

Effect of the Molecular Architecture of Graft Copolymers on the Phase Morphology and Tensile Properties of PS/EVA Blends

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ABSTRACT: Graft copolymers of poly(ethylene-co-vinyl acetate) (EVA) grafted with polystyrene (PS) with different molecular weight and different EVA/PS ratio were prepared by coupling reaction between acyl chloride functionalized PS (PS-COCl) and hydrolyzed EVA. PS-COCl with controlled molecular weight was prepared by anionic polymerization of styrene, followed by end capping with phosgene. The effect of the molecular architecture of the graft copolymer on the compatibilization of PS/EVA blends was investigated. Substantial improvement in the elongation at break and ductility was observed using the graft copolymer with PS segments with molecular weight as high as 66,000 g/mol and with a PS

proportion equal or higher than EVA. The effect of the compatibilization on the morphology was also investigated by scanning electron microscopy and atomic force microscopy. The blend that presented the highest value of elongation at break also displayed dispersed phase constituted by inclusions of the PS phase inside the EVA particle forming a cocontinuous structure, as observed by AFM. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 930–938, 2008

Key words: polystyrene; EVA; compatibilization molecular architecture; morphology; scanning electron microscopy; atomic force microscopy

INTRODUCTION

It is well known that the properties of incompatible polymer blends can be improved by the addition of compatibilizers, generally constituted by block or graft copolymers, whose segments are miscible or compatible with the blend components.^{1,2} These copolymers should be located at the interface of two immiscible polymers, reducing the interfacial tension between the phases and improving the interfacial adhesion.^{3–5} Lowering the interfacial tension leads to a smaller dispersed phase size,^{5,6} and sufficient interfacial adhesion enables the matrix to withstand the stress and strain due to an applied load. As a consequence, improved mechanical performance is expected to be reached. The interfacial action of these copolymers is believed to have depended on their molecular architecture, molecular weight, composi-

tion, and their proportion in the blend. Most of the reports in this field are related to the effect of the molecular architecture of the block copolymers on the compatibilization of heterogeneous polymer blends.^{7–14} This is because their molecular parameters are easy to control using anionic polymerization process, and also because it was stated that block copolymers are more efficient than graft copolymers as compatibilizing (interfacial) agents.⁵ In addition, there are many commercially available block copolymers (mainly those based on styrene-butadiene or -isoprene block copolymers) that can be used as compatibilizing agents. Some authors have concluded that block copolymers with short segments are preferentially located at the interface, which is a necessary condition for a good interfacial action.^{10,13,14} Other authors have suggested that long diblock copolymers, which are capable of entangling in both homopolymer phases, are more effective as compatibilizing agents.¹⁵ Some other papers have suggested that the molecular weight of the block copolymer does not affect the compatibilization in melt blending.^{7,8}

Graft copolymers have been employed as compatibilizing agents for several binary blends,^{16–22} but studies related to the effect of the molecular architecture and/or molecular weight of the graft copolymers are not common because the control of the

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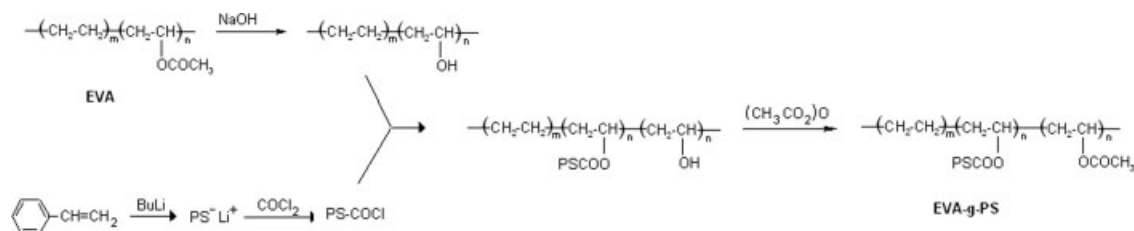


Figure 1 Scheme for the synthesis of EVA-g-PS copolymer.

copolymer structure is not so easy as in the case of block copolymer. Asaletha et al.²¹ studied the effect of the compatibilization of natural rubber-graft-polystyrene in natural rubber/polystyrene blends and observed a better interfacial action when graft copolymers with a higher molecular weight of PS grafted segments were employed.

