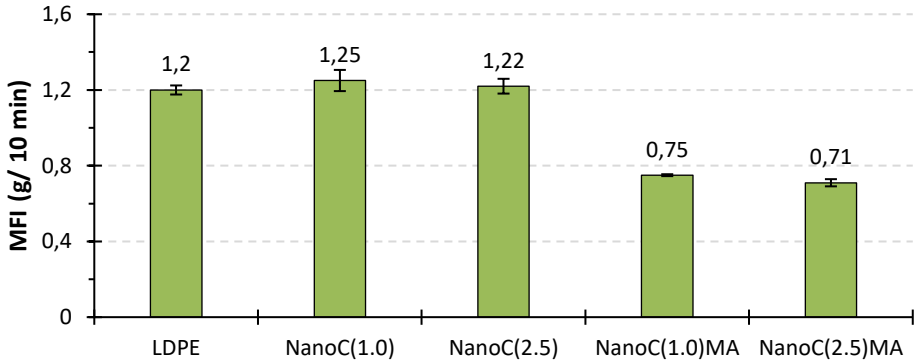


Figure 3-6 MFI for LDPE and nanocomposites.

Table 3-7 shows the results related with post-processing operations (heat sealing and printing), the average maximum sealing force and the contact angles. One sees that the minimum sealing temperature is not affected and it is similar to LDPE film (around 125 °C) for all the samples. However, differences in the sealing mechanical resistance are noticeable, samples collected in the MD present higher maximum sealing force than the TD samples, which is in agreement with the higher MD mechanical resistance. This is due to higher MD molecular orientation promoted by a higher stretching in this direction. Moreover, it is possible to verify that when the added NC is accompanied by compatibilizer, the differences between the two main directions almost vanish, while keeping higher values.

Table 3-7 Maximum sealing force and contact angles of the films.

Sample		Maximum force (N) AVE, SD	Contact Angle (degree) AVE, SD
LDPE	MD	10.6 ± 0.6	89.08 ± 2.38
	TD	7.8 ± 0.9	
NanoC(1.0)	MD	10.5 ± 0.8	87.82 ± 3.63
	TD	8.1 ± 0.2	
NanoC(2.5)	MD	7.6 ± 1.3	85.73 ± 3.56
	TD	7.4 ± 0.7	
NanoC(1.0)MA	MD	10.7 ± 0.5	87.06 ± 2.23
	TD	9.0 ± 0.3	
NanoC(2.5)MA	MD	9.8 ± 0.6	87.24 ± 2.45
	TD	9.1 ± 0.1	

The added NC in the LDPE matrix does not change the contact angles (Table 3-7). These might be associated to the low NC amount at the film surface, which leaves the film topography unchanged, keeping the same contact angle.

3.4 Conclusions

LDPE/NC nanocomposite films were produced by blown film extrusion with and without compatibilizer, PE-g-MA. Through the joint analysis of several characterization techniques, it was possible to draw conclusions about the performance of the produced nanocomposites. SEM and XRD results showed that samples with the added 5 wt.% PE-g-MA present better NC dispersion and higher interlayer distance compared to samples without compatibilizer. This homogeneity allows producing films with better and more balanced mechanical properties (for the monolithic films and their heat sealing strength), and slightly better barrier properties, which were the main objective of this study. Although, the reduction in O_2 permeability did not improve the barrier performance enough to replace high barrier polymers, such as EVOH.

The nanocomposite that presented the best results for structural and physical properties was NanoC(1.0)MA, with 1 wt.% NC, apart from the mechanical properties, which was NanoC(2.5)MA with 2.5 wt.% NC. Since good barrier properties are extremely important for food

packaging production, the choice of a nanocomposite with better mechanical properties cannot be made at the expense of barrier properties. Thus, it was possible to conclude that the barrier properties as well as the other properties studied, to produce flexible films for food packaging, can be improved with by adding 1 wt.% NC.

While the turbidity increased with the increased NC, the film transparency was not significantly affected. Therefore, the films produced can be used in food packaging, still enabling product visualization.

Moreover, properties such as melting temperature, heat sealing temperature and contact angles were not significantly affected by the added NC or compatibilizer, preserving the conditions for packaging production.

As for future studies, it may be relevant to study the eventual migration of NC from the film to the food packaged, as the packaging must comply with the regulations on migration of substances into food imposed by the European Commission.

3.5 References

[1] M. Alexandre and P. Dubois, "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials," Materials Science and Engineering, Reports: A Review Journal, vol. 28, pp. 1–63, 2000.

[2] K. Müller et al., "Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields," Nanomaterials, vol. 7, no. 74, p. 47, 2017, doi: 10.3390/nano7040074.

[3] International Organization for Standardization (ISO), "ISO/TS 80004-4 Nanotechnologies — Vocabulary — Part 4: Nanostructured materials." Accessed: May 14, 2021. [Online]. Available: https://www.iso.org/obp/ui/fr/#iso:std:iso:ts:80004:-4:ed-1:v1:en

[4] I. Pleşa, P. V. Noţingher, S. Schlögl, C. Sumereder, and M. Muhr, "Properties of polymer composites used in high-voltage applications," Polymers (Basel), vol. 8, no. 173, p. 63, 2016, doi: 10.3390/polym8050173.

[5] A. B. Asha and R. Narain, "Nanomaterials properties," in Polymer Science and Nanotechnology, Edmonton: Elsevier Inc., 2020, pp. 343–359. doi: 10.1016/B978-0-12-816806-6.00015-7.

[6] F. Hussain, M. Hojjati, M. Okamoto, and R. E. Gorga, “Review article: Polymer-matrix nanocomposites, processing, manufacturing, and application: An overview,” J Compos Mater, vol. 40, no. 17, pp. 1511–1575, 2006, doi: 10.1177/0021998306067321.

[7] D. Nath, S. R, K. Pal, and P. Sarkar, “Nanoclay-based active food packaging systems: A review,” Food Packag Shelf Life, vol. 31, no. December 2021, p. 100803, 2022, doi: 10.1016/j.fpsl.2021.100803.

[8] A. Durmus, M. Woo, A. Kasgoz, C. Macosko, and M. Tsapatsis, “Intercalated linear low density polyethylene (LLDPE)/ clay nanocomposites prepared with oxidized polyethylene as a new type compatibilizer: Structural, mechanical and barrier properties,” Eur Polym J, vol. 43, pp. 3737–3749, 2007, doi: 10.1016/j.eurpolymj.2007.06.019.

[9] M. G. Davoodi and A. H. Sourki, “Influence of environmental conditions on permeability of low density polyethylene/ clay nano composites used in bread packaging,” Int J Biosci, vol. 5, pp. 12–15, 2014, doi: http://dx.doi.org/10.12692/ijb/5.7.12-15.

[10] N. Bumbudsanpharoke and S. Ko, “Nanoclays in Food and Beverage Packaging,” J Nanomater, p. 13, 2019, doi: https://doi.org/10.1155/2019/8927167.

[11] J. Bandyopadhyay and S. S. Ray, “Are nanoclay-containing polymer composites safe for food packaging applications? — An overview,” 2019, doi: 10.1002/app.47214.

[12] H. Yamada, K. Tamura, Y. Watanabe, N. Iyi, and K. Morimoto, “Geomaterials: their application to environmental remediation,” Sci Technol Adv Mater, p. 13, 2011, doi: 10.1088/1468-6996/12/6/064705.

[13] F. R. Passador, D. R. Travain, E. H. Backes, A. C. R. Filho, and L. A. Pessan, “Nanocompósitos de Blendas HDPE / LLDPE e OMMT – Parte II : Avaliação das Propriedades Térmica , Óticas e de Transporte a Gases,” Polímeros, vol. 23, no. 6, pp. 748–757, 2013.

[14] S. Dadbin, M. Noferesti, and M. Frounchi, “Oxygen Barrier LDPE / LLDPE / Organoclay Nano-Composite Films for Food Packaging,” Macromol Symp, pp. 22–27, 2008, doi: 10.1002/masy.200851404.

[15] A. Mengual, D. Juárez, R. Balart, and S. Ferrándiz, “PE-g-MA, PP-g-MA and SEBS-g-MA compatibilizers used in material blends,” Procedia Manuf, vol. 13, pp. 321–326, 2017, doi: 10.1016/j.promfg.2017.09.083.

[16] M. Khajavi et al., “Strategies for Producing Improved Oxygen Barrier Materials Appropriate for the Food Packaging Sector,” Food Engineering Reviews, vol. 12, no. 3, pp. 346–363, 2020, doi: 10.1007/s12393-020-09235-y.

[17] K. Majeed, R. Arjmandi, and A. Hassan, “Mechanical and oxygen barrier properties of LDPE/MMT/MAPE and LDPE/MMT/EVA nanocomposite films: A comparison study,” Journal of Physical Science, vol. 29, no. 1, pp. 43–58, 2018, doi: 10.21315/jps2018.29.1.4.

[18] H. Yamada, K. Tamura, Y. Watanabe, N. Iyi, and K. Morimoto, “Geomaterials: their application to environmental remediation,” Sci Technol Adv Mater, p. 13, 2011, doi: 10.1088/1468-6996/12/6/064705.

[19] K. Majeed, A. Hassan, and A. A. Bakar, “Influence of maleic anhydride-grafted polyethylene compatibiliser on the tensile, oxygen barrier and thermal properties of rice husk and nanoclay-filled low-density polyethylene composite films,” Journal of Plastic Film and Sheeting, vol. 30, no. 2, pp. 120–140, 2014, doi: 10.1177/8756087913494083.

[20] D. Li, L. Zhou, X. Wang, L. He, and X. Yang, “Effect of crystallinity of polyethylene with different densities on breakdown strength and conductance property,” Materials, vol. 12, 2019, doi: 10.3390/ma12111746.

[21] T. Poltimäe, E. Tarasova, A. Krumme, J. Roots, and A. Viikna, “Thermal Analyses of blends of hyperbranched linear low-density polyethylene (LLDPE) with high-density polyethylene and LLDPE prepared by dissolving method,” Materials Science (Medziagotyra), vol. 17, no. 3, pp. 254–259, 2011, doi: 10.5755/j01.ms.17.3.589.

[22] S. I. Hong and J. W. Rhim, “Preparation and properties of melt-intercalated linear low density polyethylene/clay nanocomposite films prepared by blow extrusion,” LWT - Food Science and Technology, vol. 48, no. 1, pp. 43–51, 2012, doi: 10.1016/j.lwt.2012.03.009.

[23] V. Siracusa, “Food Packaging Permeability Behaviour: A Report,” Int J Polym Sci, vol. 2012, p. 11, 2012, doi: 10.1155/2012/302029.

[24] A. M. Díez-Pascual, “Inorganic-Nanoparticle Modified Polymers,” Polymers (Basel), vol. 14, no. 10, p. 1979, 2022, doi: 10.3390/polym14101979.

[25] A. G. Pedroso and D. S. Rosa, “Effects of the compatibilizer PE-g-GMA on the mechanical, thermal and morphological properties of virgin and reprocessed LDPE/corn starch blends,” Polym Adv Technol, vol. 16, no. 4, pp. 310–317, 2005, doi: 10.1002/pat.581.

4. TOWARDS MECHANICAL RECYCLABILITY OF HIGH BARRIER FOOD PACKAGING FILMS THROUGH FILLER INCORPORATION ON THE EVOH LAYER

Abstract

To preserve food from high levels of moisture and oxygen, polymers like ethylene vinyl alcohol (EVOH) are used in multilayer structures for oxygen barrier, and low-density polyethylene (LDPE) for water vapor barrier. Although this material combination is ideal from a functional standpoint, it may not meet the new guidelines for recycling multilayer packaging. Rules imposed by some European markets already restrict the weight percentage of EVOH in flexible LDPE films. To keep the packaging's oxygen barrier properties while reducing the percentage of EVOH, this study evaluated the incorporation of nanoclays (NC), cellulose microcrystals (MCC), silicon dioxide nanoparticles (SiO_2) and cellulose nanocrystals (CNC) in an EVOH matrix. Masterbatches were produced in a twin-screw extruder, with a screw configuration that promoted intensive mixing, and then were diluted to produce EVOH monolayer films. The results indicate that some types of particles induce a stable blown film extrusion process and have a better dispersion in the EVOH matrix, as is the case of NC and MCC. Thus, three-layer films (with ABA configuration) of LDPE (A) and EVOH with MCC and NC (7 μm layer) (B) were produced to protect EVOH from humidity and to support the blown film processing, with low percentages of micro and nanoparticles (0.5 and 1 wt.%). The lowest oxygen transmission rate (OTR) values were obtained for 0.5 wt.% NC and 1 wt.% MCC incorporation. Although haze has increased in films with micro and nanoparticles, this did not affect the good visibility of the packaged food.

This study demonstrated that it is possible to reduce the EVOH thickness layer by adding micro and nanoparticles, maintaining the overall barrier performance.

Keywords: Blown film; barrier properties; montmorillonite; microcrystalline cellulose; nanomaterial.

This chapter is based on the article: **Barros, C.,** Azevedo, A. G., Cerqueira, M. A., Carneiro, O. S., & Machado, A. v. (2024). Towards mechanical recyclability of high barrier food packaging films through filler incorporation on the EVOH layer. *Submitted to Applied Polymer Science*

4.1 Introduction

One of the most important properties of food packaging films is their ability to prevent permeability to oxygen and water vapor, which slows lipid oxidation and the growth of mold and fungi in the food. This double barrier in flexible plastic packaging is achieved by combining different polymers in a multilayer structure, where polymers, such as polyethylene (PE) or polypropylene (PP) constitute the water vapor barrier, and ethylene vinyl alcohol (EVOH) or polyamide (PA) serve as oxygen barrier [1]. Unfortunately, this combination of polymers does not allow to recycle the films at the end of its life time [2].

The incompatibility between the PE, or PP, and EVOH, or PA, layers makes it mandatory to use a compatibilizer between these layers [3]. Given the current packaging sorting and recycling methods, it is nearly impossible to separate these materials at the packaging end-of-life. Many recyclers consider plastic packaging recyclable if 95 wt.% of its composition is made of the same material, or if the density of a flexible polyolefin film is not higher than 0.97 g/cm^3 [4-6]. Therefore, if monomaterial packaging is not an option, it is necessary to keep the inclusion of different materials to a maximum of 5wt.%.

One of the strategies to reduce the number of polymers used in a package involves replacing some layers with composite or nanocomposite materials. For example, in a film mainly composed of LDPE, the incorporation of particles in the EVOH inner layer can improve its properties, enabling the reduction of layer thickness, and thus reducing the percentage of EVOH in the film. Several studies demonstrate that composites, especially nanocomposites, improve the mechanical and barrier properties of flexible plastic films, while also showing good stability at different temperatures [7, 8].

Polymer nanocomposites with good dispersion and distribution of nanoparticles exhibit better thermal, mechanical, and optical properties when compared to virgin polymer and microcomposites [9-11].

There are several studies on the incorporation of nanoparticles in EVOH matrices, with the aim of improving the properties of this polymer for use in food packaging. The chemical structure of EVOH, consisting of polar segments, vinyl alcohol, and nonpolar segments of ethylene, improves the EVOH/particle bond through hydrogen bonding interactions [12, 13]. For this reason, in several studies related to the production of EVOH matrix nanocomposites, the use of a compatibilizer is not detected [14-17].

Nanoclays (NC) are currently one of the most widely used materials for the production and development of nanocomposites in the field of food packaging. There are several types of mineral clays namely chlorite, montmorillonite (MMT), illite, and kaolinite, which differ in chemical structure, composition, and source. Of all types of nanoclays, MMT are the best known and most used in the packaging area, mainly to improve oxygen barrier and mechanical properties [18, 19]. Studies carried out on the effect of NC on the properties of EVOH nanocomposites show that the NC incorporation helps in reducing the permeability to oxygen and water vapor, and increases the glass transition temperature (T_g), melting temperature (T_m), and percentage of crystallinity (X_m) [15, 20-22]. Increasing the incorporation rate of NC in the EVOH matrix has advantages for the permeability and thermal stability of the nanocomposite, but above 5 wt.% leads to a decrease in film transparency, which is an important requirement for food packaging films [22].

Regarding CNC, the incorporation of only 1 wt.% of these nanoparticles in an EVOH matrix allows to obtain a 71% decrease in the water vapor transmission rate and an increase in T_g, T_m, X_m, and mechanical properties when compared to a 100% EVOH film [23, 24].

Recent studies compare EVOH composites produced with MCC and CNC and evaluate the effect of shear forces on the dispersion of micro and nanoparticles during the production of the composites by extrusion. EVOH microcomposites with 5 and 15 wt.% MCC prepared with a high shear screw configuration exhibit better mechanical and thermal properties than microcomposites produced with a low shear screw configuration [17]. The properties improvement of the microcomposite with 5 wt.% MCC is not significantly different from that corresponding to the nanocomposite with the same percentage of CNC incorporation [17]. Therefore, the incorporation of MCC into a polymeric matrix can be a low-cost alternative to replace the use of CNC when using melt compounding as a dispersive method of particles in a polymeric matrix.

Also, nano-SiO_2, widely used as an antiblocking additive, can be used in flexible food packaging to improve barrier, antimicrobial and mechanical properties [25, 26]. Liu et al. (2010) demonstrate that the incorporation of nano-SiO_2 into an EVOH matrix decreases the moisture permeability and increases the film tensile strength. Above 2 wt.% of incorporation of nano-SiO_2, the increase in tensile strength is not noticeable, but the decrease in the moisture permeability coefficient increases considerably with the incorporation of 5 wt.%. The same authors conclude that to reduce the turbidity associated with the increase in wt.% of nano-SiO_2 the take-up ratio (TUR) used in the film extrusion line should be increased [16].

In spite of the studies published in the literature, none have used samples manufactured through co-extrusion, the industry's most prevalent processing technique. Furthermore, there is a lack of comprehensive studies on the incorporation of several types of particles in the EVOH layer of multilayer films.

The micro and nanoparticles used in the current research have been approved for food contact by commission Reg. (EU) No. 10/2011 dated January 14, 2011, with the exception of CNC. CNC have a smaller particle size than microparticles, which can result in different toxicological properties. However, further studies are needed to assess their behaviour as food contact material [27, 28].

Considering these findings, the focus of the current research is the incorporation of four types of particles in the EVOH layer with a view to produce multilayer food packaging films with improved properties, namely oxygen barrier. These particles are: cellulose nanocrystals (CNC), microcrystalline cellulose (MCC), nanoclays (NC) and nano- silicon dioxide (SiO_2). The micro and nanocomposites were prepared by extrusion compounding and the respective films were produced through blown film coextrusion.

The work is organized in two parts. Initially, the dispersion of particles and properties of the EVOH film and respective nanocomposites was investigated. After this analysis, films with three layers (LDPE/EVOH/LDPE) were produced, with LDPE outer layers, a hydrophobic non-polar polymer, and an inner layer of EVOH or of its micro and nanocomposites. Due to the stability provided by the support of the two LDPE layers during blown film extrusion, it was possible to reduce the thickness of the EVOH layer to 7 μm, a value similar to that used in commercial films. The LDPE layers also played an important role in limiting the diffusion of water vapor into the EVOH layer, promoting the maintenance of the oxygen barrier characteristics of this polymer.

4.2 Experimental

4.2.1 Materials

EVOH Soarnol DC3203RB, from NIPPON GOHSEI (Osaka, Japan), containing 32 mol% of ethylene (density = 1.19 g/cm^3, melt temperature = 83 °C, and MFI (210 °C, 2.16 kg) = 3.8 g/10min) was used as matrix. Dow (Michigan, EUA) LDPE 352 E, a low-density polyethylene blown film extrusion grade (density = 925 kg/m^3, MFI (190 °C/2.16 kg) = 2.0 g/10 min and Vicat softening temperature = 96.0 °C) was used for coextrusion purposes. The NC used was Cloisite

20A, from BYK (Wesel, Germany), which is a MMT with organic modifier dimethyl, dihydrogenated tallow, quaternary ammonium with an X-Ray Diffraction d-Spacing (001) of 31.5 Angstroms, and a particle size of 2 to 13 µm. The CNC (reference NCV100) was supplied by CelluForce (Montreal, Canada). This is a cellulose hydrogen sulphate sodium salt with a particle size of 1 to 50 µm. The MCC Vivapur 105, was supplied by J. Rettenmaier & Sohne (Rosenberg, Germany) and has a medium size particle of 15 µm. The nano-SiO_2 avanSi-40 was supplied by Avanzare (La Rioja, Spain) and has a medium size particle of 3.5 µm.

