Influence of SEBS-MA and SBS compatibilizers on properties and morphology of blends of polystyrene/rubber residue (SBRr) from the footwear industry

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Abstract

The reuse of rubber waste is very important today, both to reduce the harmful effects on the environment, and to reduce the cost of new material development. Considering that most of the studies reported in literature refer to the reuse of tire waste, this article aims to evaluate the influence of styrene-butadiene-styrene (SBS) and styrene-(ethylene-butylene)-styrene grafted with maleic anhydride (SEBS-MA) compatibilizers on the blend performance of polystyrene (PS)/styrene-butadiene rubber residue (SBRr), which come from the footwear industry. The blends were prepared in a co-rotating twin screw extruder and then were molded by injection. They were analyzed by impact and tensile tests, heat deflection temperature (HDT), ductile-brittle transition temperature, dynamic mechanical thermal analysis (DMTA) and transmission electron microscopy (TEM). The results evidenced that the use of any of the compatibilizers on the PS/SBRr blend significantly increased the impact strength, while the tensile properties and HDT were lower when compared to the polymer matrix. The ductile-brittle transition temperature remains at approximately 25°C range for all the blends. In general, it has been proved that the SBS was the most effective compatibilization process in the PS/SBRr system. The DMTA test shows the presence of two distinct temperature peaks. The morphologies obtained by TEM of binary and ternary blends were quite different and typical of immiscible blend. The results show a good perspective regarding the use of industrial waste (SBRr), since it may enhance a material that would be discarded.

Keywords: rubber residue, polystyrene, compatibilizer, polymer blends.

1. Introduction

The problem of rubber waste, both industrial and post-consumer, is of great importance today (Weber *et al*., 2008). Footwear industry rubber residues are a source of environmental pollution and a waste of raw materials which have good properties and high added value. It is known that these materials have relatively high resistance to biological agents and to climate changes, thus causing serious problems to the environment at large when discarded. Both economic aspects and environmental pollution are justification for the efforts to promote the recycling of these polymer materials (Luna *et al*., 2015a). These materials cannot be melted or remolded as thermoplastics because of their cross linking structure.

One of the ways to reuse rubber waste is through mixtures with thermoplastics, i.e., the development of polymer blends. In these cases, infusible residues are dispersed in the thermoplastic matrix during processing, acting as flexible loads (Brennan *et al*., 2002; Silva *et al*., 2016). The mixture constitutes an alternative to produce materials with physical, chemical and chemical-physical characteristics better than those of pure polymers as well as obtaining materials with specific properties. Generally, the constituents of the polymer mixtures are selected so as to preserve the advantages of each polymer (Piorkowska *et al*., 1990). Furthermore, other advantages for the use of mixtures are: improve the processability and/or properties; reduce product cost; and reuse of polymer waste.

A great majority of thermoplastic mixtures with rubber waste are immiscible, which often leads to material with lower mechanical properties. To solve this problem, a compatibilizer that acts at the interface of the constituents of the mixture can be used, promoting a reduction in interfacial tension and improving dispersion (Joseph *et al*., 2005).The appropriate choice of compatibilizer can improve the mixture with rubber waste and favor the properties. Therefore, the possibility of reusing rubber waste in mechanical mixtures, as well as the fact that it adds value to a material that would be discarded in the production chain, is a reason that encourages research of the best combination of thermoplastic/waste rubber/compatibilizer, i.e., the search for the optimization of properties (Libyan *et al*., 2012; Luna *et al*., 2015b). Some papers about the development of polymer mixtures based on rubber waste and thermoplastics have been reported in literature, as noted below.

Veilleux and Rodrigue (2016) developed blends of polystyrene with rubber waste of styrene-butadiene (SBRr) in a co-rotating twin screw extruder, which then were injection molded. The objective of this study was to investigate the effect of concentration (0-94 wt%) and pretreatment of rubber waste in toluene solution. The results showed that the pretreatment improves the interaction between the phases of polystyrene with rubber waste and consequently better mechanical properties were obtained. However, it was evidenced that the pretreatment is more effective for concentration above of 50% of SBRr.

