From multilayer LDPE/EVOH flexible film scraps to new multilayer films

Carolina Barros [a,b,*] , O.S. Carneiro [a] , A.V. Machado [a]

[a] IPC - Institute for Polymers and Composites (IPC), University of Minho, Guimarães, Portugal

[b] Centre for Innovation in Polymer Engineering (PIEP), Guimarães, Portugal

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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, and the other has Ethylene Vinyl Alcohol (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.

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 (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 $\geq 5\, wt\,\%$) 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 multimaterial 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 a previous article [15], 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.

Experimental procedure

Materials

Lotrène FD0270, a virgin LDPE blown film extrusion grade from QAPCO (with 923 kg/m^3 density and melt temperature of $112^{\circ}C$) 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 (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) and characterized in more detail in Ref. [15].

Film production

After studying the mechanical behaviour and optical properties of single-layer films produced with the recycled materials mentioned in Ref. [15], 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 $60^{\circ}C$ 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 1.

The outer layer of the three-layer film containing recycled material is composed of either 100 % LDPE or 80 % virgin LDPE. This choice is driven by the fact that, when used in packaging applications, the external layer enhances consumer appeal by offering superior gloss and a more tactilely pleasing surface.

The films thickness was measured using a micrometer (Digimatic thickness gauge 547-301, Mitutoyo, Japan) with a measuring accuracy of 0.01 mm , was $40 \pm 5\ \mu\ m$.

Characterization techniques

Scanning Electron Microscopy (SEM) analysis was conducted on gold-coated film samples fractured in liquid nitrogen using a Nano SEM FEI Nova 200 system.

The haze of the films was measured with an XL-211 Hazegard System transmittance meter, following ASTM D1003-00, with five

Table 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 +20 M	r-Metallocene | r-Metallocene | LDPE +20 % r-Metallocene
E |E | LDPE	r-EVOH | r-EVOH | LDPE
E |E | LDPE +20 E	r-EVOH | r-EVOH | LDPE +20 % r-EVOH

measurements taken per sample.
Gloss properties were assessed in accordance with ISO 2813 using a BYK Micro-TRI-gloss S meter at 20° and 60° angles.

Tensile tests were performed on the produced films using a ZWICK universal mechanical testing machine with a 5 kN load cell at a speed of $50\ \ mm/min$, under controlled conditions of $23 \pm 2^{\circ}C$. Specimens ($25\ mm \times 160\ \ mm$), were taken from the extruded film bubble in both the machine (MD) and transverse (TD) directions according to ASTM D882-10.

The tensile and haze results are presented as mean ± standard deviation, with statistical analysis performed with one-way ANOVA using IBM SPSS Statistics and Tukey's method for mean comparison, at a 95 % confidence level.

Results and discussion

Through the SEM images (Fig. 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, highlighted within the circles in red in Fig. 1. 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 $40 \pm 5\ \mu\ \ m$, with a thickness variation between layers of $4.61\ \mu\ \ m$ for the film with Recycled EVOH and $2.04\ \mu\ \ m$ for the film with Recycled Metallocene.

Regarding the optical properties, haze 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 Fig. 2. Due to the incompatibility between EVOH and LDPE, the material has separate phases that scatter light differently than a homogeneous one. This can affect the visual appeal of packaged products, such as strawberries, where clear visibility is desirable for consumer attraction. Recycled EVOH films may be more suitable for less demanding applications where product visibility is not critical, such as packaging with labeling or non-transparent uses. This approach could allow the use of recycled materials while addressing visual shortcomings.

The films with recycled Metallocene showed a similar haze to the LDPE film. Regarding gloss, Fig. 3, all the films presented high values for this property, except for the *E* ∨ *E* ∨ ¿ LDPE +20 E 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 Supplementary Material.

The tensile tests results, depicted in Figs. 4 and 5 and in Table S2, demonstrate that the mechanical properties slightly decreased in the E | E | LDPE +20E multilayer film. For M |M | LDPE + 20 M 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.

Conclusions

Multilayer flexible films incorporating recycled material, from postindustrial waste, exhibited good overall properties.

