# The Effect of Mercapto-Modified Ethylene–Vinyl Acetate (EVA) on Curing Parameters, Mechanical Properties, and Thermal Properties of Vulcanized Styrene–Butadiene Rubber (SBR)/EVA Blends

**Bluma G. Soares, Fabrício F. Alves, Marcia G. Oliveira, Ana C. F. Moreira**

*Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bl. J, Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brasil*

**ABSTRACT:** The effect of EVA functionalized with mercapto groups (EVALSH) on the compatibilization of SBR and EVA copolymer blends was investigated in vulcanized systems based on sulfur or dicumyl peroxide (DCP). The presence of EVALSH resulted in an improvement of the tensile properties, indicating the reactive compatibilizing effect of this compound. The best mechanical performance was achieved with the sulfur-curing system for both compatibilized and noncompatibilized blends. The blend systems were also analyzed by scanning electron microscopy, differential scanning calorimetry, and dynamic-mechanical analysis. The crystallinity of the EVA phase was significantly affected by the presence of the EVALSH, whereas no substantial change was detected on the damping properties or the glass transition temperature of the SBR phase. Considering the aging properties, the presence of EVALSH increases the thermal stability of the blends vulcanized with DCP. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 239–249, 2002

**Key words:** blends; compatibilization; elastomers

## INTRODUCTION

SBR is a general purpose synthetic rubber that presents high filler-loading capacity, good flex resistance, crack-initiation resistance, and abrasion resistance. However, as other unsaturated rubbers, its aging resistance is not good, due to unsaturation of the butadiene component. In order to minimize the oxidative degradation of SBR during service at high temperature, it is important to blend it with a saturated or low unsaturated polymer. EVA copolymers may be considered a good partner for this purpose because of their excellent aging resistance, weather resistance, and mechanical properties. In addition, they can provide an easier melt processability to the corresponding blends.

Blends of EVA with several unsaturated rubbers such as polychloroprene,[1–4] nitrile rubber,[5–7] and natural rubber[8–10] have been developed. SBR/EVA blends have been also reported to produce thermoplastic moldable shoe sole material by dynamic vulcanization.[11] Except for polychloroprene/EVA blends, which have been reported to be miscible in all proportion,[1] the other EVA–rubber blends are incompatible, and normally display gross phase separation morphologies and low physical attraction forces across the phase boundaries, which contribute for a decreasing of their mechanical performance. These problems can be minimized by the addition of a third component able to act at the blend interface, thus promoting an effective interaction between the phases.[12,13] When one of the blend component is an unsaturated rubber, the compatibilization can be successfully achieved using polymers carrying mercapto groups because this group normally reacts with the double bond of unsaturated polymers.[14–16]

Recently, we have introduced mercapto groups on the hydrolized EVA copolymer and used this mercapto-functionalized EVAL (EVALSH) in natural rubber/EVA[17–21] and nitrile rubber/EVA blends.[22] A large amount of insoluble material has been isolated from nonvulcanized blends, indicating that the mercapto groups have reacted with the double bond of the high-diene rubbers during blending, which characterizes the reactive compatibilization. These compatibilized blends also displayed better mechanical performance and ageing properties.

The reactive compatibilization of nonvulcanized SBR/EVA blends by EVALSH has been also observed in our previous work.[23] Insoluble material has been also formed after blending, whose composition involved both component, i.e., the SBR and the EVALSH, which is also an indication of reactive compatibilization.

In this paper, we discuss the results concerning the compatibilization effect of EVALSH in vulcanized SBR/EVA blends. For these studies, the curing processes were performed with the dicumyl peroxide system (DCP) and sulfur system [S/dibenzothiazyl disulfide (MBTS)/tetramethyl thiuram disulfide (TMTD)]. Dicumyl peroxide can crosslink both SBR and EVA components, whereas sulfur is able to crosslink only the unsaturated SBR phase.

## EXPERIMENTAL

### Materials

SBR [containing 23 wt % styrene; = 125,000; Mooney viscosity (ML 1 +4 at 100°C = 52] was kindly supplied by Petroflex Ind. Com. Ltda., Brasil. EVA copolymer [containing 18 wt % of vinyl acetate; melt flow index (MFI) = 2.3 g/10 min at 120°C] was kindly supplied by Petroquímica Triunfo S. A., Brasil. EVALSH was synthesized in our laboratory by esterification of hydrolyzed EVA with mercaptoacetic acid.[24] The mercapto content in the EVALSH copolymer was in the range of 69–73 mmol/100 g of copolymer, as determined by thermogravimetric (TGA) and Fourier transform infrared (FTIR) analyses.[24] Zinc oxide (ZnO), stearic acid, sulfur, MBTS, TMTD, and DCP were of laboratory reagent grade.

### Blend preparation

The blends were prepared at 80°C, in a Haake internal mixer model Rheomix 600, using Cam rotors at 60 rpm. SBR was blended with EVALSH for 2 min in order to promote interactions between the mercapto groups and the double bond of the diene rubber. Then, EVA was added and blended for 7 min. The blends were compounded in a Berstoff two-roll mill, operating at 80°C and 20 rpm. The compounding recipes of these blends are given in Table I.

The cure characteristics of the mixes were determined by using an oscillating disk rheometer (ODR) (Tecnologia Industrial-Argentina) at 160°C and 1 arc degree, following the ASTM D-2084-81 method. The cure rate, $RH$, is defined by the ratio between torque and time as determined from the following relationship:

$$RH = \frac{M_{90} - M_{s1}}{t_{90} - t_{s1}}$$

**TABLE I**
**Formulations of Mixes in Phr (g per 100 g of Rubber)**

| Ingredients | Sulfur system | DCP system |
|---|---|---|
| Polymer | 100.0 | 100.0 |
| EVALSH | 0–5 | 0–5 |
| Zinc oxide | 5.0 | — |
| Stearic acid | 0.5 | — |
| MBTS | 2.0 | — |
| TMTD | 1.0 | — |
| Sulfur | 0.3 | — |
| DCP | — | 0.7 |

where $M_{90}$ corresponds to the value of 90% of the maximum torque, $M_{s1}$ is the minimum torque, $t_{90}$ is the time required to achieve 90% of the maximum torque (optimum cure time) and $t_{s1}$ is the scorch time.

