

Reactive Compatibilization of Polystyrene/Poly(Ethylene-co-Vinyl Acetate) (EVA) Blends

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Received 13 January 2005; accepted 5 March 2005

DOI 10.1002/app.21856

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A reactive compatibilizer, mercapto-functionalized EVA (EVASH), in combination with styrene-butadiene block copolymer (SBS), was used to compatibilize the blends of polystyrene (PS) and ethylene-vinyl acetate copolymer (EVA). The reactive compatibilization was confirmed by the presence of insoluble material and from dynamic-mechanical analysis. In addition to a more uniform morphology with small phase size, the compatibilization also provided excellent stabilization of the morphology, with an

almost complete suppression of coarsening during annealing. As a consequence, a substantial increase on the elongation at break without significant influence on ultimate tensile strength was achieved for compatibilized blends with different compositions. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 14–22, 2006

Key words: blends; morphology; polystyrene; reactive compatibilization

INTRODUCTION

There is commercial interest in multiphase polymer blends because of the possibility of improvement in the properties by the suitable selection of ingredients and their ratios. The majority of known polymers is usually immiscible and shows large interfacial tension in the melt, giving rise to materials with gross phase-separated morphology. This feature, associated with poor interfacial adhesion at the interface of each phase in the solid state, normally results in poor mechanical properties. The use of a compatibilizing agent is a common practice to achieve improved mechanical performance because it can control the morphology and suppress the coalescence of the dispersed phase, in addition to reducing the interfacial tension.¹ Graft or block copolymers having identical or similar segments as the blend components have been extensively studied.^{2–4} Although this method is very effective in compatibilization, it is not necessarily the preferred one because of the sophisticated polymerization procedures normally required to prepare block and graft copolymers with defined molecular architecture and also the large amount of expensive components required to achieve good compatibilization.

An alternative way to compatibilize heterogeneous polymer blends involves *in situ* reactive process in the melt. This method employs functionalized polymer pairs having coreactive chemical groups that are able to react to each other at the interface. These *in situ*-

formed copolymers tend to stay at the interface as the reaction between the coreactive groups occurs at the interface.⁵ Therefore, a little amount of the copolymer (0.5 to 2.0 wt %) is normally sufficient to achieve stabilization in reactive compatibilization. Classic examples of reactive compatibilization involve blends containing polymers with functional groups as polyamides and polyesters.

Polystyrene is one of the most popular commodities plastics because of its low price associated to its low mold shrinkage, excellent printability, and broad thermoforming processing window. However, it is very brittle and must be combined to elastomer materials to improve impact resistance. The classic method for that consists of the polymerization of styrene in the presence of polybutadiene, giving rise to so-called high-impact polystyrene (HIPS). Other rubbery materials can be used to improve the mechanical resistance of PS. Among these, ethylene-vinyl acetate copolymers are good candidates for this purpose because they have elastomeric characteristics depending upon the vinyl acetate content and also there is no unsaturation in their structure, which makes them very resistant against oxygen and ozone. Blends of PS/EVA have been investigated by several researchers.^{6–16} Because of the incompatibility between the components, different strategies have been employed to improve the mechanical performance of these blends. Tang and coworkers used EVA with 28 wt % of vinyl acetate to improve the compatibility with polystyrene.^{10,12} Cheng and colleagues developed the *in situ* polymerization of styrene in the presence of EVA to obtain graft copolymers with outstanding properties.^{13,15} This procedure is interesting from the technological point of view, but there is no control about the graft

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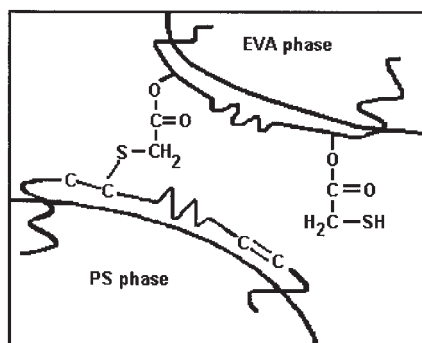


Figure 1 The schematic diagram for the compatibilizing concept involving SBS and EVASH coreactive copolymers.

copolymer structure. Block copolymers based on polystyrene and polybutadiene have been also employed as non reactive compatibilizers for PS/EVA blends.¹⁴ Graft copolymers consisting of EVA as the backbone grafted with PS segments have been developed by our research group to compatibilize PS/EVA blends.⁶⁻⁸

Reactive compatibilization is also an interesting approach for the compatibilization of PS/EVA blends. In this sense, Tang and coworkers have recently reported the use of styrene-maleic anhydride to promote the reactive compatibilization of PS and partially hydrolyzed EVA.¹⁰

Based on the technological interest of reactive compatibilization, we decided to develop a new strategy for the compatibilization of PS/EVA blends by using a combination of mercapto-functionalized EVA (EVASH) and styrene-butadiene triblock copolymer (SBS). This idea came from the success of the reactive compatibilization of blends containing EVA¹⁷⁻²⁵ or EPDM^{26,27} and unsaturated elastomers by EVASH. In these systems, the mercapto groups situated along the EVA backbone are able to react with the double bond of the unsaturated elastomer phase, thus promoting an effective anchorage between the phases.