Zhao *et al*. (2015) evaluated the influence of SBS compatibilizer and aromatic oil in the performance of high impact polystyrene (HIPS) blends with SBR rubber waste. The blends were prepared by mechanical mixture, and then the mechanical and morphological properties were evaluated. The results evidenced that the mixture combined of SBS with aromatic oil in HIPS/rubber waste blend significantly improved mechanical properties. It was shown that the composition of 9% of SBS with 15% of aromatic oil optimized the results, being observed an increase of 220% in elongation, as well as an improvement in elastic modulus. The morphology showed that the addition of SBS combined with the aromatic oil promoted a better interfacial adhesion as well as reduced the amount of voids and the size of the rubber particles.

Zhang *et al*. (2013) prepared rubber waste powder/polystyrene (WRP/PS) blends in different weight ratios with polystyrene grafted with styrene -butadiene (SBR-g-PS) rubber copolymer as a compatibilizer. The effects of proportion of WRP/PS and the compatibilizer on the mechanical properties were investigated. PS/WRP blends in a proportion of 80/20% showed a high impact strength. And the impact strength was even higher with the addition of SBR-g-PS. However, the impact strength was reduced with a high content of compatibilizer. The morphology and thermal properties WRP/PS blends were examined by differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and thermogravimetry (TG). The DSC results showed that the glass transition temperature (T_g) of the polystyrene in PS/WRP/SBR-g-PS blend shifted to lower temperature values because of the formation of chemical crosslinks between PS and WRP, and because the T_g of WRP phase of both the PS/WRP and PS/WRP/SBR-g-PS blends did not appear. SEM results indicated that the interfacial adhesion in mixtures with PS-g-SBR copolymer was improved.

Most researches about the reuse of rubber waste come from tire waste, since approximately 75% of all rubber consumed is used in tire production. Therefore, this paper aims to evaluate the influence of SBS and SEBS-MA compatibilizers on the mixture performance of PS/rubber waste that comes from the footwear industry in the mechanical, thermomechanical properties and morphology.

2. Materials and methods

Materials

A crystal polystyrene (PS) was used as polymer matrix, 158K Q611 code, melt flow index (MFI) = 4.5 g/10 min in the form of granules, manufactured by Unigel S.A. Waste rubber of styrene-butadiene (SBRr) from the São Paulo Alpargatas S.A. footwear industry of Campina Grande, Brazil was used as the dispersed phase. The compound formulation is based on: mineral fillers, and styrene butadiene elastomer, pigments, accelerators, foaming agents, flow agents and vulcanizing agent. The approximate partial composition of the residue is: 31% SBR, 26.8% $CaCO_3$, 21.5% oil, 7% of carbon black and 13.7% residual mass. As compatibilizers were used, triblock copolymer styrene-butadiene-styrene (SBS), D1101 code and styrene (ethylene-butylene) styrene copolymer grafted with 1.7% maleic anhydride (SEBS-MA), FG1901 code, in the form of granules, acquired from Activas S.A, were used.

Blend preparation

Before preparation of the blends, the dispersed phase passed through an ABNT sieve N^o. 18 (1mm). PS/SBRr blends in the proportion of 50/50% and 5% compatibilizer were processed in a twin screw co-rotating extruder from Coperion, ZSK 18 mm, with seven zones in temperature of 190°C in zones 1 and 2 and 200°C in the other zones, at 250 rpm and feed rate of 4 kg/h. To study the SBS and SEBS-MA copolymer effect on PS/SBRr blend compatibilization through the properties, the mixing sequences below (1, 2 and 3) were made, as well as the non-compatibilized mixture.

1. PS/SEBS-MA + SBRr (Weight ratio: 47.5/5 + 47.5%) - PS is pre-mixed with SEBS-MA on an extrusion step and then granulated. To this mixture, SBRr was added in a second extrusion step.
2. PS/SBS + SBRr (Weight ratio: 47.5/5 + 47.5%) - PS is pre-mixed with the SBS in

an extrusion step and then granulated. To this mixture, SBRr was added in a second extrusion step.

3. PS/SBRr (Weight ratio: 50/50%) - all components were mixed simultaneously in a single extrusion step.

Upon termination of the processing sequences of all mixtures, extruded granules were dried in a vacuum oven with 60°C for 48 hours. After drying, the extruded granules were injection molded in the form of test specimens for Izod impact tests (ASTM D256), stress (ASTM D638) and HDT (ASTM D648). The specimens were injection molded in a FLUIDMEC machine, at a temperature of 180°C in zone 1 and 190°C in zone 2, mold temperature of 20°C and 25s injection cycle.

