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ABS/Recycled PCTG blend compatibilized with SBS: effect on mechanical properties and morphology

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Abstract

The reuse of plastic polymers is one of the ways to reduce the negative environmental impact caused by these products. This work presents a study of mechanical and morphological properties of ABS and PCTG residue blend using SBS as compatibilizing agent to make copolyester recycling process feasible. It was observed that the incorporation of SBS in the mixture decreased the stiffness and increased the impact resistance compared to the results obtained in the non-compatible mixture, indicating that the SBS acted as a toughening agent in the mixture. Additionally, according to the results obtained by DSC and SEM, the blends obtained can be considered partially miscible, since two glass transition temperatures were evidenced shifted by a few degrees from neat components. Micrograph suggests that there are SBS small domain inclusions dispersed in the PCTG matrix and partial compatibility occurred by partial interaction of the SBS in the interface.

Keywords: *ABS, PCTG, SBS, polymeric blends, compatibilization.*

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1. Introduction

The manufacture of plastic products has undergone a great expansion recently due to global demand [1]. In general, the increase in production contributes to increased waste.

Advanced materials with specific and sustainable properties have been extensively developed through the manufacturing of engineering polymer commodities and/or blends. The great advantage of this type of mixture is the possibility of reusing residues whose original application does not allow the return of the reprocessed material [2].

Evaluating the feasibility of obtaining blends of two polymers for industrial applications involves studying their miscibility and mechanical properties. However, if the polymers are immiscible, the mixture between them will be brittle and morphologically unstable. Thus, the use of compatibilizers that stabilize the phases and promote synergy between them is recommended.

Acrylonitrile-butadiene-styrene (ABS) copolymer is widely used in the automotive, aeronautics, home appliances and packaging industries, among others, precisely because of its unique characteristics of mechanical resistance and brightness [3].

Poly (1,4-cyclohexylene di-methylene terephthalate glycol) (PCTG) is a copolymer formed by the esterification and polycondensation reactions (with metallic catalyst) of cyclohexane di-methanol (CHDM), terephthalic acid (TPA) and ethylene glycol (EG). PCTG has excellent processing and optical properties that allow the use of this polymer to obtain transparent thermoformed products with complex shapes, being widely used in the packaging industry [4].

Once copolyesters such as PCTG can undergo hydrolytic thermal oxidation when reprocessed, which can cause discoloration or yellowing, chain splitting, and molar mass reduction, it is difficult to recycle or reuse them [4]. The proposed alternative to use PCTG residues is to blend it with ABS, using block copolymer styrene-butadiene-styrene (SBS) as a compatibilizing agent. As ABS is opaque, it contributes to minimize visual effects of the yellowing process that occurs to PCTG in the proposed blend.

This work aimed to develop a new route to reuse industrial PCTG waste. For this, blending PCTG residues with virgin ABS was evaluated, using block copolymer butadiene-styrene (SBS) as a compatibilizing agent. The influence on the mechanical properties were evaluated by tensile and Charpy impact tests and morphology of the blend was evaluated by scanning electron microscope (SEM) and DSC.

2. Experimental

2.1. Materials

The materials used included ABS polymer, Terluran® GP22, compatibilizing agent, SBS Styroflex® 2G66, both produced by Styrolution ™ and PCTG waste obtained from grinded injection molding channels (SKYGREEN® JN400, from SK Chemicals).

2.2. Preparation methods

The blends were prepared according to the proportions shown in the Table 1, varying the concentration of the blend components and compatibilizing agent. For the compatibilized samples, different levels of SBS were added and the amount sum 100 %.

Polymers were first weighted, cold mixed and then extruded using a twin screw extruder to ensure adequate homogeneity of the blend. Prior to the injection of the test specimens, all extruded mixtures were maintained in the dehumidifier at 80 °C for 4 hours.

Table 1. Compositions of the ABS/PCTG blends without SBS (control samples) and with SBS (compatibilized samples).

Sample	ABS (%)	PCTG (%)	SBS (%)
Control samples	67	33	0
	33	67	0
	50	50	0
Compatibilized samples	67	30	3
	64	30	6
	47	50	3
	44	50	6
	36	60	4
	33	60	7

2.3. Characterization

2.3.1. Mechanical properties

Tensile tests were performed according to ASTM D638, using test specimens of ASTM D638-Type I. Samples were tested on an Instron Model 5569 universal test machine using a load cell of 5,000 N at room temperature (23 °C).