In this study, SBS was employed as the unsaturated component that was combined with EVASH. The schematic diagram for this compatibilizing concept is illustrated in Figure 1. The polystyrene segment in the SBS copolymer is miscible with the PS phase, and the EVASH backbone is miscible with the EVA phase. The reactive compatibilization was achieved by the reaction between the mercapto groups of EVASH and the double bond of SBS located at the interface. The effect of the reactive compatibilization on the mechanical, morphological, and dynamic mechanical properties, as well as on the stabilization of the morphology, was investigated.

EXPERIMENTAL

Materials

The PS used in this study was purchased from EDN do Brasil, Pernambuco, Brazil. It was a 6.13 g/10 min

melt flow index (MFI) material (at 200°C/2.16 Kg). EVA copolymer, kindly supplied by Petroquímica Triunfo S. A., Rio Grande do Sul, Brazil, has a vinyl acetate content of 18 wt % and an MFI of 2.1g/10 min at 200°C/2.16 Kg. Styrene-butadiene-styrene triblock copolymer (SBS) was obtained from Shell Chemicals (The Netherlands) as Kraton D-1101 with 31 wt % of styrene content. EVA functionalized with mercapto groups was synthesized in our laboratory, according to the procedure reported elsewhere.²⁸ The amount of mercapto groups incorporated on the EVA was 64.7 ± 5 mmol/100g.

Blend preparation

The melt blends were performed in a Haake, Rheomix 600 (Dallas, TX) internal mixer, which has a 69 cm³ mixing head with rotor roller blades. The mixer was operated at 160°C and 60 rpm for 10 min. Different addition order of the components was performed, which are specified in Results and Discussion. To follow the development of the blend morphology, the rotor was quickly stopped from time to time, and a small aliquot was immediately withdrawn from the melt and quenched in liquid nitrogen to freeze the blend morphology. The blends were then compression-molded in a laboratory hydraulic press at 160°C and 6 MPa for 10 min, followed by cooling at the same pressure.

Testing and dynamic mechanical properties

Tensile experiments were performed with an Instron 4204 tensile tester (Boston, MA) at room temperature in accordance with ASTM D638. For PS-rich blends, the crosshead speed was set at 1 mm·min⁻¹, and for EVA-rich blends, the crosshead speed corresponding to 50 mm·min⁻¹ was employed.

Dynamic mechanical measurements were carried out on a Rheometric Scientific MKIII dynamic mechanical analyzer (Piscataway, NJ). The experiments were conducted in a flexure mode at a frequency of 1 Hz. The compression-molded samples (2 × 10 × 25 mm³) were heated at 2°C/min over a range from -50 to 150°C.

Morphological characterization

The morphologies of the samples were examined with a JEOL JSM-5610LV scanning electron microscope (Tokyo, Japan) at an electron voltage of 20kV and a secondary electron detector, with cryogenically fractured specimens whose surface was treated with methyl ethyl ketone (MEK) to selectively extract the PS phase. After this treatment the surfaces were coated with a thin film of gold.

TABLE I
The Effect of the Reactive Compatibilization on Tensile Properties of PS/EVA (60 : 40 wt %) Blends

Compatibilizing system (%)		Blending procedure	Ultimate tensile strength (MPa)	Elongation at break (%)
SBS	EVASH			
0	0	dry-blend	11.6 ± 0.5	8 ± 2
3	0	dry-blend	9.5 ± 0.9	21 ± 2
3	3	dry-blend	12.0 ± 0.7	31 ± 3
3	3	PS/SBS + EVA/EVASH (master batch)	11.5 ± 0.7	17 ± 2
3	3	EVA/EVASH/SBS/PS (sequential addition)	11.6 ± 0.5	22 ± 4
3	3	PS/SBS/EVASH/EVA (sequential addition)	10.6 ± 0.8	29 ± 3

RESULTS AND DISCUSSION

Tensile properties

The effect of the compatibilization on the mechanical properties of PS/EVA (60 : 40 wt %) blends is summarized in Table I. Except for the blend containing 3 wt % of SBS as the single non reactive compatibilizer, all other blends displayed similar values of ultimate tensile strength. Nevertheless, the elongation at break was significantly influenced by the compatibilization as well as the addition order of the components in the mixing chamber. The presence of SBS contributes an important improvement on this property because of the affinity between the PS phase and the PS segment in SBS. The compatibilizing efficiency of SBS was also reported for other polystyrene-polyolefin blends.^{29,30} The combination of SBS with EVASH resulted in a substantial increase of elongation at break of PS/EVA blends.

