Henrique Ajuz Holzmann
João Dallamuta
(Organizadores)

ENGENHARIAS: Pesquisa, desenvolvimento e inovação

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APRESENTAÇÃO

Um dos grandes desafios enfrentados atualmente nos mais diversos ramos do conhecimento, é o do saber multidisciplinar, aliando conceitos de diversas áreas. Hoje exige-se que os profissionais saibam transitar entres os conceitos e práticas, tendo um viés humano e técnico.

Neste sentido este livro traz capítulos ligados a teoria e prática em um caráter multidisciplinar, apresentando de maneira clara e lógica conceitos pertinentes aos profissionais das mais diversas áreas do saber.

Apresenta temas relacionados as áreas de engenharia, como civil, materiais, mecânica, química dentre outras, dando um viés onde se faz necessária a melhoria continua em processos, projetos e na gestão geral no setor fabril. Destaca-se ainda a busca da redução de custos, melhoria continua e automação de processos.

De abordagem objetiva, a obra se mostra de grande relevância para graduandos, alunos de pós-graduação, docentes e profissionais, apresentando temáticas e metodologias diversificadas, em situações reais.

Aos autores, agradeço pela confiança e espirito de parceria.

Boa leitura

Henrique Ajuz Holzmann
João Dallamuta

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CAPÍTULO 4

SELECTIVE DISPERSION OF STYRENE-BUTADIENE CROSS-LINKED WASTE IN THE POLYSTYRENE MATRIX: A TRANSMISSION ELECTRON MICROSCOPY (TEM) RESEARCH

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ABSTRACT: The aim of this study was to observe the morphological development in polystyrene (PS) non-reactive blends with a recycled styrene-butadiene compound (SBRr), using the styrene-butadiene-styrene (SBS) copolymer as a compatibilizing agent. The effect of different mixing sequences in the preparation of PS/SBRr/SBS (47.5/47.5/5 wt %) blends on the morphology were investigated. The blends were prepared in a co-rotating twin-screw extruder and molded via injection. The samples analyzed were taken from the Izod impact test specimens, subsequently prepared using cryo-ultramicrotomy, and observed through transmission electron microscopy (TEM). The blend prepared by the simultaneous mixing of all components in a single extrusion has a morphology with elongated particles. When the PS and SBRr were pre-mixed in the first extrusion before incorporating SBS in the second extrusion, the morphology exhibited a co-continuity tendency in the SBRr phase. On the other hand, when the PS premix is performed together with the SBS initially in the first extrusion prior to the incorporation of the SBRr into the second extrusion, the morphology is apparently more stable, with smaller particles, which are better distributed in the PS matrix. Therefore, the results show that, depending on the processing route, the morphology changes significantly.

KEYWORDS: Polymer blends. Mixing sequence. Morphology. TEM.

DISPERSÃO SELETIVA DE RESÍDUOS RETICULADOS DE ESTIRENO-BUTADIENO NA MATRIZ DE POLIESTIRENO: UMA INVESTIGAÇÃO POR MICROSCOPIA ELETRÔNICA DE TRANSMISSÃO (MET)

RESUMO: O objetivo deste estudo foi observar o desenvolvimento morfológico em blendas não reativas de poliestireno (PS) com um composto de estireno-butadieno reciclado (SBRr), utilizando o copolímero de estireno-butadieno-estireno (SBS) como agente compatibilizante. O efeito de diferentes sequências de mistura na preparação das blendas PS/SBRr/SBS (47,5/47,5/5% em peso) sobre a morfologia foi investigado. As blendas foram preparadas em uma extrusora de dupla rosca co-rotacional e moldadas por injeção. As amostras analisadas foram retiradas das amostras do teste de impacto Izod e, preparadas posteriormente, por crio-ultramicrotomia e observadas por microscopia eletrônica de transmissão (MET). A blenda preparada pela mistura simultânea de todos os componentes, em uma única extrusão, possui uma morfologia com partículas alongadas. Quando o PS e o SBRr foram pré-misturados na primeira extrusão, antes de incorporar o SBS na segunda extrusão, a morfologia exibiu uma tendência de cocontinuidade da fase SBRr. Por outro lado, quando a pré-mistura do PS é realizada em conjunto com o SBS inicialmente na primeira extrusão, antes da incorporação do SBRr na segunda extrusão, a morfologia é aparentemente mais estável, com partículas menores e melhor distribuídas na matriz PS. Portanto, os resultados mostram que, dependendo da rota de processamento, a morfologia muda significativamente.