4.2.2 Micro nanoparticles thermal stability

The micro and nanoparticles were subjected to thermal analysis (TGA) to investigate their viability when subjected to the EVOH processing temperatures (190 - 200 °C). The results in Table 4-1 indicate that, with the exception of SiO_2, the initial weight loss occurs at temperatures above 200 °C. In silica particles the start of weight loss and the degradation temperature occur between 100 and 200 °C, which can be attributed to the physisorbed water in SiO_2 particles [29, 30]. However, SiO_2 particles have the lowest total weight loss and are the only that present unchanged colour (white) after being exposed to high temperatures (up to 700 °C). The NC weight loss of 31.49% is associated to the presence of organic groups used to modify the surface of these inorganic particles, and was also observed by Voorn et al. (2006) [31].

Table 4-1 TGA results of CNC, MCC, NC and SiO_2

Materials	Initial decomposing temperature (°C)	1st derivate peak temperature (°C)	Residue (%)
CNC	299	308	4
MCC	319	343	3
NC	263	314	69
SiO_2	83	127	82

4.2.3 Masterbatch preparation

EVOH masterbatches with NC, SiO_2, MCC and CNC were produced for posterior dilution in EVOH and film production. These materials were processed in a model ZSK 26 Coperion co-rotating twin-screw extruder (L/D = 40, D = 25 mm), with ten independent heating zones, and a screw configuration including five distinct mixing zones, composed by kneading blocks staggered at 30°,

45° and 90°, separated by conveying zones. Initially, the masterbatches were produced with 20 wt.% particle incorporation, using a temperature of 210 °C (in zones 1, 2, 3, 4, 9, and 10) and 200 °C (in zones 5, 6, 7, and 8), with screws rotation speed of 180 rpm. Before compounding, all micro and nanoparticles and EVOH were dried for 24 h at 55 °C in a forced convection oven.

The EVOH was fed to the extruder hopper using a single-screw gravimetric feeder K-Tron K-CL-24-KQX4, and the particles were fed by a double-screw volumetric K-Tron K- CL-24-KT20 side feeder, located in zone 5. This downstream location was intended to reduce the particles residence time in the extruder, preventing their thermal degradation. With this percentage of incorporation (20 wt.%), all particles except NC presented problems during extrusion, namely: non-uniform extruded filament diameter in SiO_2 nanocomposites, and visible thermal degradation (darkening of the composites) of micro and MCC and CNC nanocomposites. To overcome this issue, EVOH/SiO_2, EVOH/MCC, and EVOH/CNC masterbatches were produced only with the incorporation of 10 wt.%, with a temperature profile of 190 °C (zones 1 - 4) and 180 °C (zones 5 - 10).

4.2.4 EVOH film production

In order to produce single layer EVOH micro and nanocomposite films, co-extruded LDPE/EVOH blown film samples were produced using two Periplast single screw extruders, L/D = 25 and D = 25, coupled to a two-layer co-extrusion head. The extruder 1 processed the EVOH or the EVOH micro and nanocomposites, diluting the masterbatch, and extruder 2 processed LDPE. The use of the LDPE layer was required to enable the production of an EVOH film, since this polymer does not have sufficient melt strength (extensional viscosity) to form a stable bubble during the blown film process. The monolayer EVOH and EVOH composite films were obtained by separating the EVOH layer from the incompatible LDPE layer, by simply pulling it off.

The extruder 1 temperature profile was set at 200 – 210 – 210 °C (except for nanocomposites with NC, where the profile was 210 – 230 – 220 °C). The extruder 2 temperature profile was set at 170 – 180 – 195 – 200 °C, and the extrusion head were set at 210 °C. A blow-up ratio (BUR) of 2.0 and a 10.6 take-up ratio (TUR) were used in the films production. The films thickness was measured with a micrometer (Digimatic thickness gauge 547-301, Mitutoyo, Japan) with a measuring accuracy of 0.01 mm. The final film thickness ranged from 22 to 40 μm. In total, 17 films were produced, including one with neat EVOH, using four different incorporation rates of each type of particles (0.5, 1.0, 2.5, and 5.0 wt.%) in the EVOH layer.

Due to the high thickness of the EVOH film obtained through the process described (around 30 μm), and despite the presence of the LDPE layer, it was not possible to keep the extruded bubble stability. As a consequence, the films obtained had many creases and a pronounced thickness distribution, in both machine direction (MD) and transverse direction (TD).

4.2.5 Three-layer LDPE/EVOH/LDPE film production

The previous stage of this research enabled the selection of the best nanocomposites for incorporation in three-layer films. These films were produced with an ABA configuration (LDPE|EVOH|LDPE), with NC and MCC incorporated in the inner EVOH (B) layer at 0.5 and 1.0 wt.%, obtained by diluting the masterbatches produced. The five films were named as follows:

- LDPE|EVOH|LDPE
- LDPE|EVOH + 0.5% NC|LDPE
- LDPE|EVOH + 1.0% NC|LDPE
- LDPE|EVOH + 0.5% MCC|LDPE
- LDPE|EVOH + 1.0% MCC|LDPE.

The production of these films was carried out with a temperature profile of 180 to 190 °C, in the LDPE extruder, 200 °C in the EVOH extruder and 200 °C in the co-extrusion head. A BUR of 1.7 and TUR of 13.8 were used. The total thickness of these films varied from 60 to 70 μm.

4.2.6 Characterization techniques

Scanning Electron Microscopy (SEM) - SEM analysis allowed to observe the surface and cross-sectional morphology of the samples using a scanning electron microscope (Quanta 650 FEG, FEI, USA) with an operating voltage of 5 kV.

Optical properties - The films haze was determined in a XL-211 Hazegard System transmittance meter, according to ASTM D1003-00. For each sample, five measurements were performed.

Films gloss measurements were performed according to ISO 2813 standard using a BYK Micro-TRI-gloss S gloss meter, with 20° and 60° measurement geometries. The analysis of particle distribution in EVOH monolayer films was done using a digital microscope with a low to medium magnification range, Leica DMS1000, with image collection through LAS EZ software in three different zones of the film.

Barrier properties - The oxygen transmission rate (OTR) tests were carried out on a OTR analyzer OX-TRAN model 2/21 from MOCON, using a coulometric sensor. The multilayer films were tested at two values of relative humidity (RH: 0% and RH: 60%), at a temperature of 23 °C. This test was carried out in accordance with the ASTM D 3985 standard.

The water vapor transmission rate (WVTR) tests were performed according to the desiccant method from ASTM E96/E96M-10. The samples with 8 cm diameter were sealed to the open mouth of a test cup, containing calcium chloride pre-dried at 200 °C. The samples were placed inside a desiccator at 23 ± 2 °C and weighed every 24 hours for a period of 25 days for monolayer films, and 50 days for multilayer films. The samples were weighted on an analytical balance, with a 1 mg sensitivity. The WVTR is the slope obtained by fitting the weight change over time via a linear regression.

X-ray diffraction (XRD) - XRD system (Malvern Panalytical Ltd., Malvern, UK) was used to evaluate the crystallographic structure of MCC. PANanalytical X'Pert HighScore Plus was the software used to gather data and to analyse peak diffractions. The film samples were fixed by a tape in the sample holder. The XRD diffractograms were acquired at 23 ± 2 °C. Angular scans from 5° to 50° (2θ) were performed with a Cu source, X-ray tube (λ = 1.54056 Å) at 45 kV and 40 mÅ. The fine calibration offset for 2θ was -0.0372◦. One measurement was performed in each sample.

Small angle X-ray scattering (SAXS) measurements were carried out to characterise the structural and crystallinity changes over time of nanoclays (NC) films**.** The samples were measured with a SAXSess mc^2 Kratky camera (Anton Paar GmbH, Austria) using Cu-Kαradiation (λ = 1.54056 Å) and operating at 40 kV and 50 mA. An image plate system covering the q-range from 0.23 to 26 nm^{-1} was used. The exposure time for all samples was 60 minutes being the temperature 25 °C. The measurements were performed in line collimation mode to maximise scattering intensity. The 2D scattering images were converted to 1D radial intensity profiles using the SAXS-quant software (Anton Paar GmbH, Austria).

Thermogravimetric analysis (TGA) - TGA of the micro and nanoparticles was performed on a TGA Q500 (TA Instruments, New Castle, EUA) at 10 °C/min in a temperature range of 40 - 700 °C, under a nitrogen atmosphere. The extrapolated onset temperature (where the weight loss begins), the maximum weight loss temperature, and the total weight loss were calculated.

Statistical Analyses - The results of OTR, WVTR and haze measurements are provided in the mean ± standard deviation format. The statistical analysis was carried out using the software

IBM SPSS Statistics, using a one-way analysis of variance (ANOVA), with comparison procedures assuming equal variances with Tukey method for differences of means, with a confidence level of 95%.

4.3 Results and Discussion

4.3.1 Dispersion and barrier properties of micro and nanoparticles in EVOH

The SEM images of the samples surface (Figure 4-1) exhibited a high number of agglomerates and deterioration of the film surface, in the MCC, SiO_2, and CNC composites, which is intensified when the incorporation rate increases. The MCC agglomerates are smaller in size, than the SiO_2 and CNC ones, and are better distributed. The NC composite films show better dispersion and distribution of these particles when compared to the remaining films. For MCC, CNC and SiO_2 composite films with 2.5 and 5.0 wt.% of incorporation, large agglomerates are observed, which affect the surface roughness of these films.

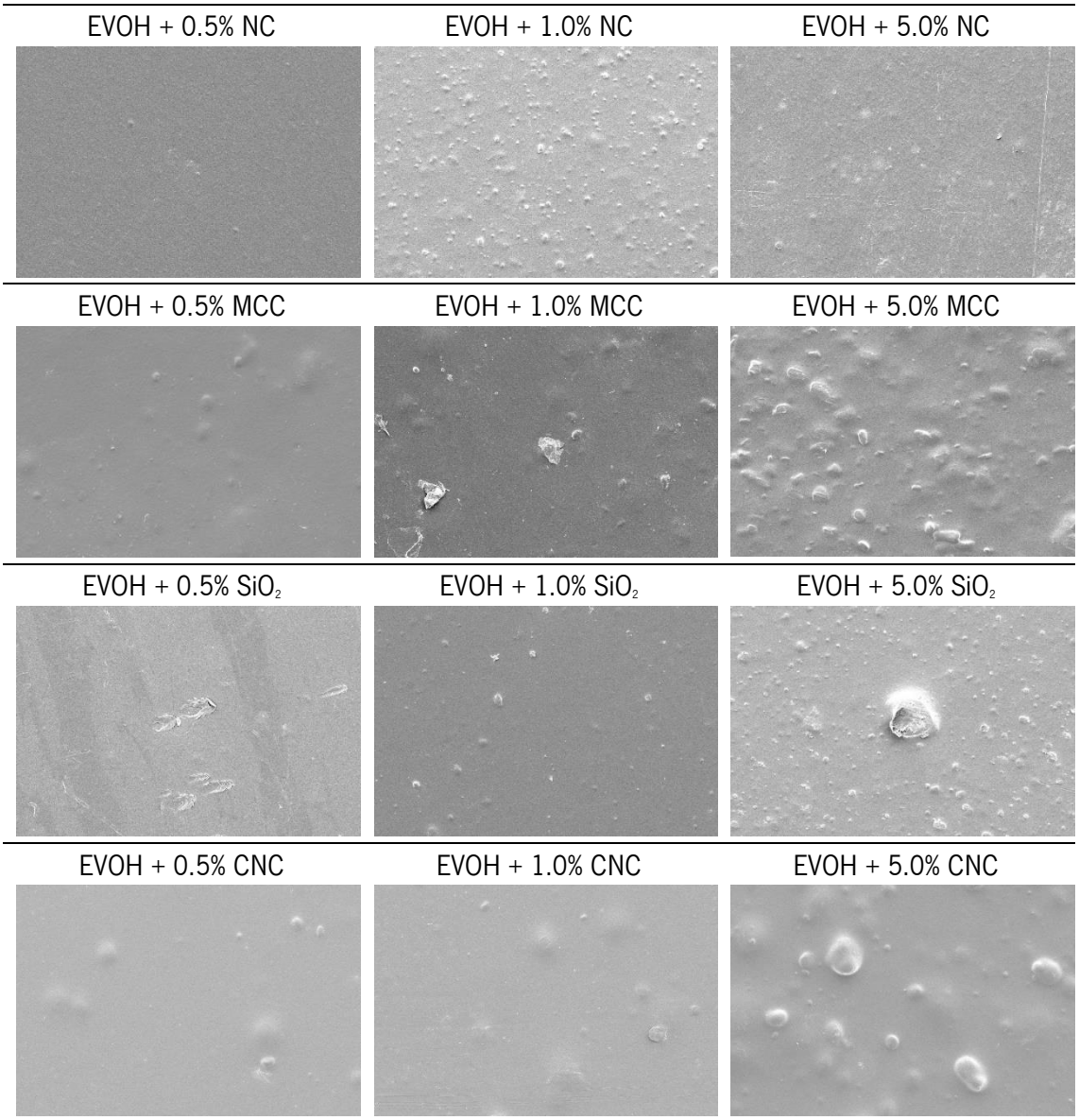


Figure 4-1 SEM micrographs, with a 750x magnification, of the surface of EVOH films incorporating NC, MCC, SiO_2 and CNC

Figure 4-2 shows the digital microscope images of the monolayer films surface showing the particle distribution. In most formulations, the incorporation of 5.0 wt.% of particles into the EVOH matrix leads to a visible increase in particle agglomerates on the surface of the films, except for the NC films. The surface images of the NC formulations are similar, even for the higher concentrations. This effect may be related to the better dispersion of these particles, as observed in the SEM images. The films that showed more surface defects were clearly those containing MCC and CNC. The formation of bubbles was observed during the production of these films, which may be associated with the humidity existing in these particles, as observed by Graninger et al. (2020) and Santos et al. (2017), despite their prior drying before masterbatch and film production [17,

32]. The poor dispersion of these particles can also induce bubble instability during extrusion, causing its rupture where agglomerates exist, as observed by Santos et al. (2017) and also noticed during the extrusion of the 5.0% MCC and 5.0% CNC formulations [32]. Since SiO_2 is widely used in films as an anti-blocking agent, especially in PP and PE matrices, a high surface roughness would be expected for these composite films; in fact, particles/agglomerates of SiO_2 are easily observed in the EVOH + 5.0% SiO_2 film [33].

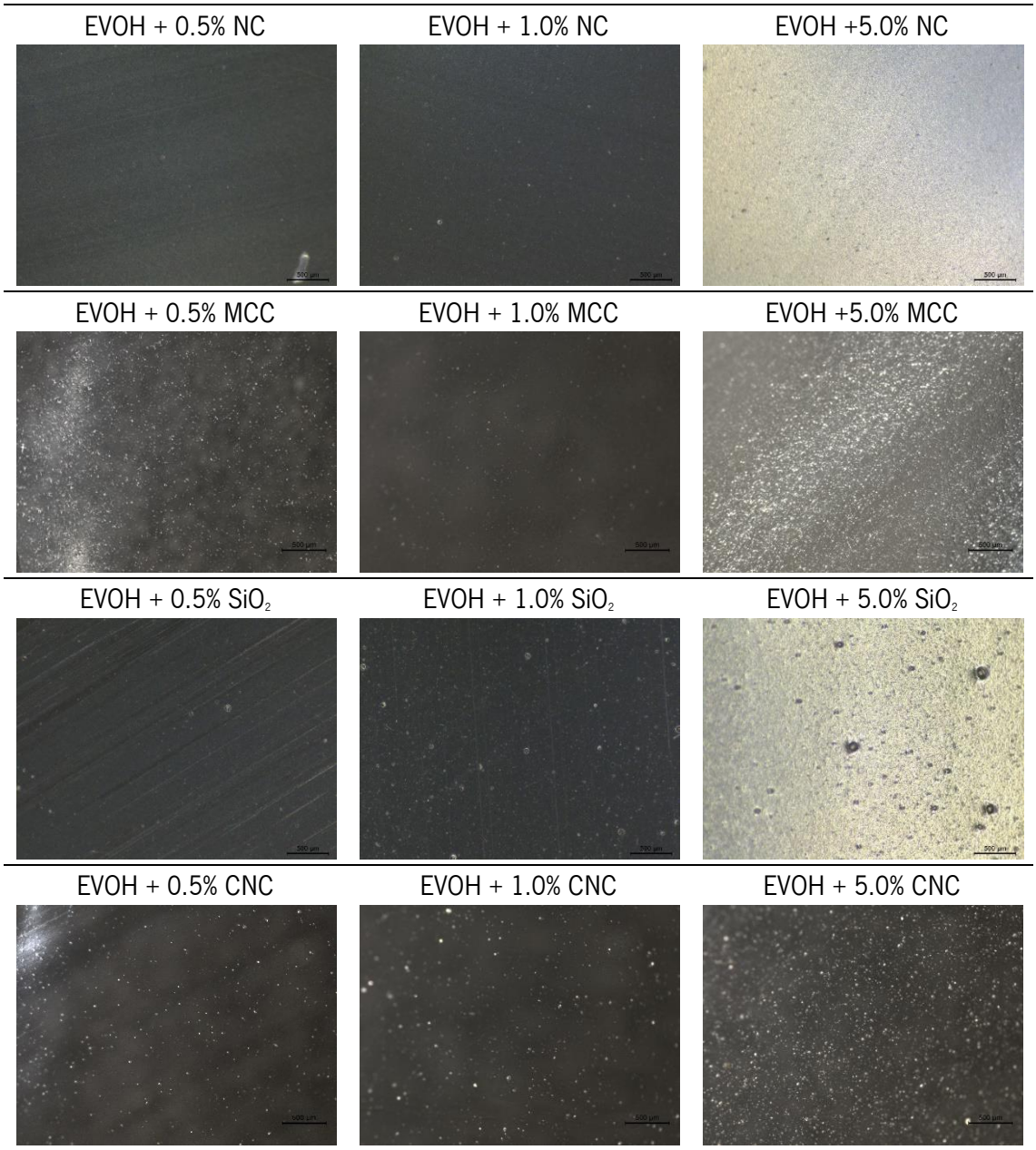


Figure 4-2 Surface images of EVOH films incorporating NC, MCC, SiO_2 and CNC through low magnification microscopy

As expected, all composite films exhibited higher turbidity than the EVOH film and an increase in haze as the incorporation rate of nano and microparticles increases, as can be seen in Table 4-2. This is in agreement with the observations made by microscopy. The EVOH + 0.5 SiO_2, EVOH + 1.0% SiO_2, and EVOH + 0.5% CNC films have turbidity values closer to that of EVOH film. These results indicate that low incorporation rates of nanoparticles originate their better dispersion and distribution in the matrix, leading to fewer aggregates and better light transmission as it was also observed by Mountain & Keating (2021) and Yao et al. (2014) [34, 35]**.**

Table 4-2 Haze of pure EVOH and the EVOH micro and nanocomposites films

Monolayer film samples	**Haze (%)**
EVOH	7.7 ± 0.2^{F}
EVOH + 0.5% NC	12.8 ± 0.8^{D}
EVOH + 1.0% NC	14.9 ± 1.6^{C}
EVOH + 2.5% NC	16.4 ± 0.0^{B}
EVOH + 5% NC	16.5 ± 0.0^{B}
EVOH + 0,5% MCC	15.2 ± 0.7^{C}
EVOH + 1% MCC	16.5 ± 0.0^{B}
EVOH + 2.5% MCC	16.6 ± 0.0^{B}
EVOH + 5% MCC	16.8 ± 0.0^{B}
EVOH + 0.5% SiO_2	9.2 ± 0.7^{E}
EVOH + 1% SiO_2	9.6 ± 0.5^{E}
EVOH + 2.5% SiO_2	16.6 ± 0.0^{B}
EVOH + 5% SiO_2	16.6 ± 0.0^{B}
EVOH + 0.5% CNC	9.8 ± 0.2^{E}
EVOH + 1% CNC	12.7 ± 0.2^{D}
EVOH + 2.5% CNC	18.7 ± 0.0^{A}
EVOH + 5% CNC	19.0 ± 0.1^{A}
Note: Means that do not share a letter are significantly different.	