The specimens for mechanical testing were compression-molded into sheets of 2 mm thickness in an electrically heated laboratory hydraulic press at 160°C, under a 6.7 MPa pressure and at the optimum cure time ($t_{90}$) as determined by the rheometric analysis.

### Measurement of the mechanical properties

Tensile–strain experiments were performed by means of an Instron 4204 testing machine at room temperature with a speed of 100 mm/min following DIN procedure 53504. The samples were conditioned at 21°C and 53% of air humidity for 24 h before the testing.

### Degree of equilibrium swelling measurement

Cured test pieces of dimension 20 × 10 × 2 mm were swollen in toluene until equilibrium swelling. After reaching the equilibrium, the swollen test pieces were weighted, then dried under vacuum and weighted again. The swollen and deswollen weights were used to calculate the volume fraction of rubber in the network swollen to equilibrium, $V_r$, according to the following expression:

$$V_r = \frac{D \times \rho_r^{-1}}{D \times \rho_r^{-1} + (S - D) \times \rho_s^{-1}}$$

where $D$ is the deswollen weight, $S$ the swollen weight, $\rho_r$ the density of rubber blend, and $\rho_s$ the density of solvent.

### Aging experiments

Accelerated aging of the compression molded specimens was carried out in an air-circulating oven at 70°C for 24 and 72 h.

**TABLE II**
**Curing Parameters of SBR/EVA Blends as Function OF composition, Curing System,**
**and Compatibilization (Curing Temperature = 160°C)**

| Blend composition (phr) | | | $t_{s1}$ (min) | $t_{90}$ (min) | $t_{90} - t_{s1}$ (min) | $M_{s1}$ (dN m) | $M_{90}$ (DN m) | $[M_{90} - M_{s1}]$ (dN m) | $RH$ (dN m/min) |
|---|---|---|---|---|---|---|---|---|---|
| SBR | EVA | EVALSH | | | | | | | |
| | | | | Sulfur system | | | | | |
| 100 | 0 | 0 | 3.0 | 9.0 | 6.0 | 10 | 60 | 50 | 8.3 |
| 100 | 0 | 5 | 2.2 | 8.6 | 6.4 | 13 | 60 | 47 | 7.3 |
| 80 | 20 | 0 | 3.8 | 11.5 | 7.7 | 9 | 49 | 40 | 5.2 |
| 80 | 20 | 5 | 2.6 | 10.5 | 7.9 | 12 | 49 | 37 | 4.7 |
| 70 | 30 | 0 | 3.8 | 11.5 | 7.7 | 8 | 40 | 32 | 4.1 |
| 70 | 30 | 5 | 2.5 | 10.0 | 7.5 | 10 | 40 | 30 | 4.0 |
| 60 | 40 | 0 | 4.6 | 13.0 | 8.4 | 7 | 28 | 21 | 2.5 |
| 60 | 40 | 5 | 2.8 | 12.5 | 9.7 | 8 | 28 | 20 | 2.1 |
| 50 | 50 | 0 | 5.8 | 13.0 | 7.2 | 5 | 17 | 12 | 1.7 |
| 50 | 50 | 5 | 3.9 | 11.0 | 7.1 | 7 | 17 | 10 | 1.4 |
| | | | | DCP system | | | | | |
| 100 | 0 | 0 | 1.0 | 19.0 | 18.0 | 12 | 69 | 57 | 3.2 |
| 100 | 0 | 5 | 1.4 | 22.0 | 21.6 | 15 | 88 | 73 | 3.5 |
| 80 | 20 | 0 | 1.8 | 20.0 | 18.2 | 11 | 62 | 51 | 2.8 |
| 80 | 20 | 5 | 1.8 | 22.0 | 20.2 | 15 | 67 | 52 | 2.6 |
| 70 | 30 | 0 | 1.8 | 23.0 | 21.2 | 11 | 53 | 42 | 2.0 |
| 70 | 30 | 5 | 1.9 | 26.0 | 24.1 | 11 | 52 | 41 | 1.7 |
| 60 | 40 | 0 | 2.4 | 23.0 | 20.6 | 8 | 37 | 29 | 1.4 |
| 60 | 40 | 5 | 2.4 | 25.0 | 22.6 | 9 | 33 | 24 | 1.1 |
| 50 | 50 | 0 | 2.4 | 22.0 | 19.6 | 10 | 36 | 26 | 1.3 |
| 50 | 50 | 5 | 2.5 | 28.0 | 25.5 | 9 | 26 | 17 | 0.7 |

## Blend characterization

The crystallinity of the EVA phase in the blends was determined by using a differential scanning calorimeter (Perkin-Elmer, model DSC7). The samples were heated under nitrogen atmosphere at 10°C/min to 200°C, then rapidly cooled to −30°C and heated again at 10°C/min.

Dynamic mechanical measurements were carried out on a dynamic mechanical thermal analyzer, Rheometric Scientific MKIII. The experiment was conducted in a bending mode at a frequency of 1 Hz. The temperature was increased at 2°C/min over the range of −100–30°C.

Scanning electron microscopy (SEM) was performed on a Zeiss DSM 160 equipment using a backscattered electron detector and a voltage of 20 kV. The samples were cryogenically fractured and the surface was treated with osmium tetroxide ($OsO_4$) for 5 min in order to stain selectively the unsaturated phase. The samples were first coated with carbon.

## RESULTS AND DISCUSSION

### Curing characteristics

Table II presents the vulcanization parameters of SBR/EVA blends with different compositions, as functions of curing system and compatibilization. Blends vulcanized with both DCP and sulfur systems

present an increase of scorch time with increase of the EVA content in the blend. This result may be attributed to the dilution of part of the curatives inside the EVA phase, resulting in a decrease of the curative concentration in the SBR phase and consequently a delay of the curing process.