Many important polymer blends are constituted by components, whose corresponding block copolymers are difficult to prepare. This is the case, for example, of PS/EVA blends. EVA copolymer can be considered a promising material for toughening PS because of its elastomeric nature (which depends on the vinyl acetate content) and also due to its saturated chain, which avoid thermal degradation of the corresponding blend during processing or service life. Several papers deal with the use of graft copolymers for improving the compatibility and also the mechanical properties of the PS/EVA blends.^{23–25} EVA grafted with PS segments (EVA-g-PS) was prepared by several procedures involving the polymerization of styrene initiated by free radical species, which was generated along the EVA backbone. Cheng et al. have used directly the *in situ* radical graft copolymerization for the manufacture of EVA-toughened PS.²³ Our group have reported the use of mercapto-modified EVA as the macrotransfer agent for the polymerization of styrene,^{26,27} and studied the efficiency of these graft copolymers as the compatibilizing agent for PS/EVA blends.^{24,27} Unfortunately, these techniques cannot provide a good control of the molecular weight and frequency of the PS segments along the EVA backbone. More than 10 years ago, our group developed an interesting methodology to prepare EVA-g-PS with controllable molecular architecture.²⁵ This methodology involved the preparation of polystyrene end capped with acyl chloride group, through anionic polymerization, followed by coupling reaction of this telechelic polymer onto hydrolyzed EVA copolymer. The synthetic scheme is illustrated in Figure 1.

This article deals with the synthesis of EVA-g-PS copolymers with different EVA/PS ratio and different molecular weights of the PS segments and the study of their effect on the morphology and tensile properties of PS-rich (PS/EVA) blends.

EXPERIMENTAL

Materials

Styrene (Sty) (free of an inhibitor) was first distilled under reduced pressure in the presence of calcium hydride and then distilled under reduced pressure in the presence of fluorenyl lithium just prior to the polymerization, according to the procedure developed by Teyssié and coworkers.²⁸ EVA [vinyl acetate (VA) content = 19 wt%; melt flow index = 2.3 g/10 min at 160°C] was kindly supplied by Petroquímica Triunfo S.A., Brazil. PS (Styrol 688G) [melt flow index = 3.5 g/10 min at 160°C; $\langle Mn \rangle = 110,000$] was kindly supplied by Dow Chemical, Brasil S.A. Phosgene was synthesized in our laboratory by reacting carbon tetrachloride and sulfuric acid in an appropriated apparatus. The phosgene was recovered in dry toluene and stored in a freezer. Hydrolyzed EVA used for the graft copolymer preparation was obtained by reacting a toluene solution of EVA with 10% methanolic solution of sodium hydroxide at 70°C, followed by neutralization of the reaction medium with aqueous solution of chloridric acid.²⁶

Synthesis of EVA-g-PS

PS samples with different molecular weight were prepared by anionic polymerization in toluene at 25°C, using *n*-butyl lithium as initiator, according to the literature.²⁸ After 12-h reaction, the polymer solution was added to the phosgene solution in toluene, under vigorous stirring, as described in literature.^{29,30} The resulting solution was heated to withdraw the excess of phosgene and transferred to another reactor containing hydrolyzed EVA solution in dry toluene and few drops of pyridine. The graft copolymerization was performed by heating the reaction medium under reflux and nitrogen atmosphere for 24 h. After the reaction was completed, an excess of acetic anhydride was added and the reaction was performed for 3 h to transform the non-reacted hydroxyl groups into acetate groups. The graft copolymer was precipitated into methanol, filtered, washed, and dried under reduced pressure.

Before and after the treatment with phosgene, aliquots were withdrawn from the reaction medium

TABLE I
Characteristics of the EVA-g-PS Copolymers

Code	<Mn> of grafted PS (g/mol)	Graft composition (wt %)	
		PS	EVA
LG20	15,500	20	80
LG50	15,500	48	52
LG80	15,500	80	20
MG20	27,000	26	74
MG50	27,000	52	48
MG80	27,000	80	20
HG20	66,000	20	80
HG50	66,000	50	50
HG80	66,000	80	20

and precipitated into methanol. The corresponding polymers were characterized by size exclusion chromatography with the help of a Waters 600 equipment to determine the molecular weight of the telechelic PS.

Blend preparation and testing

Noncompatibilized and compatibilized PS/EVA (80 : 20 wt %) blends were prepared. The polymers were melt blended in a Haake batch mixer (Rheomix 600) at 200°C for 10 min, using roller blades-type rotors at 60 rpm. The graft copolymer was first blended with the minor phase (EVA) before adding the major constitutive component (PS). After mixing, the blends were compression-molded into 1-mm thick sheets at 200°C for 10 min. Test specimens for tensile measurements were prepared from these plates, according to ASTM D 638. The tensile parameters were measured with the help of an Instron tensile tester Model 4204 at 25°C with six specimens for each sample. The strain rate was 1 mm/min.

Morphological analysis

Scanning electron microscopy (SEM) was performed in a JEOL JSM-L5300 microscope, using an accelerator power of 20 kV and secondary electron detector. The fracture surface of the samples obtained from tensile test was coated with a thin layer of gold before analysis. The micrographs were treated by image analysis using the AnalySIS@3.0, supplied by the microscope manufacturer. The obtained image was converted to the inverted binary image and the surface area of the particle was computed.