Characterization techniques

The Izod impact test was performed on notched specimens according to ASTM D256, on a CEAST Resil 5.5 J model instrument, operating with hammer 2.75 J. The results were analyzed with an average of eight specimens at room temperature and different temperatures. For the tests at different temperatures, the specimens were placed in a suitable oven coupled to the device, where they remained, after temperature stabilization, for at least 40 minutes.

The heat deflection temperature (HDT) was obtained according to ASTM D648, on a CEAST, model HDT 6 VICAT device, at a load of 1.82 MPa and heating rate of 120°C/h (method A). The temperature was determined after the sample deflected 0.25 mm. A series of three samples was tested and heat deflection temperature was measured.

The uniaxial tensile strength tests were performed in injected specimens, according to ASTM D638 using a Universal Testing Machine of Shimadzu, with load speed of 5 mm/min. The tests were conducted at room temperature and results were analyzed with an average of 10 specimens.

The dynamic mechanical thermal analysis (DMTA) was performed in a DMTA equipment, TA Instruments Explorer, Q 800 model. The dynamic-mechanical request mode used was flexural at three points, suitable for Izod type specimens used in the tests. The heating rate used was 10°C/min and frequency of 1 Hz in the temperature range of -100 to 150°C.

The blend morphology was analyzed by transmission electron microscopy (TEM). The analyzed samples were obtained from Izod impact test specimens. The area of the observed samples was located in the middle of its length in a direction that was perpendicular to the injection flow. Then the samples were submitted to the "trimming" (cut in a trapezoid shape) and were cryogenically microtomed, that is they were cut into ultrathin sections 20 nm thick with diamond knives, by a Riechert-Jung Ultracut type E microtome at around -50°C.Grids of copper were used to collect the sliced samples that were immersed in a solution of DMSO: water (3:2). The samples were exposed to vapor of osmium tetroxide (OsO_4) for 15 hours to stain the rubber phase of SBRr. After staining, the "grids" with the samples were analyzed in a Philips model CM120 transmission electron microscope at an accelerating voltage of 120 KV.

3. Results and discussion

Mechanical properties and heat deflection temperature (HDT)

Table 1 shows the results of the mechanical properties and heat deflection temperature of PS, of binary and ternary blends.

Table 1
Results of mechanical properties and heat deflection temperature of PS, of binary and ternary blends.

Materials	Impact Strength (J/m)	Tensile Stress (MPa)	Elastic Modulus (MPa)	HDT (°C)
PS	24 ± 2.0	27.5 ± 2.8	1200 ± 36	80 ± 4.4
PS/SBRr	54.4 ± 3.8	14.5 ± 1.8	670 ± 27	60 ± 3.3
PS/SEBS-MA + SBRr	70 ± 3.3	12.7 ± 2.2	435 ± 18	66 ± 3.2
PS/SBS + SBRr	96.5 ± 5.9	11.6 ± 2.1	640 ± 22	71 ± 3.7

According to Table 1, it is observed that the PS showed the lowest impact strength around 24 J/m. The direct mixture of polystyrene with rubber residue (PS/SBRr) caused an improvement of impact strength due to the presence of the rubber phase in the toughening of matrix. It is observed that the impact strength binary mixture of PS/SBRr increased substantially compared to the PS matrix, corresponding to a 126.6% increase. However, it is noted that the binary mixture has the lowest impact properties of the compatibilized blends.

Table 1 shows that the PS/SBS + SBRr mixing sequence was the most effective in the toughening process, with an increase of 302% in impact strength, when compared to the PS matrix, while the PS/SEBS-MA + SBRr sequence increased approximately by 192%. Possibly, SBS and SEBS-MA remained in the interface, providing greater adhesion between the glassy and rubbery phases, and thus allowing greater impact energy transfer of matrix to the disperse phase (Coutinho *et al.*, 2008). According to

Table 1, it is noted that the sequence PS/SBS + SBRr increased 37% in impact strength in relation to PS/SEBS-MA + SBRr blend. This lower efficiency of SEBS-MA compatibilizer in relation to the SBS may possibly be attributed to the polarity difference among system components. This polarity difference did not favor the system (PS/SBRr), probably because none of the polymers (PS and SBRr) have functional groups in their molecular structures that can react with the maleic anhydride (MA), stabilizing the interface.