In both the sulfur and DCP systems, the minimum and maximum torque decrease with the increase of the EVA content in the blend. Since the difference between maximum and minimum torque, $[M_{90} - M_{1s}]$, is normally related to the crosslink degree, these results suggest a decrease of the crosslink den-
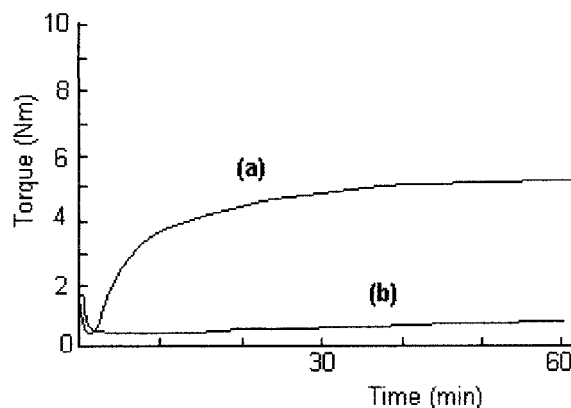


**Figure 1** Torque curves of EVA containing 0.7 phr of DCP (a) without EVALSH and (b) with 5 phr of EVALSH.

**TABLE III**
**Volume Fraction of Rubber in the Network Swollen to Equilibrium ($V_r$) of SBR/EVA Blends,**
**as a Function of Blend Composition and Compatibilization**

| Blend composition (phr) | | Sulfur system | | DCP system | |
| --- | --- | --- | --- | --- | --- |
| SBR | EVA | Without EVALSH | With 5 phr of EVALSH | Without EVALSH | With 5 phr of EVALSH |
| 100 | 0 | 0.14 | 0.16 | 0.17 | 0.21 |
| 80 | 20 | 0.14 | 0.18 | 0.20 | 0.24 |
| 70 | 30 | 0.15 | 0.21 | 0.22 | 0.26 |
| 60 | 40 | 0.22 | 0.23 | 0.27 | 0.28 |
| 50 | 50 | 0.23 | 0.22 | 0.28 | 0.30 |

sity as the EVA content in the blend increases. As observed in Table II, the $[M_{90} - M_{1s}]$ values are generally higher in blends vulcanized with DCP probably because of its ability to promote the vulcanization of both SBR and EVA components and also because of the structure of crosslinks formed during the vulcanization with DCP, which is characterized by stable and rigid carbon–carbon bonds.

The presence of EVALSH resulted in a little increase of minimum torque ($M_{1s}$), which can be related to an increase of the blend viscosity as a consequence of the reactions, which occur during blending process, between the double bond of the SBR phase and the mercapto groups of the compatibilizing agent. Such reactions were confirmed in our previous report concerning the compatibilization of nonvulcanized SBR/EVA blends.[23] In that study, we have observed the formation of insoluble material in blends containing EVALSH. The analysis of this insoluble material by FTIR spectroscopy revealed the presence of both EVALSH and SBR.

The addition of EVALSH resulted in a decrease of the scorch time in sulfur-vulcanized blends, although the overall cure rate was not significantly affected. The difference between the maximum and minimum torque $[M_{90} - M_{1s}]$ presented a little decreasing with the compatibilization for blends vulcanized with the

sulfur system, indicating that the crosslink degree was not significantly influence by the presence of EVALSH.

In the case of DCP vulcanized blends, this behavior depends upon the blend composition. The addition of 5 phr of EVALSH in the DCP-vulcanized SBR results in a substantial increase of maximum torque, indicating a considerable increase of the crosslink degree. As the amount of SBR in the blend decreases, the difference between $[M_{90} - M_{1s}]$ values between compatibilized and noncompatibilized blends becomes very small (80–70 phr of SBR). However, for blends containing 50% of SBR, the compatibilizing effect displays an opposite behavior, that is, the $[M_{90} - M_{1s}]$ decreases with the compatibilization. This behavior may be explained as follows: The primary free radicals originated from the DCP decomposition (RO•) give rise to a crosslink process inside both SBR and EVA phases, although it should be faster inside the SBR phase because of the high reactivity of the unsaturated rubber toward free radical attack. The RO• species or even the free radicals formed in the polymer backbone (SBR or EVA) may also be deactivated by the mercapto groups of EVALSH, since it is a well-known free radical chain transfer agent. When the system is composed by SBR, the curing is faster then the deactivation and occurs together with the addition of mercapto
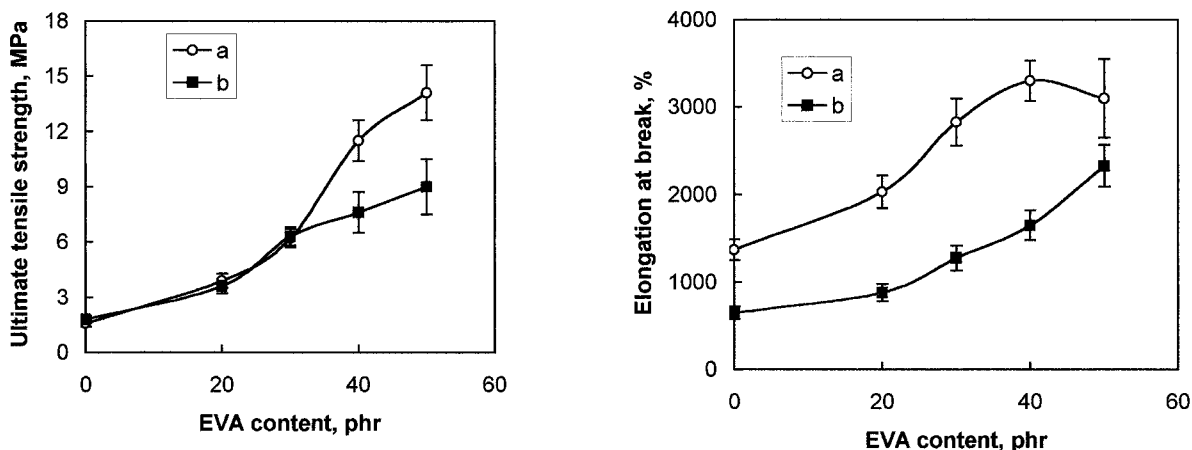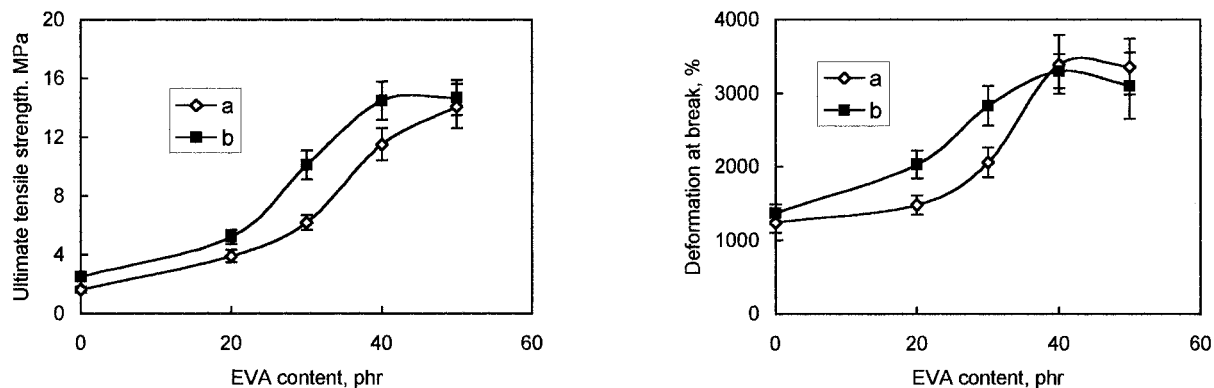