PALAVRAS-CHAVE: Blendas poliméricas. Sequência de Mistura. Morfologia. MET.

1 I INTRODUÇÃO

Polystyrene (PS) is one of the most used thermoplastics in the polymer industry worldwide, as it is easily synthesized, processed, and recycled (Calleja et al., 2004; Luna et al., 2015; Yousif and Haddad, 2013). PS at room temperature is a glassy and amorphous homopolymer, presenting limitations in ductility and possessing a low impact strength, due mainly to its high glass transition temperature (Tg) in the range of 90–100°C (Grassi et al., 2001). Therefore, for certain applications, polystyrene (PS) needs to be toughened (Wang et al., 2019; Kasavan et al., 2018).

Toughness is one of the most important parameters that determines if a given polymer can be used in several applications (Coutinho et al., 2007). In the polymer literature (Zhu et al., 2012; Cai et al., 2013), toughening is associated with an increase in the impact strength of fragile polymers, such as polystyrene (PS). The main technique used by the polymer industry has been the development of polymer blends, wherein a fragile matrix is reinforced with dispersed rubber particles (Fang et al., 2004; Libio et al., 2012). Thus, some recent work has reported on the development of polystyrene blends with rubber (Zhou et al., 2015; Hassan et al., 2019). In particular, the toughening of polystyrene with recycled rubber has been investigated, aiming to reduce the environmental impact (Rosas and Juan, 2013; Veilleux and Rodrigues, 2016; Luna et al., 2018). These works have emphasized the mechanical, thermal, and morphological properties observed via scanning electron microscopy (SEM). However, studies on the morphological evolution of polystyrene blends with recycled rubber while modifying the mixing sequences in a twin-screw extruder are not in evidence. Hence, this study is doubly convenient, as it affects the properties of interest directly and fills a gap in the literature.

The processing of a polymer blend is an extremely important step, since the conditions strongly influence the morphology of the material and, consequently, its mechanical properties (Cao et al., 2019; Torrecillas et al., 2018; Thomann et al., 2009). There are several studies in the literature (Gao et al., 2006; Rovere et al., 2008; Zhang et al., 2013) that have investigated the morphology of high-impact polystyrene (HIPS) developed in a reactor with butadiene rubber via transmission electron microscopy (TEM). However, investigations on toughened polystyrene with recycled rubber via TEM are practically nonexistent.

Therefore, the present research aims to investigate the use of TEM to analyze the evolution of the morphology of polystyrene mixtures with a recycled rubber compound using styrene-butadiene-styrene (SBS) as a compatibilizing agent. It will show that the mixing sequences used affect the morphology significantly.

2 I BIBLIOGRAPHIC REVIEW

In recent decades, technological advances, despite having increased countless benefits, have contributed negatively to a significant increase in the volume of urban and industrial solid waste generated, which often have an inadequate or unacceptable final destination from an economic point of view and environmental (Lima et al., 2015; Merrington, 2017; Santos et al., 2015). In this context, one of the industrial waste most aggressive to the environment is vulcanized rubber.

The reuse of post-consumer rubber waste represents a major challenge, especially in the tire and footwear industries, since the vast majority are vulcanized. One of the major obstacles in the recycling of vulcanized rubbers lies in the fact that these materials have cross-links in their structure, preventing their fusion and reprocessing (Garcia et al., 2015).