According to Table 1, it is observed that the presence of SBRr in mixtures drastically altered the tensile strength and rigidity properties in relation to the PS matrix. In general, all values of tensile strength and elastic modulus of the ternary and binary mixtures were lower than those obtained for PS. This decrease of the mixture properties compared to the PS is related to the fact that the disperse particles are elastomeric and hence increase the chain flexibility. According to Tang *et al.* (2001), PS toughened with elastomer under the stress action changes in the stress state of the matrix phase leading to dissipation of that energy due to the elastomeric particles of the disperse phase. Therefore, the lower the stress value presented by the mixture during the tensile test, the more energy dissipated by the material.

This is confirmed with the impact strength results (Table 1), where it is found that the PS/SBS + SBRr system showed the greatest impact strength, ie, there was a higher level of energy dissipated in the system. As can be seen in Table 1, there was a reduction in the values of elastic modulus for mixtures compatibilized in relation to the non-compatibilized mixture. The introduction of the SBS 5 wt.% in the PS/SBRr system caused a decrease in elastic modulus at 4.5%, while the use of SEBS-MA provided the mixture a 35% reduction when compared to the binary mixture. Probably the best performance of the SBS compatibilizer compared with the SEBS-MA in relation to the tensile modulus may be related to the SBS central block which is constituted by unsaturation units derived from butadiene, which are more chemically similar to SBRr chains and consequently promoting better interaction among the constituents of the PS/SBS + SBRr system. Furthermore, the MA group, present in the SEBS-MA compatibilizer, is polar and should lead to less physical interaction among the mixture constituents, promoting lower values in the properties.

It is evidenced in Table 1 that all mixtures showed a heat deflection temperature that is below the PS. It was verified that the SBRr addition to the PS decreased the HDT, and also that 50% of SBRr in the binary mixture caused a 25% decrease in HDT when compared to the PS. This probably happens because SBRs have a high value of butadiene and it therefore makes the PB/SBRr more flexible and generates a loss in HDT behavior. It can be seen in Table 1 that the compatibilizing agents have promoted a positive effect on the HDT properties of the ternary mixture in relation to the non-compatibilized mixture PS/SBRr (50/50%), an effect that was more pronounced in the compatibilized mixture with SBS. However, the HDT values of ternary mixtures remain below the PS. According to Table 1, it is possible to note that when using SEBS-MA, there was an increase of 10%, while when using SBS, the increase in HDT was 18% when compared with the binary mixture. The value observed for PS/SBS + SBR mixture (~ 71°C) is very interesting from a technological point of view, as it had a decrease of only 11.2% of HDT when compared to PS, whereas there was an increase of approximately 302% in impact strength, even using 47.5% of footwear waste.

Ductile-Brittle Transition Temperature

Figure 1 shows the impact strength values of notched samples of the binary and ternary blends ternaries with 5% compatibilizer as a function of different temperatures.

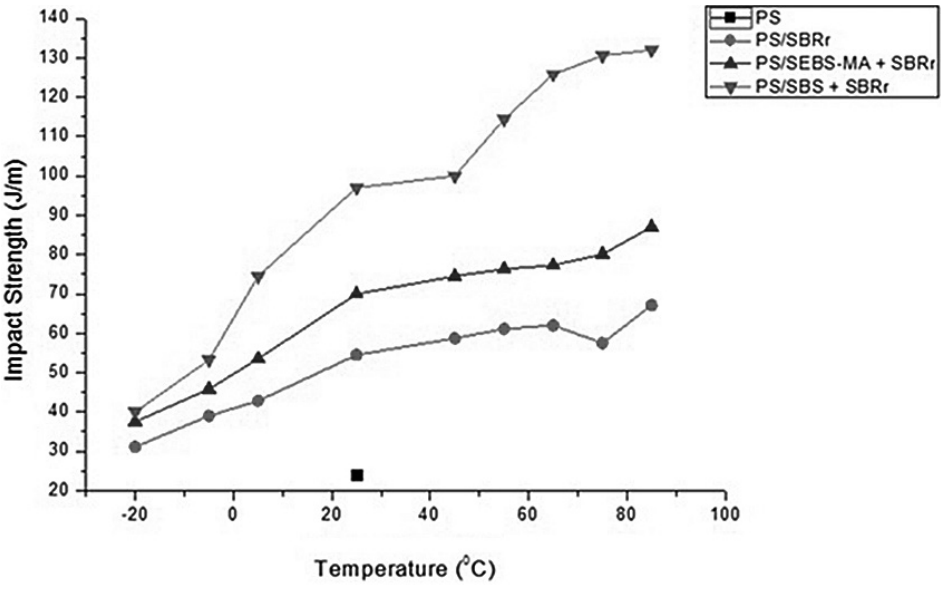

Figure 1
Impact strength of the PS/SBRr blend and compatibilized with 5% SBS and SEBS-MA as a function of temperature.