**Figure 2** Tensile properties of noncompatibilized SBR/EVA and vulcanized with the (a) sulfur and (b) DCP systems.

**Figure 3** Tensile properties of SBR/EVA blends vulcanized with the sulfur system (a) without EVALSH and (b) with 5 phr of EVALSH.

groups inside the SBR backbone. All these processes contribute to an increase of the torque. When the blend contains a significant amount of EVA, the deactivation process becomes important because part of EVALSH must be inside the EVA phase and the curing of this phase is slow. This hypothesis has been confirmed by studying the curing behavior of both EVA pure component and EVA/EVALSH binary blend in the presence of DCP. As observed in Figure 1(a), DCP promotes the vulcanization of the EVA matrix, as expected. However, the addition of 5 phr of EVALSH in the system resulted in an almost complete suppression of the vulcanization of the EVA matrix [see Fig. 1(b)], indicating that the primary free radicals originated from DCP were consumed by the EVALSH.

### Swelling degree

The degree of equilibrium swelling can also provide additional information concerning the crosslink degree. Table III presents these results for compatibilized and noncompatibilized SBR/EVA blends of different compositions, as a function of the curing system. In all systems, the $V_r$ values increase with the increase of the

EVA content in the blend, whereas the maximum torque obtained from optical rotary dispersion (ORD) measurements decreases. The torque values are normally related to the crosslink degree. On the other hand, the $V_r$ values depend upon the crosslink degree and also the polymer–solvent interactions. In rubber systems constituted by only one component, the increase of $V_r$ is usually followed by an increase of the torque values, both being proportional to the crosslink degree. In elastomer blends, this comparison cannot be made. For example, in SBR/EVA blends, the degree of swelling must be different in each phase. For the same crosslink degree, SBR should swell to a larger extent because it has more affinity toward toluene than EVA. Therefore, a lower degree of swelling (higher $V_r$ values) in blends with higher EVA content may be mainly attributed to the lower ability of this component to swell.

However, for the same blend composition, the $V_r$ values may be related to the crosslink degree. In this sense, blends with the same composition and vulcanized with DCP always display higher values of $V_r$ than those vulcanized with the sulfur system, because of the higher crosslink degree and also because the
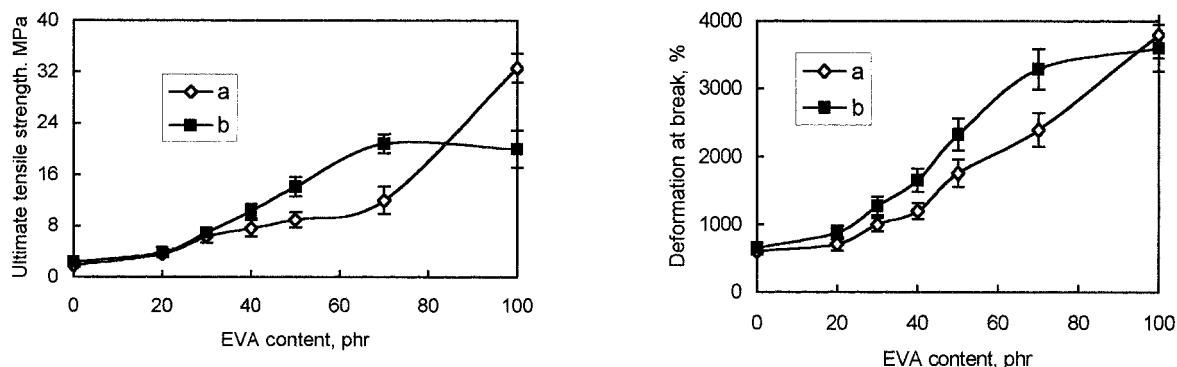


