

EFFECT OF SEBS CONTENT ON MORPHOLOGICAL AND MECHANICAL PROPERTIES OF LDPE/SEBS BLEND COMPATIBILIZED WITH PE-g-MA

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Abstract: This work discusses the preparation and analysis of films made from a blend of LDPE (low-density polyethylene) and SEBS (styrene-ethylene-butylene-styrene) that is compatible with PE-g-MA (polyethylene-graft-maleic anhydride). The study explores the influence of SEBS content on the film formation capacity and morphological and mechanical properties of the blend. The results indicate that the film formation capacity is affected by the strain-softening property of SEBS. A blend with 10% SEBS demonstrated better film formation compared to the one containing 30% SEBS. Despite the challenges in blown film production due to the strain-softening property of SEBS, the blend has potential for other applications.

Keywords: Blown extrusion, LDPE, SEBS, PE-g-MA.

EFEITO DO CONTEÚDO DE SEBS NAS PROPRIEDADES MORFOLÓGICAS E MECÂNICAS DA MISTURA LDPE/SEBS COMPATIBILIZADA COM PE-G-MA

Resumo: Este trabalho discute a preparação e análise de filmes feitos de uma blenda de PEBD (polietileno de baixa densidade) e SEBS (estireno-etileno-butileno-estireno) compatibilizada com PE-g-MA (polietileno-graftizado-anidrido maleico). O estudo explora a influência do teor de SEBS na capacidade de formação de filme e nas propriedades morfológicas e mecânicas da blenda. Os resultados indicam que a capacidade de formação do filme é afetada pela propriedade de amolecimento sob tensão do SEBS. A blenda com 10 % de SEBS demonstrou melhor formação de filme em comparação com aquela contendo 30 % de SEBS. Apesar dos desafios na produção de filmes soprados, devido à propriedade de amolecimento do SEBS, a blenda tem potencial para outras aplicações.

Palavras-chave: Extrusão sopro, PEBD, SEBS, PE-g-MA.

1. INTRODUCTION

Low-density polyethylene (LDPE) is a semicrystalline polyolefin thermoplastic with easy processability, high ductility, some chemical resistance, and barrier properties. Thus, it is widely used to produce films for packaging purposes. It can be an excellent candidate for coating the outside of the soft robot. However, the low thermal and mechanical stability at high temperatures limits its application [1].

One way to improve thermal and mechanical stability is to blend the LDPE with materials that present those properties. Polymeric blends are the easiest and low-cost way to modify interesting properties and create new materials [2]. To overcome the low thermal and mechanical stability of LDPE and make it suitable for casing the soft robot, we proposed to produce a polymer blend of LDPE with thermoplastic elastomers (TPEs) such as styrene/ethylene-butylene/styrene (SEBS) block copolymers, which presents superior thermal, mechanical, and UV stability. Furthermore, the SEBS presents high impact resistance and elongation, which can also improve LDPE's mechanical properties [3].

Most polymer blends are immiscible due to the lack of physical and chemical interaction between both polymeric chains, which leads to total phase separation and poor mechanical properties. Compatibilizers or interfacial agents can be added to the polymer blend to improve phase interaction, and consequentially improve physical, thermal, and/or mechanical properties. Functionalized polymer with maleic anhydride (MA) has been used as compatibilizing agents in several polymeric blend systems. Researchers have reported that MA-grafted polymers can act as both reactive and non-reactive compatibilizers, therefore it is possible to obtain two different mechanisms for blend compatibilization. The mechanism of compatibilization with MA depends on the polymeric blend pair's chemical structure and physical interactions [4].

John et al., 2003 evaluated the effect of blend ratio and reactive compatibilization of high-density polyethylene (HDPE)/ethylene vinyl acetate (EVA) blends compatibilized with maleic-modified polyethylene (MA-PE). They reported that the MA-PE is able to occupy the interfacial area between HDPE and EVA, in which the PE chain from MA-PE was well dispersed into HDPE while the MA could form dipolar interactions with the EVA. Consequentially, the compatibilized blends showed an increase in the storage modulus, loss modulus, and loss factor values of the system [5].

