

Polystyrene/EVA Melt Blends Compatibilized with EVA-*graft*-Polystyrene

B. G. SOARES,¹ R. V. BARBOSA,¹ J. C. COVAS²

¹ Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Centro de Tecnologia, Bl. J, 21945-970, RJ, Brazil

² Departamento de Engenharia de Polímeros, Universidade do Minho, Braga, Portugal

Received 13 June 1996; accepted 31 January 1997

ABSTRACT: The influence of poly[(ethylene-*co*-vinyl acetate)-*g*-polystyrene] (EVA-*g*-PS) on the mechanical and morphological properties of polystyrene and the blends with EVA copolymers has been investigated. The melt blends have been performed in a twin-screw extruder. The addition of the graft copolymer enhances the mechanical properties and impact resistance of the PS matrix and PS/EVA (90 : 10 wt %) blends. Better results on impact strength and elongation at break have been achieved by using a EVA-*g*-PS graft copolymer with a higher EVA proportion by weight. This graft copolymer also contains a lower molecular weight of the PS-grafted segments than the PS matrix. Morphological studies by scanning electron microscopy revealed some interfacial adhesion between the components in the compatibilized polymer blends. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2141–2149, 1997

Key words: polystyrene/EVA blends; graft copolymer; blend compatibilization

INTRODUCTION

Blending of immiscible polymers is considered an efficient tool for the development of new polymeric materials with outstanding properties and low costs. The immiscibility promotes a desired phase segregation and gives rise to materials with better performance because the blend morphology is well controlled and a good adhesion between the phases is achieved.^{1,2} These requirements can be fulfilled by proper blending conditions (to provide good phase dispersion and uniform particle size) and by the addition of an interfacial agent.^{1–5} The choice of the interfacial agent is normally gov-

erned by its effectiveness in imparting good interfacial adhesion, good phase dispersion, and morphology stability upon processing, by the feasibility of its synthesis and by the nature of the polymer components in the blend. Block^{1–3} and graft copolymers^{1,5} have been extensively employed as compatibilizing agent in polystyrene and polyolefin blends. Recently we prepared polystyrene-grafted poly[ethylene-*co*-(vinyl acetate)] (EVA-*g*-PS) and studied its efficiency on the compatibilization of polystyrene (PS)/poly [ethylene-*co*-(vinyl acetate)] (EVA) blends.^{6,7} PS/EVA (90 : 10 wt %) blends containing 5 phr of the graft copolymers revealed superior ultimate tensile properties when compared to noncompatibilized blend.⁷ The chemical composition of the graft copolymers did not exert substantial influence on the mechanical properties of the ternary blends. The studies previously reported were carried out with blends obtained by dissolving all the components into toluene, followed by precipitation into methanol. Because the blending conditions usually affect the blend morphology and, conse-

Correspondence to: B. G. Soares.

Contract grant sponsor: Conselho Nacional de Desenvolvimento Científico e Tecnológico—CNPq.

Contract grant sponsor: Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior—CAPES.

Contract grant sponsor: CEPG-UFRJ.

Contract grant sponsor: PADCT-FINEP.

Journal of Applied Polymer Science, Vol. 65, 2141–2149 (1997)

© 1997 John Wiley & Sons, Inc.

CCC 0021-8995/97/112141-09

quently, the final product performance, it is worth investigating the behavior of the PS/EVA blends obtained in melt conditions.

This article deals with the evaluation of the effect of EVA-*g*-PS on the mechanical and morphological properties of polystyrene and their blends with EVA prepared in a corotating twin screw extruder.

EXPERIMENTAL

Materials

Styrene (Sty) (free of an inhibitor) was distilled under reduced pressure. Azo-bis-isobutyronitrile (AIBN) was recrystallized from methanol/water (1 : 1 vol %). Mercaptoacetic acid (MAA) was distilled under reduced pressure and stored under nitrogen at -20°C . Ethylene-vinyl acetate copolymer (EVA), used in the graft copolymerization [vinyl acetate (VA) content = 18 wt %; melt flow index = 2.3 g/10 min at 160°C] was kindly supplied by Petroquímica Triunfo S.A., Brazil. The synthesis of poly(ethylene-*co*-vinyl acetate-*g*-styrene) (EVA-*g*-PS) was performed by grafting reaction of styrene from mercapto-modified hydrolyzed EVA (EVALSH), according to the literature.^{6,8} Poly(ethylene-*co*-vinyl alcohol-*co*-vinyl mercaptoacetate) (EVALSH) employed in the grafting reaction contains 0.73 mmol SH/g. Polystyrene (PS) ($M_n = 133,000$) (Polystyrol-143E) was kindly supplied by BASF S.A. High-impact polystyrene (HIPS) (butadiene content = 8.0 wt %; MFI = 16 g/10 min at 200°C) was generously supplied by EDN, Brazil. EVA samples used in the blends, generously supplied by NESTE, were NCPE-5810 and NCPE5028 (with 10 wt % and 28 wt % of VA, respectively).