It can be observed in Figure 1 that the ductile-brittle transition temperature for all blends is in the range of 25°C and that above this temperature, the blends show an increase in its impact strength, reaching values greater than 130 J/m. Both at sub environment temperatures and at -20°C, the ternary blends, regardless of the compatibilizer (SBS or SEBS-

MA) showed superior impact strength to the binary blend. Probably, this behavior of the binary blend may be due to poor dispersion of SBRr domains in PS matrix (showing) forming agglomerates, making it difficult to activate the toughening mechanisms. This is also confirmed by photomicrographs obtained by TEM (Figure 3) where domains of elongated, wide as well as agglomerated particles of SBRr were verified. However, in general, the presence of SBRr and of the compatibilizers improved the impact strength of PS for all the range of evaluated temperature.

Dynamic-Mechanical Thermal Analysis (DMTA)

Figure 2 presents the tanδ, E' and E" of the PS, binary and ternaries mixtures with 5% compatibilizer.

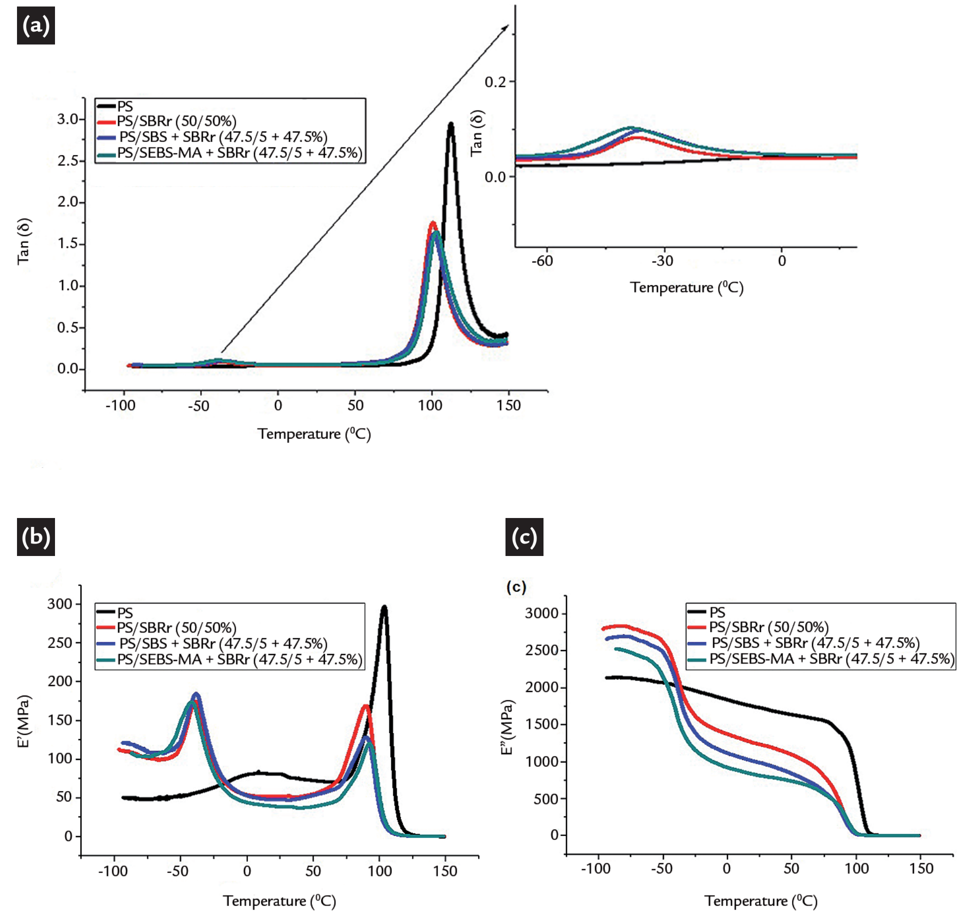

Figure 2
Dynamic mechanical thermal analysis for the PS, the binary and ternary mixtures with 5% compatibilizer: a) tan (δ) curves versus temperature; b) E" curves versus temperature and c) E' curves versus temperature.