The WVTR results of EVOH monolayer films (which, as previously stated, have an average thickness of 30 μm), were inconclusive due to the wide variation of thickness obtained (of the order of 40 %). This can be associated to the instability occurred in the extrusion process, since the bubble presented a pronounced diameter variation and, consequently, a wide thickness distribution

in both MD and TD. During the delamination of the EVOH and LDPE layers, the EVOH frequently tore and broke. This is not surprising since this material is used as an oxygen barrier, being inadequate for incorporation in structural layers.

The OTR values exceeded the maximum limit of the equipment (200 $cm^3/m^2 \cdot$ day, unmasked) for most composite films and the few results achieved were not consistent. This may also be due to the wide EVOH film thickness distribution and possible existence of micro-cracks.

Since the barrier properties of monolayer EVOH films were inconclusive, three layers (LDPE|EVOH|LDPE) films were produced with an EVOH layer thickness comparable to commercial food packaging films (around 7 μm). The use of two external layers of LDPE, as happens in commercial films, is expected to guarantee the required bubble stability, making it possible to obtain consistent barrier properties.

Anyway, monolayer films provided some relevant information concerning the inherent ability of the different types of particles to be dispersed and distributed in a EVOH matrix. From the overall analysis of monolayer micro and nanocomposite films, the NC and MCC particles showed a better dispersion. The MCC particles, when compared to CNC, had better thermal stability upon extrusion, and consequently originate less degradation and better bubble stability during extrusion. SiO_2 nanoparticles, have a tendency to migrate to the film surface, a phenomenon that increases as the particle content increases. In general, it has been noticed that all composites show a tendency to form agglomerates on the surface of the polymer film, due to their high surface area, as also stated by Gashti et al. (2013) [36].

4.3.2 Three-layer LDPE/EVOH/LDPE film

Despite the already mentioned incompatibility between LDPE and EVOH, the separation of the film layers was only achieved when fracturing the films after immersion in liquid nitrogen, for SEM analysis. This test was performed to measure the thickness of each layer, as depicted in Figure 4-3. The thickness of the EVOH layer and of its micro and nanocomposites was in the range of 7.4-7.5 μm, value typically used in commercial flexible films [1]. The difficulty in separating the layers can be an indication of more reliable OTR results, as the EVOH is protected against humidity by the LDPE side layers.

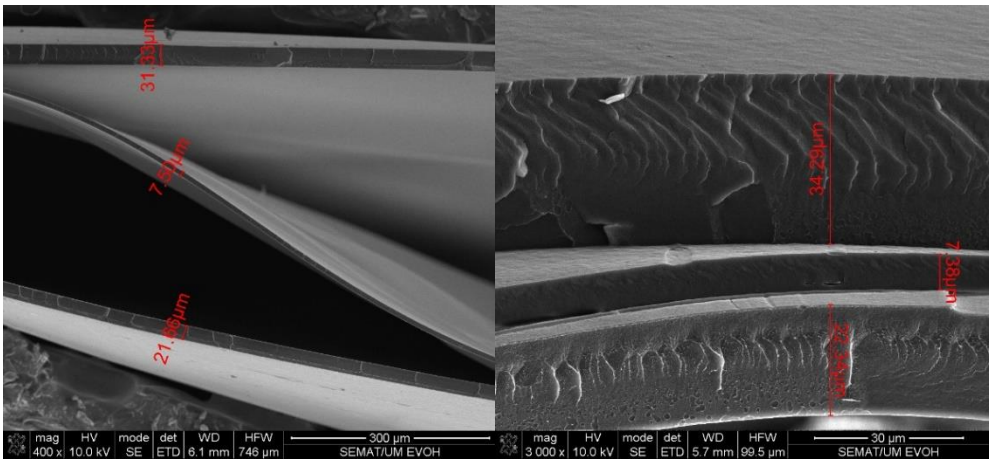


Figure 4-3 SEM micrographs of LDPE | EVOH | LDPE multilayer film

SAXS and XRD were performed to assess the dispersion of the NC and MCC particles and the results are depicted in Figures 4-4 and 4-5. On the diffractogram of the pure NC, Figure 4-4, a peak at 2θ = 1.8° (*d*-spacing 49 Å) can be noticed. Through the SAXS pattern of the NC masterbatch, it was possible to observe that the *d*-spacing and visible wave amplitude were maintained, possibly due to the high amount of NC used. For multilayer films with NC, SAXS patterns do not show any peak, which can indicate a higher intercalation or even exfoliation of NC platelets throughout EVOH matrix [37].

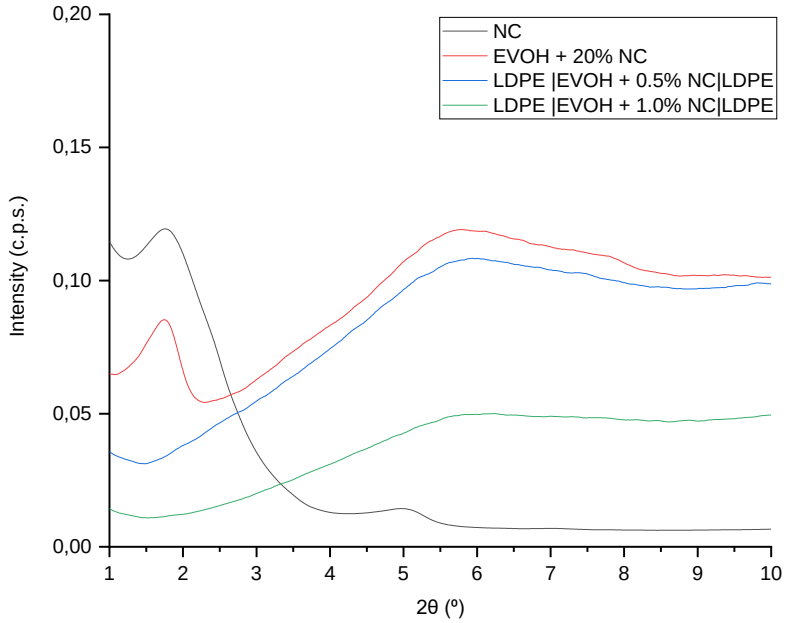


Figure 4-4 SAXS patterns of NC, and films with NC incorporation

The MCC XRD pattern, shown in Figure 4-5, presents a characteristic peak at 2θ=22.7 (d-spacing 3.91 Å), a value close to that reported in the study by Goo et al. (2021) that shows a characteristic peak at 2θ=21° for MCC Vivapur 105 [38]. For the MCC masterbatch, the

characteristic peak of MCC moved to lower angles (2θ=21.9°) leading to an increase in d-spacing to 4.06 Å. Similarly to the multilayer NC films, in these MCC multilayer films, the characteristic peak of MCC disappears, and it is only possible to observe the characteristic peaks of EVOH at 2θ = 20.1° and LDPE at 2θ of 21.4° 23.7° and 36.1° corresponding to the 110, 200, 020 lattice planes of the orthorhombic crystalline form of PE [39-43].

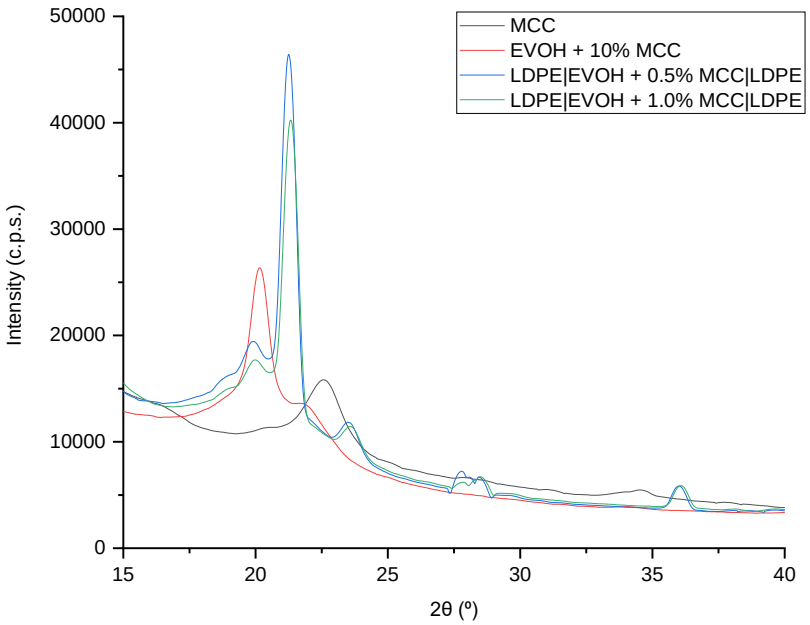


Figure 4-5 XRD patterns of MCC and films with MCC incorporation

The optical properties of the multilayer films (Table 4-3) with an inner layer of EVOH with incorporation of NC and MCC, have a slightly higher turbidity, which increases with wt. % of the particles incorporation, as it would be expected from the results obtained for the monolayer EVOH films (Table 4-2). Therefore, the best film is the one that incorporates 0.5 wt.% NC. The incorporation of EVOH composites in the inner layer did not affect the brightness of the films, since its surface was the same as in the base film, composed by LDPE.

Table 4-3 Haze and Gloss of multilayer films with LDPE, EVOH and respective micro and nanocomposites

Multilayer Film samples	Haze (%)	Gloss (60°)	Gloss (20°)
LDPE|EVOH|LDPE	7.9 ± 0.2^{C}	96.4 ± 1.4^{A}	9.80 ± 6.8^{A}
LDPE|EVOH + 0.5% NC|LDPE	7.5 ± 0.4^{D}	94.4 ± 3.5^{A}	14.1 ± 3.8^{A}
LDPE|EVOH + 1.0% NC|LDPE	8.3 ± 0.1^{B}	90.7 ± 7.8^{A}	11.8 ± 7.8^{A}
LDPE|EVOH + 0.5% MCC|LDPE	8.5 ± 0.2^{AB}	92.5 ± 2.4^{A}	15.6 ± 2.5^{A}
LDPE|EVOH + 1.0% MCC|LDPE	8.8 ± 0.2^{A}	88.3 ± 13.8^{A}	11.0 ± 9.6^{A}

Note: Values that do not share a letter are significantly different.

The OTR results, in Table 4-4, show that all the films with particles have better oxygen barrier than the base film, especially the films measured at 60% RH. The film with 1.0 wt.% NC achieved an OTR reduction of 45.3% (0% RH) and 29.0% (60% RH) when compared to the base film. However, the statistical comparison of results at 0% RH, reveals that there are no significant differences among them. Nonetheless, for the tests performed at 60% RH, the films with 0.5 wt.% NC and 1.0 wt.% MCC obtained significantly different OTR values when compared to the base film. These are promising results for the flexible packaging film industry, as they allow to reduce the EVOH layer thickness while keeping the barrier properties of the packaging film.

The incorporation of particles did not affect the WVTR (0.05 ± 0.00 g/m² h) of the control film. This is not surprising since the outer layers of the films are all composed by LDPE, a hydrophobic polymer. However, these results are interesting since no adhesive layer was used between the incompatible LDPE and EVOH layers.

Table 4-4 OTR of multilayer films with LDPE, EVOH and respective micro and nanocomposites

Multilayer Film samples	OTR ($cm^3/m^2 \cdot day$) 23 °C; 0% RH	OTR ($cm^3/m^2 \cdot day$) 23 °C; 60% RH
LDPE| EVOH| LDPE	0.777 ± 0.127^{A}	0.672 ± 0.029^{A}
LDPE| EVOH + 0.5% NC|LDPE	0.526 ± 0.135^{A}	0.399 ± 0.140^{B}
LDPE| EVOH + 1.0% NC|LDPE	0.425 ± 0.044^{A}	0.477 ± 0.021^{AB}
LDPE| EVOH + 0.5% MCC| LDPE	0.705 ± 0.146^{A}	0.439 ± 0.080^{AB}
LDPE| EVOH + 1.0% MCC|LDPE	0.565 ± 0.204^{A}	0.436 ± 0.078^{B}

Note: Values that do not share a letter are significantly different.

4.4 Conclusions

EVOH masterbatch with different types of micro and nanoparticles (NC, MCC, CNC, SiO_2) were produced and used for the production of mono and multilayer films. In the production of the NC masterbatch, it was possible to incorporate 20 wt.% of these particles, at a temperature of 210 °C. For the remaining particles, the incorporation rate was limited to 10 wt.%, and a lower temperature (180 °C and 190°C) was used. This was due to non-steady extrusion, for SiO_2 case, and thermal degradation, for the CNC and NC cases. Through microscopy, it was observed that NC showed a better dispersion and distribution in the EVOH monolayer films, for all incorporation rates (0.5, 1.0, 2.5 and 5.0 wt.%). Regarding cellulose particles, CNC exhibited larger agglomerates than MCC, originating also a more unstable film extrusion, with frequent rupture of the extruded bubble. Taking into account these results, two types of particles, MCC and NC, were selected for the production of three-layer films. Results showed that the external LDPE layers promoted excellent stability to the blown film process. The haze of all the films produced remained relatively low, enabling good visibility of the food content, while their gloss was retained, being determined by the external layers (LDPE). The WVTR remained similar for all the films, also justified by the outer LDPE layers. While the OTR results measured at 0% RH were not significantly different, at 60% RH, films with 0.5 wt.% NC and 1.0 wt.% MCC obtained significantly low OTR values, when compared to the base film.

From the overall results, it can be concluded that low incorporation rates of NC and MCC in an EVOH matrix have a great potential to be implemented in the production of industrially produced high barrier food packaging films, using a EVOH layer thickness lower than usual. This will facilitate the recycling of the multilayer films without compromising their performance during the use stage.

4.5 References

[1] N. Alipour et al., “Structure and properties of polyethylene-based and EVOH-based multilayered films with layer thicknesses of 150nm and greater,” Eur Polym J, vol. 64, pp. 36–51, Mar. 2015, doi: 10.1016/j.eurpolymj.2014.12.011.

[2] Z. Tartakowski, “Recycling of packaging multilayer films: New materials for technical products,” Resour Conserv Recycl, vol. 55, no. 2, pp. 167–170, Dec. 2010, doi: 10.1016/j.resconrec.2010.09.004.

[3] M. Paul, B. Morris, J. Weinhold, and K. Hausmann, “The effect of stretching and tie layer composition on adhesion strength of multi-layered films,” Journal of Plastic Film and Sheeting, vol. 38, no. 3, pp. 351–368, Jul. 2022, doi: 10.1177/87560879211063475.

[4] Zentrale Stelle, “Minimum standard for determining the recyclability of packaging subject to system participation pursuant to section 21 (3) VerpackG (Verpackungsgesetz – Packaging Act),” Oct. 2019.

[5] RECOUP, “Plastic Packaging Recyclability By Design,” Woodston, Peterborough, UK, 2021.

[6] Recyclass, “Recyclability Methodology Version 2.1,” Brussels, May 2022.

[7] J. H. Chen, J. G. Liu, T. Q. Yuan, and R. C. Sun, “Comparison of cellulose and chitin nanocrystals for reinforcing regenerated cellulose fibers,” J Appl Polym Sci, vol. 134, no. 22, pp. 1–8, 2017, doi: 10.1002/app.44880.

[8] M. Vähä-Nissi et al., “Cellulose nanofibrils in biobased multilayer films for food packaging,” J Appl Polym Sci, vol. 134, no. 19, pp. 2–9, 2017, doi: 10.1002/app.44830.

[9] M. Alexandre and P. Dubois, “Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials,” Materials Science and Engineering, Reports: A Review Journal, vol. 28, pp. 1–63, 2000.

[10] K. Müller et al., “Review on the processing and properties of polymer nanocomposites and nanocoatings and their applications in the packaging, automotive and solar energy fields,” Nanomaterials, vol. 7, no. 74, p. 47, 2017, doi: 10.3390/nano7040074.

[11] A. D. de Oliveira and C. A. G. Beatrice, “Polymer Nanocomposites with Different Types of Nanofiller,” in Nanocomposites - Recent Evolutions, 2018, pp. 103–128. doi: 10.5772/intechopen.81329.

[12] B. Melendez-rodriguez et al., “Development and characterization of electrospun fiber-based poly(Ethylene-co-vinyl alcohol) films of application interest as high-gas-barrier interlayers in food packaging,” Polymers (Basel), vol. 13, no. 13, Jul. 2021, doi: 10.3390/polym13132061.

[13] B. Podolyák, D. Kun, K. Renner, and B. Pukánszky, “Hydrogen bonding interactions in poly(ethylene-co-vinyl alcohol)/lignin blends,” Int J Biol Macromol, vol. 107, no. PartA, pp. 1203–1211, Feb. 2018, doi: 10.1016/j.ijbiomac.2017.09.098.

[14] J. R. Wagner, “Blown Film, Cast Film, and Lamination Processes.,” in Multilayer Flexible Packaging: Second Edition, Elsevier Inc., 2016, pp. 137–145. doi: 10.1016/B978-0-323-37100-1.00010-7.

[15] M. Rahnama, A. Oromiehie, S. Ahmadi, and I. Ghasemi, “Effect of different blend compositions on properties of low-density polyethylene/ethylene vinyl alcohol/clay toward high oxygen barrier nanocomposite films,” Polymer Science - Series A, vol. 59, no. 4, pp. 533–542, 2017, doi: 10.1134/S0965545X1704006X.

[16] Y. Liu, Y. Liu, and S. Wei, “Processing technologies of EVOH/nano-SiO2 high-barrier packaging composites,” 17th IAPRI World Conference on Packaging 2010, pp. 269–274, 2010.

[17] G. Graninger, S. Kumar, G. Garrett, and B. G. Falzon, “Effect of shear forces on dispersion-related properties of microcrystalline cellulose-reinforced EVOH composites for advanced applications,” Compos Part A Appl Sci Manuf, vol. 139, no. August, p. 106103, 2020, doi: 10.1016/j.compositesa.2020.106103.

[18] E. Garofalo, P. Scarfato, L. Di Maio, and L. Incarnato, “Tuning of co-extrusion processing conditions and film layout to optimize the performances of PA/PE multilayer nanocomposite films for food packaging,” Polym Compos, vol. 39, no. 9, pp. 3157–3167, 2018, doi: 10.1002/pc.24323.

[19] P. Scarfato, L. Di Maio, M. R. Milana, S. Giamberardini, M. Denaro, and L. Incarnato, “Performance properties, lactic acid specific migration and swelling by simulant of biodegradable poly(lactic acid)/nanoclay multilayer films for food packaging,” Food Addit Contam Part A Chem Anal Control Expo Risk Assess, vol. 34, no. 10, pp. 1730–1742, 2017, doi: 10.1080/19440049.2017.1321786.

[20] L. Cabedo, E. Giménez, J. M. Lagaron, R. Gavara, and J. J. Saura, “Development of EVOH-kaolinite nanocomposites,” Polymer (Guildf), vol. 45, no. 15, pp. 5233–5238, 2004, doi: 10.1016/j.polymer.2004.05.018.

[21] S. Seethamraju, P. C. Ramamurthy, and G. Madras, “Flexible poly(vinyl alcohol-co-ethylene)/modified MMT moisture barrier composite for encapsulating organic devices,” The Royal Society of Chemistry, vol. 3, pp. 12831–12838, 2013.