The scanning probe microscopy images of cryomicrotomed surface were obtained on a Topometrix TMX 2010 Discovery instrument, equipped with a noncontact AFM probe head and a 70- μ m tripod scanner. The tips (Topometrix 1660) were made of Si, with a spring constant of about 40 N/m and resonance frequencies in the range of 100–150 kHz. Scan-

ning was carried out at the free cantilever oscillation frequency at different amplitudes, depending on the stability and contrast obtained. The set point was fixed at 25 and 45% of the free oscillation amplitude. AFM images were obtained in air.

RESULTS AND DISCUSSION

Characteristics of EVA-g-PS copolymers

The main characteristics of the graft copolymers prepared by coupling reaction of PS-COCl and hydrolyzed EVA (EVAL) are summarized in Table I. The LG, MG, and HG codes correspond to the graft copolymers with low, medium, and high molecular weight, respectively, and the number 20, 50, and 80 correspond to the amount of the PS grafted onto the EVA backbone. It is important to emphasize that the anionic polymerization process gave rise to polymer chains with narrow molecular weight distribution. In addition, there was no significant coupling reaction of the polystyryl anion with the telechelic PS-COCl, since the PS samples

TABLE II
Mechanical Properties of PS/EVA (80 : 20 wt%) Blends Compatibilized with EVA-g-PS Copolymers with Different Molecular Architecture

Compatibilizer		Ultimate tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
Type	Conc. (%)			
0	0	25.2 \pm 0.8	13 \pm 1	258 \pm 22
LG20	2	25.7 \pm 0.5	14 \pm 1	241 \pm 20
	4	24.0 \pm 2.0	13 \pm 1	254 \pm 33
	6	24.2 \pm 0.8	13 \pm 1	248 \pm 30
LG50	2	25.8 \pm 0.7	13 \pm 1	250 \pm 30
	4	24.7 \pm 1.0	14 \pm 1	230 \pm 30
	6	24.2 \pm 1.9	12 \pm 1	250 \pm 35
LG80	2	25.2 \pm 0.9	16 \pm 1	226 \pm 14
	4	23.7 \pm 2.3	13 \pm 1	246 \pm 34
	6	24.8 \pm 1.4	15 \pm 1	270 \pm 23
MG20	2	24.3 \pm 2.4	11 \pm 1	243 \pm 33
	4	23.6 \pm 1.3	13 \pm 2	263 \pm 26
	6	23.0 \pm 1.2	12 \pm 2	239 \pm 15
MG50	2	24.1 \pm 1.9	12 \pm 2	267 \pm 20
	4	23.0 \pm 1.6	14 \pm 2	228 \pm 30
	6	22.1 \pm 1.9	15 \pm 1	215 \pm 15
MG80	2	22.8 \pm 1.3	14 \pm 2	231 \pm 20
	4	23.7 \pm 1.4	15 \pm 3	239 \pm 26
	6	23.7 \pm 2.1	12 \pm 1	249 \pm 30
HG20	2	23.2 \pm 1.2	14 \pm 2	238 \pm 22
	4	23.3 \pm 1.6	14 \pm 2	236 \pm 29
	6	22.5 \pm 1.4	12 \pm 1	248 \pm 29
HG50	2	21.5 \pm 2.1	12 \pm 2	213 \pm 18
	4	24.3 \pm 1.3	15 \pm 1	242 \pm 32
	6	19.5 \pm 1.1	122 \pm 9	219 \pm 15
HG80	2	20.4 \pm 0.6	158 \pm 36	229 \pm 42
	4	17.8 \pm 2.5	200 \pm 30	203 \pm 24
	6	27.0 \pm 0.4	12 \pm 2	271 \pm 27

withdrawn from the reaction medium before and after the addition of phosgene presented similar values of molecular weight.

Tensile properties

The effect of three different parameters of the EVA-g-PS graft copolymers on the mechanical properties of PS/EVA (80 : 20 wt %) blends was investigated: two of them were related to the molecular architecture and corresponded to the molecular weight of the PS segments (LG, MG, and HG series) and to the amount of PS in the graft copolymer (PS/EVA ratio in the copolymer). The other parameter was related to the amount of the graft copolymer in the blend. For this study, 2, 4, and 6% of the graft copolymer related to the whole blend components were employed. The main tensile properties are summarized in Table II.

No significant influence on mechanical properties was observed in blends containing graft copolymers with PS segments of molecular weight corresponding to 15,500 (LG series) or 27,000 (MG series), regardless the composition of the graft copolymer or the amount of graft copolymer in the blend. However, a significant improvement in the elongation at break was observed with the addition of EVA-g-PS copolymers constituted by PS segments with higher molecular weight (HG series). These results suggest that the molecular weight of the PS segments in HG series is higher than a critical value to promote a good entanglement with the PS matrix.

In addition to the molecular weight, the graft copolymer composition and its proportion in the blend also exerted significant influence on the mechanical performance of the PS/EVA blends, as illustrated in Figure 2. Blends containing graft copolymer with low PS/EVA ratio (20% of PS—HG20 series) presented similar properties as those found in noncompatibilized blend. The copolymer with high proportion of EVA is an asymmetric graft copolymer, which may assume a micelle configuration with EVA at the outer layer, favoring the migration of the copolymer into the EVA-dispersed phase. This behavior is explained by SEM micrographs, as it will be discussed in the next section.