Sharma and Maiti, 2014 blended polypropylene (PP) with a styrene/ethylene-butylene/styrene block copolymer grafted with maleic anhydride (SEBS-g-MA) to evaluate the role of crystallinity effects of the SEBS phase on the tensile properties and impact behavior of PP. They report that the crystallinity of the polymer blend decreases as the content of SEBS-g-MA increases. Consequently, they observed enhanced tensile elongation and impact strength [6,7].

This work is an innovative technological solution since no papers were found in the literature that reports blends constituted by the pair LDPE and SEBS compatibilized with PE-g-MA, especially to be used as casing for soft robots. The aim of this work was to produce a tubular film of LDPE/SEBS to be used for casing the robotic arm. The reason for developing this work is to select a soft and flexible material to case the soft robot externally. The benefit is to bring a technological solution in polymers to produce a new material that can accumulate interesting properties for the application, which are not possible to be achieved with pure materials. In this perspective, some doubts exist. The first is related to blend processing, because LDPE/SEBS blends processed by blow extrusion were not found in the literature. Not all materials are suitable for processing blown films since they need to have a property called strain-hardening.

Polymers need to be resistant to extensional flow or to elongational deformation to be blown. LDPE has strain-hardening, while in SEBS strain-softening predominates in wide zones of process temperatures and shear rates. This characteristic gives the material low resistance to extensional flow, present in the balloon pulling and blowing stage. Therefore, there is a concern related to the maximum SEBS content that does not affect the processing of the blend by blow extrusion and, consequently, does not affect the final properties. Another consideration for obtaining this blend is the compatibility efficiency of the two constituent phases (LDPE and SEBS). The LDPE/SEBS blend is classified as immiscible and incompatible, that is, just mixing the two phases does not guarantee the achievement of the desired properties. Incompatible blends do not have mechanical performance, thermal and chemical resistance sufficient to be intended for application [6-10].

One of the reasons why the blend in question is incompatible is related to the poor adhesion between LDPE and SEBS. The chemical structure of both polymers does not have functional groups attractive to each other, and the interactions and chemical bonds present in each one is stronger than breaking them to interact with the macromolecules of the neighboring material [10]. To overcome this factor, interfacial agents called compatibilizing agents are added, which will be responsible for reducing the interfacial tension, promoting adhesion between the phases, and stabilizing the morphology of the blend. For this work, polyethylene functionalized with maleic anhydride (PE-g-MA) was chosen to act as a compatibilizer for the LDPE/SEBS blend [11]. It is not known whether maleic anhydride can interact with SEBS during the simultaneous mixing of the three components, due to factors such as steric hindrance caused by bulky functional groups present in the chemical structure of SEBS, and low mixing power of the blowing extruder available in the SENAI/CIMATEC polymer laboratory. Therefore, this work allows us to understand how a mixture between a thermoplastic polymer and a conventional elastomer works, the need for a good mixing process, and the ideal proportion between the materials.

2. METHODOLOGY

The materials used were SEBS from Fortiprene, trade name TPE 3051; PE-g-MA from SK functional polymer, trade name Orevac®18507; LDPE from Eteno, trade name PEBD EBE853/73. The blow molding machine in the polymer processing laboratory is from the IMACOM brand, model IM .25. LD26 with a 25 mm diameter cylinder and an L/D = 26.

2.1. Processing

The proportions between the materials to process the samples are shown in Table 1. It was considered that blow extrusion needs to maintain the strain-hardening property, therefore the concentration of SEBS could not exceed 30 wt%, and, in the literature, the standard concentration of PE-g-MA is 3 wt%.

Table 1- Blend ratio for 1.5 kg of total material per sample.

SAMPLES	LDPE		SEBS		PE-g-MA	
LDPE	100 %	-	-	-	-	-
LDPE/SEBS10%	87 %	1305 g	10 %	150 g	3 %	45 g
LDPE/SEBS30%	67 %	1005 g	30 %	450 g	3 %	45 g

The amount of each material was measured on a precision scale and then dried at 80 °C for 2 hours in an oven with air ventilation to remove moisture. Before processing the blend, the blowing extruder was cleaned with pure LDPE to prepare the machine for the experiment. Before processing, the materials were mechanically mixed

by placing all blend components in a plastic bag and shaking it for at least 2 minutes. The processing parameters were 160 to 170 °C temperature profile, 40 rpm screw rotation, and 0.8 rpm of drawling up velocity.