Figure 2a shows the values of the loss tangent, tan (δ) of PS, of the 50/50% binary mixture and compatibilized mixture sequences. The presence of two clearly distinct transition peaks is observed in Figure 2a: approximately 108° C related to the glass transition temperature (Tg) of the PS and approximately -36°C related to the present polybutadiene phase in SBRr, which is characteristic of immiscible systems. To the compatibilized PS/SBRr mixture sequences, there was displacement of the peak of the PS Tg to values of approximately 101°C, while there was no displacement of the peak of the rubber phase. As reported by Poshyachinda et al. (1996), it was seen that partially miscible blends show more than one glass transition, but the temperatures are displaced in relation to the Tg of the pure components, and the displaced peaks are in a temperature range among pure components. However, it can be emphasized that the blends produced in the next research are immiscible because of the two Tg values obtained for PS/SBRr systems, which can be seen by the morphologies obtained by TEM, that will be presented.

Figure 2b evidences the loss modulus (E ") values of the PS, of the binary mixture and of the compatibilized with SBS and SEBS-MA. It is observed in Figure2b that the PS shows a peak at approximately 103°C, related to its Tg, and -38°C, related to Tg of the polybutadiene phase present in SBRr. No significant change in the glass transition peaks is observed between the binary and ternary mixtures, with the mixture displacement to approximately 101°C. It is observed that the peaks of the loss curves of the PS/SBS + SBRr and PS/SEBS-MA + SBRr mixtures both in the glass transition region of the elastomeric phase and glassphase (PS) have profiles and width slightly differentiated, characteristic of each material. However, those concerning the glass phase of the PS/SBS + SBRr mixture have a greater tendency not being bimodal, indicating a good homogenization of the PS block of the compatibilizer (SBS) with the PS matrix.

In Figure 2c, the curves for the polymer blends decrease initially, at around -36°C, which is due to the glass transition of the elastomeric phase of polybutadiene (PB) present in SBRr. It is interesting to observe that the introduction of rubber waste tends to increase the elastic modulus (E'). Under -36°C, the elastic modulus of the blends is higher because it is below the Tg of the PB. However, above this temperature, the PS is more rigid than all the blends and also the binary blend is more rigid than the ternary with the SBS compatibilizer, and in turn, the latter is more rigid than with SEBS, according to the results obtained under tensile elastic modulus.

Transmission Electron Microscope (TEM)

Figure 3 illustrates the TEM photomicrographs of the PS/SBRr binary and ternary mixture with 5% SEBS-MA and SBS, respectively. The TEM images are at a scale of 2000 nm.