Concerning the blends containing EVA-g-PS with similar PS/EVA ratio (HG50 series), a substantial increase in the elongation at break followed by a decrease of ultimate tensile strength and Young modulus were observed with the addition of 6% of this copolymer. In the case of blends containing EVA-g-PS copolymer with high PS/EVA ratio (HG80 series), a significant improvement in elongation at break was observed with the addition of only 2% of

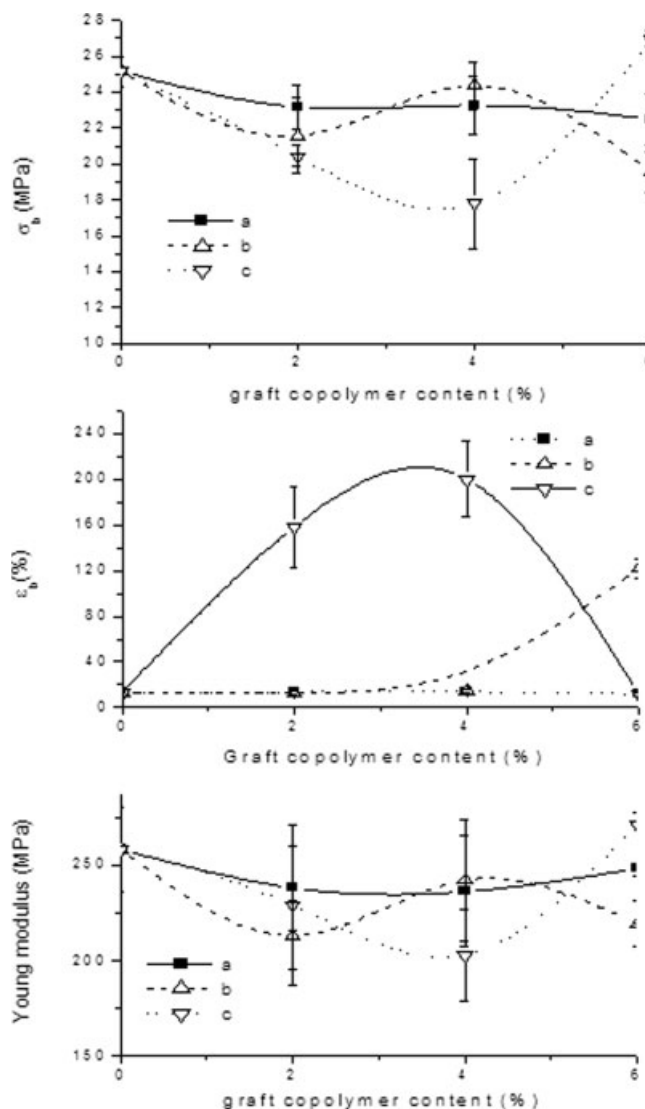


Figure 2 Mechanical properties of PS/EVA (80 : 20 wt%) blends compatibilized with EVA-g-PS copolymer (HG series), as a function of the graft copolymer composition and amount of graft copolymer.

this copolymer, reaching a maximum with 4%. Beyond this concentration, the elongation at break decreased substantially.

The stress-strain curves of the modified blends, shown in Figure 3, allow a better insight into the mechanical properties of the compatibilized blend. Blend compatibilized with 4% of HG80 graft copolymer (curve d) or 6% of HG50 graft copolymer (curve c) displayed typical curves of ductile materials, with yielding followed by high elongation until break. In addition, it was observed a small increase of tensile strength in the later stages of the tensile process, indicating the presence of strong entanglements between the blend components, imparted by the graft copolymer.

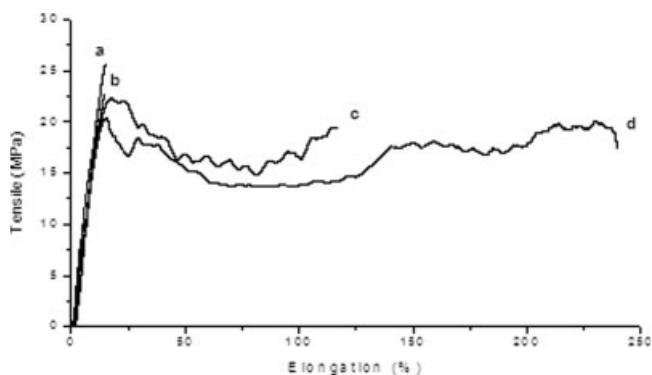


Figure 3 Stress versus strain curves of PS/EVA (80 : 20%) blends: (a) noncompatibilized; (b) containing 6% of HG20; (c) 6% of HG50; and (d) 4% of HG80.