Incompatibility between EVOH and LDPE resulted in an

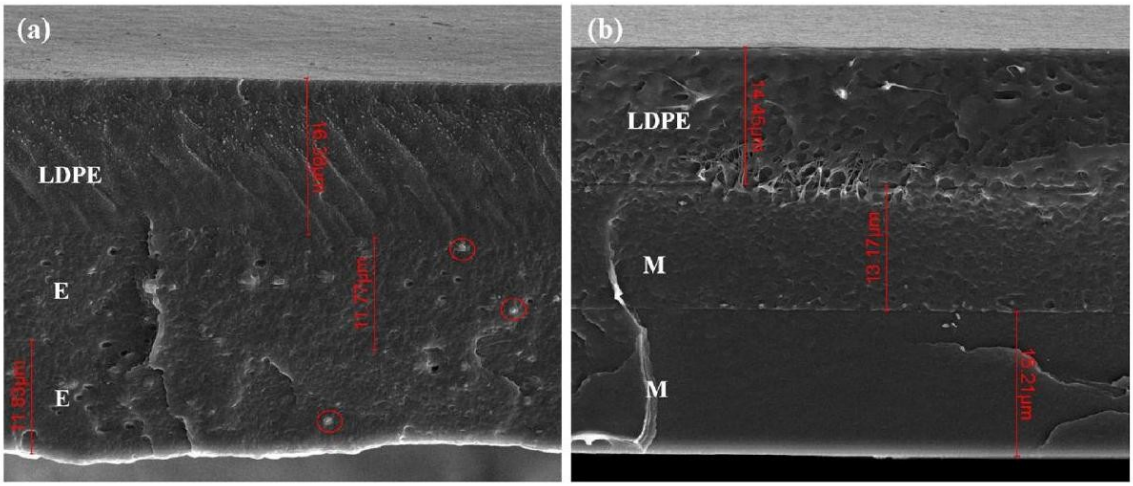

Fig. 1. SEM images of the cross-section of the *E* ∨ *E* ∨ ¿ LDPE film (a), and M ¿ *M* ∨ ¿ LDPE film (b).

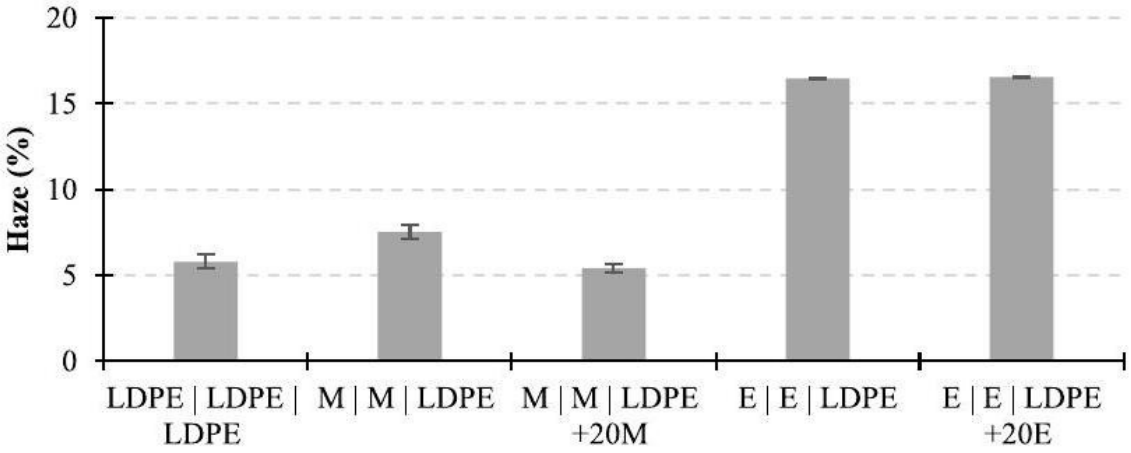

Fig. 2. Haze of the multilayer films with LDPE, Recycled Metallocene and Recycled EVOH.

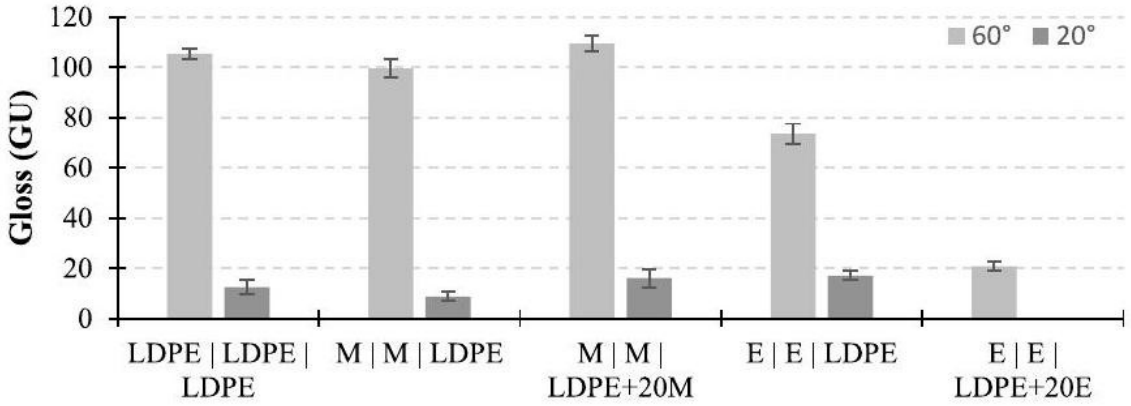

Fig. 3. Gloss at the outer LDPE layer in multilayer films with LDPE, Recycled Metallocene and Recycled EVOH.

