

INFLUENCE OF POLYPROPYLENE RANDOM COPOLYMER IN MECHANICAL PROPERTIES OF STRETCH WRAP FILMS

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Abstract: Recent developments on Stretch wrap films, usually made from polyethylene (PE), have focused more on processing conditions and film formulation redesign than on the base resin itself, aiming at continuously optimizing film performance. This paper evaluated the influence of polypropylene random copolymer (PP random), with 10% content, in stretch films of PE regarding mechanical properties such as puncture, retention ending force and stretch force, as much as dart drop impact, tear resistance and tear propagation resistance. Overall, properties evaluated at Highlight® equipment remained very similar, but adding PP random to the film increased its dart impact and tear propagation resistance. The outstanding performance in tear propagation resistance was attributed to the presence of a PP stiffer layer to the structure, well compatibilized to PE by the random ethylene-propylene chains, which increased interfacial strength, reduced interlayer slip and delayed the failure mechanism.

Keywords: *Stretch wrap films, polypropylene random copolymer, tear; tear propagation;*

Introduction

Stretch wrap films are extensible polymeric structures extremely used for industrial packaging, unitization and product transportation worldwide. Linear low density polyethylene (LLDPE) copolymerized with butene (C4), hexane (C6) or octene (C8) through catalytic systems such as Ziegler-Natta and/or Metallocene, is the most used polymer to produce these formulations, providing them great mechanical properties such as tensile strength, puncture and tear resistance, as much as great elastic recovery and cling properties as well. [1] Recent developments regarding these films have focused on achieving high performance solutions through processing conditions and/or final product redesign, aiming towards better mechanical properties, as much as emerging market needs such as packaging downgauging and more sustainable solutions.

It is known that physical properties of semicrystalline polymers depend on several variables, such as molecular structure, molecular weight and molecular weight distribution, crystallinity and morphology of chains through the polymer, as much as processing methods and product design characteristics. [2] Combining different materials is also an attractive route to modify polymers final properties. Blending polypropylene (PP) and ethylene copolymers to synergistically combine their properties, such as stiffness from PP and toughness and tear resistance from PE, is an attractive option for a variety of applications, such as polymer blends, coextrusion of multilayered films and engineering thermoplastics. [3, 4] However, these properties depend strongly on adhesion of constituents, and interfacial properties should be evaluated carefully. Due to their incompatibility, a variety of copolymers have been investigated as compatibilizers to improve the interfacial adhesion between PP and PE, including ethylene-propylene-diene-monomer (EPDM), ethylene-vinyl-acetate (EVA), styrene-butadiene-styrene (SBS) and styrene-ethylene-butadiene-styrene

(SEBS). These techniques are well known to improve the interfacial strength through imposing interfacial interaction and crystal formation [3], and compatibilized blends show substantial increases in the elongation at break and the impact strength. [4]

A previous study evaluated coextruded microlayers formulations made either with Ziegler-Natta catalyzed ethylene copolymer (ZNPE) or metallocene ethylene copolymer (mPE), both with Isotactic Polypropylene (iPP). The formulation with mPE resulted in better adhesion to iPP, characterized by an interface with regions of epitaxially crystallized ZNPE and other regions of entangled mPE chains, in which entanglement bridges promoted much better adhesion than did epitaxially crystallized lamellae. [5] Controlling parameters such as interfacial entanglement, diffusion and adhesion is determinant to reach suitable performance, since multilayer polymers share extensive interfacial area between layers. Interfacial strength and the failure mechanism at the interface is driven mainly by the density and length of interfacial entanglements, which bridge the layers together to increase adhesion and reduce interlayer slip. The failure mechanism is composed either by the pull-out mechanism for short molecules and the crazing mechanism for long molecules. In the pull-out mechanism, the entangled chains at the interface are pulled out from the shorter side of the chains while in the crazing mechanism, interface fracture occurs by chain breaking, and this normally results in stronger interface reinforcement. [3]

Researches on stretch films have become more focused on film solution and processing conditions developments rather than the base resin itself. Therefore, the central objective of this paper is to evaluate the presence of PP random copolymer on mechanical properties of stretch wrap formulations of PE, as much as subsidizing knowledge to continuously develop high performance solutions of these films.