For good effectiveness on the reactive compatibilization, the coreactive groups (double bond and mercapto groups) must reach each other at the interface. Therefore, the addition order of the functional copolymers is of paramount importance. As observed in Table I, the best result was obtained when all blend components were preblended as a dry-blend before introducing it into the mixing chamber. When masterbatches of EVA/EVASH and PS/SBS were separately prepared by melt blending at 160°C and then blended again at the same conditions, the resulting PS/EVA blend did not display as good mechanical properties as those obtained from the dry-blend process. Probably this blend procedure favors the interaction of EVASH and SBS with the EVA and PS phases, respectively, making difficult the diffusion of the reactive components towards the interface.

The sequential addition of PS/SBS/EVASH/EVA also resulted in good mechanical performance, but the dry-blend process is technologically more interesting because it reduces the number of steps necessary for the blend preparation.

Measurement of the mixing torque during the blending of polymers is a useful technique for the investigation of the chemical reaction between the two

phases. Figure 2 compares the torque-time curves of the non compatibilized PS/EVA blend and the compatibilized one with the SBS-EVASH system and prepared by the dry-blend process. The initial increase in torque results from the addition of the blend into the mixer. After this, the torque drops as the polymers soften until a value characteristic of the blend. The compatibilized blend presented a slight increase in final torque, which is the first evidence for intermolecular crosslinking between the EVASH and SBS. This phenomenon was not significant because of the low amount of mercapto groups in the blend.

The crosslink reactions in the reactive compatibilized blend were also evidenced from the presence of insoluble material after the extraction with hot toluene (around 70°C) for 24h. At this condition, polystyrene, EVA copolymer, and the non compatibilized blends were completely soluble in hot toluene. However, that containing the coreactive copolymers, EVASH/SBS, gave rise to around 18 wt % of insoluble material, confirming intermolecular crosslinking. This value is somewhat higher than the amount of SBS and EVASH in the blend, indicating that part of the EVA and/or PS phase has also been attacked by the free radicals generated during processing.

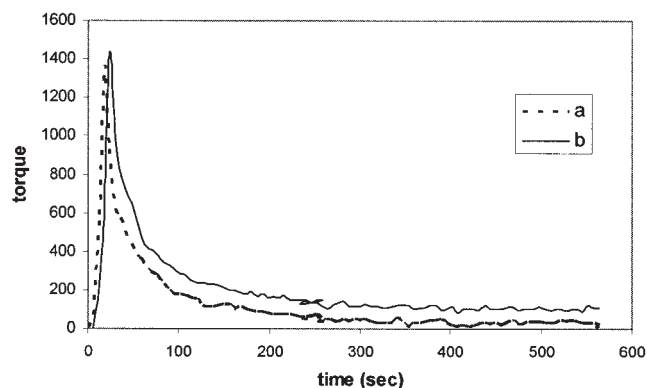


Figure 2 Torque-time curves of (a) non compatibilized PS/EVA (60 : 40 wt %) blend and (b) compatibilized blend with SBS-EVASH system, prepared by the dry-blend process.