Blend Preparation and Characterization

Blends of PS/EVA-*g*-PS were prepared in a Leistritz corotating twin extruder (model LSM 30.40; die diameter = 4 mm; screw speed = 5 rpm; barrel temperature = $195\text{--}205^{\circ}\text{C}$). The pellets obtained by the extrusion process were injection molded into specimens with dimensions according to ASTM D638 type II, on a Krauss-Maffei KM60-KM420 injector. The tensile properties were measured at room temperature, using an Instron tensile tester Model 4500, at a crosshead speed of 50 mm/min. Notched Izod impact strength was determined with the help of a TMI 43-01 impact testing machine at room temperature.

Scanning Electron Microscopy

Scanning electron microscopy was taken from the fracture surface handled at room temperature or from the surface obtained from impact measurements, as indicated in the text. The surface was coated by gold vapor and analyzed on a JEOL 5300 scanning electron microscope.

Rheological Measurements

Melt rheological measurements of the polymer material employed in the blends were carried out on a piston-type capillary rheometer (Rosand RH-7 with double piston) using diameter capillary = 1 mm, and with a piston speed adjusted to give a shear rate from 10 s^{-1} to 105 s^{-1} . The apparent shear viscosity and shear rate obtained from conventional expressions were corrected by using Bagley and Rabinovitsch corrections.

RESULTS AND DISCUSSION

Binary EVA/PS Blends

The tensile properties of the PS/EVA blends as functions of blend composition and vinyl acetate (VA) content in the EVA copolymer are illustrated in Figure 1. For this study, EVA copolymers with 10 wt % of VA (EVA10) and 28 wt % of VA (EVA28) were employed. The ultimate tensile strength (σ_B) [Fig. 1(A)] and Young's modulus [Fig. 1(B)] increase as the PS content in the blend increases. No minimum value smaller than that of either pure component was observed for both properties. Blends prepared with EVA10 (with lower VA content) presented higher values of modulus and σ_B . As reported in the literature,⁹ the crystallinity degree of EVA copolymers increases as the VA content in the copolymer decreases. Therefore, the higher crystallinity of EVA10 sample may be responsible for the improvement on the Young's modulus and σ_B of the corresponding PS/EVA blends. It is curious to observe that the Young's modulus and σ_B of both EVA10 and EVA28 pure copolymer samples present similar values.

The elongation at break (ϵ_B) [Fig. 1(C)] presents a synergism for PS-rich blends, compared to pure polystyrene. The values of energy to break (E_B) [Fig. 1(D)] also show an improvement in ductility with the addition of small amount of EVA (5–10 wt %) into the PS matrix. Although these properties are superior for pure EVA copolymer with higher VA content, the synergism ob-