For impact strength, tests were performed on a Resil 25R instrumented impact machine from Ceast using a 1.0 J impactor in test specimens injected at 23 °C with a pendulum velocity of 2.90 m/s. The samples that presented the best performance on Impact Strength test were selected to be analyzed by DSC and SEM.

2.3.2. Differential Scanning Calorimetry measurements (DSC)

For DSC, measurements were performed in the second heating from -120 °C to 250 °C at a ratio of 20 °C min^{-1} in dynamic nitrogen atmosphere (N_2) with gas flow of 50 mL min^{-1} in Mettler's model 822e equipment.

2.3.3. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was used to evaluate the fracture surface of the samples that had the best impact resistance (with and without SBS). A low vacuum Scanning electron microscope was used, model FEI Quanta 400.

3. Results and Discussion

3.1. Mechanical properties

Table 2 summarizes mechanical properties results of the ABS/PCTG blends with and without the addition of compatibilizing agent SBS.

It can be observed that the sample 67/33 had the highest values of elastic modulus and Charpy impact strength, however it had the lowest elongation at break. This behavior was expected, since neat ABS terpolymer is more rigid than PCTG. On the other hand, increasing of the proportion of PCTG in blends with SBS causes an increase in elongation at break and in Charpy impact strength, but there is a decrease of the rigidity in relation to control samples, due the highest toughness of the elastomer copolyester.

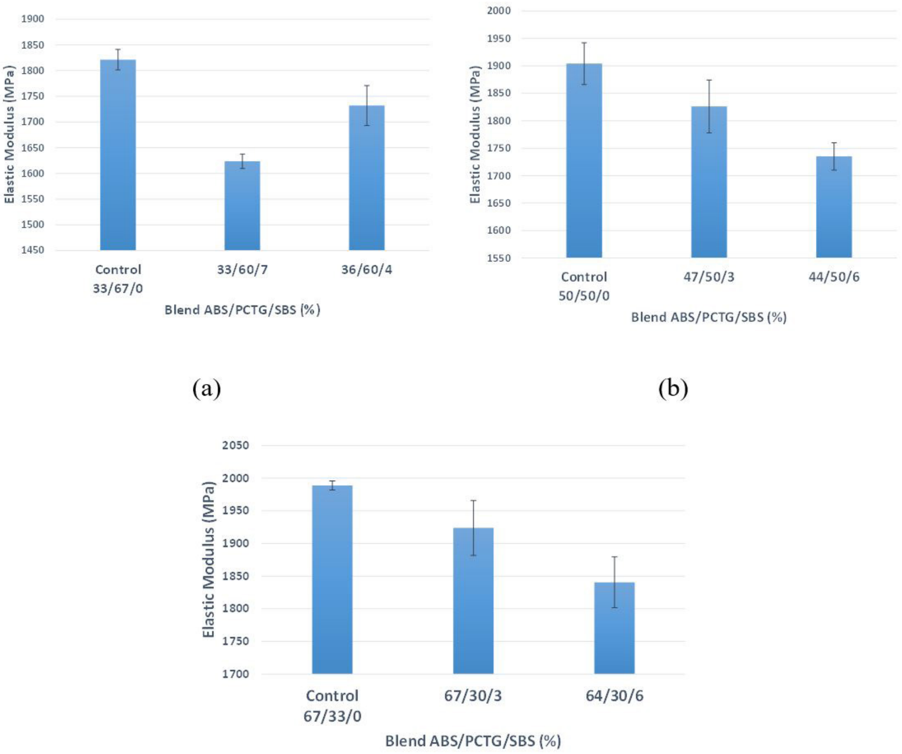
Figure 1 shows elastic modulus results obtained for the control and compatibilized blends with similar proportions. As it can be seen for the control blends, as the content of ABS in the blend increases, the elastic modulus also increases, indicating a higher rigidity. This behavior may be associated to greater rigidity of neat ABS compared to neat PCTG.