Sousa et al. (2015) reported in their studies that the vulcanized rubber waste does not decompose easily due to its reticulated structure, the presence of stabilizers and other additives, and the time required for it to degrade naturally is undetermined. Vulcanized rubbers cannot be reprocessed as thermoplastic materials as they are infusible and insoluble in organic solvents due to the presence of the three-dimensional chemical network. Currently, the recycling of vulcanized rubbers is even more difficult due to the addition of new components in the mixture and additives in order to increase their performance and useful life, in addition to the fact that the actual formulation is unknown because it is confidential.

The reuse of rubber can be a difficult process, however, it is currently being made possible in mixtures with thermoplastics. In this case, the rubber residues are dispersed in the thermoplastic matrix during processing, acting as elastomeric fillers (Mangaraj, 2005).

Zhang et al. (2013) developed polystyrene blends with rubber residues from the tire industry (PS/WRP), using polystyrene grafted with styrene-butadiene (PS-g-SBR) as a compatibilizer. The results showed that the PS/WRP blend in the proportion 80/20% (by mass) showed high impact resistance, and this was higher when the compatibilizer SBR-g-PS was added. However, the same blend reduced the properties to high levels of the compatibilizer SBR-g-PS. Differential exploratory calorimetry (DSC) analysis indicated that, compared to the PS/WRP blend, the PS glass transition temperature (Tg) in the ternary mixture PS/WRP/SBR-g-PS was shifted to more low temperatures. The images obtained by scanning electron microscopy (SEM) indicated a better interfacial adhesion for mixtures compatible with PS-g-SBR.

Silva et al. (2014) studied the mechanical properties of polystyrene (PS) blends with rubber residue from the shoe industry (SBRr), using two different types of polystyrene, as well as a styrene-butadiene-styrene (SBS) compatibilizing agent. The results showed that the tensile strength tended to decrease and the impact resistance increased, as the rubber residue content increased in the blends. The incorporation of 47.5% SBRr with 5% SBS in the PS/SBRr/SBS blend increased the impact resistance by 250%, compared to pure PS. However, it was observed that for all ternary blends a reduction in tensile properties, in comparison to PS. In general, the results showed that the mechanical properties were better for PS with higher viscosity, indicating a greater interaction with the rubber residue and, consequently, favoring a better toughening of this polymer.

Luna et al. (2020) investigated the influence of 5; 7.5 and 10% of the styrene-butadiene-styrene (SBS) compatibilizer, in the properties of polystyrene (PS) blends with a recycled styrene-butadiene rubber compound (SBRr), obtained in the shoe industry. For comparative effect, high impact commercial polystyrene (HIPS) was used. It was observed that the viscosity of the blends was higher than the HIPS. The blends made compatible with 5 and 7.5% were at the same level of resistance to the impact of HIPS, while the 10% had a gain of 80.5%, compared to HIPS. The flexural properties, Shore hardness, thermal deflection temperature (HDT) and Vicat softening temperature were close to HIPS, which was attributed to the presence of inorganic loads, minimizing losses of these properties. By atomic force (AFM) the presence of two distinct phases was observed, while the morphology obtained by SEM was typical of immiscible blends.

The reuse of rubber waste is important, as it can add value to a material that would be discarded. At the same time, it contributes to the development of materials with good properties, thereby generating a sustainable cycle. However, although there are studies on the proposed theme, there are still few investigations on the effect of the processing route on morphology.

3 I MATERIALS AND METHODS

3.1 Materials

The blends were prepared from PS crystal, commercialized with the code 158K Q611®, and melt flow index (MFI) = 4.5 g/10 min (190°C/ 5kg), supplied as pellets and manufactured by Unigel S.A. (Brazil). A recycled compound of vulcanized styrene–butadiene rubber (SBRr) in the form of white powder from the shoe industry of São Paulo Alpargatas S.A., was used as the filler or dispersed phase. The compatibilizing agent used was the SBS linear triblock copolymer in the form of pellets, commercialized with the code D1101B®, containing 31% styrene and melt flow index less than 1 g/10 min (200°C/5 kg), supplied by Activas S.A. (Brazil).