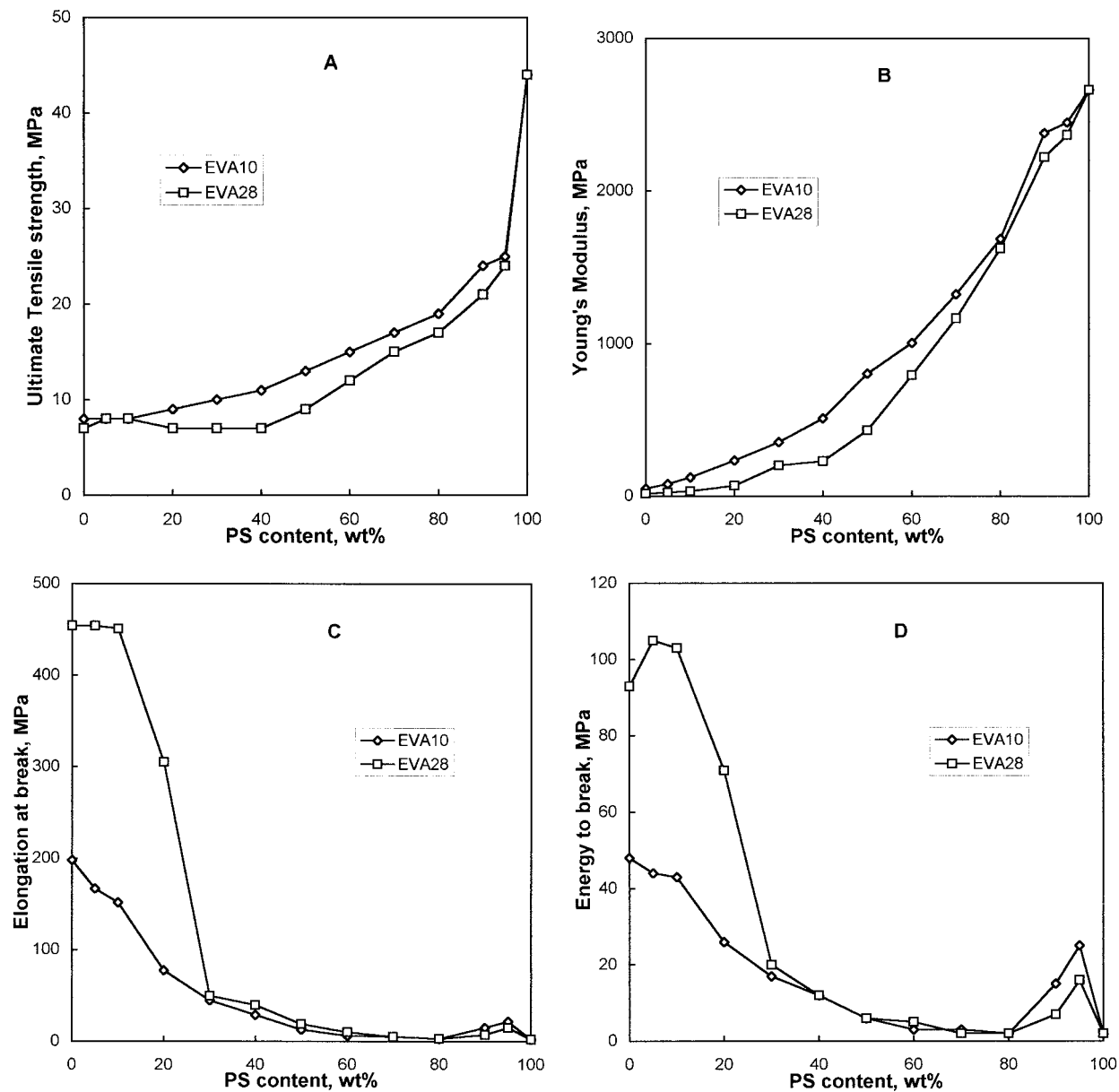


Figure 1 Tensile properties of PS/EVA blends as functions of blend composition and EVA copolymer composition.

served in PS-rich blends is more pronounced when EVA sample with lower VA content (EVA10) is employed. Because PS/EVA blends are expected to be incompatible, the improvement of the ϵ_B and E_B in PS-rich blends may be related to the good phase dispersion resulting from the processing conditions used in these experiments.

Selective extraction experiments have been performed in order to detect the phase inversion composition. For this purpose, the PS phase was selectively extracted with methyl ethyl ketone (MEK), whose results are presented in Table I. Some articles in the literature suggest that a co-

continuous two-phase morphology is achieved when one phase is completely extracted without destroying the shape of the specimen.¹⁰⁻¹² The continuity of PS is quantitatively expressed by the weight fraction of PS, which is extracted by MEK. The dimensional stability of the sample with total extraction of the PS phase, characterizing a dual cocontinuous morphology, was observed at a composition corresponding to 90 wt % of PS for PS/EVA28 blends and to 80 wt % of PS for PS/EVA10 blends. The phase inversion and cocontinuity at high proportion of PS (65 to 75%) has also been observed in PS/HDPE blends.¹² The authors have

Table I Selective Extraction Experiments of PS Phase in PS/EVA Blends^a

PS/EVA10 Blends				PS/EVA28 Blends			
PS (wt %)	EVA10 (wt %)	PS Extracted Phase (wt %)	Comments	PS (wt %)	EVA28 (wt %)	PS Extracted Phase (wt %)	Comments
95	5	100	destroyed	95	5	100	destroyed
90	10	100	destroyed	90	10	96 ^b	intact
80	20	98 ^b	intact	80	20	85	intact
70	30	90	intact	70	30	80	intact
60	40	80	intact	60	40	75	intact
50	50	70	intact	50	50	65	intact

^a Selective extraction of PS phase by using methyl ethyl ketone as a solvent.

^b Phase inversion point.

associated these results with elasticity phenomena. In this case, HDPE has a tendency to encapsulate the PS phase due to its higher elasticity.^{12–14}

Shear viscosity vs. shear rate plots of EVA10, EVA28, and PS samples are compared in Figure 2. At high shear viscosity, both EVA10 and EVA28 copolymers are more viscous than pure PS. Therefore, the phase inversion point at high proportion of PS in PS/EVA blends may be attributed to the high elasticity of the EVA phase by analogy with the studies concerning PS/HDPE blends.^{12–14} The lower viscosity of EVA28 may also explain the lower amount of this copolymer (10 wt %) in the PS/EVA blends to achieve the phase inversion point, when compared to EVA10.