Regarding the compatibilized blends, all the results showed that the addition of SBS increased the flexibility of the blends compared to the control samples, since the elastic modulus of the compatibilized blends decreased. Comparing 33/67/0 blend with the ABS/PCTG/SBS 36/60/4 and 33/60/7 blends, it can be observed a reduction on stiffness of approximately 5 % and 10 %, respectively. Therefore, the increase on the SBS content increases the flexibility of the final blend. All the compatibilized samples presented the same behavior.

Figure 2 shows the elongation at break results of control and compatibilized blends. Comparing the blends ABS/PCTG 33/67 and ABS/PCTG/SBS 36/60/4, it is possible to notice a small increase of 5 % of elongation at break. On the other hand, 33/60/7 blend showed an increase of approximately 65 % in the elongation at break. The 47/50/3 blend had a greater increase in the elongation at break (189 %) compared

Table 2. Elastic modulus, elongation at break and Charpy impact strength of the ABS/PCTG blends with and without SBS.

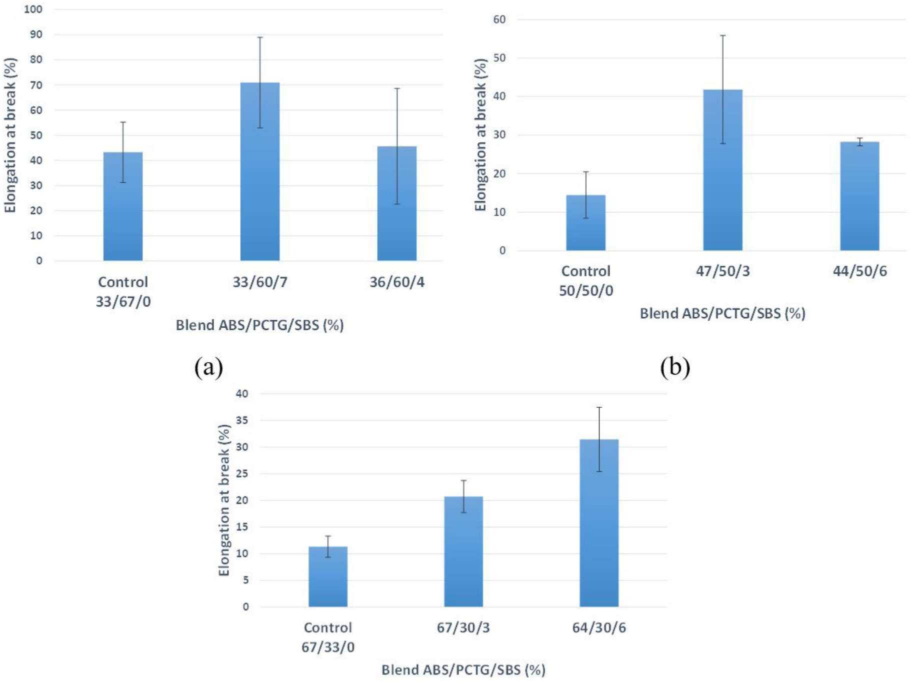
Sample	ABS (%)	PCTG (%)	SBS (%)	Elastic modulus (MPa)	Elongation at break (%)	Charpy impact strength (J/m)
Control samples	67	33	0	1,989 ± 7	11.0 ± 2	66 ± 17
	50	50	0	1,904 ± 38	14.5 ± 6	63 ± 17
	33	67	0	1,821 ± 20	43.0 ± 12	51 ± 12
Compatibilized samples	67	30	3	1,924 ± 42	21.0 ± 3	65 ± 15
	64	30	6	1,840 ± 39	31.0 ± 6	77 ± 17
	47	50	3	1,826 ± 48	42.0 ± 14	78 ± 18
	44	50	6	1,735 ± 24	28.0 ± 1	88 ± 18
	36	60	4	1,732 ± 39	45.0 ± 23	108 ± 23
	33	60	7	1,623 ± 14	71.0 ± 18	115 ± 18



(a) (b)

(c)

Figure 1. Elastic modulus (MPa) of ABS/PCTG and ABS/PCTG/SBS blends at similar contents of ABS and PCTG.



(a) (b)

(c)

Figure 2. Elongation at break (%) of ABS/PCTG and ABS/PCTG/SBS blends at similar contents of ABS and PCTG.

to the ABS/PCTG 50/50 mixture. The 33/60/7 blend also had an expressive increase of 181 % compared to the 33/67/0 control blend. It can be concluded that the increase in the ABS content in the control samples decreased the toughness of the blends. However, SBS compatibilizer attenuated this effect since there was an increase on the elongation at break of the compatibilized blends.