[22] S. W. Kim and S. H. Cha, “Thermal, Mechanical, and Gas Barrier Properties of Ethylene–Vinyl Alcohol Copolymer-Based Nanocomposites for Food Packaging Films: Effects of Nanoclay loading,” Applied Polymer Science, p. 8, 2013.

[23] N. Gray, Y. Hamzeh, A. Kaboorani, and A. Abdulkhani, “Influence of cellulose nanocrystal on strength and properties of low density polyethylene and thermoplastic starch composites,” Ind Crops Prod, vol. 115, pp. 298–305, 2018, doi: 10.1016/j.indcrop.2018.02.017.

[24] A. Kaboorani, N. Gray, Y. Hamzeh, A. Abdulkhani, and Y. Shirmohammadli, “Tailoring the low-density polyethylene - thermoplastic starch composites using cellulose nanocrystals and compatibilizer,” Polym Test, vol. 93, p. 11, 2020, doi: 10.1016/j.polymertesting.2020.107007.

[25] S. Liu et al., “Investigating the H2O/O2 selective permeability from a view of multi-scale structure of starch/SiO2 nanocomposites,” Carbohydr Polym, vol. 173, pp. 143–149, 2017, doi: 10.1016/j.carbpol.2017.05.091.

[26] C. Swaroop and M. Shukla, “Nano-magnesium oxide reinforced polylactic acid biofilms for food packaging applications,” Int J Biol Macromol, vol. 113, pp. 729–736, 2018, doi: 10.1016/j.ijbiomac.2018.02.156.

[27] Y. Huang, L. Mei, X. Chen, and Q. Wang, “Recent Developments in Food Packaging Based on Nanomaterials,” pp. 1–29, 2018, doi: 10.3390/nano8100830.

[28] C. Vasile, “Polymeric Nanocomposites and Nanocoatings for Food Packaging: A Review,” no. Ii, 2018, doi: 10.3390/ma11101834.

[29] H. Zhang, C. Li, J. Guo, L. Zang, and J. Luo, “In Situ Synthesis of Poly(methyl methacrylate)/SiO Hybrid Nanocomposites via ‘Grafting Onto’ Strategy Based on UV Irradiation in the Presence of Iron Aqueous Solution,” J Nanomater, vol. 2012, pp. 1–9, 2012, doi: 10.1155/2012/217412.

[30] N. Wu et al., “A novel surface molecularly imprinted polymer as the solid-phase extraction adsorbent for the selective determination of ampicillin sodium in milk and blood samples,” J Pharm Anal, vol. 6, no. 3, pp. 157–164, Jun. 2016, doi: 10.1016/j.jpha.2016.01.004.

[31] D. J. Voorn, W. Ming, and A. M. van Herk, “Polymer–Clay Nanocomposite Latex Particles by Inverse Pickering Emulsion Polymerization Stabilized with Hydrophobic Montmorillonite Platelets,” Macromolecules, vol. 39, no. 6, pp. 2137–2143, Mar. 2006, doi: 10.1021/ma052539t.

[32] F. A. Santos, G. C. V. Iulianelli, and M. I. B. Tavares, “Effect of microcrystalline and nanocrystals cellulose fillers in materials based on PLA matrix,” Polym Test, vol. 61, pp. 280–288, Aug. 2017, doi: 10.1016/j.polymertesting.2017.05.028.

[33] J. Markarian, “Slip and antiblock additives: surface medication for film and sheet,” Plastics, Additives and Compounding, vol. 9, no. 6, pp. 32–35, Nov. 2007, doi: 10.1016/S1464-391X(07)70156-3.

[34] M. Yao, J. Nan, and T. Chen, “Effect of particle size distribution on turbidity under various water quality levels during flocculation processes,” Desalination, vol. 354, pp. 116–124, Dec. 2014, doi: 10.1016/j.desal.2014.09.029.

[35] G. A. Mountain and C. D. Keating, “Practical considerations for generation of multi-compartment complex coacervates,” 2021, pp. 115–142. doi: 10.1016/bs.mie.2020.09.001.

[36] M. P. Gashti, H. Allahyary, P. Nasraei, and M. P. Gashti, “SiO2-kaolinite affecting the surface properties of ternary poly(vinyl chloride)/silica/kaolinite nanocomposites,” Fibers and Polymers, vol. 14, no. 11, pp. 1870–1876, Nov. 2013, doi: 10.1007/s12221-013-1870-0.

[37] A. Babaei, S. R. Ghaffarian, M. M. Khorasani, and S. Baseghi, “Influence of Compatibilizer-Type and Processing Approach on the Dispersion of OMMT in High-Density Polyethylene Matrix,” Journal of Macromolecular Science, Part B, vol. 51, no. 3, pp. 481–495, Mar. 2012, doi: 10.1080/00222348.2011.597689.

[38] Y. T. Goo et al., “Development of a Solid Supersaturable Micelle of Revaprazan for Improved Dissolution and Oral Bioavailability Using Box-Behnken Design,” Int J Nanomedicine, vol. Volume 16, pp. 1245–1259, Feb. 2021, doi: 10.2147/IJN.S298450.

[39] W. Du, W. Zhong, Y. Lin, L. Shen, and Q. Du, “Space charge distribution and crystalline structure in polyethylene blended with EVOH,” Eur Polym J, vol. 40, no. 8, pp. 1987–1995, 2004, doi: 10.1016/j.eurpolymj.2004.04.003.

[40] D. Depan, W. Chirdon, and A. Khattab, “Morphological and Chemical Analysis of Low-Density Polyethylene Crystallized on Carbon and Clay Nanofillers,” Polymers (Basel), vol. 13, no. 10, p. 1558, May 2021, doi: 10.3390/polym13101558.

[41] A. N. Shebani, A. J. Van Reenen, and M. Meincken, “The Effect of Wood Species on the Mechanical and Thermal Properties of Wood–LLDPE Composites,” J Compos Mater, vol. 43, no. 11, pp. 1305–1318, Jun. 2009, doi: 10.1177/0021998308104548.

[42] J.-T. Yeh, W.-H. Yao, Q. Du, and C.-C. Chen, “Blending and barrier properties of blends of modified polyamide and ethylene vinyl alcohol copolymer,” J Polym Sci B Polym Phys, vol. 43, no. 5, pp. 511–521, Mar. 2005, doi: 10.1002/polb.20344.

[43] N. Aktzi, Y. Nir, D. Wang, M. Narkis, and A. Siegmann, “EVOH/clay nanocomposites produced by melt processing,” Polym Compos, vol. 22, no. 5, pp. 710–720, Oct. 2001, doi: 10.1002/pc.10573.

5. FEASIBILITY OF INCORPORATING RECYCLED MULTILAYER LDPE/EVOH FILMS INTO FLEXIBLE PACKAGING

Abstract

Multilayer films are widely used in the food industry because they allow the combination of properties of different materials to increase product shelf life without sacrificing product value. Despite the associated benefits, these films are difficult to recycle due to material immiscibility and difficult layer separation. Thus, the purpose of this research is to investigate the feasibility of incorporating recycled plastic material from the multi-material film industry into extruded films for food packaging.

To simulate the thermomechanical recycling, two different post-industrial polymeric wastes of low-density polyethylene (LDPE) (with linear low-density polyethylene (LLDPE) or with ethylene vinyl alcohol (EVOH)), were reprocessed four times in a single-screw extruder. Moreover, these polymeric wastes were blended with virgin LDPE to improve the extrusion process control and to assess their effect on the blend properties. The extrusion experiments demonstrate that reprocessing of multilayer films and processing of their blends with virgin LDPE is feasible. Moreover, the mechanical and thermal properties of the corresponding films are not negatively affected when compared to those of virgin LDPE films. Nevertheless, the optical properties of recycled EVOH films were lower than those of virgin LDPE or recycled LLDPE, with high haze and low gloss.

Keywords: Packaging, blown film, recycled multilayer film

This chapter is based on the article: **Barros, C**., Carneiro, O. S., & Machado, A. v. (2024). Feasibility of incorporating recycled multilayer LDPE/EVOH films into new flexible packaging. *Accepted for Publication in Polymer Engineering & Science*.

5.1 Introduction

In recent years, the packaging sector has been dominant in the production of primary plastics and, consequently, also dominant in the production of plastic waste [1, 2]. Despite the decrease of packaging deposited in landfills and the increase in recycling, more than 18% of this waste still ends in landfills [2]. These packages can be of different types and made in a variety of ways; however, this study focuses only on food packages made of flexible films.

Plastic film packages may combine different types of materials in coextruded or laminated films, improving its aesthetic, functional, mechanical, and/or barrier properties, however it becomes difficult to recycle them [3, 4].

Polymers, such as ethylene vinyl alcohol (EVOH), polyamide (PA) and polyvinylidene chloride (PVDC) are often used in the inner layers of flexible food packaging, made up mostly of polyethylene (PE), to improve the mechanical and oxygen barrier properties of the package [5-9]. Although advantageous, the combination of PE with polymers normally used for oxygen barrier in multilayer films is extremely critical in terms of recycling cost [10, 11]. The chemical structure of these polymers differs in polarity making them incompatible [12]. For this reason, the use of a compatibilizer between the PE and EVOH layers is always necessary, with these films requiring a minimum of 5 layers: PE/tie layer/EVOH/tie layer/PE [13]. When recycling thermomechanically, this incompatibility causes poor adhesion between phases, resulting in a recycled material with lower properties and less added value [14, 15]. Despite the incompatibility of these materials, recent studies have shown that the tie layer used to bond PA and PE in the film serves as an effective compatibilizer throughout the recycling process [16].

The use of recycled plastic packaging not only mitigates its adverse impact on the environment but also reduces the need for its eventual incineration. Several studies have been developed for this purpose, to evaluate the properties of plastic films with the incorporation of different percentages of recycled material, to ensure the maintenance of the packaging quality for the food industry [17, 18].

The study of Turriziani et. al (2023) evaluated the mechanical properties of two different recycled materials from multilayer films (A and B), with 5 and 7 wt.% of polyolefin compatibilizer with maleic anhydride (PCA-MA). The samples were produced by blown film extrusion with a thickness of 50 μm. Recycled films with PCA-MA exhibited greater elongation at break and tensile strength than films without the compatibilizer, but only in the transverse direction. This study demonstrates that while the compatibilizer offers advantages for the mechanical properties of the

film, the recycled materials without it also exhibit good mechanical properties compared to virgin PE [8].

Meran, Ozturk and Yuksel (2008) investigated the change in mechanical properties of samples with varying percentages of post-consumer recycled material compared to the corresponding virgin materials. Tensile strength decreased by 35.5 % in the sample with 100 % recycled LDPE, compared to the sample without recycled material, but only 11.9 % in the sample with 20 % recycled [19]. Another significant outcome from this study was that these recycled materials did not cause any problems during processing. Studies carried out with samples of multi-layer blown films showed different results. According to Chytiri et al. (2006) the introduction of different percentages of recycled material (0 %, 50 % and 100 %) in the inner layer of a five-layer LDPE and LLDPE film, did not affect the mechanical properties of the film [20]. These findings could be explained by the fact that the layer containing recycled material is inserted between two layers of virgin material.

Most of the studies found in the literature presented a mechanical recycling with a single material, without exploring the recycling of multilayer films with different materials. Additionally, the characterized samples are not frequently produced by industrial techniques of packaging production [21-23].

The motivation for the development of the current research stems from the need to achieve scientific knowledge in the plastic film sector, particularly for the food market, aiming to promote the production of high-performance packaging with the incorporation of recycled material to reduce the deposition of plastic waste in landfills.

In this study, plastic films for the development of new packages were produced using tubular film extrusion technique. This processing technique enables the production of films with some biaxial orientation and low thickness, widely employed in the industry for manufacturing food packaging [24]. With the samples produced by this processing technique, it was possible to evaluate the properties of two different types of recycled multilayer films with different materials. Moreover, the effect of repeated thermomechanical reprocessing on these recycled materials was also assessed and compared with the film produced using a typical reference material for flexible film production, such as LDPE. Due to the increase in the standard deviation in the tensile tests results, and the increase in haze in the Recycled EVOH films, mixtures were made with virgin and recycled material. The incorporation of a fixed percentage of virgin polymer in the recycled material can also improve film reproducibility in the industrial process, minimizing composition variations.

The present study focuses on exploring the modification and preservation of the properties of recycled (post-industrial) materials, while evaluating their reprocessability and blending with virgin LDPE, for potential integration into food packaging films.

5.2 Experimental

5.2.1 Materials

Dow LDPE 352 E, a low-density polyethylene blown film extrusion grade (density = 925 kg/m^3, melt flow index (MFI) = 2.0 g/10 min (190 °C/2.16 kg) and Vicat softening temperature of 96.0 °C), was used as the virgin polymer in the blend with recycled materials. The film producer company involved in this research, Vizelpas, supplied the recycled materials recovered from multi-material multilayer films used in two food packages made with different materials, namely: 'Recycled Metallocene' – consisting of LDPE, butene LLDPE and metallocene LLDPE; and 'Recycled EVOH' – consisting of LDPE, butene LLDPE, metallocene LLDPE, polyethylene grafted maleic anhydride (PE-g-MA) as adhesive and EVOH.

To characterize the composition of the materials recovered from industry, samples were analysed by Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). The EVOH content in the 'Recycled EVOH' was determined by the dissolution of the soluble fraction (PE) in xylene. The experimental protocols used are described in section 5.2.2.

The FTIR spectra of the 'Recycled Metallocene' and 'Recycled EVOH' are shown in Figure 5-1. The spectrum of the 'Recycled Metallocene' reveals peaks at 1466 and 721 cm^{-1}, characteristic of scissoring and rocking vibrations of CH_2 groups, respectively, present in the chemical structure of PE [25, 26]. The spectrum of Recycled EVOH shows peak at 3338 cm^{-1}, characteristic of O-H bond present in the chemical structure of EVOH, as well as peaks at 1466 and 721 cm^{-1} (related to PE structure) as in the previous case.

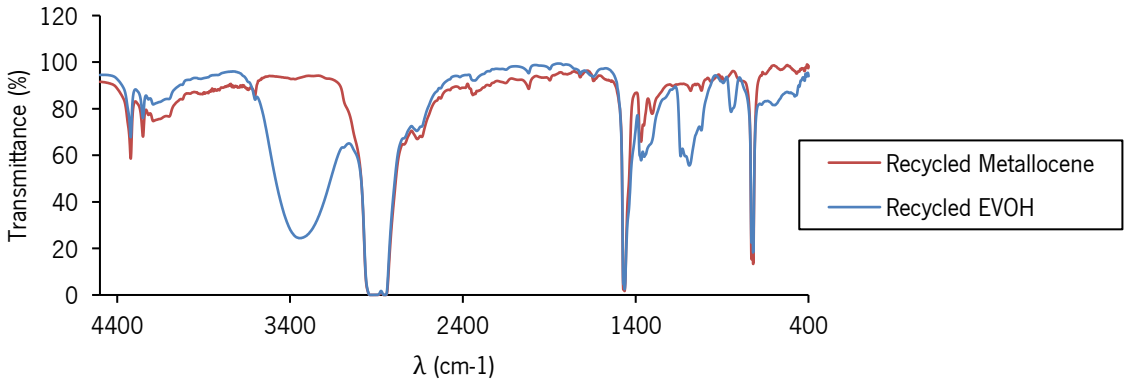


Figure 5-1 FTIR spectra of 'Recycled Metallocene' and 'Recycled EVOH'.

DSC results indicate that Recycled Metallocene has two melting peaks at 109.5 °C and 126.9 °C, corresponding to the melting temperature of LDPE and LLDPE, respectively. For Recycled EVOH, two melting peaks at 111.7 °C and 183 °C were observed, corresponding to the melting temperatures of LDPE, and EVOH, respectively. The first peak on the DSC of Recycled EVOH shows a shoulder to the right of the LDPE melting peak indicating the presence of another polymer with similar melting temperature, such as LLDPE.

After dissolution of LDPE, LLDPE, and PE-g-MA in xylene, 9.0 wt.% EVOH content was obtained.

These recycled materials were used for the production of blends with virgin LDPE and for the production of pellets with four additional reprocessing cycles, obtained through filament extrusion and subsequent pelletizing.

5.2.2 Reprocessing and films production

The supplied recycled material was reprocessed four additional times, resulting in a total of five reprocessing cycles, to evaluate the evolution of mechanical, optical, and rheological properties as the number of reprocessing cycles increased. The sample codes used for these samples are listed in Table 5-1.

Table 5-1 Sample codes of recycled reprocessed materials

Sample Code	Recycled reprocessed materials
1M	1st 'Recycled Metallocene'
2M, 3M, 4M, 5M	2nd, 3rd, 4th and 5th Reprocessing of 'Recycled Metallocene'
1E	1st 'Recycled EVOH'
2E, 3E, 4E, 5E	2nd, 3rd, 4th and 5th Reprocessing of 'Recycled EVOH'

The reprocessing was carried out in a PeriPlast single screw extruder with a screw diameter (D) of 20 mm and L/D = 20, coupled to a filament extrusion die. The Recycled Metallocene was reprocessed at 180 °C for all heating zones, while the Recycled EVOH, was reprocessed with a temperature profile of 200 °C - 230 °C - 220 °C, given the EVOH melting temperature, both at a screw speed of 40 rpm. The filament of the reprocessed materials was cooled by forced air convection and subsequently pelletized. These pellets were dried at 60 °C during 4 hours before being processed on the blown film extrusion line.

The reprocessed materials were produced in a tubular film extrusion line equipped with a Periplast single-screw extruder with D = 25 mm and L/D = 25. The extrusion head attached to this equipment terminates with an annular die with a diameter of 50 mm and a 1.25 mm gap. In all the cases, a temperature profile of 180 °C - 200 °C - 220 °C in the extruder, 220 °C in the extrusion head, a screw speed of 50 rpm, blow-up ratio (BUR) of 1.8 and a take-up ratio (TUR) of 11, were employed.

For the production of films with incorporation of recycled materials, 20, 40 and 50 wt. % of virgin LDPE granules were mixed with 80, 60 and 50 wt. %, respectively, of the recycled Metallocene and the recycled EVOH in a rotating drum mixer, as described in Table 5-2.

Table 5-2 Sample codes of recycled blends produced with incorporation of virgin LDPE

Sample code	Recycled Metallocene (wt.%)	Recycled EVOH (wt.%)	LDPE (wt.%)
50% M + 50% LDPE	50		50
60% M + 40% LDPE	60		40
80% M + 20% LDPE	80		20
50% E + 50% LDPE		50	50
60% E + 40% LDPE		60	40
80% E + 20% LDPE		80	20

These blends were utilized for film production via extrusion, as described above. The quality of the films produced was assessed through tensile, haze and brightness tests to evaluate the impact of incorporating virgin LDPE.

The thickness of the films was measured using a micrometer (Digimatic thickness gauge 547-301, Mitutoyo, Japan) with a measuring accuracy of 0.01 mm. The thickness of all the produced films was 50 ± 10 μm.

5.2.3 Characterization Techniques

FTIR - The FTIR spectra of the recycled blends were obtained using the Jasco FT/IR-4100 equipment.

Determination of EVOH content - To determine the EVOH content (insoluble fraction) two samples weighing 0.1007 g and 0.0948 g of Recycled EVOH were placed on a 120-mesh wire pouch, previously weighed, that was fold to form a cage. The content in the wire cage was dissolved in 100 ml of refluxing xylene at 46 °C during 12 h. After dissolution, the pouch was placed in a vacuum oven at 150 °C and then weighed to calculate the percentage of EVOH. This method is an adaptation of the method used for the determination of gel content of ethylene plastics present in the ASTM D2765-16 standard.

DSC - For the DSC test one pellet (4–5 mg) from each sample was placed in aluminium crucibles with pierced lid under a nitrogen flow rate of 50 mL/min using a DSC Netzsch equipment. The procedure was repeated three times for each material. The test was performed from 20 to 230 °C at a heating rate of 10 °C/min and cooled down at rate of 20 °C/min. Each sample was

subjected to two heating-cooling cycles, as recommended in ISO 11357-1. The melting and crystallization temperatures of the different materials were determined from the 2nd heating endothermic peak, and first controlled cooling exothermic peak, respectively.