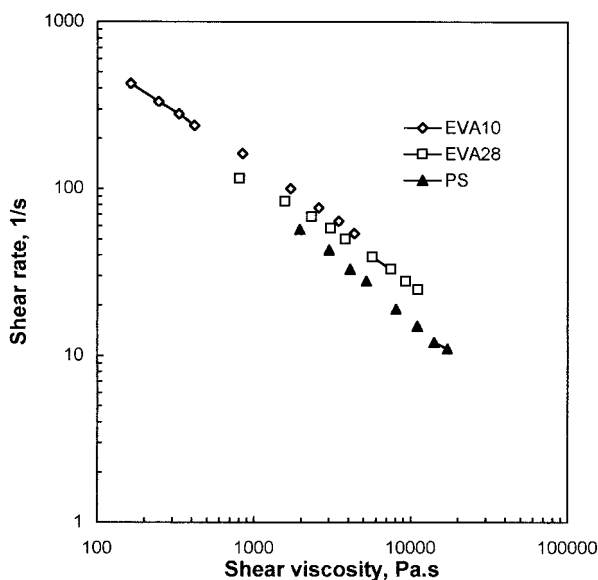


Figure 2 Shear viscosity versus shear rate of (a) EVA10, (b) EVA28, and (c) PS, at 205°C.

Melt Blends of PS with EVA-g-PS

Impact modification of thermoplastic polymers has been usually performed by adding a rubber phase. A typical example includes high-impact polystyrene (HIPS), which is normally manufactured by graft copolymerization of styrene onto the polybutadiene (PBD) backbone, followed by blending with the polystyrene homopolymer.¹⁵ The *in situ* graft copolymerization technique has been employed in EVA-based polymer systems. For example, ethylene–vinyl acetate copolymers (EVA) have been grafted with styrene, vinyl chloride, and methyl methacrylate by mixing EVA and the corresponding monomer in the presence of free radical initiators.^{16,17} The resulting materials present good mechanical and impact properties associated to better ageing resistance when compared to unsaturated elastomers.^{18,19}

As reported in literature,^{2,20} graft or block copolymers may be more effective as impact modifiers in one-component thermoplastic if the segments of these copolymers are well adjusted with the chains of the matrix polymers. This good control of molecular structure in graft copolymers is hard to achieve by *in situ* grafting reactions. Therefore, we decided to synthesize two different EVA-g-PS graft copolymers and to investigate their performance in the PS matrix. The results concerning the mechanical properties of the pure PS or their blends with EVA-g-PS are given in Table II. For comparison, the mechanical behavior of an injection-molded HIPS sample is also presented. The tensile properties of polystyrene were not substantially affected by the presence of the RG36 graft copolymer, except the tensile modulus, which increases with the addition of 1 phr of this copolymer. An increase in the notched Izod impact strength in PS/EVA-g-PS (RG36)

Table II Mechanical Properties of Polystyrene/EVA-g-PS Binary Blends

Mechanical Properties	PS	PS/RG36 ^a (100 : 1 phr)	PS/RG36 ^a (100 : 5 phr)	PS/RG44 ^b (100 : 5 phr)	HIPS
Elongation at break, %	2.1 ± 0.1	2.6 ± 0.3	3.1 ± 0.2	21.8 ± 1.1	36.0 ± 7.0
Ultimate tensile					
Strength, MPa	44.0 ± 0.3	42.8 ± 0.4	42.0 ± 0.4	26.2 ± 0.2	23.9 ± 0.4
Tensile modulus, MPa	2664 ± 54	2931 ± 36	2914 ± 59	2466 ± 29	1737 ± 46
Notched Izod Impact					
strength, J/m	146 ± 23	193 ± 12	197 ± 8	272 ± 12	1058 ± 11

^a RG36 graft copolymer: M_n of PS-grafted segments = 136,400; EVA/PS ratio (wt %) = 24/76.

^b RG44 graft copolymer: M_n of PS-grafted segments = 18,800; EVA/PS ratio (wt %) = 45/55.

blends was also observed. The mechanical behavior was not affected by the proportion of this graft copolymer in the binary blends.

The RG44 graft copolymer exerts a stronger

influence on tensile properties and impact strength. Indeed, a substantial improvement on ϵ_B was achieved by adding 5 phr of this copolymer into the PS matrix. The impact strength also pres-