**Figure 4** Tensile properties of SBR/EBA blends vulcanized with the DCP system (a) without EVALSH and (b) with 5 phr of EVALSH.
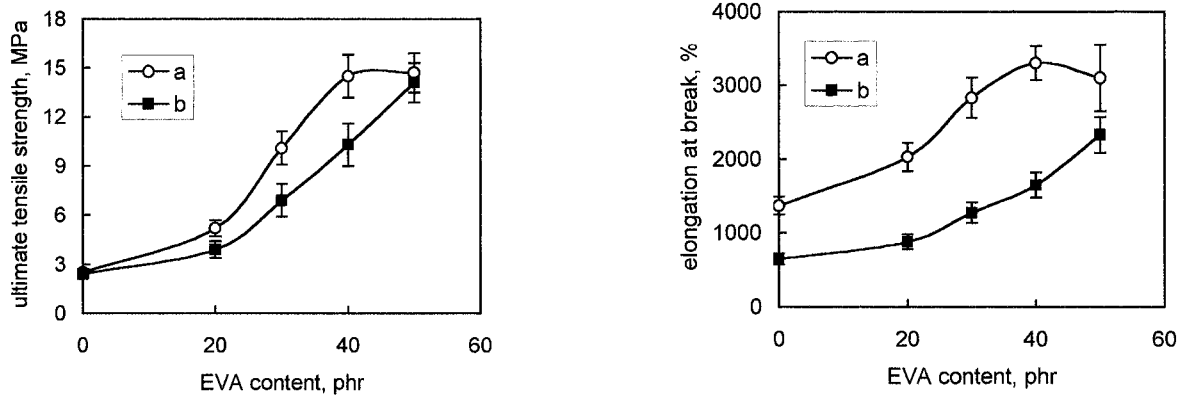
**Figure 5** Tensile properties of compatibilized SBR/EVA with 5 phr of EVALSH and vulcanized with the (a) sulfur and (b) DCP systems.

structure of the crosslinks. These results are in agreement with those of maximum torque found in ORD experiments.

As also observed in Table III, the addition of 5 phr of EVALSH resulted in a little increase of $V_r$ in both sulfur- or DCP-based curing systems. However, except for the DCP-vulcanized system containing 100 phr of SBR sample, all other blends presented a decrease of the torque values obtained from ORD measurements. These different behaviors may be better related to the morphology achieved with the compatibilization. As discussed later, the addition of EVALSH resulted in better dispersion of the EVA phase. Since EVA has lower swelling ability, it will restrict the swelling of the SBR phase, contributing toward an increase of $V_r$ of the system.
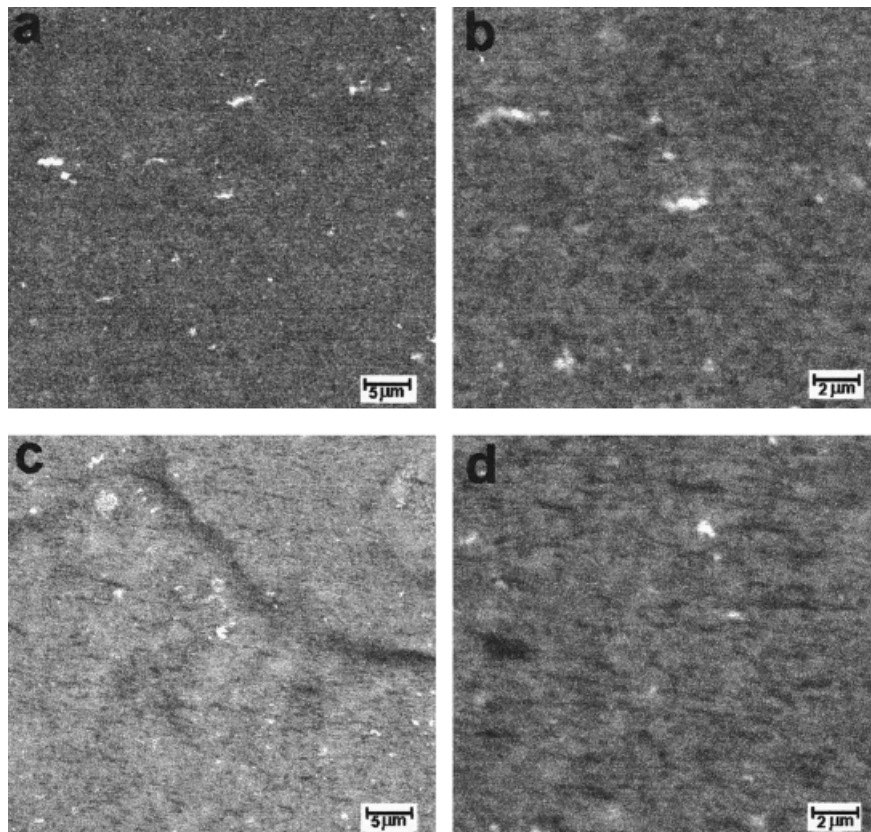


**Figure 6** SEM micrographs of SBR/EVA (50:50 phr) blends vulcanized with sulfur: (a) with EVALSH (2000× magnification), (b) without EVALSH (5000× magnification), (c) with 5 phr of EVALSH (2000× magnification), and (d) with 5 phr of EVALSH (5000× magnification).
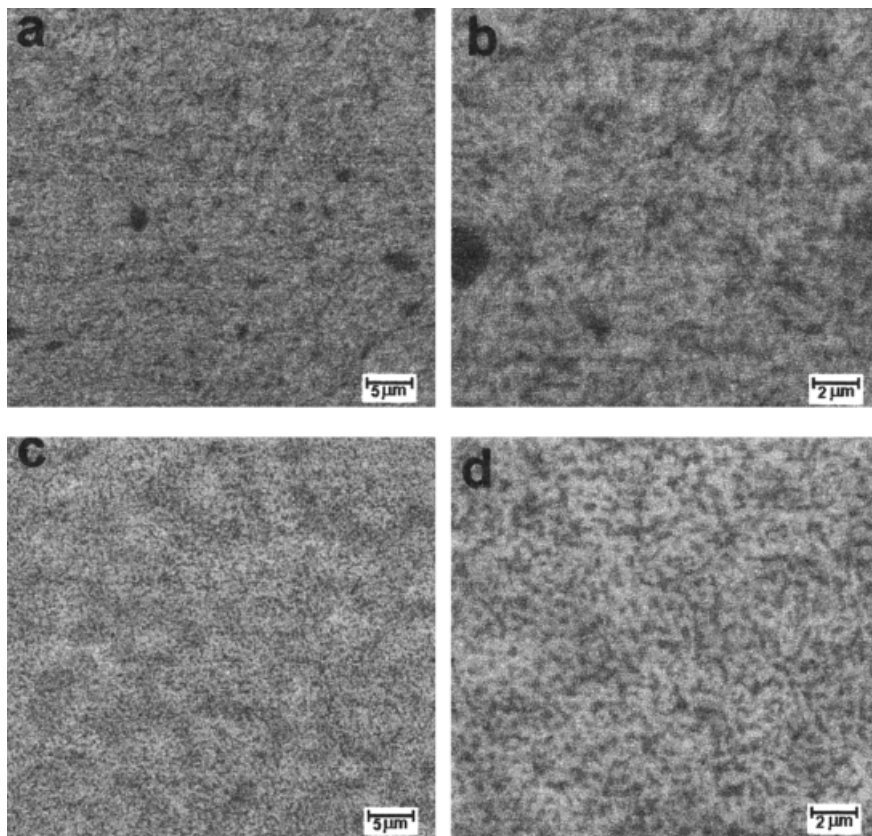
**Figure 7** SEM micrographs of SBR/EVA (50:50 phr) blends vulcanized with DCP: (a) with EVALSH (2000× magnification), (b) without EVALSH (5000× magnification), (c) with 5 phr of EVALSH (2000× magnification), and (d) with 5 phr of EVALSH (5000× magnification).