XRD - X-Ray diffraction measurements were carried out on film samples at 23 ± 2 °C using a diffractometer, Bruker AXS D8 Discover, equipped with a CuKα generator (λ = 1.5404 Å) operating at 40 kV and 40 mA. Measurements were conducted in a 2θ range from 5° to 60° with a 0.02° step and a counting time of 1 second per step. The crystallinity of the samples was calculated from their scans by dividing the area of the crystalline peaks by the total area under the diffraction curve, using the Bruker AXS DIFFRAC.EVA V4.2.2 software.

SEM - Scanning Electron Microscopy analysis was carried out on film samples coated with gold, fractured in liquid nitrogen, using a Nano SEM - FEI Nova 200 equipment.

MFI - The MFI of reprocessed granules from 'Recycled Metallocene' and 'Recycled EVOH' were carried out in an MFI Daventest equipment at temperatures of 190 °C, 210 °C and 230 °C with a 2.16 kg weight, according to ISO 1133-1.

Tensile Tests - The tensile tests of the films produced with reprocessed recycled material and the films produced with recycled material incorporating virgin LDPE were performed using a ZWICK universal mechanical testing equipment with a load cell of 5kN, at a speed of 50 mm/min, at 23 ± 2 °C. From the extruded film bubble, 5 specimens 25 mm wide and 160 mm long, were collected in accordance with ASTM D882-10 in the machine direction (MD) and in the transverse direction (TD).

Optical properties - The haze of the films was determined using a XL-211 Hazegard System transmittance meter, according to ASTM D1003-00. Five measurements were performed for each sample.

Gloss measurements of the films were analysed according to ISO 2813 standard using a BYK Micro-TRI-gloss S gloss meter, with 20° and 60° measurement geometries.

Statistical Analyses - The results of tensile tests and haze measurements are presented as mean ± standard deviation. Statistical analysis was performed using IBM SPSS Statistics software, employing one-way analysis of variance (ANOVA) with comparison procedures assuming equal variances with Tukey method for differences of means, with a confidence level of 95%.

5.3 Results and Discussion

5.3.1 Reprocessing Study

As can be seen in Figure 5-2, and corresponding Table S1 in the supplemental section, the melting and crystallization temperatures of the first and fifth reprocessing cycles of Recycled Metallocene and EVOH are similar. Additionally, a shoulder attenuation in LDPE melting peak from sample 1E to 5E, can be observed in the DSC curves, which may indicate improved homogenization of this recycled material after reprocessing.

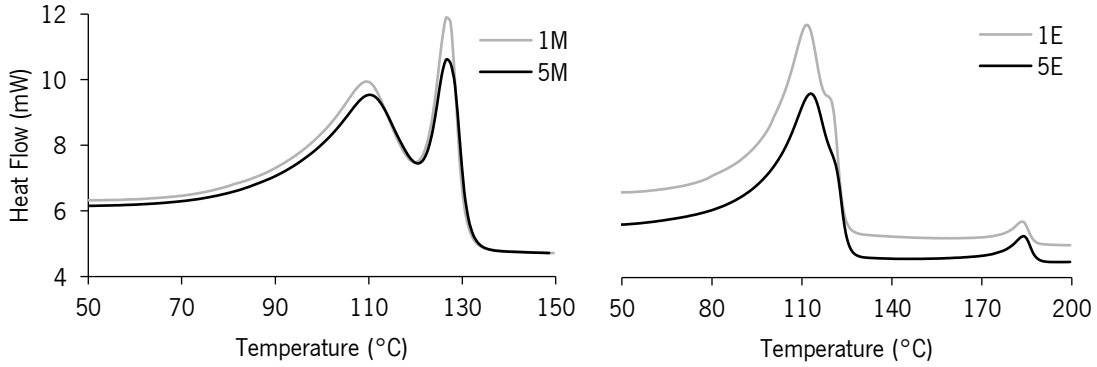


Figure 5-2 DSC second heating curves of the first and fifth reprocessed recycles

From the analysis of the MFI results depicted in Figures 5-3 and 5-4 and in Table S2 in the supplemental section, it can be noticed that material's fluidity is almost unaffected by the successive reprocessing cycles (from 1 to 5) for the recycled EVOH, only the results of the tests at 230°C show slightly differences among the recycled cycles, increase until the third and then decreases. This can be due to thermal degradation during the MFI test, since the test has a pre-heating of 5 minutes, at this temperature, thermal degradation might occur. Due to tertiary carbons present in EVOH, degradation occurs mainly through chain scission rather than crosslinking, which explains the increase of MFI as the recycled cycle increases. For Recycled Metallocene, at all tested temperature, there is a slight decreasing trend in the MFI as the number of reprocessing cycles increases, which can be associated with a slight crosslinking of LDPE and LLDPE, well-known effect for reprocessing recycled PE [27]. Nevertheless, it is not possible to associate the crosslink reaction with LDPE or LLDPE since this is a recycled material and the composition is not known. The consistent rheological performance is of great importance as it allows to keep the processing conditions throughout the reprocessing cycles.

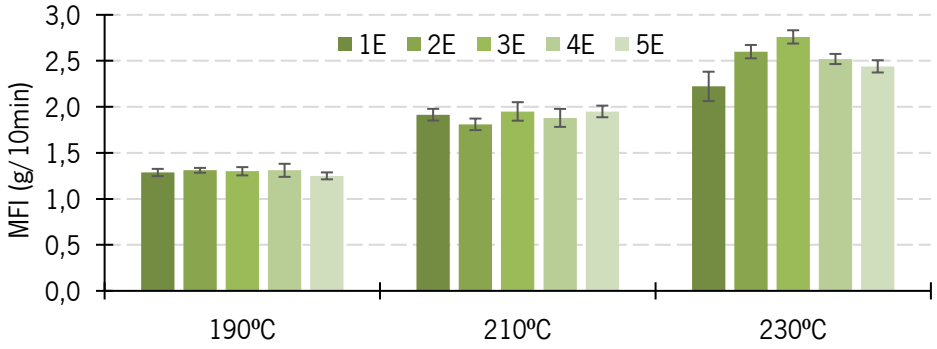


Figure 5-3 MFI of reprocessed recycled EVOH (E)

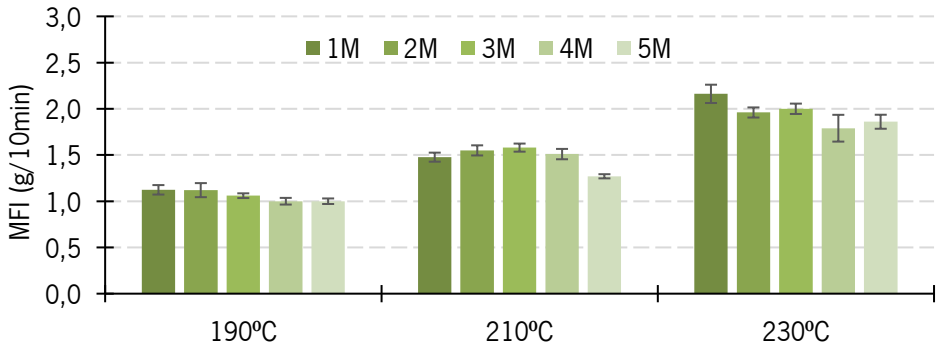


Figure 5-4 MFI of reprocessed recycled Metallocene (M)

The WAXD spectra for the first and fifth reprocessed recycled materials and virgin LDPE film samples are depicted in Figure 5-5. All samples exhibit three main crystalline diffraction peaks characteristics of PE at 2θ of 21.5°, 23.7° and 36.2°, corresponding to the 110, 200 and 020 lattice planes of the orthorhombic crystal lattice, respectively [28-30]. The characteristic EVOH diffraction peaks mentioned in other research works do not appear in any of the EVOH recycles. Since the characteristic diffraction peak of EVOH is at 21.24°, this peak is overlaid by the high intensity peak of LDPE, which hinders a clear distinction of the individual peaks [31, 32].

Table 5-3 shows that the amount of EVOH present in the 'Recycled EVOH' (9 wt.%) did not change the crystalline form of PE, a fact that was also observed by Du et al. (2004) [30]. On the contrary, the recycled Metallocene has slightly decrease in the degree of crystallinity, which might be associated with the crosslinking reactions.

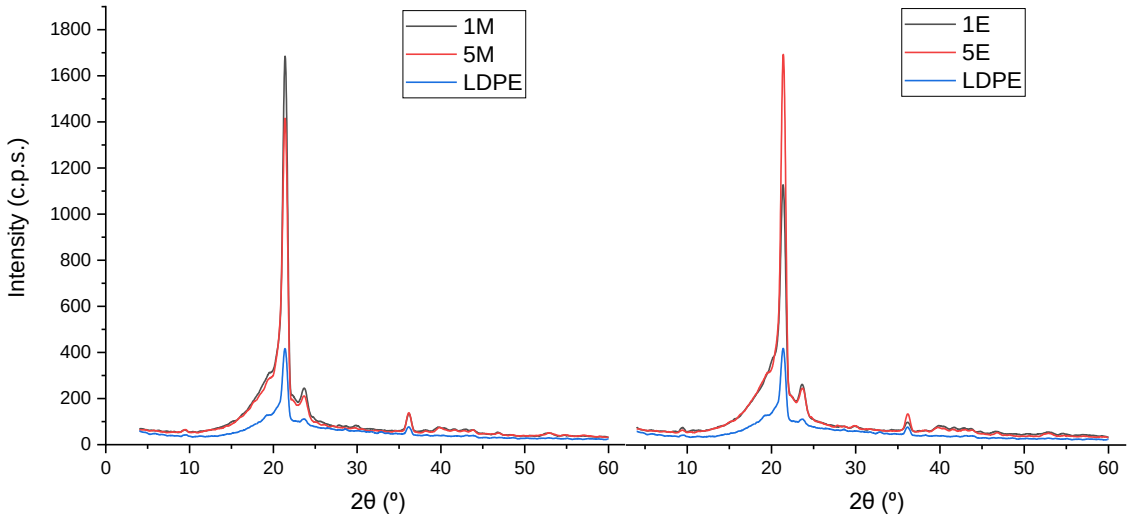
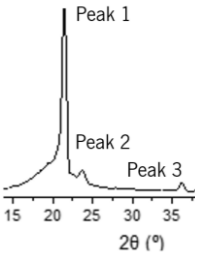


Figure 5-5 On the left, WAXD spectra for the 1st and 5th reprocessed Recycled Metallocene and LDPE and on the right WAXD spectra for the 1st and 5th reprocessed Recycled EVOH and LDPE.

Table 5-3 Diffraction peaks and crystallinity of the 1st and 5th reprocessed cycles and virgin LDPE

Samples	**Peak 1**		**Peak 2**		**Peak 3**		**Crystallinity**
	2θ (°)	Intensity (c.p.s)	2θ (°)	Intensity (c.p.s)	2θ (°)	Intensity (c.p.s)	**(%)**
1M	21.46	2010	23.82	287	36.12	158	54.1
5M	21.46	1656	23.66	231	36.06	161	51.7
1E	21.36	1322	23.74	283	36.20	137	54.0
5E	21.40	1008	23.58	270	36.16	98	53.8
LDPE	21.42	481	23.64	131	36.18	102	39.5



SEM micrographs of recycled EVOH samples in Figure 5-6 reveal circle and elongated particles of EVOH detached from the PE matrix, which demonstrate poor adhesion between PE and EVOH. Films with recycled metallocene exhibit a homogeneous morphology.

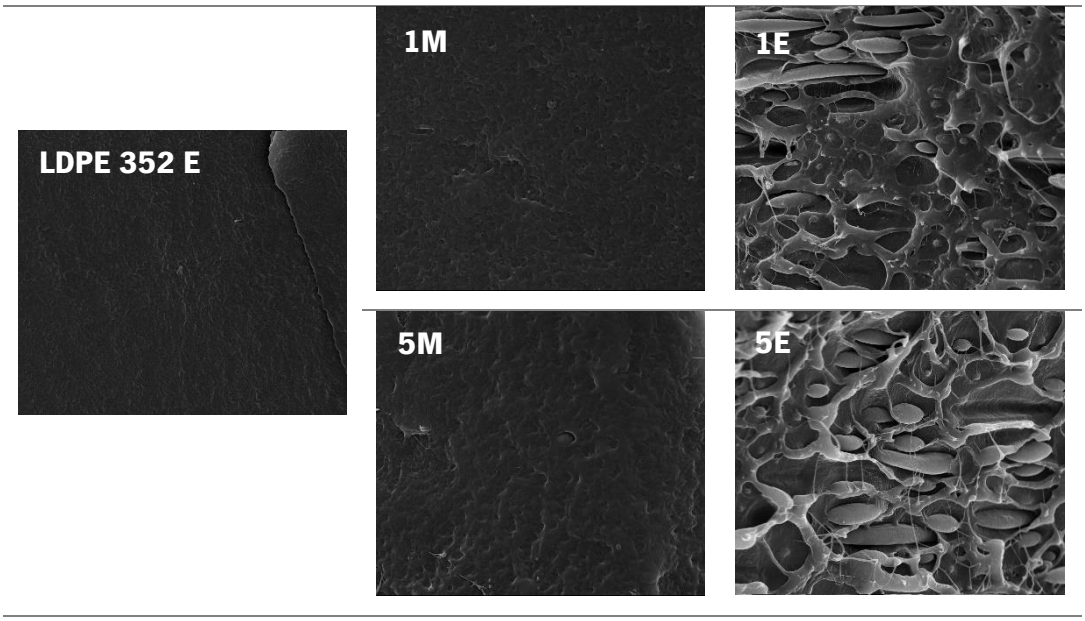


Figure 5-6 SEM micrographs, with 15000x magnification, of virgin LDPE and recycled films

The mechanical properties (Figures 5-7 and 5-8, and Tables S3 and S4 (in the supplemental section)) of the films produced with reprocessed material generally demonstrate that all the reprocessed systems have better mechanical properties than virgin LDPE, including higher Young's modulus, maximum stress, and strain at break. This improvement is attributed to the presence of materials with higher mechanical performance in the recycled films. The properties of the Recycled Metallocene improve with increasing cycles, which might be related to a progressive better homogenization of the materials present in the recycle, as already discussed in the DSC results, and possibly to a minor crosslinking of polymer chains due to repeating the extrusion processes. The crosslinking effect resulting from simulated mechanical recycling through repeated or extensive extrusion has been observed in the studies by Gonzalez Gutierrez et al. (2013) and Yin et al. (2015) [27, 33].

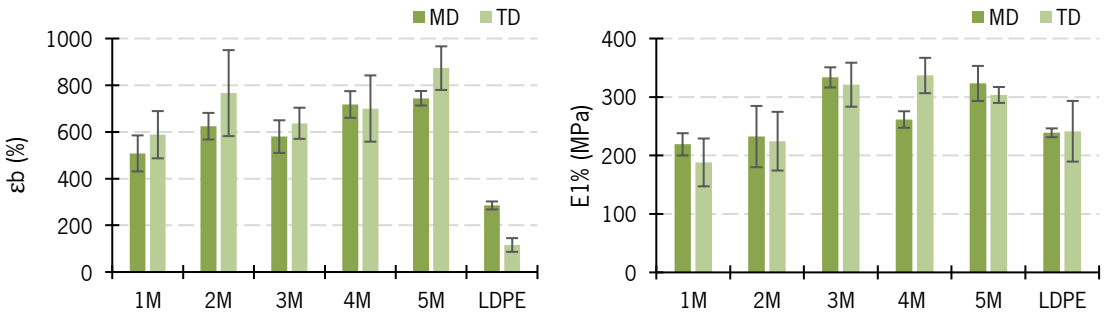


Figure 5-7 Strain at break (ε_b) and Young's Modulus ($E_{1\%}$) of films with Recycled Metallocene

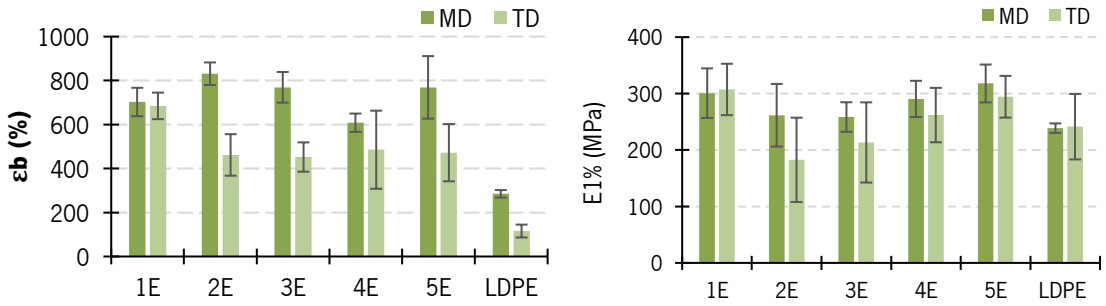


Figure 5-8 Strain at break (ε_b) and Young's Modulus ($E_{1\%}$) of films with Recycled EVOH

For the Recycled EVOH, the mechanical properties do not exhibit the same trend with the number of cycles. Due to the presence of an incompatible material (EVOH), it results in a poorly distribution in the PE matrix, as observed in SEM micrographs. This leads to an increase in the standard deviation and irregular mean values as reprocessing cycles increase. Therefore, it is not possible to observe a consistent increase or decrease in the mechanical properties. Thus, the incorporation of virgin material in this recycled one, as described in point 4 of this study, is important to evaluate the stability of the film properties with Recycled EVOH.

As indicated in Figure 5-9 and Table S5, in the supplemental section, haze decreases with the reprocessing cycles of 'Recycled EVOH', potentially resulting from a better dispersion of this material in the PE matrix. However, the haze level in this Recycled material remains significantly higher than that of LDPE (4.5 to 6.4 times higher), hindering clear visibility of the food through the film. In Recycled Metallocene, the haze slightly increases with the increase in reprocessing cycles, potentially linked to the presence of crosslinks, as previously mentioned. This observation is corroborated by the study conducted by Esmailzadeh et al. (2022), which demonstrates that crosslinks lead to an increase in haze and a decrease in gloss of LDPE and LLDPE films [34].

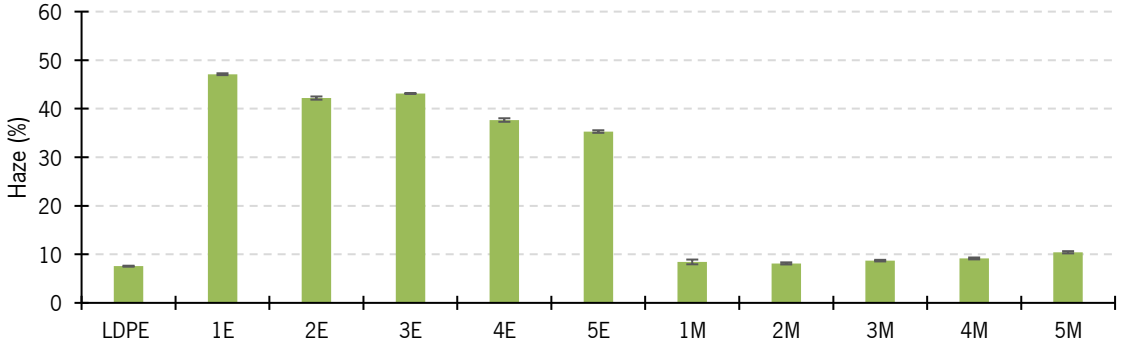


Figure 5-9 Haze values of virgin LDPE, 'Recycled EVOH' (E), and 'Recycled Metallocene' (M)

The increased reprocessing of Recycled EVOH led to a slight increase of the surface gloss of the films, as it can be observed in Figure 5-10 and Table S6 in the supplemental section. Since the gloss values obtained for Recycled Metallocene exceeded 70 GU (measurement angle of 60°), characteristic of high-gloss surfaces, it was necessary to use the 20° measurement angle for a finer analysis of the results. The Recycled Metallocene films, with low haze similar to virgin LDPE film, exhibited a high-gloss film surface. Up to the second reprocessing cycle, the Recycled Metallocene showed lower gloss than 1M and virgin LDPE film samples.