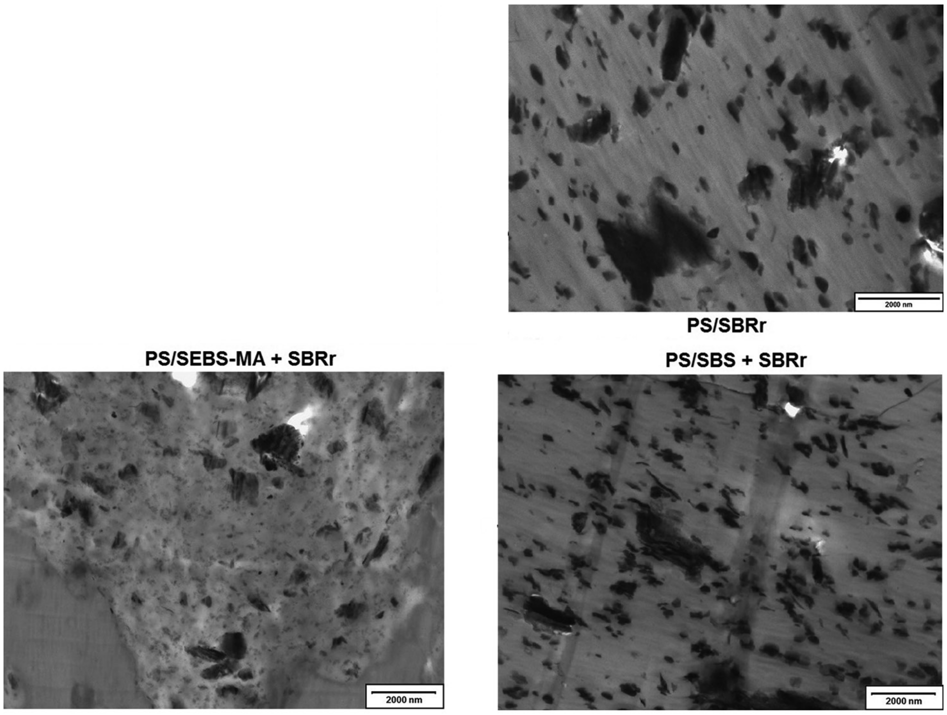

Figure 3
TEM Photomicrographs of the binary and ternary mixtureswith 5% compatibilizer (a) PS/SBRr; (b) PS/SBS + SBRr and (c) PS/SEBS-MA + SBRr.

It is observed in Figure 3 that the morphologies presented by the binary and ternary blends, are very different as well as having the characteristics of immiscible blends. The PS/SBRr blend shows domains of elongated SBRr, wide as well as agglomerated particles. This result is expected because the blend has been obtained without the use of compatibilizing agent, which prevents the coalescence of these SBRr domains during processing. This corroborates the impact strength results which were lower than the compatibilized blends, because agglomerates and larger rubber particles tend to have a smaller surface area and consequently distributed the tensions less.When 5% of SBS and SEBS-MA compatibilizers were introduced into the blends, a reduction in the size of these domains occurred, although there are still some SBRr domains relatively elongated and agglomerated.

Apparently, the blend prepared by the PS/SEBS-MA + SBRr sequence resulted in a more pronounced reduction in the size of the SBRr disperse domains. Although the rubber reduction of this mixture was greater than the one of PS/SBS + SBRr blend, this system did not present a better result of impact strength since the values obtained were less than the values found for the PS/SBS + SBRr blend (Table 1). The studies by Zhu et al. (2013) evidence that there is an upper and lower limit of critical size beyond which the rubber particles are not effective for toughening. According to the authors, particles below a certain limit are unable to cavitate, and thus do not participate of the toughening mechanism. Perhaps this is a possible cause of the lower toughening displayed by PS/SEBS-MA + SBRr blend when compared to PS/SBS + SBRr.

The blend prepared by the PS/SBS + SBRr sequence resulted in a reduction in the size of the SBRr disperse domains, as well as a higher size distribution of the rubber particles compared to PS/SBRr. According to Alfarraj and Nauman (2004), the bimodal size distribution of the rubber particles favors better toughening. Therefore, this photomicrograph of PS/SBS + SBRr blend confirms the best impact strength results among all the mixtures.

4. Conclusions

Blends of PS/rubber waste (SBRr) were produced with the SBS and SEBS-MA compatibilizers. The SBS was more effective during the compatibilizing process of the PS/SBRr system, increasing by 302% the impact strength compared to PS. The tensile test results evidenced that, overall, the elastic modulus and tensile strength of all blends reduced when compared to the PS. The value observed for PS/SBS + SBRr blend is very interesting from a technological point of view, because it fell by only 11.2% of HDT when compared to PS, as well as a high increase in impact strength. In general, the presence of SBRr and of the compatibilizers improved the impact strength of PS for all the range of evaluated temperature. The thermomechanical analysis of DMTA confirmed the immiscibility of the PS/rubber waste system. The morphologies presented typical characteristics of immiscible blends. The SBS compatibilizer was more effective in increasing the compatibility of the PS/SBRr system probably for showing a higher similarity in the molecular structure with the SBRr chains, and therefore promoting a better interaction. The SEBS-MA is polar and did not favor the physical interaction in the PS/SBRr system. Considering all the difficulties inherent to reuse rubber waste, the results show that it is possible to obtain a material with good properties, as well as promoting the reduction of production costs. In addition, it avoids incineration and disposal in landfills. It is known that the composition of rubber wastes may contain stabilizers, flame retardants and plasticizers that have low molecular weight, allowing migration to soil and groundwater contamination.

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