3.2 Preparation of the Blends

Prior to the preparation of the blends, the industry-recycled rubber compound was sieved in an 18-mesh sieve (1000 µm), and the sieved powder was used. In order to study the effect of the SBS copolymer on the PS/SBRr blend morphology and the dispersion of the SBRr particles in the compatibilized blends, three different mixing sequence were used to prepare ternary blends, according to the following procedure:

- PS/SBRr/SBS: PS, SBRr, and SBS were blended simultaneously in a single extrusion step.
- (PS/SBRr) + SBS: PS and SBRr were preblended in the first extrusion step. Subsequently, the product obtained was blended with SBS in a second extrusion step.
- (PS/SBS) + SBRr: PS and SBS were preblended in the first extrusion step. Subsequently, the product obtained was blended with SBRr in a second extrusion step.

For all mixing sequences, the amounts of PS, SBRr, and SBS were fixed at 47.5, 47.5, and 5.0 wt%, respectively. Additionally, for reference, a PS/SBRr (50/50 wt %) binary blend was also prepared in a single extrusion step. The descriptions of the three mixing sequences are shown in Figure 1.

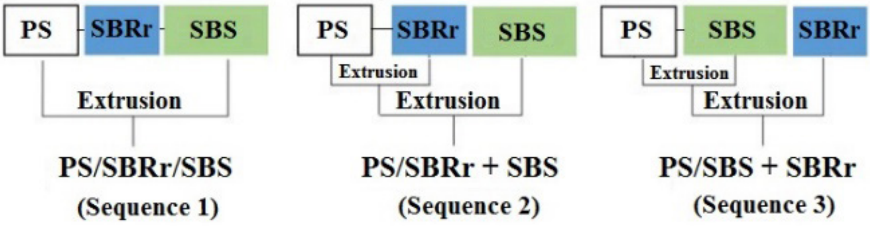

Figure 1 - Flow chart for preparing PS/SBRr blends with 5 wt % SBS via different mixing sequences.

The binary and ternary blends were dry-mixed and subsequently processed in a modular, co-rotating twin-screw extruder, model ZSK (D = 18 mm and L/D = 40) from Coperion Werner & Pfleiderer, at a temperature of 190°C in zones 1 and 2 and 200°C in the other zones, a screw rotation speed of 250 rpm, and a controlled feed rate of 4 kg/h, with the screw profile configured with distributive and dispersive mix elements.

The material was granulated and dried in a vacuum oven at 60°C for 24 hours. The dried extruded granules were molded by injection into the form of Izod impact strength specimens (ASTM D256). The injection molding was done with an injection pressure of 900 bar in a Fluidmec injector (Model H3040) at temperatures of 180ºC in zone 1 and 190ºC in zone 2. The mold temperature was 20ºC and 25s of injection time.

3.3 Transmission Electron Microscopy (TEM)

The samples analyzed by TEM were taken from the Izod impact test specimens and observed in the direction perpendicular to the injection flow. The specimens were trimmed to a trapezoid form and then cut into thin sections of about 40 nm in thickness using a diamond knife and a Riechert-Jung Ultracut E type microtome at around -60°C. Copper grids were used to collect the sliced specimens. A two-step selective staining technique was used to generate the phase contrast. The staining of the polybutadiene (PB) phase of the SBRr phase was completed in two stages.The sliced samples were immersed in a solution of DMSO: water (proportion - 3:2). After drying, the samples were stained with osmium tetroxide solution (OsO_4) vapor for 15 hours. After staining, the grids with the coated samples were viewed in a Philips transmission electron microscope, model CM120, at an acceleration voltage of 120 kV.

4 I RESULTS AND DISCUSSION

TEM has been used widely as a way to relate morphology to the properties of materials which are determinants in technological applications that require good performance (Dagli et al., 1995).