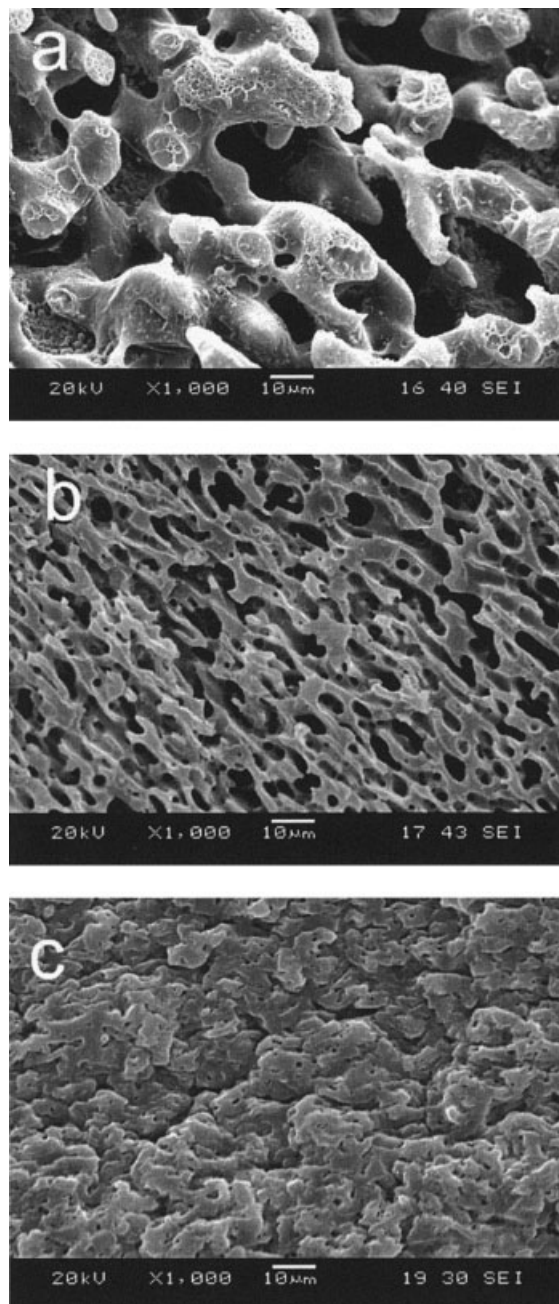


Figure 3 SEM micrographs of PS/EVA (60 : 40 wt %) blends: (a) non compatibilized; compatibilized with (b) SBS and (c) SBS-EVASH coreactive copolymers.

Blend morphology

To confirm the effect of the coreactive copolymers on dispersed phase morphology, compatibilized and non compatibilized blends were analyzed by SEM. Figure 3 shows the SEM micrographs of the cryogenically fractured surfaces of PS/EVA (60 : 40 wt %) blends as a function of the compatibilization. Since the composition of 60 : 40 wt % is in the range of cocontinuity, the PS phase was selectively extracted with MEK. The holes in the micrographs correspond to the PS phase, which was withdrawn by MEK. The non compatibi-

lized blend presents a gross phase-separated morphology, as expected for a heterogeneous blend. The presence of SBS resulted in a more homogeneous morphology, with both PS and EVA as thinner and elongated phases. The use of the coreactive copolymers imparted significant changes on the phase morphology, with a substantial decrease in phase size. This morphology may be responsible for the outstanding mechanical performance. It is important to point out that all blends at this composition present a cocontinuous morphology because it was possible to extract all the PS phase without damaging the sample.

Dynamic mechanical analysis (DMA)

DMA constitutes a very important tool for the analysis of the compatibilization effect in heterogeneous polymer blends. Figure 4 presents the variation of the loss tangent ($\tan \delta$) of the PS/EVA blends against temperature as a function of the compatibilization. Non compatibilized blends displayed two transitions: at -24°C related to the glass transition of the EVA phase and at 120°C corresponding to the transition of the PS phase. The blend compatibilized with pure SBS presented an additional transition at -67°C related to the polybutadiene segment in the SBS block copolymer. In spite of the low proportion of SBS in the blend, the great mobility of PB segments contributes to a relatively high $\tan \delta$ value. The transition of the PS phase is also broader, indicating some degree of interaction between the SBS and the PS phase, as expected.

A very interesting phenomenon is observed in blends compatibilized with the coreactive copolymers. The PS transition appears at almost the same position as that of the non compatibilized blend, with a $\tan \delta$ value a little lower, indicating a small decrease in the phase mobility, probably as a consequence of the physical entanglement between the interfacial agent and the PS phase. The transition related to the EVA

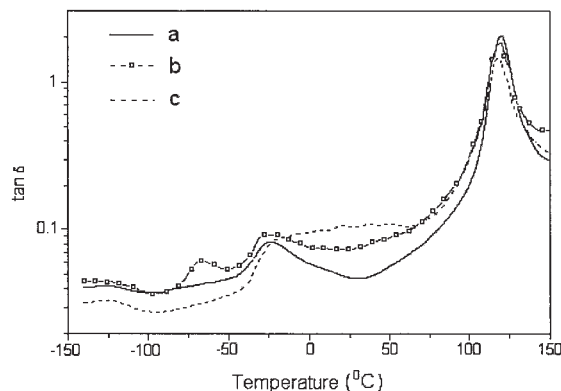


Figure 4 Loss tangent ($\tan \delta$) of the PS/EVA (60 : 40 wt %) blends against temperature: (a) non compatibilized; compatibilized with (b) SBS and (c) SBS-EVASH coreactive copolymers.