Experimental

Materials

Table 1 shows Braskem thermoplastic resins used for this study, alongside with its main controlling properties such as melt flow rate (MFI), density and type of comonomer.

Table 1: MFI, density, type of comonomer and additives of the thermoplastic resins used on this work

Resins	Properties			
	MFI 190°C/2,16kg (g/10min)	Density (g/cm ³)	Co-monomer	Additives
mPE 1	3,5	0,918	Hexene	
mPE 2	4,5	0,912	Hexene	
ZNPE	2,7	0,919	Butene	Antioxidants
PP Random	7,0*	0,900	Ethylene	
Cling Layer		**		

*MFI = 230°C/2,16kg

**Not disclosed due to confidentiality.

Methodology

Stretch film samples A e B were produced through working partnership between Braskem and SML machine producer. Resins were processed in a twin-screw extruder, medium rotation speed of 180 rpm and temperature profile of Z1=60°C, Z2=200°C, Z3=280°C, Z4=280°C, Z5=280°C, Z6=280°C, Z7=280°C; Formulations were designed with 13 layers according to film composition shown in Table 2, resulting co-extruded films with 23µm thickness. Afterwards, samples were sent to Braskem Innovation&Technology Center at Triunfo (RS) and acclimatized for further analysis.

Table 2: Formulation components and percentage between Stretch films samples A e B.

Components	Sample A (%)	Sample B (%)
mPE1	55	45
mPE2	25	25
ZNPE	10	10
PP random	0	10
Cling Layer	10	10

Characterization

Films were analyzed through Highlight Tester® (Figure 1-A,1-B), since it is an equipment specifically designed to simulate stretch film application. Films were also analyzed for Elmendorf Tear, according to ASTM D1922 and Dart Drop Impact, according to ASTM D1709; Tear Propagation Resistance was evaluated according to ESTL FPT750 at ESTL laboratory (Figure 1-C). Both Highlight results and Tear Propagation Resistance were evaluated at 300% film elongation.



Figure 1: Characterization equipment. (A) Control panel and (B) Analysis board of Highlight Tester®; (C) Illustration of tear propagation resistance analysis (FPT750 - ESTL laboratory)

Results and Discussion

Table 3 shows main film properties obtained from Highlight Tester® Center. Overall, solutions presented similar values of puncture, retention ending force and stretch force. Ultimate Highlight analysis, which represents maximum machine direction (MD) elongation that the film can withstand before breaking, showed higher values for Sample B, with PP random, than Sample A.

Table 3: Highlight Tester® properties between Stretch films samples A e B

Properties (Highlight Tester)	Units	Sample A	Sample B
Ultimate	%	431 ± 1	475 ± 4
Puncture	kg	3,1 ± 0,2	3,05 ± 0,15
Retention Ending Force	kg	2,01 ± 0,02	2,10 ± 0,01
Stretch Force	kgf	30,9 ± 0,1	31,3 ± 0,1

Figure 2 compares Dart Impact results between both stretch film formulations, obtained through dart drop analysis. It can be seen that sample B presented higher impact strength than standard solution, since the energy, indirectly measured by the dart mass that the film can sustain without breaking, was higher compared to sample A. It is reasonable to assume that PP, although stiffer than PE, might help increase impact strength through its interface with mPE, since its molecular structure has enough free volume to allow chain conformation and, therefore, energy dissipation.