Figure 2 (a-d) shows the micrographies obtained by TEM of the binary PS/SBRr blends and ternary blends with 5% SBS. For a better visualization of the present phases, the polybutadiene (PB) phase was dyeing with osmium tetroxide (OsO_4). Through this selective staining technique, it is possible to observe the polybutadiene domains (dark particles) in the polystyrene matrix (PS). In addition, gray image processing (left-hand picture) was performed and transformed into a binary digital image (right- hand picture) in order that the clear (polystyrene) and dark (polybutadiene) regions can show clearly the dispersion of the elastomeric phase (PB). ImageJ software used to convert the images obtained by TEM to binary images.

The morphologies of all blends, Figure 2 (a-d), show typical immiscible blends presenting phase separations of PS and SBRr. For the PS/SBRr blend, Figure 2 (a and a1) shows a heterogeneous morphology that presents SBRr elongated domains which are wide and have agglomerated and poorly dispersed particles along the matrix. The final morphology of an immiscible polymer blend is the result of the balance between the rupture and agglomerate formation of the particles dispersed during the process (Bassani et al., 2005). Apparently, the SBRr particles tend to predominantly form agglomerate domains in the PS/SBRr blends, and most likely the formation of agglomerates overlaps the particle disruption process, as the SBRr is shown to be roughly dispersed in the PS matrix, directly affecting mechanical properties. The presence of agglomerates reduces the ability of the matrix to withstand mechanical stresses, since they tend to have a lower surface area and, consequently, distribute stress less (Rabello, 2000).

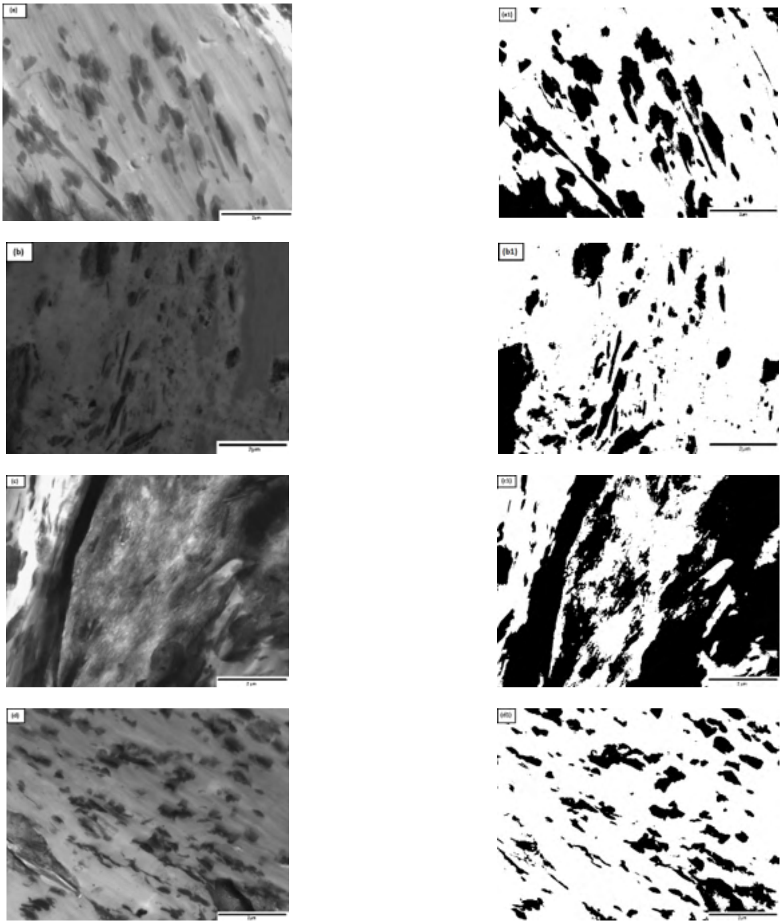

Figure 2 - Photomicrographs obtained by MET of the mixtures: a) PS/SBRr; b) PS/SBRr/SBS; c) (PS/SBRr) + SBS; and d) (PS/SBS) + SBRr. Increase of 11.500x.