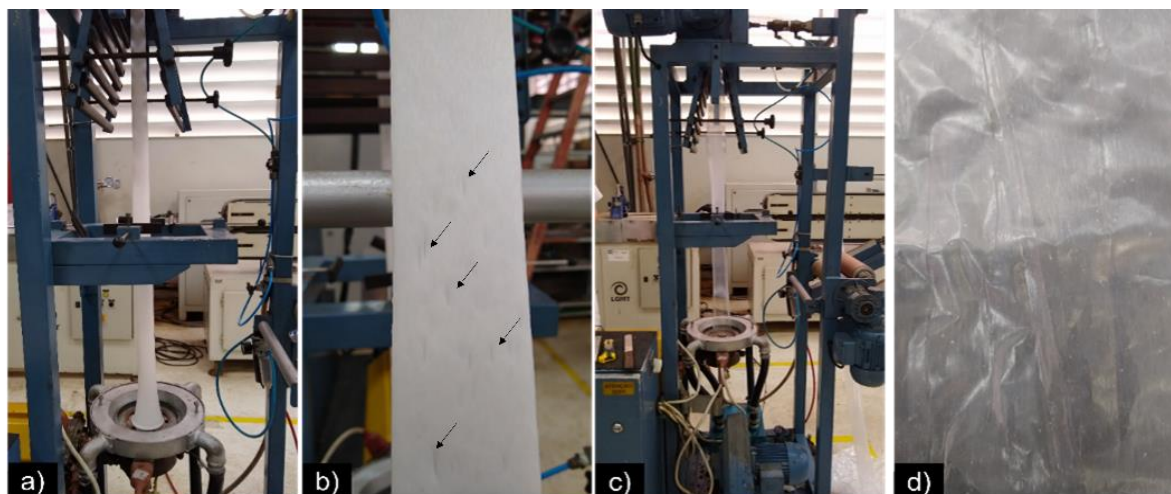
2.2. Characterization of polymer films

Film surface morphological characterization of the LDPE and LDPE/SEBS compatibilized blends was carried out on a JEOL JSM-6510LV Scanning Electron Microscope, using the detection of secondary electrons and 5-20 kV. Images were examined with Fiji image ImageJ 1.50i software. The tensile testing was performed at 23 °C as ASTM D882 standard in specimens with 100 mm length, 10 mm \pm 1 mm width, and 0.6 mm \pm 0.2 thickness on an EMIC DL-2000. The load cell used in the assay was TRD-21 with 490.5 kN and a speed of 50 mm.min⁻¹. The results reported are an average of the results obtained in the assay of at least five tested specimens.

3. RESULTS AND DISCUSSION

Figure 1 illustrates the process of film formation through blow extrusion, depicting both the LDPE/SEBS 30% composition (a and b) and the LDPE/SEBS 10% composition (c and d) films.

Figure 1- a) Film formation of the blend containing 30 %wt SEBS, evidencing of the strain-softening phenomenon; b) macro morphology of the blend containing 30 %wt SEBS; c) Film formation of the blend containing 10 %wt SEBS, evidencing of the strain-softening phenomenon; d) macro morphology of the blend containing 10 %wt SEBS.



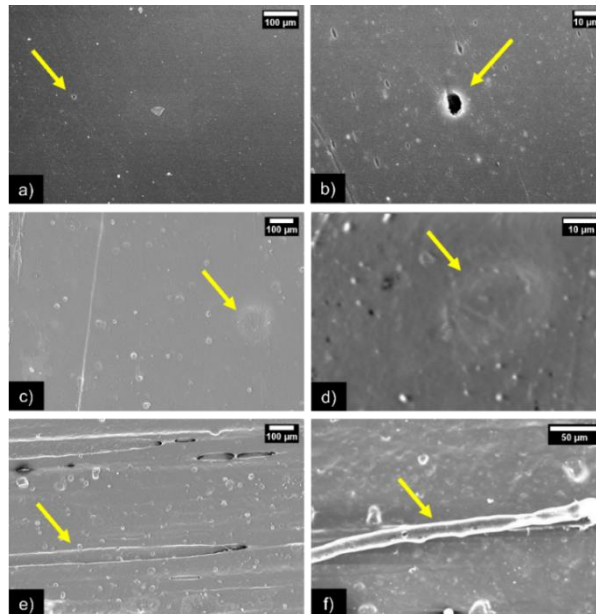
As expected, the blend with 30 %wt SEBS was not suitable for processing by blow extrusion, due to the greater influence of the strain-softening property of SEBS, as shown in Figure 1 illustrates the process of film formation through blow extrusion, depicting both the LDPE/SEBS 30% composition (a and b) and the LDPE/SEBS 10% composition (c and d) films.