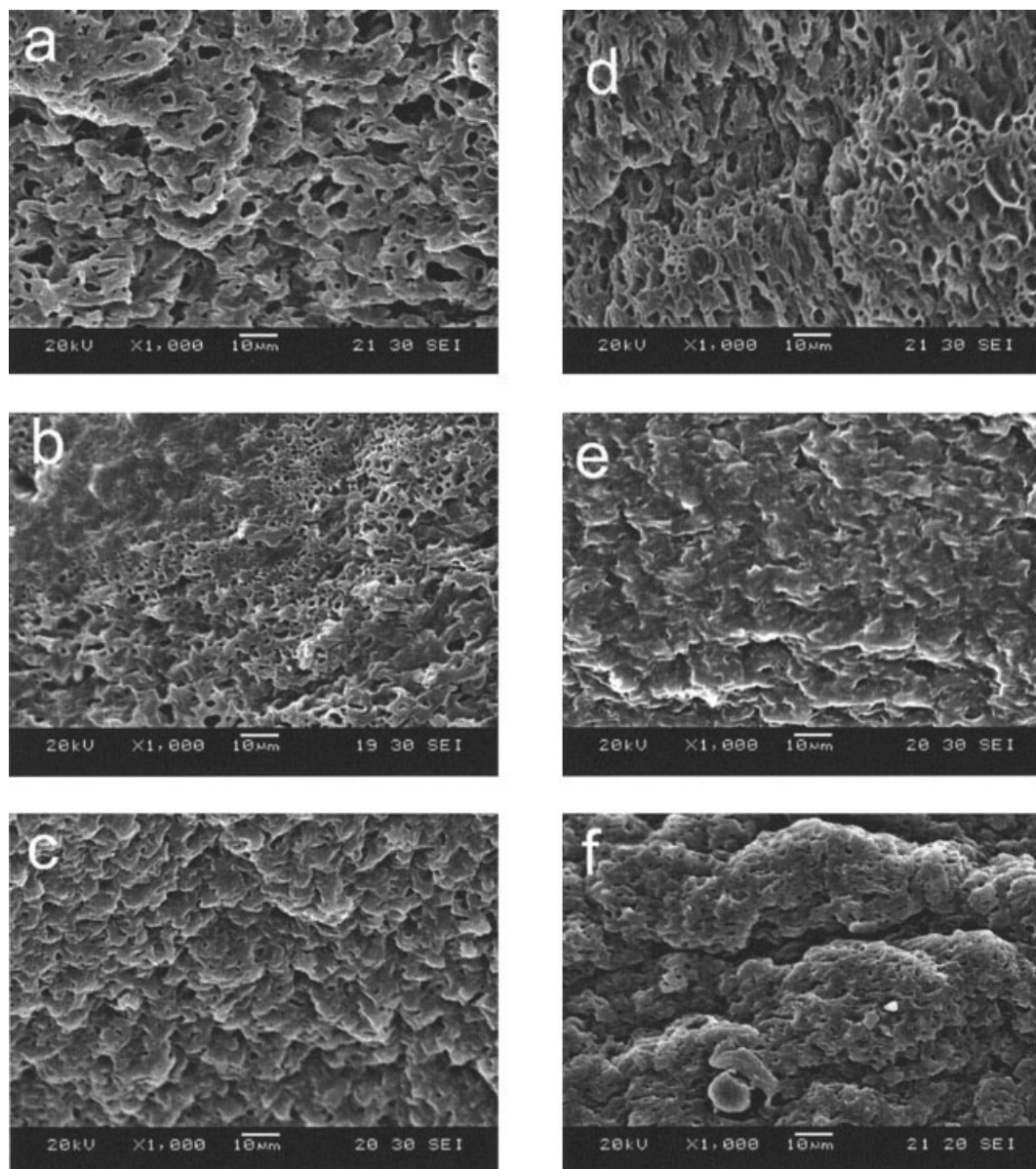


Figure 5 SEM micrographs of PS/EVA (60 : 40 wt %) non compatibilized blends processed at (a) 3 min; (b) 5 min; (c) 10 min; and compatibilized blend with SBS-EVASH system processed at (d) 3 min; (e) 5 min; (f) 10 min.

phase is also shifted towards a little higher temperature, but the peak is not well resolved as those observed in the other blends. In spite of the same amount of SBS in this blend, the transition at -67°C related to the polybutadiene segment could not be detected. Instead of this transition, it is possible to observe another non resolved transition at around 25°C , non detectable in the other blends. The absence of the transition at -67°C indicates that the polybutadiene segments have completely interacted with another blend component, the EVASH, forming a crosslinked and more rigid interphase, whose transition should correspond to the peak at 25°C , that is, in between the EVA and PS transitions. These results confirm the coreactive compatibilization and the formation of a third phase constituted by SBS, EVASH, and probably some portion

of PS or EVA, chemically jointed. This behavior is in agreement with the presence of insoluble material in extraction experiments with hot toluene.