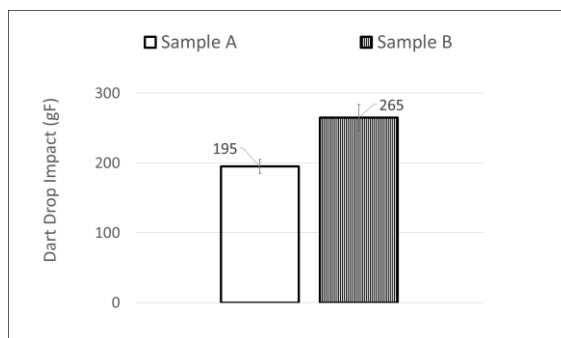


Figure 2: Dart drop impact results between Stretch films samples A e B

Figure 3 correlates tear resistance (Elmendorf) between samples A and B. For MD, it can be seen that sample B showed tear resistance around 25% higher compared to sample A. This is particularly interesting, since it was expected decrease in tear resistance due to polypropylene highly oriented chains (shish-kebab) in MD morphology, as observed in previous studies. It is not conclusive to assign this improvement observed in sample B to polypropylene only, especially due to its low content. As expected, tear resistance for transverse direction (TD) was higher than MD, but more similar between both samples considering standard deviation.

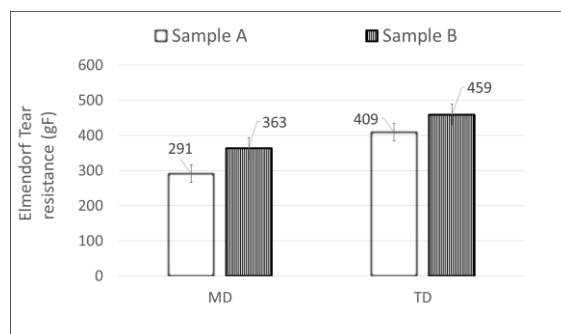


Figure 3: Tear resistance (Elmendorf) between both Stretch films samples A e B

Figure 4 shows the resistance to tear propagation, measured in time (seconds), between both samples. It can be observed that sample B presented time of tear propagation approximately 300% higher than sample A, which stood out as the main highlight of this work. It is believed that the presence of a stiffer layer of PP in the microstructure, compatibilized to the mPE layer by the ethylene-propylene random copolymer chains, helped increasing interfacial strength and crystal formation, increasing entanglement density and reducing interlayer slip. Consequently, the failure mechanism in sample B was delayed compared to sample A.

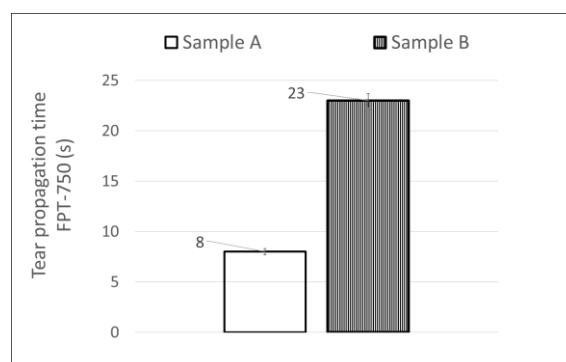


Figure 4: Time of tear propagation (FTP-750) between Stretch films samples A e B

Conclusions

Different formulations of Stretch wrap films were processed and characterized mechanically regarding Highlight Tester® properties, Dart Drop Impact, Elmendorf Tear and Time of Tear propagation, in order to evaluate the influence of polypropylene random copolymer in stretch formulations. Overall, Highlight properties remained similar for both samples. Impact dart resistance was higher for sample B, with PP, associated with energy dissipation due to structure chain conformation.

Regarding tear properties, adding polypropylene to the formulation increased both tear resistance in machine direction (MD) and the time of tear propagation through the stretch film. The first result was considered unexpected, since previous studies demonstrated that polypropylene's highly oriented structure with fibrillar chains decreased tear resistance in PE blends.

The outstanding increase in tear propagation resistance was attributed to the presence of a stiffer layer of polypropylene in between layers, which due to the good compatibilization promoted by the random copolymer sequences to the mPE layers, helped increase entanglement density and reduce interlayer slip, delaying the failure mechanism comparing to sample A. This result is considered essential to design new stretch wrap solutions with higher mechanical performance.

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