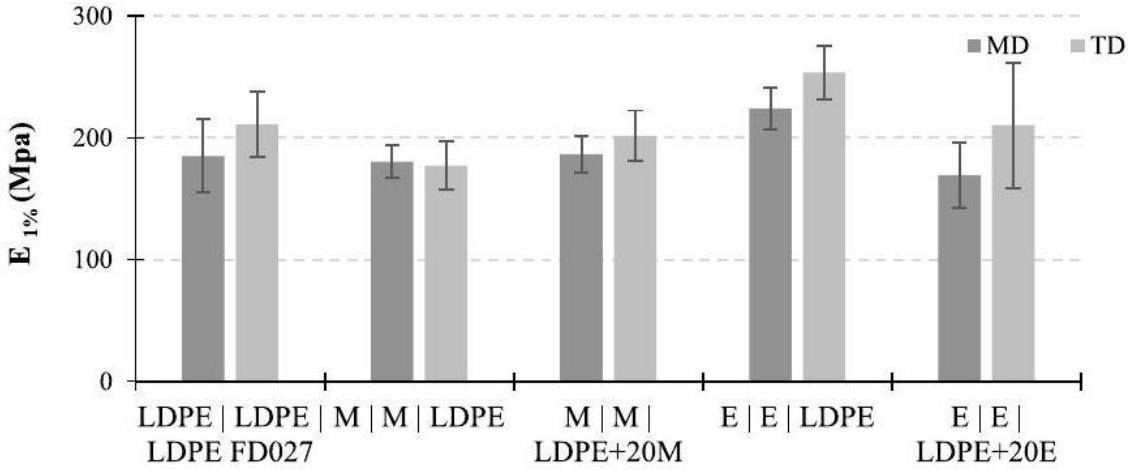

Fig. 4. Young's Modulus ($E_{1\%}$) of the multilayer films with LDPE, Recycled Metallocene and Recycled EVOH.

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 gloss and an increase in

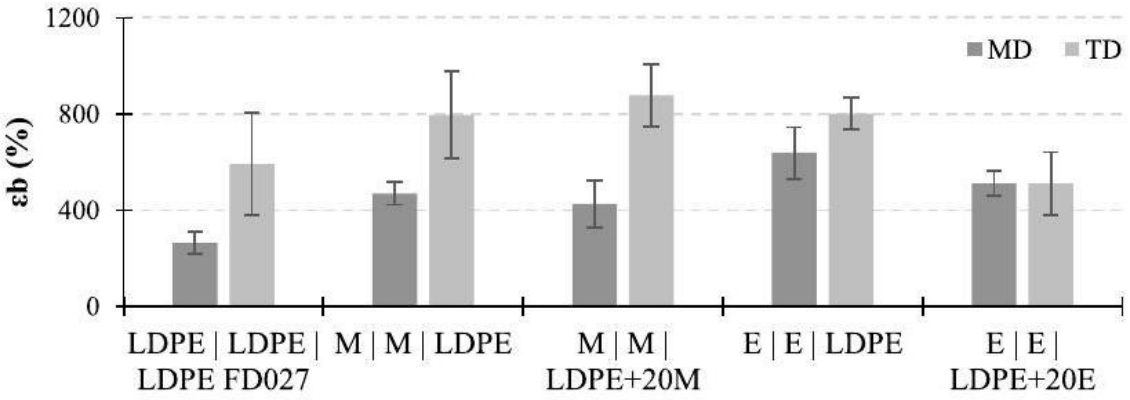

Fig. 5. Strain at break (ε_b) of the multilayer films with LDPE, Recycled Metallocene and Recycled EVOH.

haze. 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.

CRediT authorship contribution statement

Carolina Barros: Writing - original draft, Investigation, Formal analysis, Data curation, Conceptualization. O.S. Carneiro: Writing review & editing, Visualization, Validation, Project administration, Methodology. A.V. Machado: Writing - review & editing, Visualization, Validation, Project administration, Methodology.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Carolina de Lemos Barros reports financial support was provided by European Regional Development Fund. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2024.127695.

Data availability

Data will be made available on request.

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- Corresponding author. IPC - Institute for Polymers and Composites (IPC), University of Minho, Guimarães, Portugal.

E-mail address: b8453@dep.uminho.pt (C. Barros).