The stabilization of the morphology

It is normally stated that the effectiveness of a compatibilizing agent in improving the mechanical performance of a heterogeneous polymer blend is related to its ability to increase the interfacial adhesion and decrease the interfacial tension. Therefore, more homogeneous morphology with small domain size is normally achieved. In addition, its interfacial action contributes to the stabilization of the dispersed phase morphology against coalescence during the blend processing and also under annealing conditions.³¹⁻³³ In

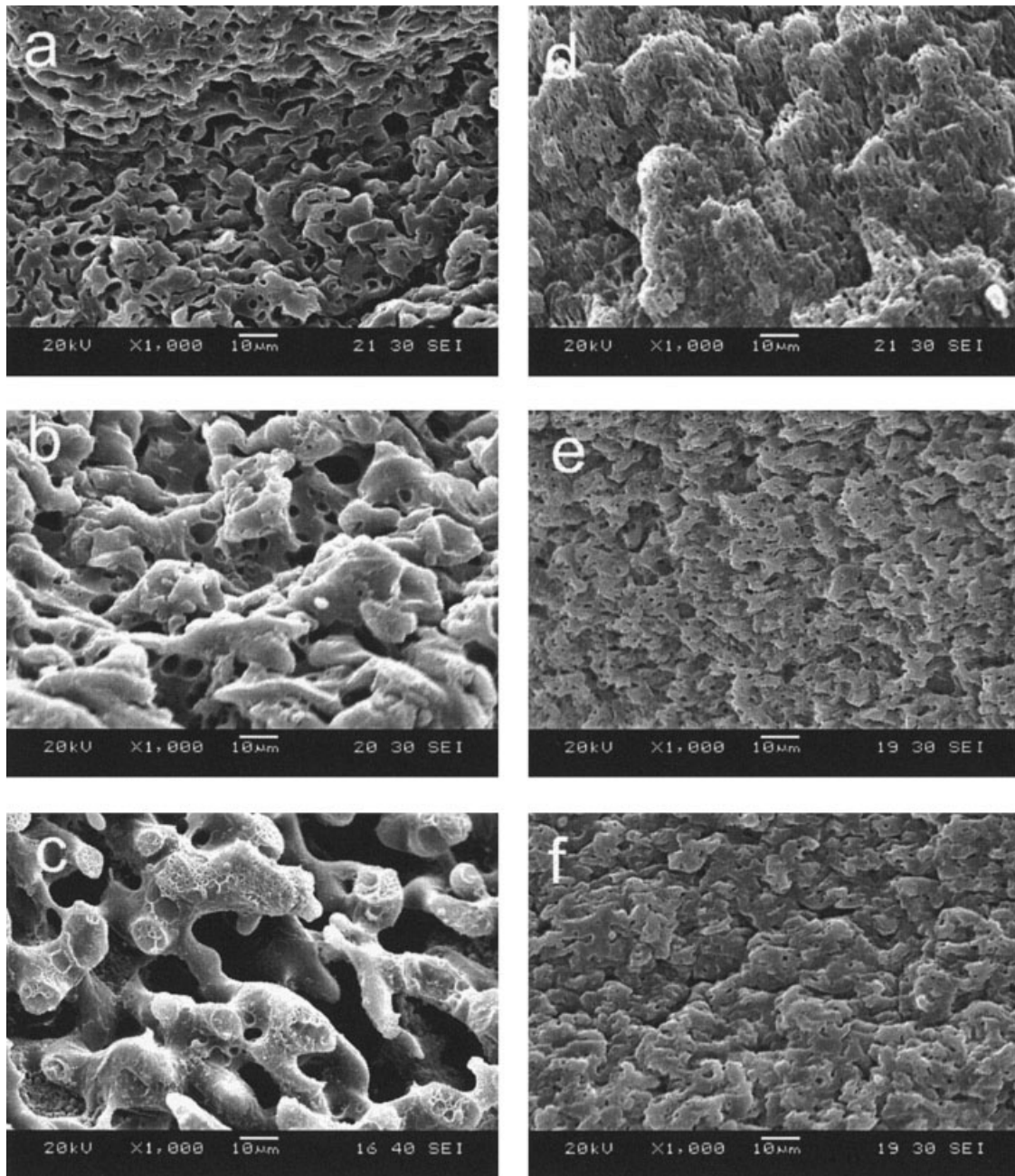


Figure 6 SEM micrographs of PS/EVA (60 : 40 wt %) non compatibilized blends compression-molded at (a) 0 min; (b) 5 min; (c) 10 min; and compatibilized blend with SBS-EVASH system compression-molded at (d) 0 min; (e) 5 min; (f) 10 min. (All blends were processed for 10 min.)