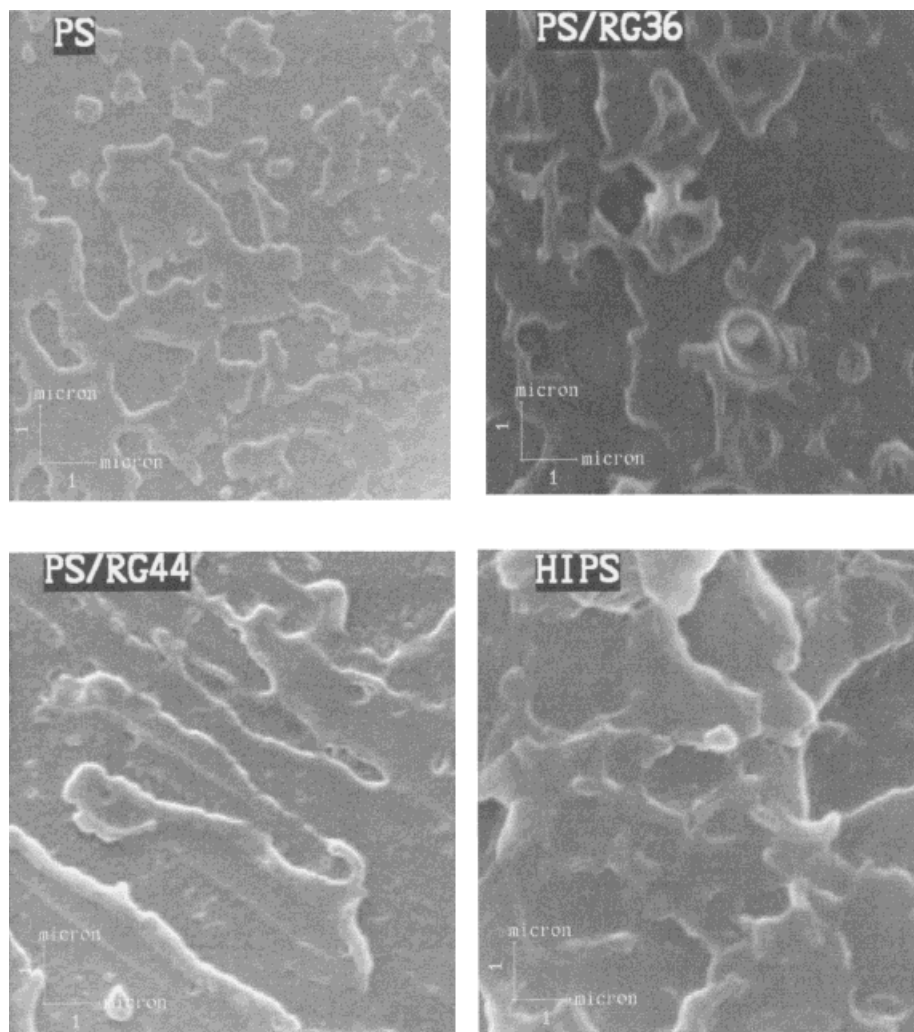


Figure 3 Scanning electron microscopy of impact fracture surface of PS, the PS/EVA-g-RG36 blend, the PS/RG44 blend, and HIPS (15,000 \times).

Table III Mechanical Properties of PS/EVA10 Blends

Mechanical Properties	PS/EVA10 (90 : 10 wt %)			
	PS	Pure	with 5 phr of EVA- <i>g</i> -PS	
			RG36 ^a	RG44 ^b
Elongation at break, %	2.1 ± 0.1	14.7 ± 4.3	16.2 ± 2.5	20.9 ± 0.9
Ultimate tensile Strength, MPa	44.0 ± 0.3	24.6 ± 0.2	24.6 ± 0.6	20.6 ± 0.2
Young's modulus, MPa	2.2 ± 0.1	2380 ± 29	2537 ± 47	2219 ± 55
Notched Isod impact strength, J/m	146 ± 23	169 ± 12	177 ± 2	196 ± 7

^a RG36 graft copolymer: M_n of PS-grafted segments = 136,400; EVA/PS ratio (wt %) = 24/76.

^b RG44 graft copolymer: M_n of PS-grafted segments = 18,800; EVA/PS ratio (wt %) 45/55.

ents a better result. As observed in several other impact-modified thermoplastic systems,^{15,21,22} the addition of EVA-PS graft copolymers is able to improve the mechanical properties of PS. These properties are, however, influenced by the chemical composition of these copolymers. The PS segments in the RG36 sample have a molecular weight of 136,000, which is similar to the molecular weight of the PS matrix ($M_n = 133,000$). According to the literature,⁴ the similarity of the molecular weights between the PS matrix and the PS segments in the graft copolymer should lead to a greater improvement in the elongation at break and impact resistance. Nevertheless, this behavior was not observed in our system. The elongation at break presents only a little increase with the addition of 5 phr of the RG36 graft copolymer.