Figure 3 shows Charpy impact strength results obtained for the compatibilized and control blends. It can be observed that the compatibilized blends produced using the following proportions of ABS/PCTG/SBS, 36/60/4 and 33/60/7, presented an increase on the Charpy impact strength of 111 % and 125 %, respectively, compared to 33/67/0 blend. However, the blends with a higher percentage of ABS, such as 47/50/3 and 44/50/6 compatibilized blends showed increase on this property of approximately 23 % and 33 %, respectively, when compared to the 50/50/0 control blend. The comparison of the 67/33/0 control sample to 67/30/3 and 64/30/6 blends showed smaller increases of approximately 2 % and 16 %, respectively.

Therefore, results of Charpy impact strength test indicated that the increase on the ABS content resulted on the increase of this mechanical property, considering the non-compatibilized blend. Blends containing SBS presented an enhance on this mechanical property compared to control samples, corroborating the results of elastic modulus and elongation at break. It can be concluded that this effect is related to the elastomeric characteristic of the SBS compatibilizer that promotes better performance in blends with higher PCTG content.

Among the control samples, the 67/33/0 blend was the one that presented the highest impact strength result whereas, among the compatibilized blends, the mixture 33/67/7 presented the best result for this property. These two compositions were evaluated by DSC and SEM techniques in order to evaluate the compatibility mechanism between the components.

3.2. Miscibility of polymeric blend

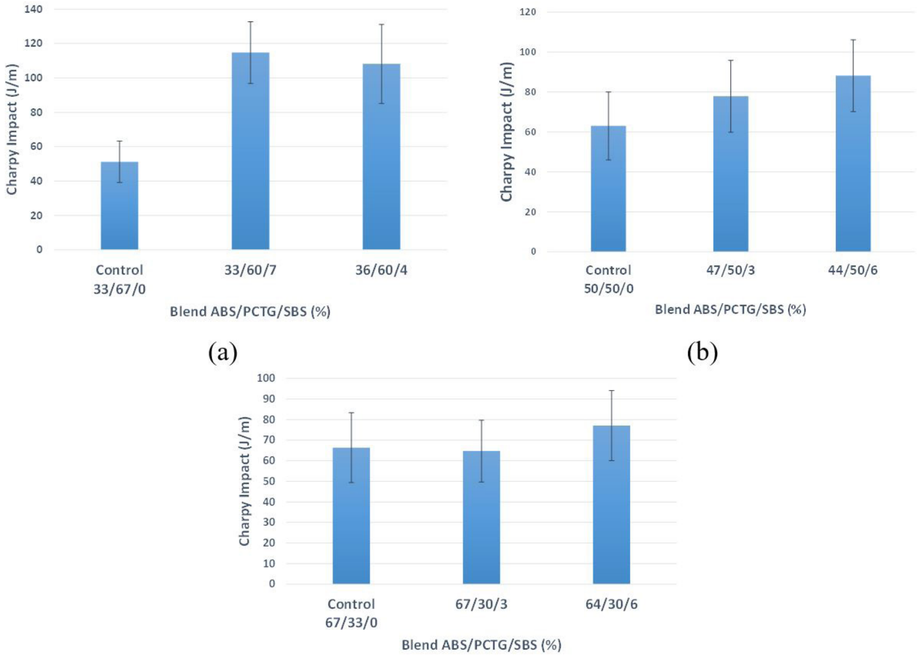
3.2.1. DSC analysis

In order to evaluate the miscibility between the components of the blends with and without compatibilizer agent, samples that presented the highest results on Charpy impact strength tests were selected to be analyzed by DSC and SEM. Thus, the samples analyzed were: 67/33/0 and 33/60/7. For DSC analysis, samples of neat ABS and PCTG were also evaluated.

According to Olabisi et al. [5], a blend can be considered miscible when the glass transition temperature (Tg) is unique and is in an intermediate range between the temperatures of the neat components.

For a partially miscible blend, the glass transition temperature is given by two or more transitions that are corresponding to the blend phases and are shifted in relation to the Tg of the neat components. In this case, each phase is formed by a miscible mixture containing different compositions [5-8].