Figure 1b, arrows pointing to macroscopic matrix defect. Processing failure has a negative impact on the film's mechanical properties since it is necessary to control the blend morphology by processing to obtain a final material with desired properties.

Scanning electron microscopy (SEM) was made on the films' surface to investigate blend morphological characteristics. Figure 2 shows film surface SEM micrography of LDPE (Figure 2a and b), LDPE/SEBS10% (Figure 2c and d), and LDPE/SEBS30% (Figure 2e and f).

Figure 2- Surface film SEM images. a) 150x magnification and b) 1000x magnification of LDPE film – arrows pointing to matrix defects, c) 100x magnification and d) 1500x magnification of LDPE/SEBS10% film – arrows pointing to a large droplet of SEBS dispersed

phase soaked into the LDPE matrix, e) 100x magnification of LDPE/SEBS30% film – arrow pointing to the void created by SEBS fiber pullout, and f) 400x magnification of LDPE/SEBS30% film – arrow pointing to a SEBS fiber.



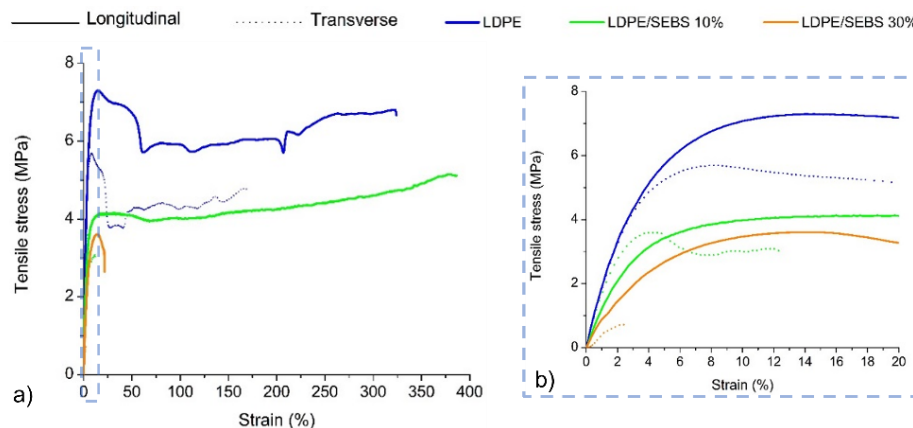
The micrographs depicted in Figure 2a and Figure 2b, which pertain to pure LDPE, reveal the existence of defects that may be linked to film pulling conditions such as blowing ratio and stretching speed, which have an impact on the melt's strength. The micrographs acquired from the LDPE/SEBS10% blends (Figure 2c and Figure 2d) exhibit the dispersed phase of SEBS as droplets encased by the LDPE matrix. These micrographs depict a sizable droplet size of the SEBS phase. The dispersion and comminution of the dispersed phase in the LDPE matrix during processing may have been compromised, primarily due to the low residence time of the material in the extruder barrel and low screw rotation speed, leading to lower shear rates. These factors hinder effective mixing and poor dispersion of SEBS in the LDPE, thereby promoting the coalescence of the dispersed phase in the matrix. This outcome is manifested in the mechanical properties of the blend, with a decrease in tensile strength and Young's modulus.

Figure 2e and Figure 2f micrographs display the combination of LDPE with 30 wt% SEBS, exhibiting the SEBS phase's arrangement as microfibrils within the LDPE matrix. The blow extrusion process made it possible to form *in situ* SEBS microfibrils in the LDPE/SEBS30%. However, poor adhesion of the microfibrils to the matrix is observed, with evidence of detachment highlighted in Figure 2e. The weak interface generated in the LDPE/SEBS30%, even in the presence of PE-*g*-MA, can be attributed to processing conditions. The low mixing time during extrusion did not facilitate interaction between the components, resulting in a blend with a weak interface and, consequently, poor mechanical properties.