The gloss of these recycles correlates with haze and SEM results. As gloss increases, haze decreases, and vice versa. The Recycled EVOH films exhibited a semi-gloss surface with high haze due to the clear immiscibility between LDPE and EVOH observed in SEM micrographs, while the films with Recycled Metallocene achieved a high-gloss surface with low haze due to a compatible PE-based constitution. This effect has been documented in several studies on extruded monolayer films [35-37].

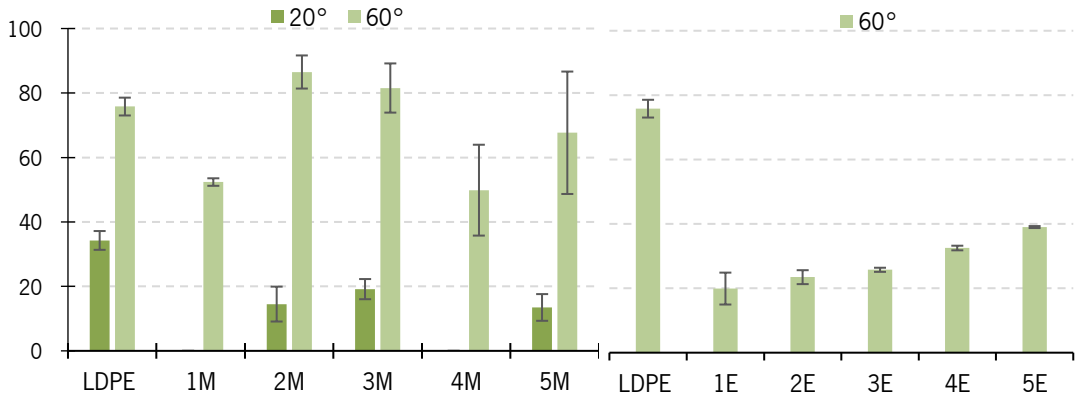


Figure 5-10 Gloss of 'Recycled EVOH', 'Recycled Metallocene', and virgin LDPE films

The reprocessing of the recycles did not affect the mechanical properties of the two different recycles but did impact the optical properties of the Recycled EVOH. As the reprocessing cycles increase, the film with recycled EVOH becomes brighter and less hazy, although not enough to compete with Recycled Metallocene or virgin LDPE. Incorporating a fixed percentage of virgin polymer with the recycled material in the industrial process can help to control and improve the optical properties of the film. Also, incorporating virgin material helps to reduce the influence of eventual variations on the composition on the recycled material, resulting in a higher film reproducibility.

5.3.2 Incorporation of virgin LDPE in Recycled material

As it can be seen in Table 5-4, haze increased with the rise in the percentage of recycled material in the film. These findings align with WAXD results presented in Table 5-6, where the degree of crystallinity decreases with the incorporation of LDPE. This decrease in crystallinity reduces the structural rearrangement within the polymeric matrix, resulting in increased transparency.

Table 5-4 Haze values of the films with the Recycled EVOH (E) and Recycled Metallocene (M), films with blends and virgin LDPE

Samples	Haze (%)	Samples	Haze (%)
1M	8.4 ± 0.2^{A}	1E	47.1 ± 0.4^{B}
50% M + 50% LDPE	7.7 ± 0.2^{B}	50% E + 50% LDPE	34.2 ± 0.2^{D}
60% M + 40% LDPE	7.6 ± 0.2^{B}	60% E + 40% LDPE	38.0 ± 0.3^{C}
80% M + 20% LDPE	8.7 ± 0.2^{A}	80% E + 20% LDPE	48.4 ± 0.1^{A}
LDPE	7.6 ± 0.1^{B}	LDPE	7.6 ± 0.1^{E}
Note: Means that do not share a letter are significantly different.			

In recycled/LDPE blends there is a decrease in brightness with the reduction in the percentage of LDPE, as can be seen in Table 5-5. The gloss results are in line with the turbidity results, as observed for the reprocessed materials.

Table 5-5 Gloss units of recycled/LDPE blends at 20° and 60° measurement geometries

Samples	Gloss Units		Samples	Gloss Units
	20°	60°		60°
1M	28.77 ± 1.76^{AB}	52.37 ± 1.17^{C}	1E	19.91 ± 0.72^{D}
50% M + 50% LDPE	27.19 ± 15.24^{B}	84.55 ± 27.65^{BC}	50% E + 50% LDPE	38.29 ± 4.95^{B}
60% M + 40% LDPE	48.04 ± 5.41^{A}	124.25 ± 21.19^{A}	60% E + 40% LDPE	30.72 ± 2.16^{C}
80% M + 20% LDPE	25.61 ± 3.13^{AB}	118.00 ± 3.61^{AB}	80% E + 20% LDPE	24.20 ± 0.64^{CD}
LDPE	34.26 ± 2.91^{AB}	75.79 ± 2.76^{BC}	LDPE	75.79 ± 2.76^{A}
Note: Means that do not share a letter are significantly different.				

The WAXD spectra for Recycled EVOH, Recycled Metallocene, their blends with 50 wt. % of LDPE, and virgin LDPE film samples are illustrated in Figure 5-11. As mentioned earlier regarding

the reprocessed recycles, all samples exhibit three main crystalline diffraction peaks characteristics of PE.

As indicated in Table 5-6, the addition of 50 wt. % virgin LDPE reduced the crystallinity of both recycles. These findings are consistent with those obtained in Li et al. (2019) study, where the crystallinity of LLDPE is found to be slightly higher than that of LDPE [38].

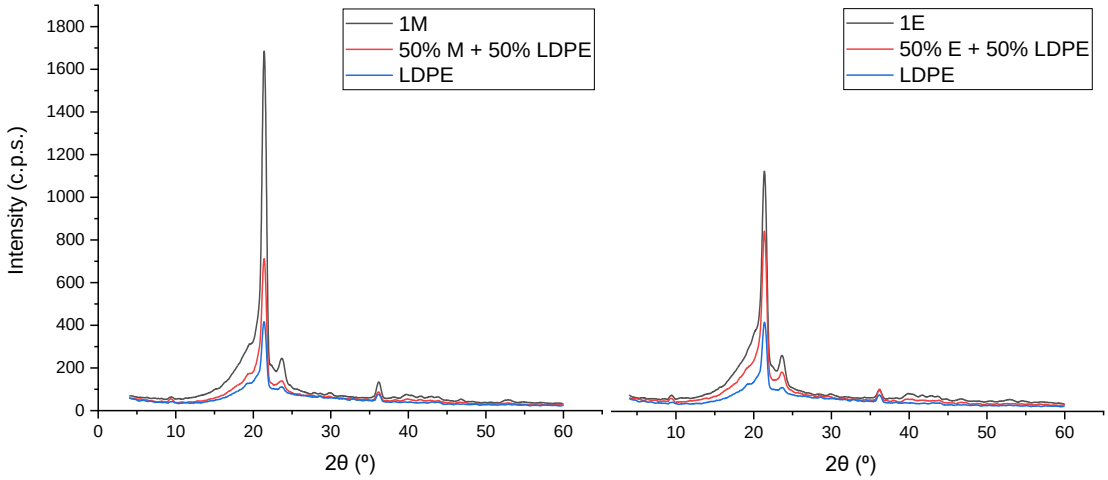


Figure 5-11 On the left, WAXD spectra of Recycled Metallocene, 50%M+50%LDPE, and virgin LDPE and on the right Recycled EVOH, 50%E+50%LDPE, and virgin LDPE.

Table 5-6 Degree of crystallinity of Recycled Metallocene and Recycled EVOH (1M, 1E), Recycled/LDPE blend and virgin LDPE films

Samples	**Peak 1**		**Peak 2**		**Peak 3**		**Crystallinity**
	2θ (°)	Intensity (c.p.s)	2θ (°)	Intensity (c.p.s)	2θ (°)	Intensity (c.p.s)	(%)
1M	21.46	2010	23.82	287	36.12	158	54.1
50% M + 50% LDPE	21.44	849	23.72	165	36.20	104	48.1
1E	21.36	1322	23.74	283	36.20	137	54.0
50% E + 50% LDPE	21.40	976	23.62	211	36.24	137	45.6
LDPE	21.42	481	23.64	131	36.18	102	39.5

Comparing Recycled EVOH (1E) with its blend containing 50 wt.% LDPE, as shown in Figure 5-12, the reduction of EVOH is clearly visible with the incorporation of virgin LDPE, while its dispersion in the LDPE matrix remains the consistent. Conversely, films with recycled Metallocene show no signs of incompatibility upon the addition of LDPE.

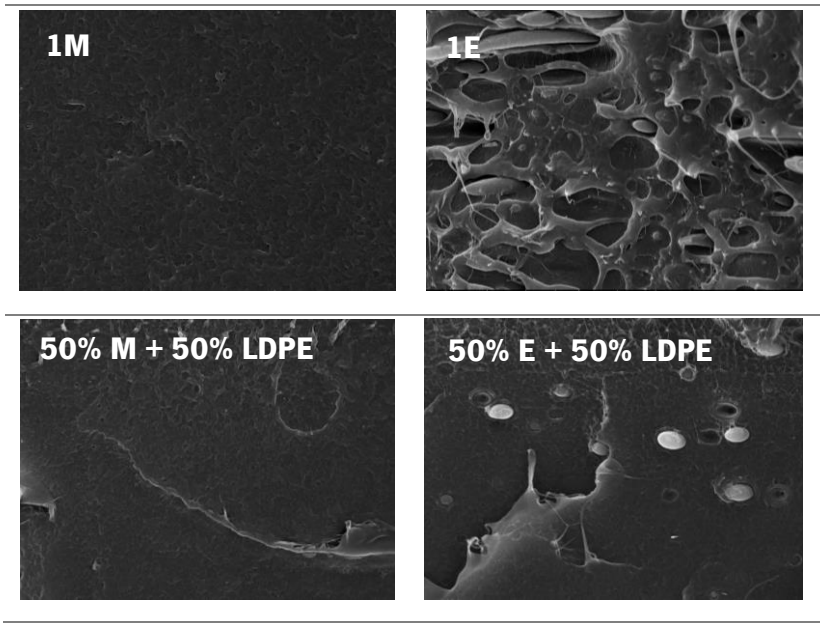


Figure 5-12 SEM micrographs, 15000x magnification, of the films with 1M, 1E and their blends with 50 wt.% LDPE

The tensile test results of the films produced with blends of recycled materials and virgin LDPE are presented in Tables 5-7 and 5-8. The tensile tests conducted on the recycled mixtures containing 20%, 40%, and 50% LDPE demonstrate positive results, even with a low incorporation of virgin LDPE.

The strain at break of both recycled blends increased considerably compared to LDPE film. However, the incorporation of virgin material did not lead to the expected control of mechanical properties or a decrease in the standard deviation of the tensile results of the samples. Therefore, in the case of applying this study in an industrial process, it may not be necessary to incorporate virgin material into the recycled one, as the results obtained for the two systems are very similar, particularly in terms of mechanical properties.

Table 5-7 Tensile test results of films with LDPE and Recycled Metallocene with LDPE

Samples		$E_{1\%}$(MPa)	σ_{max}(MPa)	ε_b(%)
LDPE	MD	238.76 ± 8.42^{A}	16.99 ± 0.42^{A}	284.96 ± 19.22^{B}
	TD	241.36 ± 58.02^{A}	9.76 ± 0.24^{C}	115.76 ± 32.8^{B}
50% M + 50% LDPE	MD	246.02 ± 32.15^{A}	15.85 ± 1.55^{AB}	590.12 ± 70.04^{A}
	TD	252.71 ± 30.31^{A}	12.55 ± 0.51^{AB}	765.81 ± 141.40^{A}
60% M + 40% LDPE	MD	225.45 ± 8.57^{A}	14.19 ± 1.15^{AB}	491.07 ± 110.28^{A}
	TD	246.13 ± 22.78^{A}	12.45 ± 0.57^{AB}	702.10 ± 106.88^{A}
80% M + 20% LDPE	MD	213.46 ± 13.89^{A}	13.59 ± 0.93^{B}	574.70 ± 46.11^{A}
	TD	242.21 ± 16.35^{A}	12.81 ± 0.78^{A}	774.70 ± 80.04^{A}
1M	MD	219.01 ± 21.32^{A}	13.80 ± 3.00^{B}	507.90 ± 86.42^{A}
	TD	188.06 ± 45.73^{A}	11.65 ± 0.78^{B}	587.98 ± 113.02^{A}

Note: Means that do not share a letter are significantly different. Statistical analysis was performed separately for the samples collected in MD and TD.

Table 5-8 Tensile test results of films with LDPE and Recycled EVOH with LDPE

Samples		$E_{1\%}$(MPa)	σ_{max}(MPa)	ε_b(%)
LDPE	MD	238.76 ± 8.42^{AB}	16.99 ± 0.42^{AB}	284.96 ± 19.22^{D}
	TD	241.36 ± 58.02^{A}	9.76 ± 0.24^{C}	115.76 ± 32.8^{B}
50%E + 50%LDPE	MD	236.80 ± 15.68^{B}	16.52 ± 1.95^{B}	525.65 ± 107.99^{BC}
	TD	294.66 ± 23.24^{A}	13.31 ± 0.84^{AB}	754.35 ± 283.75^{A}
60%E + 40%LDPE	MD	280.58 ± 52.62^{AB}	15.73 ± 1.23^{B}	478.25 ± 125.12^{C}
	TD	249.80 ± 76.08^{A}	11.93 ± 0.91^{BC}	615.24 ± 213.45^{A}
80%E + 20%LDPE	MD	256.80 ± 21.72^{AB}	18.02 ± 1.18^{AB}	691.54 ± 75.75^{AB}
	TD	270.79 ± 23.42^{A}	14.99 ± 1.06^{A}	845.41 ± 87.46^{A}
1E	MD	300.72 ± 43.93^{A}	19.86 ± 2.23^{A}	702.57 ± 72.28^{A}
	TD	307.28 ± 45.53^{A}	13.24 ± 0.88^{B}	684.93 ± 67.46^{A}

Note: Means that do not share a letter are significantly different. Statistical analysis was performed separately for the samples collected in MD and TD.

5.4 Conclusions

The present study concludes that it is feasible to incorporate materials recovered from multilayer films, consisting mainly of LDPE, into the structural layers of conventional food packaging

without compromising their mechanical and thermal properties, while maintaining the extrusion conditions.

Reprocessing the recycled material did not significantly alter the crystallization and melting temperatures, degree of crystallinity, MFI, or the stability of the tubular film production process. While Young's modulus of the Recycled Metallocene increased with reprocessing, it remained constant for films with reprocessed Recycled EVOH. Overall, all reprocessed recycles exhibited superior mechanical properties compared to virgin LDPE films. Additionally, LDPE/Recycled blends demonstrated significantly higher strain at break values than LDPE film.

Blending 50 wt.% LDPE with recycled materials can effectively control half of the raw material content in the final film packaging, given that the recycled material may vary in composition across different batches. Regarding optical properties, the haze of films containing recycled EVOH was much higher than that of LDPE and Metallocene recycled materials, which exhibited similar haze and gloss values. While haze decreased with the reprocessing of recycled EVOH material, it slightly increased for Recycled metallocene. In LDPE blends with recycled EVOH, the haze increased with the proportion of recycled material in the film. It was also observed that as turbidity increased, gloss decreased, and vice versa across all samples.

Despite the favourable mechanical results of Recycled EVOH, films with Recycled Metallocene exhibited the best overall properties, as all polymers in this recycled material are fully compatible.

Supporting information

Table S1 Melting and crystallization temperatures of virgin LDPE and the first and fifth reprocessed recycles

Samples	Melting temperatures (°C)		Crystallization temperatures (°C)	
	1st peak	2nd peak	1st peak	2nd peak
LDPE	116	-	96	-
1M	110	127	96	113
5M	110	127	96	112
1E	112	184	99	162
5E	113	184	98	161

Table S2 MFI of reprocessed recycled Metallocene (M) and EVOH (E)

Sample	190 °C	210 °C	230 °C
1M	1.12 ± 0.05	1.48 ± 0.05	2.16 ± 0.10
2M	1.12 ± 0.08	1.55 ± 0.05	1.96 ± 0.05
3M	1.06 ± 0.03	1.58 ± 0.04	2.00 ± 0.06
4M	1.00 ± 0.04	1.51 ± 0.06	1.79 ± 0.14
5M	1.00 ± 0.03	1.27 ± 0.02	1.86 ± 0.08
1E	1.29 ± 0.04	1.92 ± 0.06	2.22 ± 0.16
2E	1.31 ± 0.03	1.81 ± 0.06	2.60 ± 0.07
3E	1.30 ± 0.05	1.95 ± 0.10	2.76 ± 0.07
4E	1.31 ± 0.07	1.88 ± 0.10	2.52 ± 0.06
5E	1.25 ± 0.04	1.95 ± 0.06	2.44 ± 0.07

Table S3 Tensile results of the Recycled Metallocene films

Samples		$E_{1\%}$ (Mpa)	σ_{max} (MPa)	ε_b (%)
1M	MD	219.01 ± 21.32^{B}	13.80 ± 3.00^{B}	507.90 ± 86.42^{B}
	TD	188.06 ± 45.73^{D}	11.65 ± 0.78^{BC}	587.98 ± 113.02^{B}
2M	MD	232.26 ± 58.63^{B}	13.66 ± 0.73^{B}	624.43 ± 63.78^{AB}
	TD	224.36 ± 56.16^{CD}	16.18 ± 2.30^{A}	766.18 ± 205.88^{AB}
3M	MD	333.47 ± 19.31^{A}	16.86 ± 1.06^{A}	579.97 ± 78.09^{B}
	TD	321.01 ± 42.10^{AB}	15.19 ± 1.90^{AB}	636.98 ± 74.53^{AB}
4M	MD	261.42 ± 15.81^{B}	15.26 ± 0.62^{AB}	717.47 ± 63.86^{A}
	TD	336.70 ± 33.83^{A}	15.99 ± 3.04^{A}	700.15 ± 158.74^{AB}
5M	MD	323.16 ± 33.53^{A}	16.86 ± 1.06^{A}	744.18 ± 34.74^{A}
	TD	303.48 ± 15.22^{ABC}	14.07 ± 1.36^{AB}	873.10 ± 104.45^{A}
LDPE	MD	238.76 ± 8.42^{B}	16.99 ± 0.42^{A}	284.96 ± 19.22^{C}
	TD	241.36 ± 58.02^{BCD}	9.76 ± 0.24^{C}	115.76 ± 32.8^{C}

Note: Mean values that do not share a letter are significantly different. Statistical analysis was performed separately for the samples collected in MD and TD.

Table S4 Tensile results of the Recycled EVOH films

Samples		$E_{1\%}$ (Mpa)	σ_{max} (MPa)	ε_b (%)
1E	MD	300.72 ± 43.93^{AB}	19.86 ± 2.23^{A}	702.57 ± 72.28^{AB}
	TD	307.28 ± 45.53^{A}	13.24 ± 0.88^{B}	684.93 ± 67.46^{AB}
2E	MD	261.62 ± 55.46^{AB}	19.30 ± 0.39^{AB}	831.29 ± 57.29^{A}
	TD	182.62 ± 74.66^{B}	11.73 ± 1.84^{B}	461.88 ± 105.47^{BC}
3E	MD	258.45 ± 26.15^{AB}	17.22 ± 1.29^{BC}	769.31 ± 46.50^{AB}
	TD	213.41 ± 71.08^{AB}	13.75 ± 3.59^{B}	452.35 ± 198.63^{BC}
4E	MD	290.51 ± 32.10^{AB}	15.90 ± 1.70^{C}	608.41 ± 159.06^{B}
	TD	261.87 ± 48.20^{AB}	13.23 ± 1.69^{B}	485.65 ± 145.55^{B}
5E	MD	317.90 ± 33.56^{A}	18.23 ± 0.73^{ABC}	769.13 ± 53.99^{AB}
	TD	294.37 ± 37.00^{A}	13.69 ± 1.40^{A}	472.19 ± 115.01^{A}
LDPE	MD	238.76 ± 8.42^{B}	16.99 ± 0.42^{BC}	284.96 ± 19.22^{C}
	TD	241.36 ± 58.02^{AB}	9.76 ± 0.24^{B}	115.76 ± 32.8^{CD}

Note: Mean values that do not share a letter are significantly different. Statistical analysis was performed separately for the samples collected in MD and TD.