Table 3 shows the values of the glass transition temperature obtained for the analyzed samples. The 67/33/0 blend presented two different glass transition temperatures that were remarkably close to the neat ABS and PCTG components shifted by a few degrees. The same occurred to the 33/60/7 blend.



(a) (b)

(c)

Figure 3. Charpy impact strength (J/m) of ABS/PCTG and ABS/PCTG/SBS blends at similar contents of ABS and PCTG.

Table 3. Glass transition temperature of polymeric blends and their neat constituents.

Sample (ABS/ PCTG/SBS)	Tg1 (°C)	Tg2 (°C)	Tg2 – Tg1
100/0/0	-81.9	102.6	-
67/33/0	74.3	107.5	33.2
33/60/7	77.0	110.2	33.2
0/100/0	83.1	-	-

Chen and Zhang [9,10] observed the similar behavior for ABS/PETG blends without compatibilizer. PCTG differs from PETG by the amount of the CHDM co-monomer. PETG is defined as a copolymer containing less than 50% (in weight) of CHDM comonomer; for contents higher than 50%, the material is defined as PCTG. In their work, the 70/30 ABS/PETG blend presented Tg1 of 74.3 °C and Tg2 of 110.4 °C while for the 30/70 ABS / PETG blend, the Tg results obtained were, respectively, 76.2 °C and 111.4 °C, corresponding to ABS and PETG phases, respectively.

Considering Tg difference (Tg2 - Tg1), it is possible to notice that the 33/60/7 blend presented the same difference as the control blend. This leads to the conclusion that the 33/60/7 blend was not totally miscible.

3.2.2. Morphology and interface observations

The morphology of a fracture surface may provide information about the compatibilization mechanism of polymeric blends. The component that is presented in the smallest proportion is called the dispersed phase while the component in the highest proportion is the continuous phase. When the dispersed phase is incompatible with the continuous phase, or matrix, it appears in spherical forms, large and with a well-defined interface [7,8].

Figures 4a and b show the fracture region of the impact specimen at 41 and 38x magnification, respectively, while Figures 4c and d show the micrographs at 5000x magnification and Figures 4e and f, with 10000x magnification, for 67/33/0 and 33/60/7 blends.

It can be observed that the fracture surface of the compatibilized blend with SBS is rougher (Figure 4b), with several cracks, but with well-defined reliefs that indicates a ductile failure compared to the blend produced without the addition of compatibilizer.

Figure 4c shows a good dispersion of the PCTG in the ABS matrix that has “fibers” form. The opposite is seen in Figure 4d, where the PCTG is the continuous phase (matrix), and the ABS is regularly dispersed in the mixture with different domain sizes. ABS, as an acrylonitrile, butadiene, and styrene terpolymer, presents a more heterogeneous aspect, due to its different co-monomers, while the PCTG has a smoother and more homogeneous surface. This aspect can be seen in Figures 4c and 4d, respectively.

Micrographs of the 67/33/0 and 33/60/7 blends show an interface that do not present any adhesion between the phases as indicated by the circles in Figures 4 c-d. In addition, there are some regions, represented by the diamonds in Figures 4 c-d, with better adhesion in the interface.

Micrograph of the 67/33/0 blend (Figure 4e) shows regions where PCTG-rich phase is dispersed in the ABS-rich matrix with a larger domain size and regions with a smaller domain size with a tendency to appear in the form of fibers, as indicated by the arrows in the micrograph.

According to Zhang et al. [11], the smaller the diameter of the fiber, the better the adhesion at the interface and, consequently, the greater the tendency of the fibers to break or not to detach from the matrix. Thus, the 67/33/0 blend showed a lower result of impact strength due to the weak adhesion in the interface region between the components and due to the larger diameter of the dispersed phase in the matrix. However, the interface was not weak enough to allow the complete detachment of the PCTG fibers from the ABS matrix.

Joseph et al. [12] studied ABS/PETG blends using SBS as a compatibilizer; the mixture of ABS in PETG as a dispersed phase presented larger domain sizes than when PETG is the dispersed phase. The phenomenon of coalescence is more pronounced in high concentrations of the dispersed ABS phase, due to the high mobility of the ABS domains in the PETG matrix. This phenomenon can also explain the morphology of the 33/60/7 ABS/PCTG/SBS blend.