Morphology

Figure 4 compares the micrograph of noncompatibilized PS/EVA blend with those of compatibilized blends containing 4% of graft copolymer with similar PS/EVA ratio (50 : 50 wt %) and different molecular weight of the PS segments. Noncompatibilized blend displayed relatively good EVA phase dispersion in spite of the incompatibility between the components. The presence of graft copolymers with shorter PS segments (LG50 and MG50) resulted in an increase of the EVA domain size, suggesting that

part of the graft copolymer was trapped inside this phase, probably together with some portion of polystyrene homopolymer. The highest domain size was observed with MG50 [Fig 4(c)]. The higher molecular weight of the PS segments in the graft copolymer resulted in a decrease of the particle size and an improved interfacial adhesion [Fig 4(d)].

The effect of the chemical composition of the graft copolymer on the morphology is illustrated in Figure 5, for blends compatibilized with the HG-graft copolymers. Graft copolymer with low PS/EVA ratio resulted in blend with increased EVA domain size, compared to noncompatibilized blend. Blends compatibilized with EVA-g-PS with similar PS/EVA proportion [HG50 – Fig 5(b)] or with higher proportion of PS [HG80 – Fig 5(c)] displayed better dispersion of the EVA domains and smaller domain size.

The domain size distribution curves of PS/EVA blends compatibilized with the HG series graft copolymer are illustrated in Figure 6. The dependence of the number-average diameter of the EVA dispersed phase as a function of the graft copolymer concentration is shown in Figure 7. Noncompatibilized blend displayed dn value around 1.5 μm , which is considered a good dispersion for an heterogeneous blend. The addition of HG20 copolymer resulted in an increase of dn values. In addition, the domain size distribution curves of these blends are broad and bimodal in the case of 2 or 4%, indicating

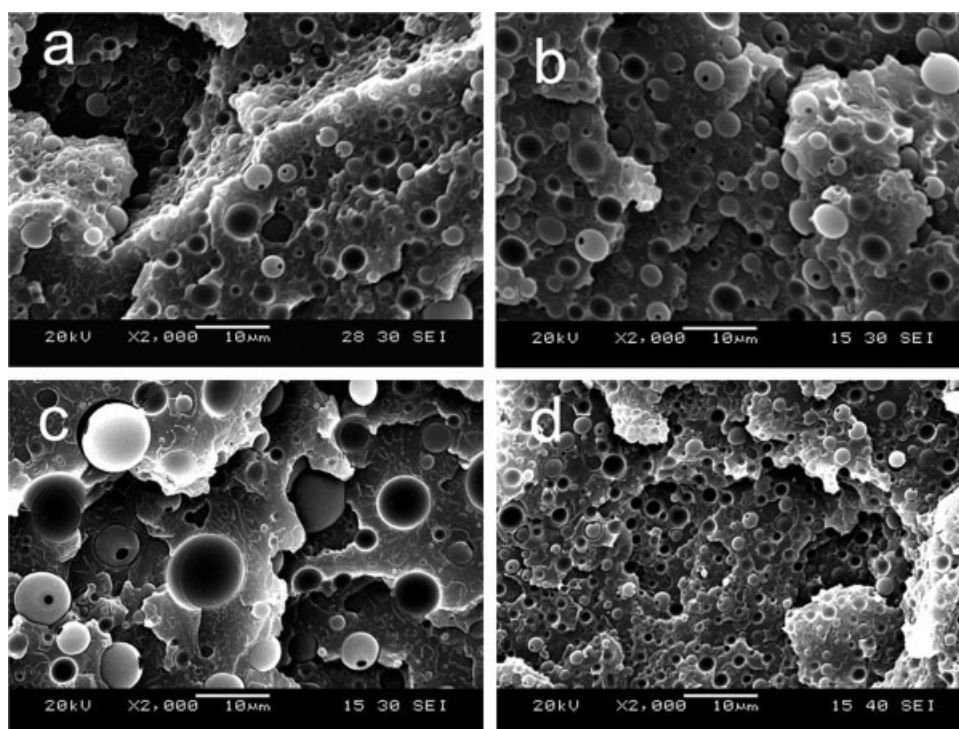


Figure 4 SEM micrographs of PS/EVA (80 : 20%) blends: (a) noncompatibilized; (b) containing 6% of LG50; (c) 6% of MG50; and (d) 6% of HG50.