Table S5 Haze values of the 'Recycled EVOH' (E), 'Recycled Metallocene' (M), and virgin LDPE films

Samples	Haze (%)	Samples	Haze (%)
1M	8.4 ± 0.2^{CD}	1E	47.1 ± 0.4^{A}
2M	8.1 ± 0.2^{D}	2E	42.2 ± 0.3^{C}
3M	8.7 ± 0.1^{C}	3E	43.1 ± 0.5^{B}
4M	9.2 ± 0.1^{B}	4E	37.7 ± 0.2^{D}
5M	10.4 ± 0.2^{A}	5E	35.3 ± 0.2^{E}
LDPE	7.6 ± 0.1^{E}	LDPE	7.6 ± 0.1^{F}

Note: Mean values that do not share a letter are significantly different.

Table S6 Gloss of recycled reprocessed materials films measured at 20° and 60°

Samples	Gloss Units		Samples	Gloss Units
	20°	60°		60°
1M		52.37 ± 1.17^{BC}	1E	19.91 ± 0.72^{E}
2M	14.51 ± 4.14^{B}	86.51 ± 5.13^{AB}	2E	23.45 ± 0.31^{DE}
3M	19.15 ± 5.92^{B}	86.89 ± 7.63^{A}	3E	25.74 ± 2.21^{D}
4M		49.86 ± 14.09^{C}	4E	32.51 ± 1.21^{C}
5M	13.47 ± 2.94^{B}	67.66 ± 18.99^{ABC}	5E	39.02 ± 1.62^{B}
LDPE	34.26 ± 2.91^{A}	75.79 ± 2.76^{ABC}	LDPE	75.79 ± 2.76^{A}

Note: Mean values that do not share a letter are significantly different.

5.5 References

[1] Plastics Europe, “Plastics – the Facts 2019 An analysis of European plastics production, demand and waste data,” Accessed March 15, 2022. [Online]. Available: https://www.plasticseurope.org/en/resources/publications/1804-plastics-facts-2019

[2] Plastics Europe, “Plastics – the Facts 2020 An analysis of European plastics production, demand and waste data,” Accessed March 15, 2022. [Online]. Available: https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts-2020

[3] K. Kaiser, M. Schmid, and M. Schlummer, “Recycling of polymer-based multilayer packaging: A review,” Recycling, vol. 3, no. 1, 2017, doi: 10.3390/recycling3010001.

[4] D. D. P. Moreno and C. Saron, “Influence of compatibilizer on the properties of low-density polyethylene/polyamide 6 blends obtained by mechanical recycling of multilayer film waste,” Waste Management and Research, vol. 36, no. 8, pp. 729–736, Aug. 2018, doi: 10.1177/0734242X18777795.

[5] L. Marangoni Júnior, L. M. de Oliveira, P. F. J. Bócoli, M. Cristianini, M. Padula, and C. A. R. Anjos, “Morphological, thermal and mechanical properties of polyamide and ethylene vinyl alcohol multilayer flexible packaging after high-pressure processing,” J Food Eng, vol. 276, Jul. 2020, doi: 10.1016/j.jfoodeng.2020.109913.

[6] Yasmine Nasri, Mohamed Tahar Benaniba, and Michel Bouquey, “Elaboration and characterization of polymers used in flexible multilayer food packaging,” Mater Today Proc, vol. 53, pp. 91–95, 2022, doi: https://doi.org/10.1016/j.matpr.2021.12.390.

[7] D. Ferrari et al., “PVDC multilayer films: Chemical recycling by means of catalytic conversion into aromatics (BTX),” Sustainable Chemistry for the Environment, vol. 2, p. 100010, Aug. 2023, doi: 10.1016/j.scenv.2023.100010.

[8] B. B. Turriziani, R. P. Vieira, L. Marangoni Júnior, and R. M. V. Alves, “Mechanical Recycling of Multilayer Flexible Packaging Employing Maleic Anhydride as Compatibilizer,” J Polym Environ, vol. 32, no. 3, pp. 1393–1405, Mar. 2024, doi: 10.1007/s10924-023-03057-9.

[9] D. Ferrari, A. Sanguineti, M. Mirenda, and Y. Vanderveken, “Compatibility of polyvinylidene chloride with mechanical recycling of polyolefins,” Progress in Rubber, Plastics and Recycling Technology, vol. 39, no. 3, pp. 264–280, Aug. 2023, doi: 10.1177/14777606231152268.

[10] C. T. de M. Soares, M. Ek, E. Östmark, M. Gällstedt, and S. Karlsson, "Recycling of multi-material multilayer plastic packaging: Current trends and future scenarios," Resour Conserv Recycl, vol. 176, Jan. 2022, doi: 10.1016/j.resconrec.2021.105905.

[11] Sina Ebnesajjad, "11 - Extrusion," in Fluoroplastics (Second Edition), vol. 2, 2015, pp. 282–347. doi: https://doi.org/10.1016/B978-1-4557-3197-8.00011-0.

[12] John R. WagnerJr., "10 - Blown Film, Cast Film, and Lamination Processes," in Multilayer Flexible Packaging (Second Edition), Rochester, NY, United States: William Andrew, 2016, pp. 137–145. doi: https://doi.org/10.1016/B978-0-323-37100-1.00010-7.

[13] Bruna Bonato Turriziani, Mary Ângela Fávaro Perez, Paulo Henrique Massaharu Kiyataka, Roniérik Pioli Vieira, Luís Marangoni Júnior, and Rosa Maria Vercelino Alves, "Effect of maleic anhydride-based compatibilizer incorporation on the properties of multilayer packaging films for meat products," Journal of Polymer Research, vol. 30, no. 194, May 2023, doi: https://doi.org/10.1007/s10965-023-03584-y.

[14] A. Ghosh, "Review Performance modifying techniques for recycled thermoplastics," Resour Conserv Recycl, vol. 175, 2021, doi: 10.1016/j.resconrec.2021.105887.

[15] M. Roosen et al., "Detailed Analysis of the Composition of Selected Plastic Packaging Waste Products and Its Implications for Mechanical and Thermochemical Recycling," Environ Sci Technol, vol. 54, no. 20, pp. 13282–13293, Oct. 2020, doi: 10.1021/acs.est.0c03371.

[16] Heike Scheurer, "Certification of the recyclability of multilayer films containing polyamide expanded." Accessed: Apr. 14, 2024. [Online]. Available: https://www.basf.com/global/en/media/news-releases/2023/11/p-23-376.html

[17] I. Jönkkäri, V. Poliakova, V. Mylläri, R. Anderson, M. Andersson, and J. Vuorinen, "Compounding and characterization of recycled multilayer plastic films," J Appl Polym Sci, vol. 137, no. 37, Oct. 2020, doi: 10.1002/app.49101.

[18] D. Czarnecka-Komorowska, K. Wiszumirska, and T. Garbacz, "FILMS LDPE/LLDPE MADE FROM POST - CONSUMER PLASTICS: PROCESSING, STRUCTURE, MECHANICAL PROPERTIES," Advances in Science and Technology Research Journal, vol. 12, no. 3, pp. 134–142, Sep. 2018, doi: 10.12913/22998624/92205.

[19] C. Meran, O. Ozturk, and M. Yuksel, "Examination of the possibility of recycling and utilizing recycled polyethylene and polypropylene," Mater Des, vol. 29, no. 3, pp. 701–705, 2008, doi: 10.1016/j.matdes.2007.02.007.

[20] S. Chytiri, A. E. Goulas, K. A. Riganakos, and M. G. Kontominas, “Thermal, mechanical and permeation properties of gamma-irradiated multilayer food packaging films containing a buried layer of recycled low-density polyethylene,” Radiation Physics and Chemistry, vol. 75, no. 3, pp. 416–423, 2006, doi: 10.1016/j.radphyschem.2005.07.005.

[21] F. P. La Mantia and M. Morreale, “Mechanical properties of recycled polyethylene ecocomposites filled with natural organic fillers,” Polym Eng Sci, vol. 46, no. 9, pp. 1131–1139, Sep. 2006, doi: 10.1002/pen.20561.

[22] V. Pistor, A. Chiesa, and A. J. Zattera, “Estudo do Reprocessamento de Polietileno de Baixa Densidade (PEBD) Reciclado do Processamento de Extrusão de Filmes Tubulares,” Polímeros, vol. 20, no. 4, pp. 269–274, 2010, doi: 10.1590/S0104-14282010005000045.

[23] D. D. P. Moreno and C. Saron, “Low-density polyethylene/polyamide 6 blends from multilayer films waste,” J Appl Polym Sci, vol. 136, no. 18, May 2019, doi: 10.1002/app.47456.

[24] Chi-Hsien Huang, Jiann-Shing Wu, Chun-Chin Huang, and Li-Shin Lin, “Morphological, Thermal, Barrier and Mechanical Properties of LDPE/EVOH Blends in Extruded Blown Films,” Journal of Polymer Research, vol. 11, no. 1, pp. 75–83, 2004, doi: DOI: 10.1023/B:JPOL.0000021796.41800.e9.

[25] R. G. Snyder, S. L. Hsu, and S. Krimm, “Vibrational spectra in the C□H stretching region and the structure of the polymethylene chain,” Spectrochim Acta A, vol. 34, no. 4, pp. 395–406, Jan. 1978, doi: 10.1016/0584-8539(78)80167-6.

[26] S. Abbate, G. Zerbi, and S. L. Wunder, “Fermi resonances and vibrational spectra of crystalline and amorphous polyethylene chains,” J Phys Chem, vol. 86, no. 16, pp. 3140–3149, Aug. 1982, doi: 10.1021/j100213a017.

[27] S. Yin, R. Tuladhar, F. Shi, R. A. Shanks, M. Combe, and T. Collister, “Mechanical reprocessing of polyolefin waste: A review,” Polym Eng Sci, vol. 55, no. 12, pp. 2899–2909, Dec. 2015, doi: 10.1002/pen.24182.

[28] A. N. Shebani, A. J. Van Reenen, and M. Meincken, “The effect of wood species on the mechanical and thermal properties of wood-LLDPE composites,” J Compos Mater, vol. 43, no. 11, pp. 1305–1318, 2009, doi: 10.1177/0021998308104548.

[29] D. Depan, W. Chirdon, and A. Khattab, “Morphological and chemical analysis of low density polyethylene crystallized on carbon and clay nanofillers,” Polymers (Basel), vol. 13, no. 10, 2021, doi: 10.3390/polym13101558.

[30] W. Du, W. Zhong, Y. Lin, L. Shen, and Q. Du, “Space charge distribution and crystalline structure in polyethylene blended with EVOH,” Eur Polym J, vol. 40, no. 8, pp. 1987–1995, 2004, doi: 10.1016/j.eurpolymj.2004.04.003.

[31] N. Artzi, Y. Nir, D. Wang, and M. Narkis, “EVOH/Clay Nanocomposites Produced by Melt Processing,” Polym Compos, vol. 22, no. 5, pp. 710–720, Oct. 2001.

[32] J.-T. YEH, W.-H. YAO, Q. DU, and C.-C. CHEN, “Blending and Barrier Properties of Blends of Modified Polyamide and Ethylene Vinyl Alcohol Copolymer,” J Polym Sci B Polym Phys, vol. 43, pp. 511–521, 2005.

[33] J. Gonzalez-Gutierrez, P. Oblak, B. Zupančič, I. Emri, and H. Jin, “Effect of extensive recycling on flow properties of LDPE,” 2013. [Online]. Available: https://www.researchgate.net/publication/259656619

[34] R. Esmailzadeh, S. Hosseini, R. Rashedi, S. Houshmandmoayed, K. Afzali, and A. Sepahi, “Study on the Rheological, Thermal, Mechanical, and Optical Properties of LDPE/LLDPE Blown Films Containing Recycled LDPE/LLDPE Pellets For Circular Economy,” 2022, doi: 10.21203/rs.3.rs-2185814/v1.

[35] R. Patel, V. Ratta, P. Saavedra, and J. Li, “Surface haze and surface morphology of blown film compositions,” Journal of Plastic Film and Sheeting, vol. 21, no. 3, pp. 217–231, Jul. 2005, doi: 10.1177/8756087905057247.

[36] X. Y. Chen and M. Xiang, “Formulating of a novel polyolefin hazy film and the origins of haze thereof,” Polymer Bulletin, vol. 64, no. 9, pp. 925–937, May 2010, doi: 10.1007/s00289-009-0229-6.

[37] Robert Shanks, “Technology of Polyolefin Film Production,” in Handbook of Plastic Films, 2003, pp. 5–38.

[38] D. Li, L. Zhou, X. Wang, L. He, and X. Yang, “Effect of crystallinity of polyethylene with different densities on breakdown strength and conductance property,” Materials, vol. 12, no. 11, Jun. 2019, doi: 10.3390/ma12111746.

6. FROM MULTILAYER LDPE/EVOH FLEXIBLE FILM SCRAPS TO NEW MULTILAYER FILMS

Abstract

This study explores the mechanical and optical properties of multilayer films incorporating recycled materials, mimicking the structure of industrial films. Using a coextrusion blown film line with a three-layer ABC configuration extrusion head, films were produced using two different recycled multilayer films, from post-industrial scraps, in layers A and B and virgin low-density polyethylene (LDPE) in one of the external layers (C). These recycles result from multilayer films mainly constituted of LDPE; one has also linear-LDPE (LLDPE) Metallocene, referenced as Recycled Metallocene, and the other has Ethylene Vinyl Alcohol (EVOH), referenced as Recycled EVOH. Both recycled materials enabled to maintain blown film extrusion process stability during film production. The multilayer films produced with the incorporation of recycles were characterized using scanning electron microscopy (SEM), haze and gloss measurements, and tensile tests. Films with Recycled EVOH presented haze values much higher than those obtained for the Recycled Metallocene. However, all films presented good mechanical properties when compared to single layer virgin LDPE film. Anisotropic behaviour was observed, emphasizing the directional dependence of mechanical properties. The findings provide insights into the behaviour of multilayer films with recycled content, offering valuable information for the development of sustainable packaging solutions.

Keywords: multilayer recycles, recycles incorporation, packaging, blown film, polyethylene

This chapter is based on the short communication: **Barros, C**., Carneiro, O. S., & Machado, A. V. (2024). Feasibility of incorporating recycled multilayer LDPE/EVOH films into new flexible packaging. *Submitted to Polymer*

6.1 Introduction

The packaging sector, the largest consumer of virgin plastics, faces sustainability challenges in managing the end-of-life phase [1-3]. According to the Ellen MacArthur Foundation, 26% of flexible packaging consists of multilayer films incorporating different materials, complicating recycling efforts [4]. Chemical recycling is still not a solution for this type of packaging due to the low yields of the reactions and the production of solvent waste. Also, eventual change of a multimaterial/multilayer structure to a monomaterial/monolayer structure, would improve recyclability, but harm important functional properties of the packaging, such as mechanical, and barrier properties [5, 6].

Despite the impossibility of separating materials and potential risk of their thermal degradation during mechanical recycling, the multilayer approach remains the most cost-effective and environmentally friendly, with the lowest carbon footprint and widespread adoption [7, 8].

Zenon Tarakowski's (2010) assessed the properties of recycled multilayer packaging films composed of polyethylene (PE) and polyamide (PA), from leftovers from the industrial co-extrusion process. After being modified with inorganic fillers, the produced materials demonstrated comparable properties to virgin materials, highlighting the potential to repurpose industrial waste to reduce pollution and replace virgin materials [9].

The study of Gabriel Uehara et al. (2015) also explored the feasibility of recycling multilayer films, using different blends of virgin polyethylene terephthalate (PET) and PE to simulate multilayer thermomechanical recycling. Their findings, utilizing PE grafted with maleic anhydride (PE-g-MA) and ethylene-glycidyl methacrylate (E-GMA) as adhesion promoters, underscored improved impact strength and elongation at break for blends with compatibilizers. Although the use of PE-g-MA and E-GMA (with incorporations ≥ 5 wt.%) increased the impact strength and elongation at break of the blends, the PET/PE blends without compatibilizer showed similar results compared to previous for the strength at break and Young's modulus [10].

Soto et al. (2018) analysed samples produced with recycled material from post-consumer waste, mainly PE, by blown film extrusion and concluded that the recycled material exhibited mechanical properties close to those of virgin PE, endorsing its suitability for blown or cast film extrusion [11].

Although there are many studies on the mechanical recycling of flexible packaging, it is necessary to deepen this research for multi-material packaging and to evaluate the possibility of using this material for the same application [12-14].

The present study aims to complement the work carried out by the present research team, described in Chapter 5, using the same materials but incorporating them in two layers of a three-layer film having an external layer of virgin low density PE (LDPE). Characterization techniques such as SEM, haze and gloss measurements, and tensile tests, were used to assess the feasibility of incorporating flexible multilayer films recycled materials into new multilayer films.

The findings of this research stand to contribute to the development of eco-friendly packaging solutions, meeting industry standards, and addressing environmental concerns.

6.2 Experimental

6.2.1 Materials

Lotrène FD0270, a virgin LDPE blown film extrusion grade from QAPCO (with 923 kg/m^3 density and melt temperature of 112 °C) was used in the outer layer of the film and for the blend with recycled materials. This LDPE is an additive free grade currently used in flexible food packaging because of its high gloss. The recycled materials used in this study are referred as Recycled Metallocene and Recycled EVOH and described in the section 5.2.1 of Chapter 5.

6.2.2 Film production

After studying the mechanical behaviour and optical properties of single-layer films produced with the recycled materials mentioned in chapter 5, multilayer films with the same recycled materials were developed to mimic the structure of packaging films produced in industry. The films were produced in a blown film coextrusion line with three single screw extruders attached to an ABC extrusion head configuration, with an annular die of 50 mm diameter and 1.25 mm gap. All the materials were pre-dried at 60 °C for 4 h in a drying oven. A control film with three layers of virgin LDPE was produced, alongside the four films incorporating recycled materials, as described in Table 6-1.

Table 6-1 Sample codes of the multilayer films with recycled (r-) materials and virgin LDPE

Sample code	Structure (A | B | C)
LDPE | LDPE | LDPE	All three layers of virgin LDPE
M | M | LDPE	r-Metallocene | r-Metallocene | LDPE
M | M | LDPE+20M	r-Metallocene | r-Metallocene | LDPE + 20% r-Metallocene
E | E | LDPE	r-EVOH | r-EVOH | LDPE
E | E | LDPE+20E	r-EVOH | r-EVOH | LDPE +20% r-EVOH

The films thickness was measured using a micrometer (Digimatic thickness gauge 547-301, Mitutoyo, Japan) with a measuring accuracy of 0.01 mm, was 40 ± 5 μm.

6.3 Characterization Techniques

The film samples were analysed through SEM, haze and gloss measurements, and tensile tests. The equipment and methods used for the respective characterization techniques are described in the section 5.2.3 of Chapter 5, as well as the statistical analysis performed.

6.4 Results and discussion

Through the SEM images (Figure 6-1), the three layers in both types of films produced (with recycled EVOH and with recycled Metallocene) are clearly discernible. In the film with Recycled EVOH, the phase with the lowest percentage, EVOH, is encapsulated by the LDPE matrix. As expected, the incompatibility of these materials does not allow adhesion between their surfaces, resulting in empty voids where the EVOH would be, in the fractured section. In the film with recycled Metallocene all the materials are compatible, being all polyethylene based, but there is a clear division between layers, mainly between virgin and recycled LDPE. The films have a total thickness of 40 ± 5 μm, with a thickness variation between layers of 4.61 μm for the film with Recycled EVOH and 2.04 μm for the film with Recycled Metallocene.