Analysis of the micrograph of the 33/60/7 blend (Figure 4f) suggests that there are rubber small domain inclusions dispersed in the PCTG-rich matrix (arrows) and regions of irregular sizes of the dispersed phase, ABS, suggesting phase distortion and co-continuous morphology.

Bo Li et al. [13] studied the toughening mechanism of the blend ABS/PETG and a co-continuous morphology was also evidenced.

The toughening mechanism with this co-continuous morphology can be explained by energy dissipation with the interfacial debonding, energy absorption with the distortion of ABS phase [13] and the presence of elastomeric phase, from SBS, which influences in the crack propagation process, turning the material more ductile (Figure 5).

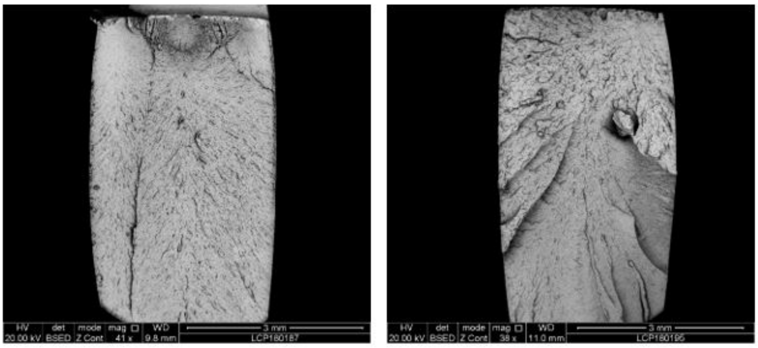
According to the model proposed by Macosko [14], a co-continuous morphology should enhance the fluidity, toughening and rigidity of the final blend, depending on the properties of the components and the dispersion of energy, corroborating the results of mechanical properties obtained previously for impact resistance.

Figure 6 summarizes how the blends components acted in the interface and on the compatibilization of the systems ABS/PCTG and ABS/PCTG/SBS, at the proportions 67/33/0 and 33/60/7, respectively.

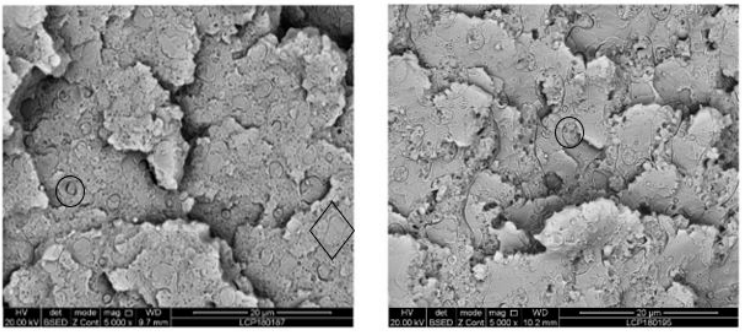
Therefore, the evaluation of all micrographs suggests that the main mechanism of action of the SBS in the blend was by dispersion and increase of rubber content, which attenuates the transference of mechanical stresses to the matrix and increases the impact strength and by the co-continuous morphology of the ABS-rich phase, which can enhance the toughness of the material.

According to the theory proposed by Joseph et al. [11], if the compatibilization of ABS in the PCTG had occurred by emulsification, the morphology would be more homogeneous and with smaller domains.

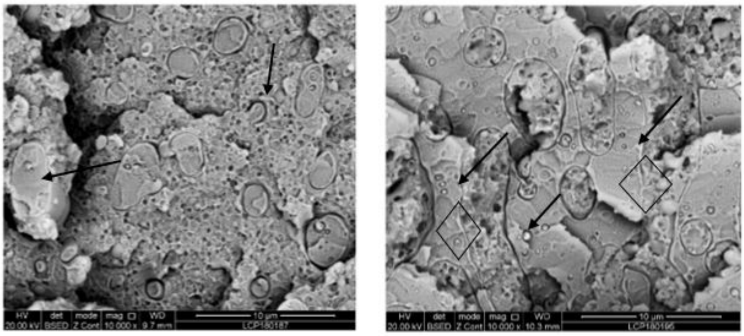
Considering the present study, for regions where it is possible to identify a better affinity between the ABS-rich phase and PCTG-rich matrix, there may have been a small



(a) 67/33/0 (b) 33/60/7



(c) 67/33/0 (d) 33/60/7



(e) 67/33/0 (f) 33/60/7

Figure 4. Micrographs of the fracture surface of the ABS/PCTG/SBS samples at different magnifications.