Although the RG44 graft copolymer has shorter PS segments ($M_n = 18,400$), the elongation at break and impact resistance of the PS/RG44 (100 : 5 phr) blend are superior when compared to the blend with RG36. The most probable explanation for this behavior is based on the EVA/PS proportion by weight in these copolymers. The EVA/PS weight ratio in the RG44 graft copolymer was found to be 45 : 55 wt %. The RG36 graft copolymer contains a lower amount of EVA (EVA/PS = 26 : 74 wt %). The higher amount of the EVA soft component in the RG44 sample results on a substantial increase of elongation at break and may enhance the partial microphase separation, which is responsible for the improved impact resistance. The ultimate tensile strength is also affected by the amount of EVA component in the graft copolymer. A higher amount of EVA results in a decrease of σ_B . In the studies concerning the mechanical properties of compatibilized polyeth-

ylene-polystyrene blends reported by Fayt et al.,³ the addition of HPB-*b*-PS into polystyrene resulted into a little increase on both σ_B and ε_B . Considering that the HPB proportion in the block copolymer used in the Fayt's experiments is similar to the EVA proportion in the RG44 graft copolymer, the lower value of σ_B found in our experiments may be related to the softer nature of EVA.

As observed in Table II, the impact performance of the PS/EVA-*g*-PS binary blends is still lower than HIPS. The last material displays improved elongation at break and impact strength values. Several factors must be contributing to its outstanding performance when compared to the PS/EVA-*g*-PS blends. One important feature to be considered is related to the overall amount of the soft component in the PS matrix. The RG44 graft copolymer, considered the best impact modifier between the EVA-*g*-PS samples used in our experiments, contains 45 wt % of EVA. Because this copolymer is present in the PS/EVA-*g*-PS blend at a proportion of 5 phr, the overall EVA content in the blend corresponds to 2.14 wt %. On the other hand, the rubber content in the HIPS sample corresponds to nearly 8 wt %, which is approximately four times higher than the EVA amount employed in our system. As reported in several articles, the impact strength increases with increase of the rubber content.^{21,22} Probably the low amount of EVA in the RG44 graft copolymer is not enough to provide an appropriated particle size and size distribution of the EVA particles, which should be responsible for a higher impact resistance. The chemical nature of the impact modifier must also be taken into account. Polybutadiene has a high elastomeric characteristic, while EVA used in the EVA-*g*-PS synthesis, is considered a thermoplastic due to the low vinyl

acetate content in the backbone (18 wt %). Therefore, polybutadiene particles must be more effective in dissipating the energy during impact measurements. Such effect is enhanced by the chemical crosslinking in the rubber phase.

The scanning electronic micrographs of pure polystyrene and their blends with the EVA-*g*-PS graft copolymers are shown in Figure 3. For comparison, the photography of the fracture surface of HIPS is also included. These photographs were taken from the surface of impact test specimens after impact measurements. Pure polystyrene is known to be a brittle material and exhibits typical brittle fracture. Practically no plastic deformation is accepted by this material. PS blended with 5 phr of the RG36 graft copolymer presents a little plastic deformation, indicating some ductile character of the fracture. In addition, some shear band growing from debonded domains are also observed. Similar plastic deformation and the formation of shear bands can also be suggested in the fracture of HIPS sample. It is curious to note, however, the presence of some nonuniform spherical domains along the PS matrix in the micrography of the PS/RG36 binary blend. The amount of EVA in this blend corresponds to 1.2 wt %, which is too small to present a visible phase separation. Therefore, these spherical domains may be constituted by graft copolymer with some encapsulated homopolymer chains. Because such domains are not evident in the PS/RG44 binary blend, it is supposed that the similarity between the molecular weights of the homopolymer matrix and the PS grafted segments in the RG36 copolymer, in addition to the low grafting frequency (0.018 mmol of graft/gram of copolymer) may be responsible for this type of morphology. The solubilization of the PS homopolymer in the polystyrene domains of styrene-butadiene triblock copolymer has also been suggested in the literature when the molecular weight of the PS terminal blocks approaches that of the PS homopolymer.²³

The PS/RG44 binary blend displays better mechanical properties than the PS/RG36 blend, as discussed. The fracture surface in the PS/RG44 blend shows also a higher plastic deformation, suggesting a higher ductility than the PS/RG36 blend. Moreover, a U-shaped pattern is observed, which is a characteristic feature of tear fracture.²⁴

PS/EVA/EVA-*g*-PS Ternary Blends

The effect of EVA-*g*-PS as interfacial agent in PS/EVA (90 : 10 wt %) blends was investigated. The mechanical properties of these blends, composed

with EVA10 (with lower VA content), are summarized in Table III. The noncompatibilized PS/EVA10 blend presents higher values of elongation at break and impact strength than pure polysty-