In Figure 2 (b-d), it is possible to see that the morphologies presented by the ternary blends prepared with different mixing sequences are quite different. These differences indicate that the mixing sequences of the components affect the blend morphology. In addition, the compatibilizer acts on the blend interface, reducing the domain size and improving the distribution of the dispersed phase in the matrix, as well as increasing the adhesion between the phases (Graziano et al., 2018).

When the SBS copolymer is introduced into the blends PS/SBRr/SBS and (PS/SBS) + SBRr, Figure 2 (b, d) shows a decrease in the size of the SBRr domains in relation to the PS/SBRr blends, although some relatively elongated SBRr domains and agglomerates are still present. The blend prepared via the sequence (PS/SBS) + SBRr shows a better dispersion of the SBRr domains when compared to the simultaneous mixing of all PS/SBRr/SBS components. It is speculated that the formation of a more stable morphology for the blend (PS/SBS) + SBRr during the first processing of the PS with SBS possibly favors a better interaction with the SBRr during the second processing, thereby promoting a better dispersion of the rubber's particles. It is also possible to visualize that the sequence (PS/SBS) + SBRr shows a greater tendency towards bimodal particles in the range of 2 to 5 µm, thus favoring better toughening (Hobbs, 1986). The only change and inversion in morphological behavior occurred in the mixing sequence (PS/SBRr) + SBS, where there was a co-continuity tendency in the SBRr phase. It is possible to observe that, in this mixture, i.e., (PS/SBRr) + SBS, certain regions of the polystyrene matrix were surrounded by the rubber, possibly because the PS/SBRr system underwent two processing cycles, i.e., a more intense blending.

Figure 3 shows the micrographies obtained by TEM of the PS/SBRr binary blends and the ternary blends with 5% SBS at an increase of 66.000x. The mechanical behavior of rubber toughened polymers is related directly to their morphology, average particle size, and elastomer content (Costa et al., 2012). Therefore, it is interesting to analyze the morphology at higher magnifications.

The non-compatibilized blend (PS/SBRr) in Figure 3(a) shows a morphology with a tendency towards forming relatively large particles which are agglomerated and poorly distributed in the PS matrix as well as a short interparticle distance. On the other hand, the blend prepared using the sequence (PS/SBS) + SBRr resulted in a more marked decrease in the size of the dispersed SBRr domains. Apparently, it is also possible to verify the phenomenon of fine-scale cavitation (black arrow), in which case there is a generation of voids inside the rubber particle (Dompas and Groeninckx, 1994).

Figure 3(b) shows the micrograph of the PS/SBRr/SBS blend, where the SBRr domains are larger and more elongated than they are in the (PS/SBS) + SBRr blend. In addition, the PS/ SBRr/SBS sequence shows few particles per area, indicating poor dispersion of the particles in the PS matrix. Again, the mixture (PS/SBRr) + SBS, shown in Figure 3(c), exhibits a morphology with a co-continuity tendency, with SBRr particles having an interconnected structure. This type of co-continuous morphology is not made in a single volumetric fraction but rather in a composition range. The range of co-continuity depends on the interfacial tension, presence of crosslinks, and processing conditions (Boer et al., 1998; Willemse et al., 1998; Veenstra et al., 2000). In the (PS/SBRr) + SBS mixing sequence, it is reasonable to suggest that the preponderant effect in terms of changing the morphology is the PS and SBRr phase feed conditions during the extrusion process, since the morphology differed significantly from the (PS/SBS) + SBRr sequence when feeding PS and SBS initially.