## Mechanical properties

The effect of the curing system on the tensile properties of SBR/EVA blends is illustrated in Figure 2, as a function of the blend composition. For blends with EVA content up to 30 phr, the tensile strength values are similar for both curing systems employed. Beyond this point, the sulfur-based curing system resulted in a better tensile strength. Concerning deformation at break, the vulcanization with peroxide (curve b) displays lower deformation probably because of the higher crosslink degree.

**TABLE IV**
**Crystallinity Behavior of the EVA Phase in SBR/EVA (50:50 phr) Blends as a Function**
**of the Compatibilization and Curing System**

| EVA (phr) | SBR (phr) | EVALSH (phr) | $\Delta H$ (J/mol) | | Crystallinity ($\chi$) (%) | | $T_m$ (°C) |
|---|---|---|---|---|---|---|---|
| | | | Theor.[a] | Esp.[b] | Theor.[c] | Exp.[d] | |
| Blends vulcanized with sulfur system | | | | | | | |
| 50 | 50 | 0 | 21.1 | 20.7 | 16 | 15.8 | 85.4 |
| 50 | 50 | 5 | 21.1 | 15.8 | 16 | 12.0 | 84.9 |
| Blends vulcanized with DCP system | | | | | | | |
| 50 | 50 | 0 | 21.1 | 19.8 | 16 | 15.0 | 83.9 |
| 50 | 50 | 5 | 21.1 | 15.7 | 16 | 12.0 | 85.5 |

[a] $\Delta H$ calculated by the expression = $42.2x[EVA]/100$.
[b] $\Delta H$ determined from the area of the melting endotherm.
[c] Fractional crystallinity calculated from the $\Delta H$ values, assuming that 42.2 J/mol corresponds to 32% of crystallinity of EVA18.
[d] Crystalinity determined from the experimental values of $\Delta H$.
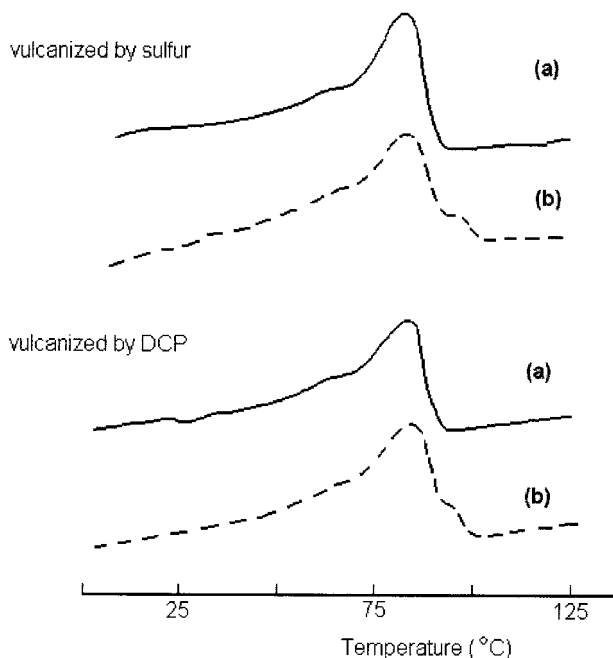
**Figure 8** DSC curves of vulcanized SBR/EVA (50:50 phr) blends (a) without EVALSH and (b) with 5 phr of EVALSH.

The effect of EVALSH on the mechanical properties of SBR/EVA blends was also studied as a function of blend composition. Figure 3 illustrates the mechanical behavior of blends vulcanized with the sulfur system. The addition of 5 phr of EVALSH resulted in an increasing of the ultimate tensile strength and elongation at break. These phenomena were more important in blends at a composition around 30 phr of SBR. The compatibilization was also efficient in blends vulcanized with DCP. As observed in Figure 4, there is a significant improvement of both ultimate tensile strength and elongation at break with the addition of EVALSH. Although the presence of EVALSH im-
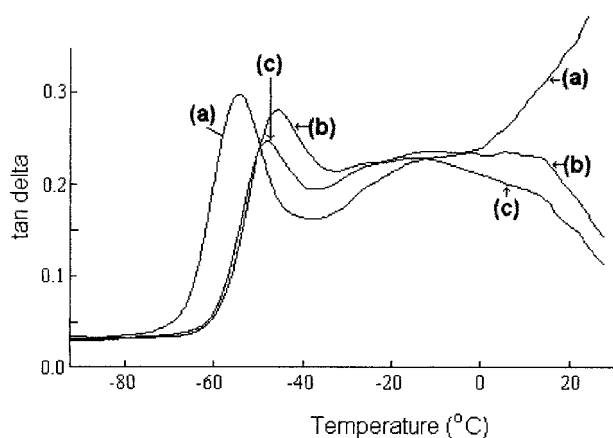