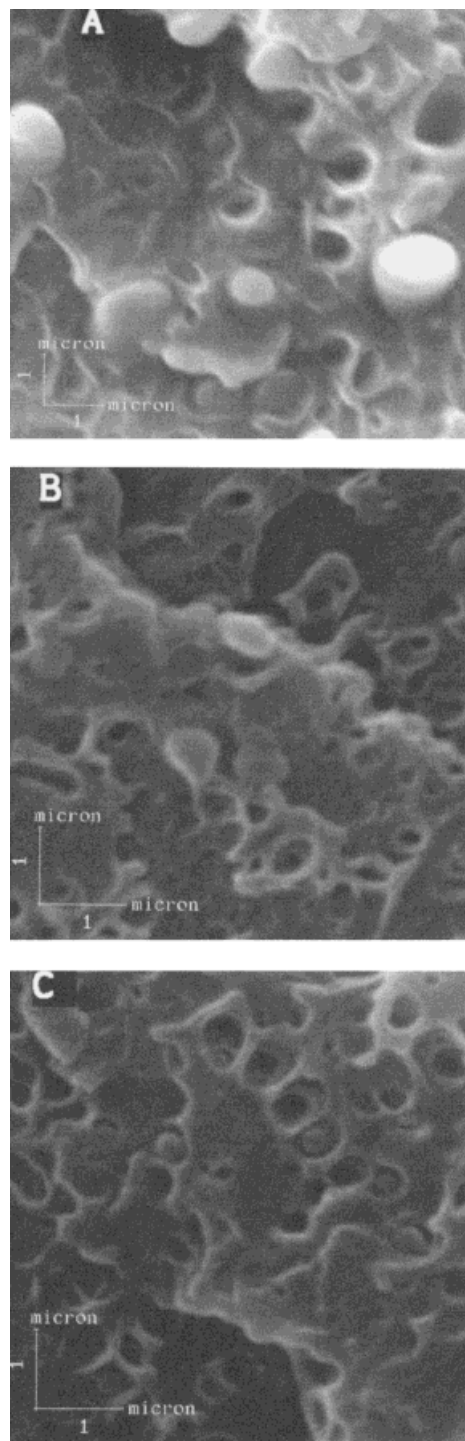


Figure 4 Scanning electron microscopy of fracture surface at room temperature of the PS/EVA10 blends (A) with 5 phr of RG36 (15,000 \times), (B) with 5 phr of RG44 (20,000 \times), and (C) pure blend (20,000 \times).

Table IV Mechanical Properties of PS/EVA28 Blends

Mechanical Properties	PS/EVA28 (90 : 10 wt %)			
	PS	Pure	with 5 phr of EVA- <i>g</i> -PS	
			RG36 ^a	RG44 ^b
Elongation at break, %	2.1 ± 0.1	7 ± 1	14 ± 3	18 ± 2
Ultimate tensile				
Strength, MPa	44.0 ± 0.3	21.2 ± 0.5	23.7 ± 0.5	22.5 ± 0.7
Young's modulus, MPa	2.2 ± 0.1	2224 ± 49	2448 ± 30	2381 ± 23
Notched Isod impact				
Strength, J/m	146 ± 23	151 ± 20	197 ± 9	229 ± 18

^a RG36 graft copolymer: M_n of PS-grafted segments = 136,400; EVA/PS ratio (wt %) = 24/76.

^b RG44 graft copolymer: M_n of PS-grafted segments = 18,800; EVA/PS ratio (wt %) 45/55.

rene. The addition of 5 phr of the RG36 graft copolymer does not exert any considerable influence on the blend properties. On the other hand, an improvement on these properties was reached with the presence of the RG44 graft copolymer, which has a higher EVA content when compared to the RG36 sample (see Table III). Figure 4 compares the morphological aspects of these blends. The photographs were taken from the surface of the fracture handled at room temperature. Non-compatible PS/EVA10 samples [Fig. 4(C)] present several holes and debonded domains, characteristics of low interfacial adhesion. The compatibilized blends [Fig. 4(A) and (B)] display some EVA domains well adhered to the PS matrix, indicating some interfacial adhesion between the blend components. The adhesion promoted by the RG36 graft copolymer [Fig. 4(A)] was not enough to improve the mechanical properties of the PS/EVA10 blend, probably because of the high particle size in the sample. The PS/EVA10 blend compatibilized with the RG44 graft copolymer sample presents a finer phase dispersion. This behavior can be observed in the micrography of Figure 3(B), taken at higher magnification than that related to the PS/EVA10/RG36 blend in Figure 3(A).

The influence of the EVA-*g*-PS graft copolymer on the mechanical properties of PS/EVA28 blends is more significative. As indicated in Table IV, an improvement on the elongation at break and impact resistance was achieved with the addition of 5 phr of the graft copolymer. Again, the RG44 sample exerts a higher influence on the mechanical performance.