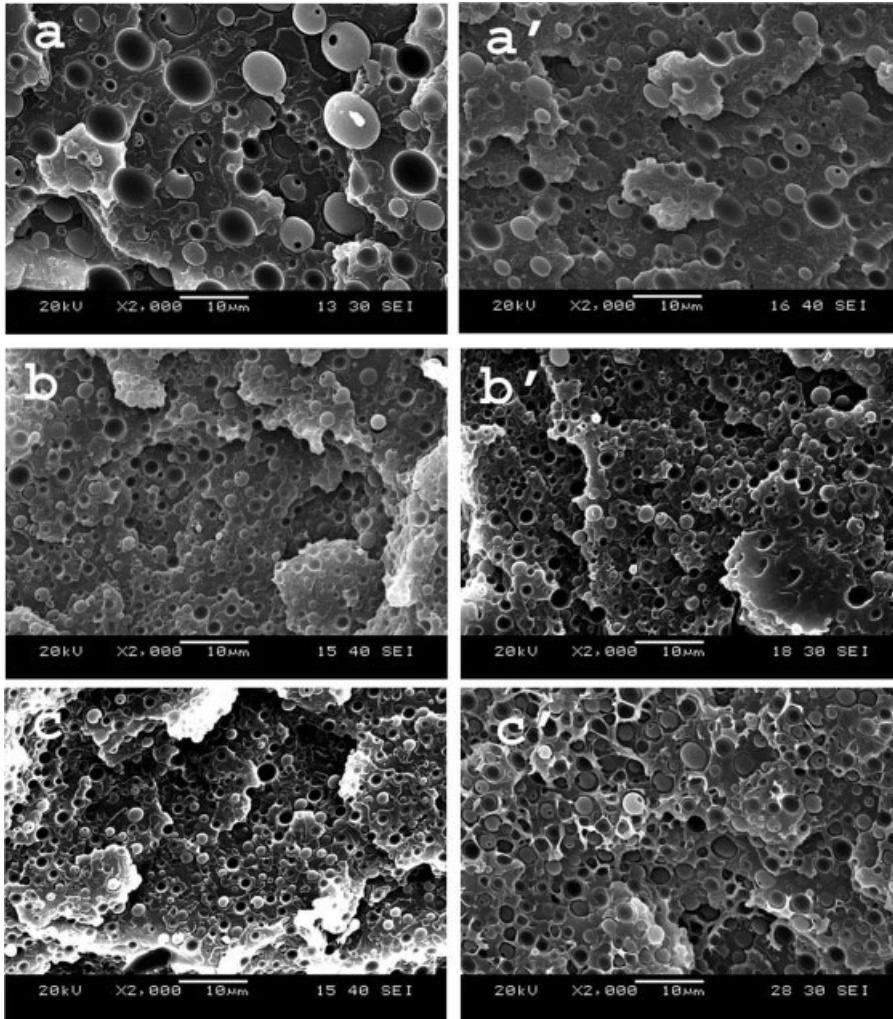


Figure 5 SEM micrographs of PS/EVA (80 : 20%) blends containing (a) 4% and (a') 6% of HG20; (b) 4% and (b') 6% of HG50; (c) 2% and (c') 4% of HG80.