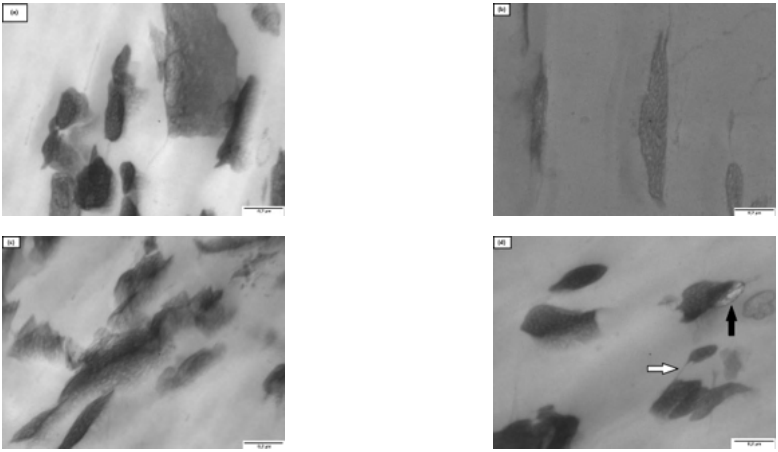

Figure 3 - Photomicrographs obtained by TEM of the mixtures: a) PS/SBRr; b) PS/SBRr/SBS; c) (PS/SBRr) + SBS; and d) (PS/SBS) + SBRr. Increase of 66.000x.

The impact strength results of PS/SBRr blends; PS/SBRr/SBS; (PS/SBRr) + SBS and (PS/SBS) + SBRr can be found in the literature (Luna et al., 2015b). The PS/SBRr blend was found to have the lowest impact strength, due to the morphology with coarse and poorly dispersed particles. However, by adding the compatibilizer a higher performance in impact strenght was obtained, suggesting a greater stability in morphology. As a consequence, significant increases in impact strenght were verified. When PS and SBS were mixed together in a first extrusion step, before incorporation of SBRr in a second extrusion step, impact resistance was optimized with a 302% increase over the polystyrene matrix. On the other hand, when performing simultaneous PS/SBRr/SBS mixing, impact strength was reduced compared to the sequence (PS/SBS) + SBRr, indicating that the generated morphology reduced the ability of SBRr particles to dissipate energy. Good impact strength was verified for the sequence (PS/SBRr) + SBS, including a performance comparable to the sequence (PS/SBS) + SBRr, considering the experimental error. This indicates that a co-continuous morphology favored good energy dissipation when subjected to the impact strength test.

Rabello (2000) reports that a decrease in the size of the rubber particles results in a better distribution of stresses and, consequently, an increase in the surface area of fissures, representing a positive aspect in terms of toughening. Therefore, by changing the mixing sequences, the morphology can be modified to include a greater degree of refinement in the rubber particles, which affects the mechanical properties. A number of investigations have been carried out to monitor the modification of phase morphology during extrusion with the aim of improving properties (Castro et al., 201; Oliveira et al., 2011). Apparently, the modification of the mixing sequence in blends has a major influence on impact strength. However, no significant influence on the results of tensile properties is observed. Castro et al. (2016) showed that the modification of the mixing sequence affects the morphology of PA6/ABS blends compatibilized with MMA-MA. When PA6 is mixed with the premixed (ABS/MMA-MA) system, the compatibilizer migrates preferentially to the ABS phase, forming a co-continuous structure, which favors increased toughness. On the other hand, when the ABS is mixed with the premixed (PA6/MMA-MA) system, the compatibilizer is preferably located in the PA6 phase, inducing a morphology of encapsulated particles.

5 I CONCLUSION

In this study, the morphology of PS/SBRr blends compatibilized with the SBS copolymer was analyzed using three mixing sequences prepared in a co-rotating twin-screw extruder. The study of the morphological behavior of the blends showed that they are immiscible and dependent on the feeding conditions during the extrusion process. The evolution of the morphology when changing the mixing sequence during the extrusion process is quite different for the compatibilized systems, indicating that it probably impacts directly on the mechanical properties. Apparently, the sequence (PS/SBS) + SBRr forms a more stable morphology, with smaller particles and better dispersion along the PS matrix. The study of the modification's effect on the mixing sequences is relevant since by modifying the feed sequence in the blend (PS/SBS) + SBRr to (PS/SBRr) + SBS, there was a change in morphology, with dispersed particles of SBRr exhibiting a co-continuity tendency.

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