CONCLUSIONS

The present investigation demonstrates that the addition of a small amount of EVA-*g*-PS graft co-

polymers provides an improvement on the mechanical properties of PS and PS/EVA blends. The performance of these graft copolymers depends on their structural feature. A more ductile material was obtained by blending PS or PS/EVA (90 : 10 wt %) with 5 phr of the RG44 graft copolymer, whose PS-grafted segments display a lower molecular weight ($M_n = 18,400$) than that of the PS matrix. These results are different from those reported in the literature. For example, Hu and co-workers⁴ have observed that the compatibilization of polystyrene/polyacrylate rubber blends by graft copolymers having poly(butyl acrylate) as the backbone and PS as the side chains, results in improved impact-resistant materials when these compatibilizing agents contain longer PS branches and fewer grafts. In our system, the better performance of the RG44 graft copolymer in these ternary blends may be related to the higher proportion of EVA in this copolymer and/or to the higher grafting frequency. The RG36 graft copolymer is characterized by a low grafting frequency and long PS branches whose molecular weight is close to that of the PS homopolymer. This structural feature may be responsible for the presence of large and debonded domains in the fractured surface of the PS/EVA-*g*-PS blend. Such a morphology suggests that the long PS segments should be mainly inside the domains encapsulating some homopolymer chains. In this case, the adhesion with the PS matrix is not as effective and, consequently, no substantial improvement on the mechanical properties was observed in the PS/RG36 binary blends.

The authors are indebted to Conselho Nacional de Desenvolvimento Científico e Tecnológico—CNPq, Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior—CAPES, CEPG-UFRJ, and PADCT-FINEP

for financial support. The authors would also like to thank Miss N. B. Sanches for the technical support in the microscopy analysis.

REFERENCES

1. D. R. Paul, in *Polymer Blends*, Vol. 2., D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978.
2. Ph. Teyssié, *Makromol. Chem., Macromol. Symp.*, **22**, 83 (1988).
3. R. Fayt, R. Jérôme, and Ph Teyssié, *J. Polym. Sci., Phys. Ed.*, **27**, 775 (1989); and references therein.
4. S. C. Tang, C. P. Hu, and S. K. Ying, *Polym. J.*, **22**, 70 (1990).
5. D. Heikens, N. Hoen, P. Barentsen, P. Piet, and H. Ladan, *J. Polym. Sci., Polym. Symp.*, **62**, 309 (1978).
6. R. V. Barbosa, B. G. Soares, and A. S. Gomes, *J. Appl. Polym. Sci.*, **47**, 1411 (1993).
7. R. V. Barbosa, B. G. Soares, A. S. Gomes, *Macromol. Chem. Phys.*, **195**, 3149 (1994).
8. R. C. L. Dutra, V. L. Lourenço, M. F. Diniz, M. F. P. Azevedo, R. V. Barbosa, and B. G. Soares, *Polym. Bull.*, **36**, 593 (1996).
9. K. W. Doak, in *Encyclopedia of Polymer Science and Engineering*, Vol. 6, J. I. Kroschwitz, Ed., Wiley, New York, 1986.
10. R. M. Ho, C. H. Wu, and A. C. Su, *Polym. Eng. Sci.*, **30**, 511 (1990).
11. C. J. Nelson, G. N. Avgeropoulos, F. C. Weissert, and G. G. A. Böhm, *Angew. Makromol. Chem.*, **60/61**, 49 (1977).
12. D. Bourry and B. D. Favis, *Technical Paper, vol. XLI, 53rd Annual Technical Conference, SPE*, 2001 (1995).
13. B. D. Favis and J. P. Chalifoux, *Polymer*, **29**, 1761 (1988).
14. F. Gubbels, S. Blacher, E. Vanlathem, R. Jérôme, R. Deltour, F. Brouers, and Ph. Teyssié, *Macromolecules*, **28**, 1559 (1995).
15. C. B. Bucknall, in *Comprehensive Polymer Science*, Vol. 7, G. Allen, and J. C. Bevington, Eds., Pergamon Press, London, 1989.
16. H. Bartl and D. Hardt, *Adv. Chem. Ser.*, **91**, 477 (1969).
17. I. Alberts, H. Bartl, and R. Kuhn, *Adv. Chem. Ser.*, **142**, 214 (1975).
18. N. Koyanagi, Jpn. Pat. 7214,713; *Chem. Abstr.*, **77**, 153135n (1972).
19. I. Iwami, T. Nishikage, and H. Kawasaki, Jpn. Pat. 7232,829; *Chem. Abstr.*, **78**, 112117k (1973).
20. D. Braum, M. Fisher, and G. P. Hellmann, *Macromol. Symp.*, **83**, 77 (1994).
21. B. K. Kim and G. S. Shin, *J. Appl. Polym. Sci.*, **48**, 945 (1993).
22. H. Keskkula, H. Kim, and D. R. Paul, *Polym. Eng. Sci.*, **30**, 1373 (1990).
23. S. L. Aggarwal and R. A. Livigni, *Rubber Chem. Technol.*, **51**, 775 (1978).
24. L. Engel, H. Klingele, G. W. Ehrenstein, and H. Schaper, *An Atlas of Polymer Damage*, Wolfe Publishing Ltd, Munich, 1981, translated by M. S. Welling.