A tensile test analysis was conducted to evaluate the mechanical properties of both films in longitudinal and transverse modes. Figure 3 and Table 2 show the tensile properties of LDPE and LDPE/SEBS blends. Figure 3a show the full stress-strain curves of longitudinal (full line) and transverse (dotted line) films of LDPE and LDPE/SEBS blends. Figure 3b shows a zoom into the 0-20 % strain region of the stress-strain curves. The overall analysis shows that inserting SEBS into LDPE reduces the matrix tensile yield strength, Young's modulus, and strain at break. However, the blend with 10 % SEBS presented higher stability during tensile

deformation for longitudinal films, which can be noticed in Figure 3a by a more linear curve in the plastic zone of LDPE/SEBS10% compared to neat LDPE. The lower tensile yield strength of all blends was expected since the SEBS phase has low stiffness and contributes to lower the stiffness of the composite. However, the poor adhesion between SEBS and LDPE was responsible for the poor mechanical properties observed in all compositions. This outcome can be explained by the low shear rate, low residence time, and poor mixture capacity of the processing method.

Figure 3- Tensile stress-strain curve of LDPE (blue), LDPE/SEBS10% (green), and LDPE/SEBS30% (orange) longitudinal films (full line) and transverse films (dotted line). a) Stress-strain full curve of all samples and b) zoom in into 0 - 20 % strain region.



The results were attributed to several factors. First, it is necessary to consider that the LDPE/SEBS blend is classified as immiscible and incompatible, which means that just mixing the two phases does not guarantee the achievement of the desired properties. Incompatible blends do not have good mechanical, thermal, and chemical resistance to be intended for application. One of the reasons why the blend in question is incompatible is related to the poor adhesion between LDPE and SEBS [13].

The chemical structure of both polymers does not have functional groups attractive to each other, so the physical interactions and chemical bonds presented in each one are stronger than breaking them to interact with the macromolecules of the neighboring material. To overcome this factor, interfacial agents called compatibilizing agents are added to reduce the interfacial tension, promote adhesion between both phases, and stabilize the morphology of the blend. For this PoC, polyethylene functionalized with maleic anhydride (PE-g-MA) was chosen to act as a compatibilizer for the LDPE/SEBS blend [3,13-15].

Table 2- Tensile Properties of LDPE and LDPE/SEBS blends longitudinal and transverse films.

Film orientation	Samples	Young's modulus (MPa)	Tensile yield strength (MPa)	Strain at break (%)
Longitudinal	LDPE	199.9 ± 18.6	8.4 ± 0.9	341.6 ± 209.2
	LDPE/SEBS10%	135.4 ± 34.8	4.3 ± 1.0	237.6 ± 139.0
	LDPE/SEBS30%	88.1 ± 12.7	3.8 ± 0.3	25.4 ± 4.8
Transverse	LDPE	212.8 ± 14.7	5.6 ± 0.9	175.1 ± 96.6
	LDPE/SEBS10%	187.1 ± 18.7	3.6 ± 0.6	13.4 ± 8.0
	LDPE/SEBS30%	15.9 ± 15.4	0.4 ± 0.3	1.9 ± 0.9

Some factors could have affected the blend compatibility process. The first one to consider is the steric impediment caused by bulky functional groups present in the chemical structure of SEBS, which makes physical interaction with maleic anhydride difficult. Another important factor is the limitations of the blow extruder from the SENAI/CIMATEC polymer laboratory: low mixing power with restricted screw operation capacity up to 48 rpm and low $L/d = 26$. In order to obtain satisfactory mechanical properties of the incompatible blend, it is necessary that the polymers are well mixed and have a sufficient residence time in the machine.

4. CONCLUSION

The LDPE/SEBS blend is an attractive choice for various applications, especially in the automotive industry, where thermal stability and impact resistance are determining factors. This study addressed the production of films from the PEBD/SEBS blend, compatibilized with PE-g-MA, revealing that the SEBS content in the mixture exerts a notable influence on the blown film-forming capacity, consequently affecting its mechanical properties. This occurs due to the inherent stress-softening property of this component. The results pointed out that a concentration of 10 wt% of SEBS in the mixture resulted in the best film-forming capacity, surpassing the mixture with 30 wt% of SEBS. However, it is important to note that the tensile mechanical properties obtained did not reach satisfactory levels. Therefore, optimizing the manufacturing process of this blend and selecting the most suitable processing method are critical steps to fully harness the potential of this material in specific industrial applications.

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