**Figure 9** Damping properties of SBR/EVA (50:50 phr) blends as a function of the vulcanized system: (a) nonvulcanized blend, (b) vulcanized with the sulfur system, and (c) with DCP.
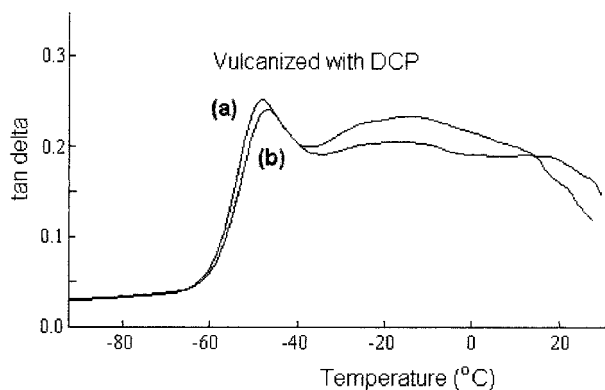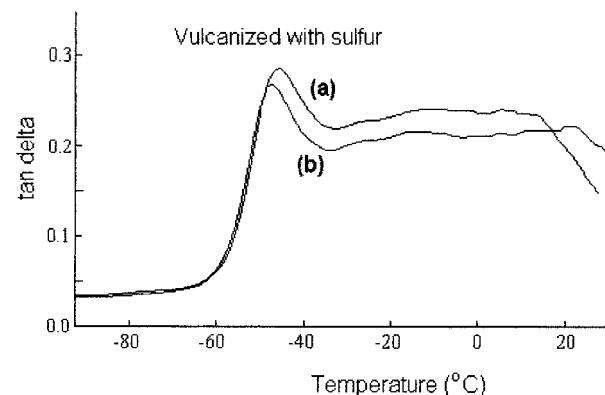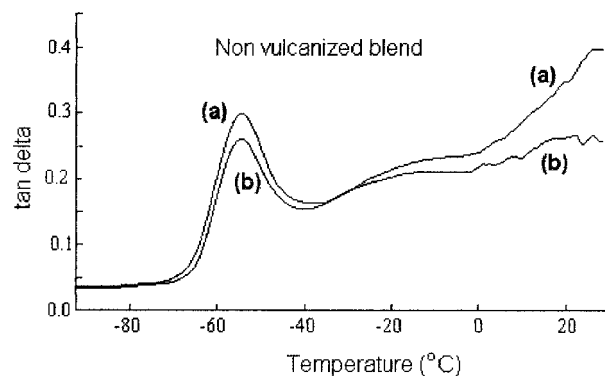


**Figure 10** Damping properties of SBR/EVA (50:50 phr) blends (a) without EVALSH and (b) with 5 phr of EVALSH.

proves the mechanical properties of both sulfur and DCP vulcanized blends, the best properties were achieved with the sulfur system, as indicated in Figure 5.

**Morphological aspects**

The micrographs of the SBR/EVA (50:50 phr) blend vulcanized with the sulfur system are presented in Figure 6. The gray region corresponds to the SBR phase, which was stained by $OsO_4$ and the dark points are related to the unstained EVA phase. Both noncompatibilized and compatibilized blends present well dispersed phase morphology although that containing
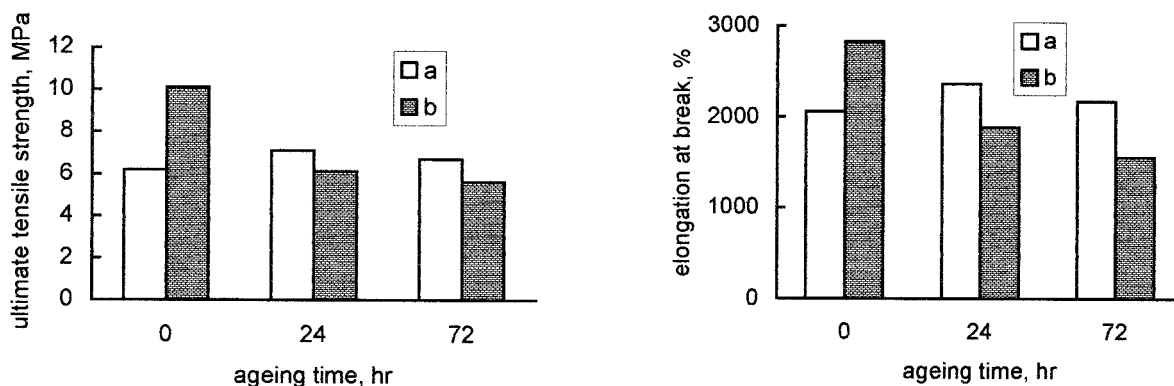
**Figure 11** Variation of the tensile properties of sulfur-vulcanized SBR/EVA (70:30 phr) blends with thermal ageing (a) without EVALSH and (b) with 5 phr of EVALSH.

5 phr of EVALSH [Fig. 6(c)] displays a more elongated EVA phase (black region). This behavior is better illustrated in the micrograph taken at higher magnification [Fig, 6(d)] and may be attributed to an increasing of the viscosity of the SBR phase in compatibilized blend as a consequence of the interaction of the mercapto groups of EVALSH and the unsaturated rubber phase. This difference in viscosity contributes for a higher deformation of the EVA phase in compatibilized blend. An increasing of the viscosity with the reactive compatibilization was also observed in nonvulcanized nitrile rubber/EVA blends and compatibilized with EVALSH.[25]

The morphologies of the SBR/EVA (50:50 phr) blend vulcanized with the DCP system are presented in Figure 7. In these cases, the co-continuous morphology is evident. The presence of EVALSH resulted in a more homogeneous morphology. The difference in morphology with the curing system may be attributed to the ability of DCP in vulcanizing also the EVA phase. The crosslink formation inside this phase resulted in an increase of its viscosity, which make the dispersion more difficult. These morphological differences related to sulfur and DCP vulcanized blends may explain the best mechanical performance of the sulfur system as vulcanizing system in both compatibilized and noncompatibilized blends.

### Thermal analysis

DSC analyzed the effect of the compatibilization on thermal properties. The melting temperature ($T_m$), fractional crystallinities, $\chi_c$, and heat of fusion ($\Delta H$) of EVA and some blends are reported in Table IV. DSC results of compatibilized and noncompatibilized blends are compared in Figure 8, for blends cured with sulfur or DCP systems. The area of the melting endotherm was reported as the heat of fusion. The crystallinity of EVA was established as 32%, according to the literature data for EVA containing 18 wt % of vinyl acetate.[8] The fractional crystallinities of the

blends were calculated from the $\Delta H$ values, assuming that EVA18 is 32% crystalline and present a heat of fusion of 42.2 J/mol. This value of heat of fusion was obtained from nonvulcanized EVA component in the pure form.