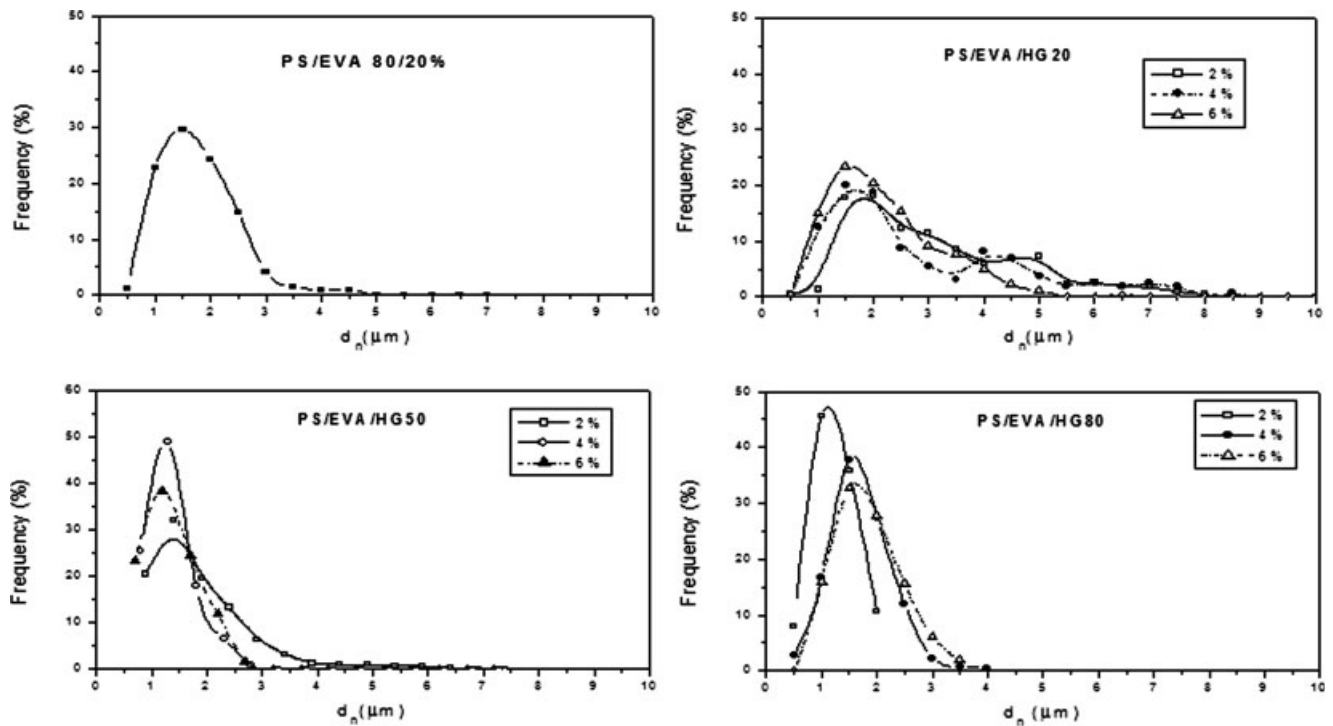


Figure 6 Domain size distribution curves of PS/EVA (80 : 20%) blends as a function of the graft copolymer composition and amount of graft copolymer (HG series).

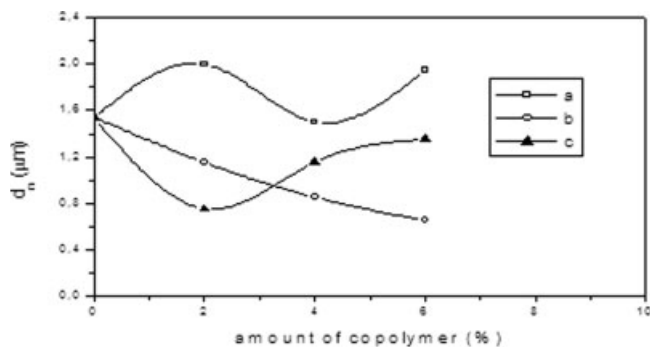


Figure 7 Dependence of the number-average diameter of EVA dispersed phase with the graft copolymer concentration (HG series).

that some amount of the graft copolymer are in the form of aggregates located inside the EVA domain. This morphological feature is in agreement with the mechanical behavior of these blends.

Blends containing HG50 graft copolymer resulted in narrow domain size distribution of EVA phase. In addition, the number-average diameter of EVA domain decreased as the graft copolymer concentration in the blend increased. This behavior is typical of a compatibilized system and suggests that the critical concentration for emulsification is higher than that used in our study, because no plateau value was observed within the concentration range employed. The presence of 6% of this graft copolymer resulted in EVA-dispersed phase with small d_n value (around 0.6 μm) and an improved mechanical performance.

A significant reduction of d_n value (from 1.5 to 0.7 μm) was also observed in blends compatibilized with 2% of HG80. Further increase of the graft copolymer concentration resulted in an increase of EVA domain particle size (Figs. 6 and 7). Blend containing 4% of this copolymer presented a particle size in the range of 1.1 μm and broader domain size distribution curve, but a very good response in terms of elongation at break and ductility.

The improved mechanical performance of these compatibilized blends should be attributed to a reduced particle size and also to a good interfacial adhesion. Figure 8 compares the micrographs (taken at higher magnification) of the blends containing 6% of HG50 with that containing 4% of HG80, both of them characterized by outstanding mechanical performance. The former presented smaller particle size and some adhesion between the phases. In addition, it is possible to observe some holes with a well-adhered inner layer. Since these micrographs were taken from the surface after tensile testing, it was suggested that during the tensile experiment, the rupture started inside the EVA domains, whose interface was adhered to the PS matrix. Blend containing 4% of HG80 graft copolymer also presented good interfacial adhesion. The micrograph is also characterized by the presence of some holes containing a thin layer inside them, which can be attributed to part of the EVA domain that stayed adhered to the matrix after the testing experiment.

To explain the morphological behavior of the blends containing HG80 graft copolymer, the surface obtained from the tensile test was cryomicrotomed and analyzed by atomic force microscopy. Figure 9 compares the micrographs of the noncompatibilized blend with those containing 2 and 4% of HG80 graft copolymer. The dispersed particles in the blend containing 2% of HG80 are constituted by EVA component with some inclusions of the PS component. However, the morphology of the blend compatibilized with 4% of HG80 is quite different. The dispersed phase contains a large amount of the PS matrix included in it, forming a cocontinuous structure together with the EVA component. These inclusions of the PS phase inside the EVA dispersed particles increased the domain size of EVA in this blend. The cocontinuous morphology formed inside the dispersed particles promotes a smooth phase separation, which may be responsible for the outstanding elongation until breaking.