the case of cocontinuous polymer blends, the compatibilization also slows the phase coarsening.^{34–36}

With the aim of explaining the causes of the better mechanical performance of the compatibilized PS/EVA (60 : 40 wt %) blend, it was decided to follow the morphological changes of the blends during the mixing process and also under annealing conditions. Figure 5 compares the SEM micrographs of these blends processed at different times. After 3 min of blending, both compatibilized and non compatibilized blends presented small phase domains of the polystyrene phase, indicated by the holes after selective extraction

of this phase. The irregularity of the surface in the non compatibilized blend suggests that some large domain of the PS phase was extracted by MEK. The compatibilized blend presented a more uniform morphology, characterized by thinner and more elongated phases of PS and EVA. As the time of blending increased, the morphology of both blends became more homogeneous. After 10 min, the morphology was not affected by the compatibilization.

After the mixing process, the blends were kept under quiescent conditions (without heat and pressure) and then compression-molded at 160°C for different

TABLE II
The Effect of the Reactive Compatibilization on Tensile Properties of PS/EVA Blends as a Function of the Composition

Blend composition (wt %)		Ultimate tensile strength (MPa)		Elongation at break (%)	
PS	EVA	non comp	compatib	non comp	compatib
100	0	26.7 ± 0.5	—	3 ± 1	—
80	20	14.8 ± 0.3	17.0 ± 0.5	5 ± 2	14 ± 4
60	40	11.6 ± 0.5	12.0 ± 0.7	8 ± 2	31 ± 3
40	60	5.9 ± 0.3	3.6 ± 0.8	19 ± 5	78 ± 15
20	80	3.1 ± 0.2	3.8 ± 0.5	1750 ± 50	1950 ± 60