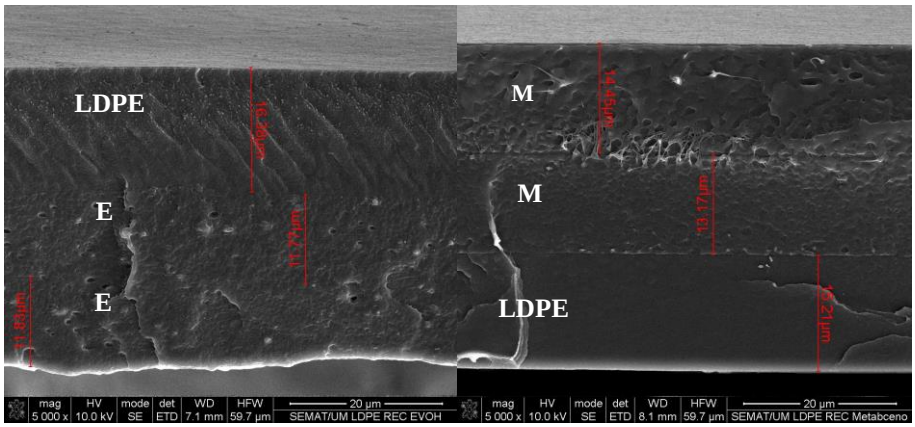


Figure 6-1 SEM images of the cross-section of the E | E | LDPE film (on the left), and M |M | LDPE film (on the right)

Regarding the optical properties, turbidity increased considerably from 5.8%, for the LDPE three-layers film, to 16.5 and 16.6% for films with recycled EVOH, as can be seen in Figure 6-2. The films with recycled Metallocene showed a similar turbidity to the LDPE film. Regarding brightness, all the films presented high values for this property, except for the E | E | LDPE+20E film. This film does not have an outer layer only composed of virgin LDPE, presenting, therefore, a semi-gloss of 20.9 GU. It should be mentioned that the gloss was measured only in the outer LDPE layer. The values obtained for the haze and gloss of the films are shown in Table S1 in the Supporting Information section.

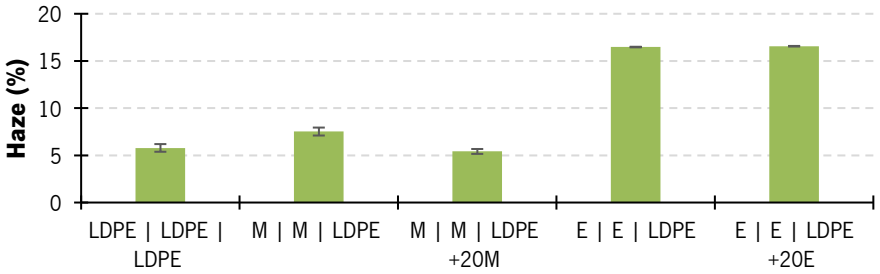


Figure 6-2 Haze of the multilayer films with LDPE, Recycled Metallocene and Recycled EVOH

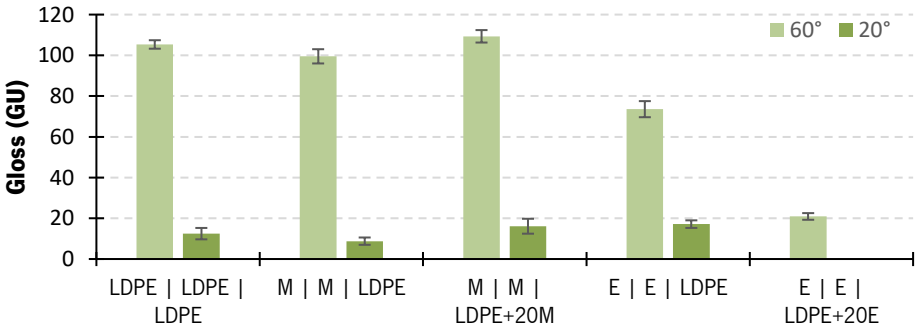


Figure 6-3 Gloss at the outer LDPE layer in multilayer films with LDPE, Recycled Metallocene and Recycled EVOH

The tensile tests results, depicted in in Figures 6-4 and 6-5 and in Table S2, demonstrate that the mechanical properties slightly decreased in the E | E | LDPE+20E multilayer film. For M | M | LDPE+20M film in Transverse Direction (TD) and E | E | LDPE film in Machine Direction (MD), the elongation at break was significantly higher than for the control film with 3 layers of virgin LDPE. Variations in mechanical properties between MD and TD indicate anisotropic behaviour.

The tensile strength was similar for all samples, indicating that films with a high percentage of recycled material (> 67%, in this case) can withstand similar stresses during packaging processes, and are expected to present tearing or puncture resistance comparable to the virgin LDPE film.

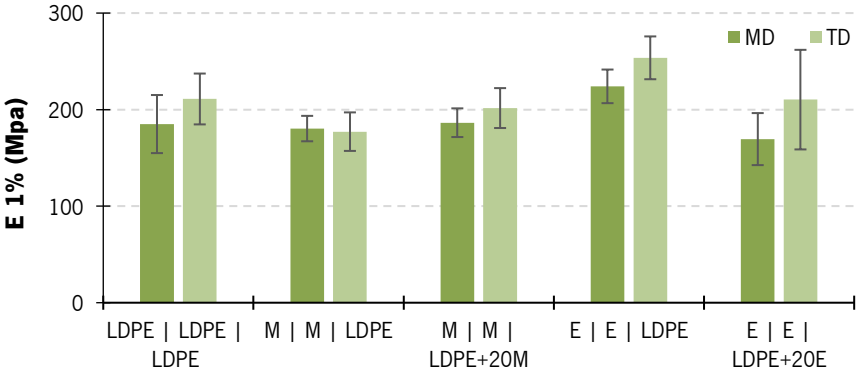


Figure 6-4 Young's Modulus ($E_{1\%}$) of the multilayer films with LDPE, Recycled Metallocene and Recycled EVOH

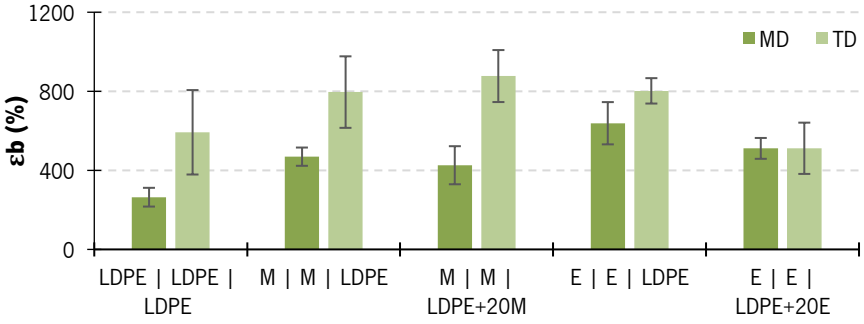


Figure 6-5 Strain at break (εb) of the multilayer films with LDPE, Recycled Metallocene and Recycled EVOH

6.5 Conclusions

Multilayer flexible films incorporating recycled material, from post-industrial waste, exhibited good overall properties.

Incompatibility between EVOH and LDPE resulted in an encapsulated EVOH phase, observed by SEM, and high haze values of 16.5% and 16.6%, indicating reduced clarity when compared to the LDPE film that has 5.8% haze. The gloss measurements on the outer virgin LDPE layer, demonstrated high performance for all films, except for E | E | LDPE+20E, which showed semi-gloss with 20.9 GU, due to the presence of encapsulated EVOH in the LDPE layer.

The incorporation of recycled EVOH negatively affected the optical properties of the films, promoting a decrease in brightness and an increase in the turbidity. However, the overall mechanical properties of the films incorporating both recycled materials were very similar to those of the LDPE control film, with the former showing increased elongation at break.

As a conclusion, this study demonstrates that it is possible to incorporate a high percentage of recycled material from post-industrial multilayer films without significant loss of films strength and transparency, offering a basis for further improvements in the development of sustainable film packaging solutions. Future research and development efforts shall focus on optimizing the compatibility between incompatible materials co-existing in the recycles, in order to enhance overall film performance and to address specific application requirements.

Supporting information

Table S-1 Haze and gloss results of the multilayer films

Samples	Haze (%)	Gloss Units	
		20°	60°
LDPE | LDPE | LDPE	5.8 ± 0.4^{C}	12.47 ± 2.79^{AB}	105.33 ± 2.08^{AB}
M | M | LDPE	7.5 ± 0.4^{B}	8.77 ± 1.8^{B}	99.5 ± 3.5^{B}
M | M | LDPE+20M	5.4 ± 0.3^{C}	16.10 ± 3.66^{A}	109.33 ± 3.06^{A}
E | E | LDPE	16.5 ± 0.0^{A}	17.13 ± 1.86^{A}	73.57 ± 3.95^{C}
E | E | LDPE+20E	16.6 ± 0.0^{A}	-	20.9 ± 1.64^{D}
Note: Means that do not share a letter, are significantly different.			

Table S-2 Tensile test results of the multilayer films with LDPE, Recycled Metallocene and Recycled EVOH

Samples		$E_{1\%}$(Mpa)	σ_y(MPa)	σ_{max}(MPa)	ε_b(%)
LDPE | LDPE | LDPE	MD	185.04 ± 30.08^{B}	-	14.33 ± 1.42^{AB}	264.24 ± 47.43^{C}
	TD	211.04 ± 26.34^{AB}	8.54 ± 0.94^{BC}	12.94 ± 3.47^{A}	595.60 ± 213.64^{BC}
M | M | LDPE	MD	180.37 ± 13.17^{B}	-	15.20 ± 0.55^{A}	469.21 ± 46.20^{B}
	TD	177.18 ± 19.94^{B}	7.8 ± 0.23^{C}	14.35 ± 1.28^{A}	795.99 ± 180.87^{AB}
M | M | LDPE+20M	MD	186.45 ± 14.85^{B}	-	14.45 ± 1.00^{AB}	425.95 ± 96.30^{B}
	TD	201.61 ± 20.68^{B}	8.85 ± 0.21^{AB}	13.35 ± 1.34^{A}	877.10 ± 131.50^{A}
E | E | LDPE	MD	224.09 ± 17.41^{A}	-	13.16 ± 0.56^{B}	638.42 ± 106.87^{A}
	TD	253.66 ± 22.18^{A}	9.59 ± 0.48^{A}	13.48 ± 0.79^{A}	802.24 ± 64.22^{AB}
E | E | LDPE+20E	MD	169.47 ± 26.95^{B}	-	13.78 ± 0.86^{B}	511.11 ± 52.79^{B}
	TD	210.36 ± 51.57^{AB}	7.99 ± 0.67^{BC}	8.49 ± 0.50^{B}	511.70 ± 129.73^{C}

Note: Means that do not share a letter are significantly different. Statistical analysis was performed separately for the samples collected in MD and TD.

6.6 References

[1] Plastics Europe, "Plastics - the fast Facts 2023," 2023, Accessed: Dec. 24, 2023. [Online]. Available: https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2023/

[2] Z. O. G. Schyns and M. P. Shaver, "Mechanical Recycling of Packaging Plastics: A Review," Macromolecular Rapid Communications, vol. 42, no. 3. Wiley-VCH Verlag, Feb. 01, 2021. doi: 10.1002/marc.202000415.

[3] WRAP, "Plastic Recycling Reimagined: A High-Level Overview of Non-mechanical Recycling, Prepared by Adam Herriott," Banbury, 2023. [Online]. Available: www.wrap.org.uk

[4] Ellen MacArthur Foundation, "The New Plastics Economy: Rethinking the Future of Plastics & Catalysing Action," Ellen MacArthur Foundation. 2017. Accessed: Dec. 24, 2023. [Online]. Available: https://www.ellenmacarthurfoundation.org/the-new-plastics-economy-catalysing-action

[5] Manu C. Mulakkal et al., "Advancing mechanical recycling of multilayer plastics through finite," Resouces, Conservation & Recycling, 2021, doi: https://doi.org/10.1016/j.resconrec.2020.105371.

[6] C. Bascucci et al., "Investigating thermomechanical recycling of poly(ethylene terephthalate) containing phosphorus flame retardants," Polym Degrad Stab, vol. 195, Jan. 2022, doi: https://doi.org/10.1016/j.polymdegradstab.2021.109783.

[7] A. Saush, U. Schulte, and E. Angelidou, “Plastic Solid Waste Management - A Report of The Conference Board Plastics Working Group,” 2021. Accessed: Dec. 30, 2023. [Online]. Available: https://www.conference-board.org/topics/plastic/plastic-solid-waste-management

[8] BASF, “Mechanical Recycling.” Accessed: Dec. 30, 2023. [Online]. Available: https://www.basf.com/global/en/who-we-are/sustainability/we-drive-sustainable-solutions/circular-economy/mechanical-recycling.html

[9] Z. Tartakowski, “Recycling of packaging multilayer films: New materials for technical products,” Resour Conserv Recycl, vol. 55, no. 2, pp. 167–170, Dec. 2010, doi: 10.1016/j.resconrec.2010.09.004.

[10] G. A. Uehara, M. P. França, and S. V. Canevarolo Junior, “Recycling assessment of multilayer flexible packaging films using design of experiments,” Polimeros, vol. 25, no. 4, pp. 371–381, Jul. 2015, doi: 10.1590/0104-1428.1965.

[11] J. M. Soto, G. Blázquez, M. Calero, L. Quesada, V. Godoy, and M. Á. Martín-Lara, “A real case study of mechanical recycling as an alternative for managing of polyethylene plastic film presented in mixed municipal solid waste,” J Clean Prod, vol. 203, pp. 777–787, Dec. 2018, doi: 10.1016/j.jclepro.2018.08.302.

[12] M. Larrain et al., “Techno-economic assessment of mechanical recycling of challenging post-consumer plastic packaging waste,” Resour Conserv Recycl, vol. 170, Jul. 2021, doi: 10.1016/j.resconrec.2021.105607.

[13] J. Maris, S. Bourdon, J. M. Brossard, L. Cauret, L. Fontaine, and V. Montembault, “Mechanical recycling: Compatibilization of mixed thermoplastic wastes,” Polymer Degradation and Stability, vol. 147. Elsevier Ltd, pp. 245–266, Jan. 01, 2018. doi: 10.1016/j.polymdegradstab.2017.11.001.

[14] I. S. Lase et al., “Material flow analysis and recycling performance of an improved mechanical recycling process for post-consumer flexible plastics,” Waste Management, vol. 153, pp. 249–263, Nov. 2022, doi: 10.1016/j.wasman.2022.09.002.

7. CONCLUSIONS

In this work, flexible films for food packaging were developed using the blown film extrusion technique for four different case studies. The incorporation of different micro and nanoparticles into LDPE and EVOH matrices was carried out and analysed in Chapters 3 and 4. Also, the feasibility of incorporating two different types of recycled polymers, one with incompatible materials, into new flexible packaging was examined in Chapter 5 and 6.

Chapter 3 describes the preparation of LDPE nanoclay composites with and without PE-g-MA compatibilizer. It was concluded that the incorporation of 5 wt.% compatibilizer improved NC dispersion, by promoting adhesion of nanoparticle/matrix surfaces, leading to a decrease in aggregates and improving the film oxygen barrier. It was also concluded that the incorporation of NC did not considerably affect other relevant characteristic properties of films for the food industry, such as the heat-sealing strength and temperature, processing conditions and films transparency. Although the incorporation of NC improves the oxygen barrier of the matrix, the resulting permeability for these nanocomposites is not good enough to replace high barrier polymers, such as EVOH and PA. As an alternative strategy, the incorporation of micro and nanoparticles was carried out into the EVOH matrix. This was intended to improve their oxygen barrier properties, enabling a reduction of this layer thickness, as described in Chapter 4. This chapter presents a more comprehensive study comparing the performance of different micro and nanoparticles (NC, MCC, CNC, SiO_2), used at different incorporation rates (0.5, 1.0, 2.5 and 5.0 wt.%) in an EVOH matrix. This study also comprises the characterization of EVOH composite single-layer films (with high EVOH thickness) and multi-layer (with very low EVOH thickness) LDPE/EVOH/LDPE films. Masterbatch production at 210 °C with incorporation rates of 20 wt.% was only possible for NC. With this rate, the extrusion process did not remain stable for SiO_2. Furthermore, MCC and CNC suffered thermal degradation during this process. As a result, new masterbatches were produced with lower temperatures (180 °C and 190 °C) and incorporation rates of 10 wt.%, showing again a darkening (from white to soft brown) of the CNC particles. In single-layer films, the distribution and dispersion of particles was characterized through microscopy, which demonstrate that NC particles achieved a better dispersion. The WVTR and OTR tests were not conclusive for monolayer films, since EVOH loses its characteristic barrier when exposed to humidity, and due to a large thickness gradient throughout the film (from 22 to 40 μm) originated by the bubble instability

during film production. Multilayer LDPE/EVOH/LDPE films were produced with EVOH micro and nanocomposites in an inner layer and LDPE in the outer layers, to promote blown film stability. The EVOH layer thickness was reduced as much as possible, to 7.4 - 7.5 μm, to get closer to typical values used in commercial films. For this stage of the study, and taking into account the results previously obtained, low incorporation rates (0.5 wt.% and 1.0 wt.%) of MCC and NC were selected for incorporation into the EVOH matrix. Surprisingly, delamination of these films was not manually possible, probably due to the low thicknesses of EVOH layer and to the adhesion promoted by the blow-up ratio. Therefore, the OTR and WVTR tests were carried out on the three-layer structure. The WVTR results remained the same for all samples, as expected, due to the LDPE outer layers, and the OTR results decreased significantly with the incorporation of 0.5 wt.% NC or 1.0 wt.% MCC.

Therefore, the incorporation of low percentages of NC in LDPE and EVOH matrices, and MCC in EVOH matrices, showed to be a good strategy to reduce the thickness of the EVOH layer of a typical food packaging film, facilitating its recycling.

The recycling of multilayer films is reported in Chapter 5 and 6, which presents the possibility of incorporating plastic recovered from post-industrial multilayer films, mainly of LDPE base, into new food packaging without significant alteration of the mechanical and thermal properties of the films, when compared to the virgin LDPE ones. The study presented in Chapter 5 showed that all the reprocessed recycles, up to 5 cycles, have better mechanical properties than the LDPE films, provide a good extrusion process stability, and maintain the critical material properties (crystallization and melting temperatures, degree of crystallinity, and MFI). Although the two recycled materials tested were mostly LDPE based, they also contained LLDPE, and one of the recycled materials also contained EVOH, being LLDPE responsible for the good mechanical properties observed in these recycles. Chapter 6 is a continuation of the work reported in Chapter 5, further emphasizing that recycles with LDPE and EVOH (incompatible materials) exhibit inferior optical properties, while the mechanical properties of all films with recycled content remained comparable to LDPE control films.

7.1 Future Work

Concerning future work, it is important to perform migration tests for micro and nanocomposites, as the packaging must comply with the regulations on migration of substances into food imposed by the European Commission. It would also be relevant to optimize the dispersion of the particles used, during the masterbatch production stage. For this sake, simulations of the twin-screw extrusion process, encompassing the use of different processing conditions and screws design, would be a possible strategy.

Regarding recycled multilayer films, promoting the affinity between incompatible polymers (LDPE/EVOH) by the incorporation of a compatibilizer (PE-g-MA) could improve the mechanical, optical and barrier properties. In addition, producing films using virgin materials with the polymers that constitute the recycles can lead to a fairer comparison. In the studies presented in chapters 5 and 6, only LDPE films were used for control purposes, while LLDPE is a material with superior mechanical properties.

A Life Cycle Analysis (LCA) of the developed films should be conducted in order to compare their environmental impact with that of traditional packaging materials.

These future work ideas aim to further enhance the performance, functionality, and sustainability of the developed films, providing a roadmap for continued research and development in the field of flexible food packaging.