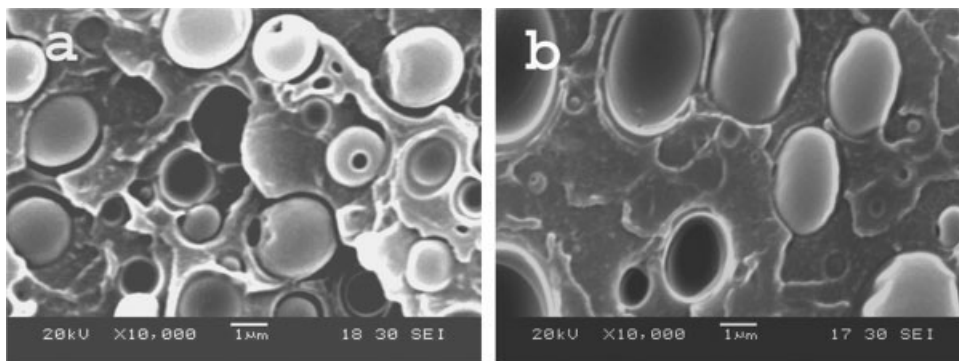


Figure 8 SEM micrographs of PS/EVA blends containing (a) 6% of HG50 and (b) 4% of HG80 at higher magnification.

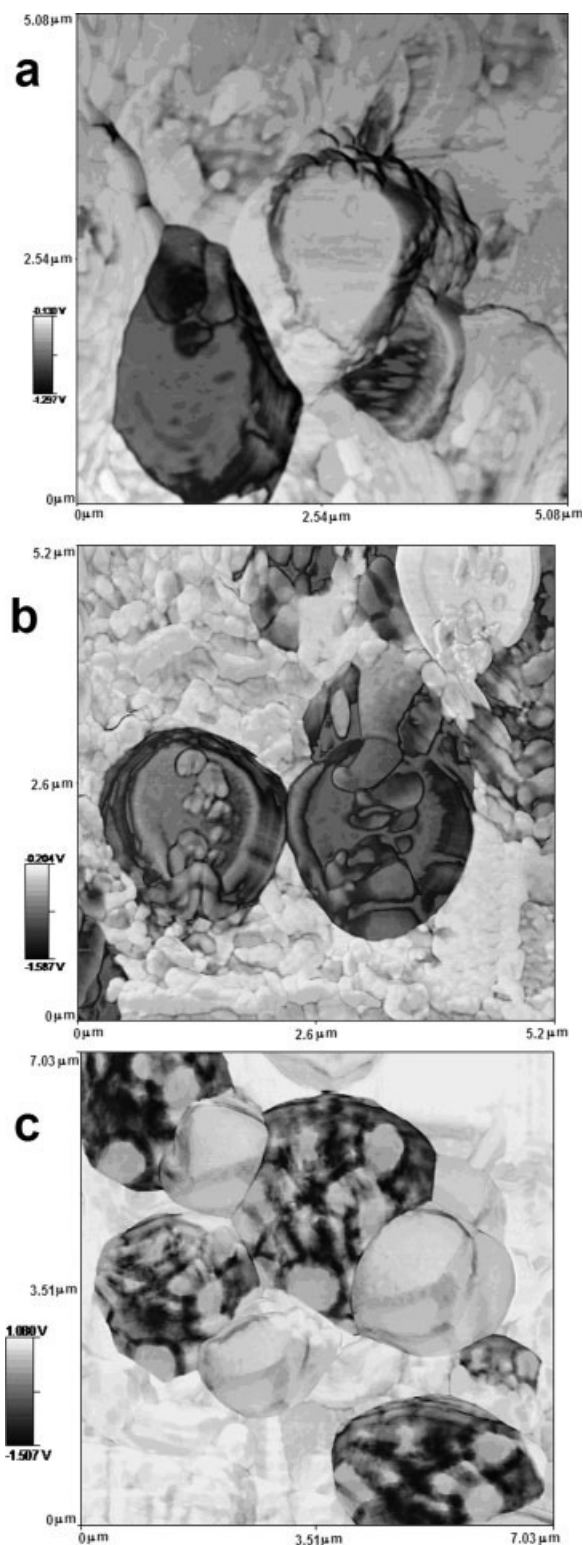


Figure 9 AFM micrographs of PS/EVA blend containing (a) 0, (b) 2, and (c) 4% of HG80.

CONCLUSIONS

EVA-g-PS graft copolymers with different molecular architecture were employed as interfacial agent in PS/

EVA (80 : 20%) blends. Graft copolymers containing PS segments with molar mass lower than 27,000 could not provide a good interfacial action and an improvement of mechanical performance, probably because the entanglements between the PS segments and the PS homopolymer chains were not strong enough. Significant improvement in elongation at break and ductility of the blends was achieved with the addition of EVA-g-PS copolymer with longer PS segments ($\langle M_n \rangle = 66,000$). The graft composition was also another important parameter for the compatibilization process. Only graft copolymers with similar or higher proportion of PS related to the EVA backbone were effective. In these cases, the smallest particle size was achieved with 6% of the EVA-g-PS copolymer with similar PS/EVA ratio. However, the increased elongation at break was observed in blend containing 4% of the EVA-g-PS copolymer with higher PS/EVA ratio. This behavior may be attributed to a peculiar morphology of the dispersed phase, constituted by PS phase included in the EVA particle forming a cocontinuous structure.

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