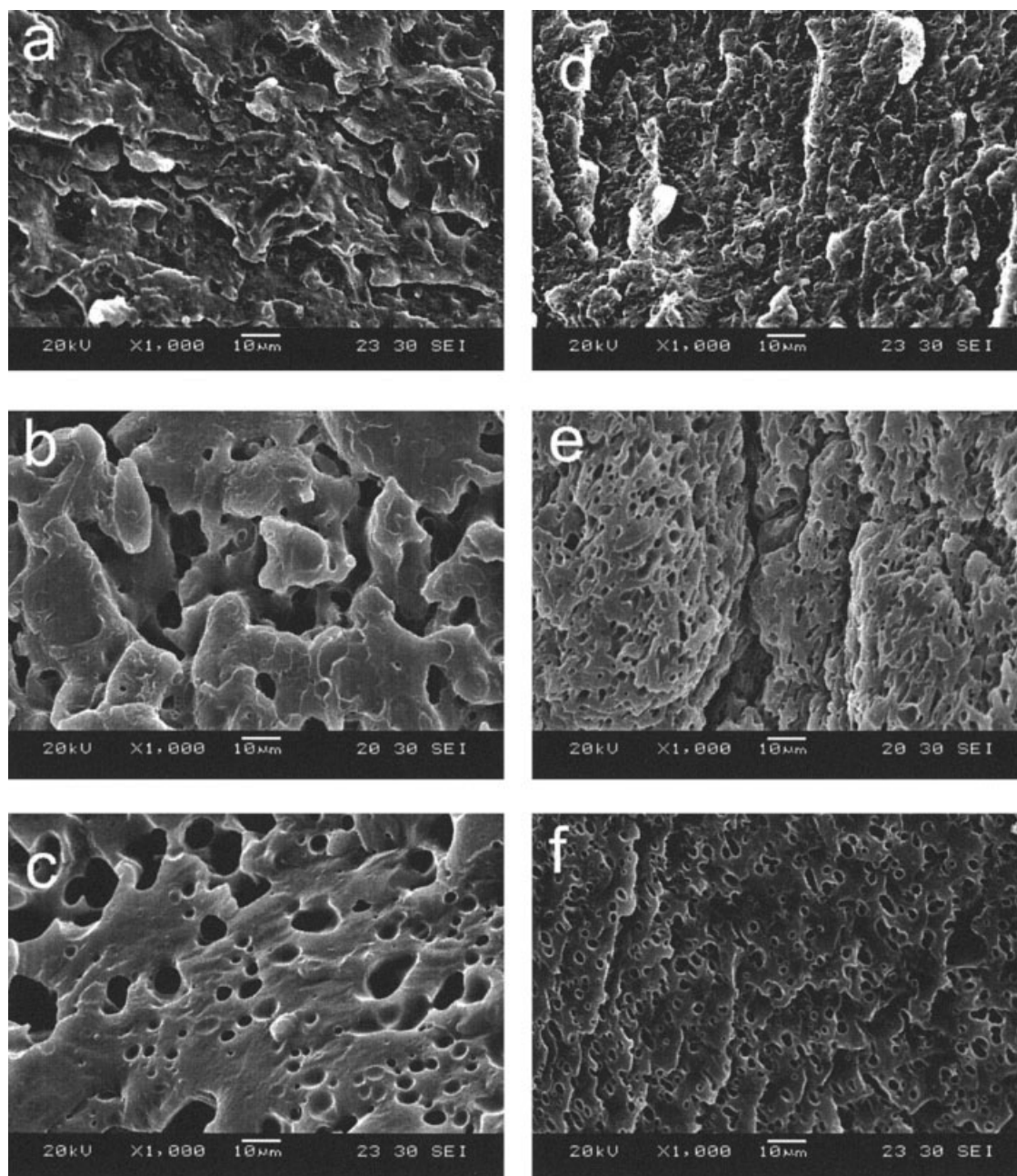


Figure 7 SEM micrographs of PS/EVA non compatibilized blends with (a) 20, (b) 60, and (c) 80 wt % of EVA and compatibilized blends with SBS-EVASH system and (d) 20, (e) 60, and (f) 80 wt % of EVA. (All blends were processed during 10 min and compression-molded for 10 min).

times. Figure 6 compares the morphological changes of these blends. Even without heat and pressure (0 min of molding), the non compatibilized blend presented a coarsening effect [Fig. 6(a)] as compared to the same blend which was immediately submersed in liquid nitrogen after blending [Fig. 5(c)]. A dramatic change in the size scale of this blend was observed between the sample quenched after mixing and after 10 min of compression-molding [Fig. 6(c)]. In spite of the increased coarsening of the blend morphology, the cocontinuity was still retained.

The presence of the coreactive compatibilizing agents resulted in a great stabilization of the morphology. Indeed, all compatibilized blend samples submitted to different treatment displayed similar morphology, characterized by a significant suppression of coarsening. These results confirm the effective interfacial action of the SBS-EVASH system. Besides a decrease of the interfacial tension, the coreactive copolymers were able to keep the uniform morphology with small domain size.

The variation of blend composition

The effect of the coreactive compatibilization was also evaluated in blends with different compositions. Table II presents the corresponding tensile properties. In all compositions studied, the compatibilization resulted in a substantial improvement of the elongation at break. For PS-richer blends, there was also an increase of the ultimate tensile strength. These behaviors are attributed to a more uniform morphology achieved with the compatibilization. Figure 7 illustrates the SEM micrographs of the cryogenically fractured surface of the blends as a function of composition and compatibilization. The composition corresponding to PS/EVA = 60 : 40 wt % was previously shown in Figure 3. Except for the blends containing 20 wt % of EVA, all other surface blends were submitted to selective extraction of the PS phase to highlight the phase contrast. In all composition studied, the decrease of phase size and a more uniform morphology in compatibilized blends is evident.

CONCLUSIONS

The efficiency of SBS in combination with mercapto-modified EVA (EVASH) on the reactive compatibilization of PS/EVA blends was investigated. The mercapto groups along the EVASH backbone reacted with the double bond of the SBS component during processing, giving rise to a crosslinked material, as indicated by the presence of insoluble material after the treatment of the blend with hot toluene. From dynamic mechanical analysis, it is possible to confirm the formation of this crosslinked material as a third phase of the blend, probably located at the interface. This conclusion was based on the presence of a third tran-

sition that occurred at a temperature in between those corresponding to the EVA and PS phases.

As shown above, the postmixing processing can dramatically affect the morphology of immiscible polymer blends. The non compatibilized PS/EVA (60 : 40 wt %) blend showed a substantial coarsening of the cocontinuous morphology after annealing. The presence of a small amount of SBS-EVASH as the coreactive system dramatically reduced the phase size and provided excellent stabilization of the morphology during annealing, confirming its excellent interfacial action. The decrease of phase size and the stabilization of the morphology are the key factors responsible for the outstanding mechanical performance, especially the elongation at break, achieved with the compatibilization.

We would like to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico—CNPq and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro—FAPERJ for financial support for this project.

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