The noncompatibilized blends display a single peak point temperature whose maximum was taken as the melting point. The melting point of the EVA phase in compatibilized blends appears at almost the same temperature as for noncompatibilized blends. The compatibilized blends also display a small peak at higher temperature. This second peak is related to the presence of EVALSH, which is also a semicrystalline polymer.

The crystallinity degree of noncompatibilized blends is close to the theoretical value whatever is the curing agent employed. However, for compatibilized systems, there is a decreasing in the overall crystallinity, which may be attributed to the fact that the interaction of the blend components inhibits the crystal growth in the EVA phase. This behavior is similar for sulfur- and DCP-curing systems.

### Dynamic mechanical analysis

Figure 9 illustrates the tan δ of SBR/EVA (50:50 phr) blends over a temperature range of −100–30°C, as a function of the curing system. All blends present two damping peaks, confirming the incompatibility of the components. Nonvulcanized blend (curve a) displays a sharp loss tangent peak at around −56°C, which corresponds to the glass transition of the SBR phase. The EVA component in the blend displays a two peaks at around −15 and 10°C. According to the literature,[1] the transition at around −15°C corresponds to the crystal unconstrained glass–rubber transition and that one at around 10°C is associated to the segment motion in the amorphous zone and corresponds to crystal constrained glass–rubber transition. The vulcanization with both the sulfur system (curve b) and DCP (curve c) shifts the glass transition temperature of the SBR
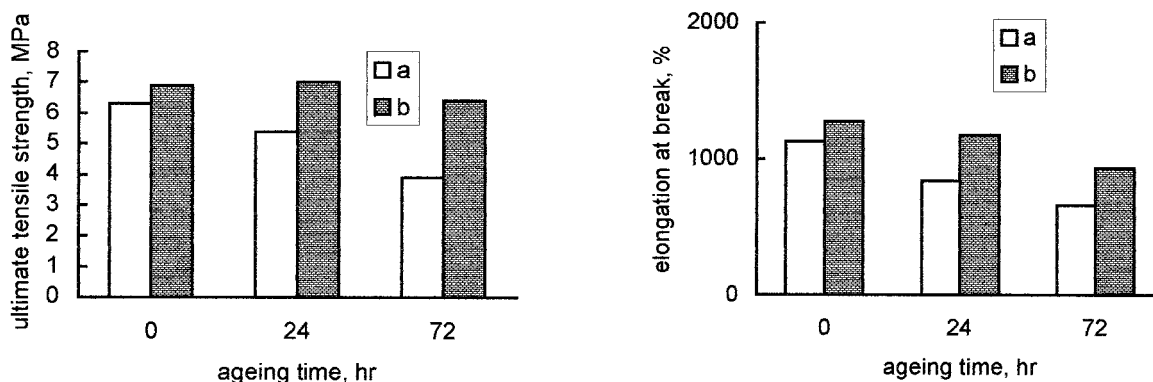
**Figure 12** Variation of the tensile properties of DCP-vulcanized SBR/EVA (70:30 phr) blends with thermal aging (a) without EVALSH and (b) with 5 phr of EVALSH.

phase toward higher values. These features are related to a decreasing of the molecular mobility of this phase, as a consequence of the crosslink.

The effect of the compatibilization on the damping properties of these blends is illustrated in Figure 10. The presence of EVALSH resulted in a small decreasing of the damping related to both SBR and EVA phase in all systems studied as a consequence of the interactions between the EVALSH and the SBR phase. The glass transition temperature of the SBR phase was not influenced by the compatibilization, except in blends vulcanized with DCP where a very small shift towards higher temperature can be observed.

### Aging properties

The effect of EVALSH on the aging properties was also investigated for SBR/EVA (70:30 phr) blends vulcanized with sulfur or DCP systems. Figure 11 illustrates the variation of the tensile properties of the sulfur-vulcanized blends after aging in an air circulating oven at 70°C for 24 and 72 h. The noncompatibilized blend presents similar values of ultimate tensile properties after aging, indicating the ability of the EVA component to stabilize the SBR component against aging under heating. The presence of EVALSH resulted in a considerable decreasing of both properties.

Considering blends vulcanized with DCP, one can observe a better stability of the SBR/EVA blend with the addition of EVALSH. Indeed, as observed in Figure 12, there is retention of the ultimate tensile property even after 72 h of aging in compatibilized blend.

### CONCLUSIONS

SBR/EVA blends display better tensile properties when vulcanized with the sulfur system. This curing system also displays a lower crosslink degree and better aging properties as compared to the DCP-curing system. The addition of EVALSH in vulcanized

SBR/EVA blends resulted in an improvement of the mechanical properties, for both sulfur- and DCP-vulcanizing systems, indicating the compatibilizing effect of the functionalized copolymer. Concerning aging properties, the presence of EVALSH contributes to a better thermal stability only in blends vulcanized by DCP. The crystallinity of the EVA phase in the blends was affected by the compatibilization. Indeed, a considerable decreasing of the heat of fusion and crystallinity were observed for compatibilized blends, whatever the curing system employed. The morphology of the SBR/EVA (50:50 phr) blends was not significantly affected by the presence of EVALSH. Only a relatively more elongated EVA phase was observed in the sulfur-vulcanized blend, probably because of an increasing of the viscosity of the SBR phase as a consequence of the interactions between the mercapto groups of the EVALSH component and the double bonds of the SBR phase. In the case of DCP-vulcanized blend, the compatibilization resulted in a more uniform morphology, characterized by dual-phase continuity. This morphological situation may be responsible for an increase of $V_r$ values in swelling experiments. To conclude, the presence of mercapto groups in EVALSH resulted in a reactive compatibilization, which occurs through a chemical reaction between the mercapto groups along the EVALSH backbone and the double bond of the SBR phase. Such interactions resulted in an improvement of the mechanical performance of the blends without affecting the damping properties.

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