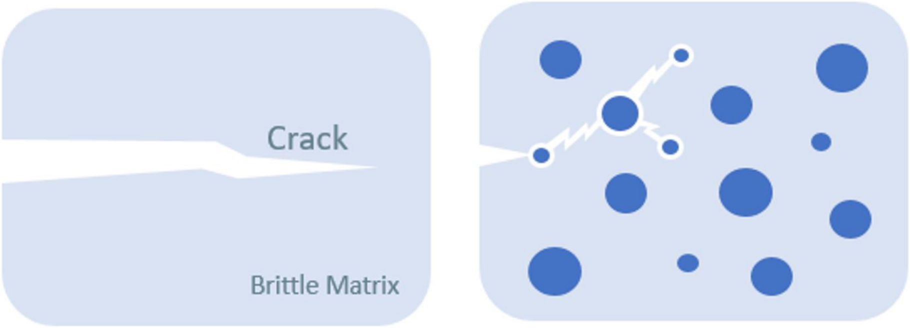


Figure 5. Crack propagation process in a brittle matrix and in a tenacified matrix.

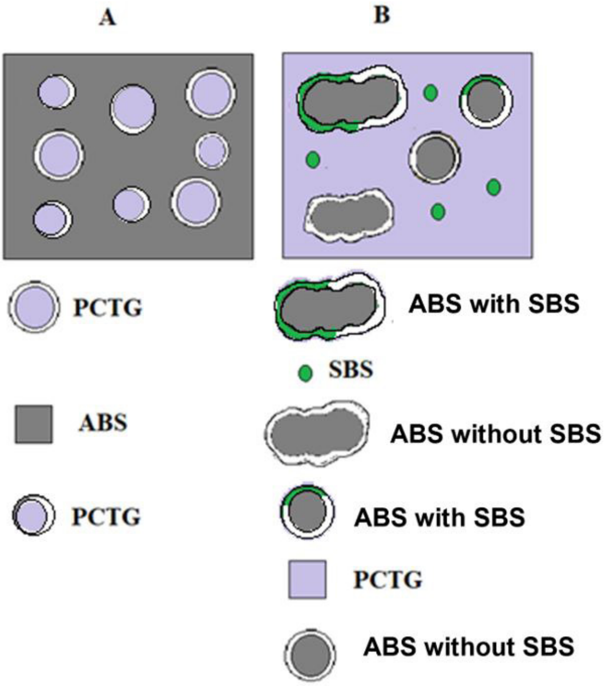


Figure 6. Scheme of the morphology and mechanism of action of the compatibilizers for the ABS/PCTG and ABS/PCTG/SBS blends at the following contents: (a) 67/33/0; (b) 33/60/7, respectively.

interaction between the butadiene phase of SBS and PCTG, as well as an interaction of the styrene phase with the ABS. Nevertheless, this was not the main mechanism responsible for the results that were found.

4. Conclusion

According to the results, it was found that the inclusion of SBS as a compatibilizing agent in the blend between ABS and PCTG, promoted an increase on the toughness of the blend and it enhanced impact strength, when compared to the control blend.

It was observed that, in the 67/33 ABS/PCTG blend, PCTG is dispersed in the ABS matrix in the form of fibers of different sizes and homogeneous distribution with regions where the interface is easily observed and regions with a certain affinity of the phases.

For 33/60/7 ABS/PCTG/SBS blend, it was verified the coalescence of the dispersed ABS phase in the PCTG matrix, since that the SBS acted, primarily, as an impact modifier in the matrix, but there may also exist a small interaction between them, this corroborates with the results of glass transition temperature obtained, in which there was a slight displacement in relation to the neat polymers.

Therefore, it is suggested that SBS promoted a toughening effect due to the increase in the rubber content in the final blend, since a significant increase in elongation at break was observed, although there was a decrease in the elastic modulus.

Thus, it can be concluded that the blend between virgin ABS and residues of PCTG using SBS as compatibilizer, in the proportion of 33/60/7, can be used in several applications, like packaging and home appliances, for example, once that the impact properties have improved with the toughening.

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