

Use of EVA-Containing Mercapto Groups in Natural Rubber–EVA Blends. I. Mechanical, Thermal, and Morphological Properties

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SYNOPSIS

The effect of ethylene–vinyl acetate (EVA) modified with mercaptoacetic acid on mechanical, thermal, and morphological properties of blends of natural rubber (NR) and EVA copolymers has been investigated. The introduction of EVASH promotes a crosslinking of natural rubber phase as indicated by extraction experiments and microscopy analysis. This crosslinking may be attributed to bonding between sulfhydryl groups along the EVASH backbone and double bonds in rubber phase and may be responsible for the hardness improvement of most of the studied blends. Better results on hardness and ultimate tensile strength with EVASH addition were achieved for NR–EVA (60 : 40) ratio, probably due to cocontinuous morphology of this composition. The influence of EVASH on crystallinity degree of NR–EVA blends was also studied by differential scanning calorimetry. The morphology of the blends was studied through scanning electronic microscopy. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The development of new polymeric materials with new commercial applications and lower costs has stimulated several studies on polymer blends. In this field, the thermoplastic elastomers are receiving special attention to obtain products with elastomeric properties while maintaining excellent thermoplastic processing. Several studies and books deal with this subject.^{1–4} Blending rubber with plastic to achieve good mechanical properties is not an easy process because of the incompatibility of most of these blends. Several strategies have been employed to minimize the phase separation and increase interfacial adhesion that include the addition of physical or chemical compatibilizers.^{4,5} Considering rubber-based blends, other parameters such as cure system and aging stability must be taken into account.

Ethylene–vinyl acetate (EVA) copolymers are being considered as a good partner for several poly-

mers. Besides their improved impact resistance at low temperature and flex crack resistance, they can impart melt processing and aging properties.⁶ Blends with natural rubber, for example, have been studied to improve processing characteristics and resistance against the action of degradating agents as thermal aging, γ radiation, and ozone attack.⁷ To improve the mechanical properties, some cure systems such as dicumyl peroxide (DCP) and/or sulfur were employed.

In a previous study, the reaction between natural rubber (NR) and mercaptoacids or their esters to introduce carboxyl groups along the rubber backbone was reported.⁸ Recently, we have introduced mercapto groups along the EVA backbone by the simple esterification reaction between hydrolyzed EVA and mercaptoacetic acid.⁹ As in the case of low-molecular-weight mercaptan compounds earlier reported,⁸ EVA modified with sulfhydryl (SH) groups (EVASH) can also react with the rubber through an *in situ* graft copolymerization.

This study deals with the evaluation of mechanical properties of NR–EVA blends in the presence of EVASH. The reaction between NR and EVASH is also studied through extrac-

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tion experiments and microscopic and thermal analysis.

EXPERIMENTAL

Materials

Natural rubber SMR10 grade rubber (Malaysia) was supplied by Irwin, Brazil. Molecular weight = 580,000; specific density = 0.93 g/cm³. Ethylene-vinyl acetate copolymer was supplied by Petroquímica Triunfo S.A., Brazil. Vinyl acetate content = 18 wt %; melt flow index (MFI) (g/10 min) = 2.3. SH-modified-EVA was prepared by esterification of hydrolyzed EVA (EVAL) with mercaptoacetic acid, according to the literature procedure.⁹ The chemical structure of EVASH is illustrated below.

Blend Preparation

Blends were prepared in a Berstoff two-roll mill as follows: NR was masticated for 2–3 min and then blended with EVASH and EVA for 2–3 min until homogenization. Mixing was performed at 130°C and 30 rpm. The compounded blends were pressed into a sheet of 3 mm thickness using a hydraulic press at 150°C for 5 min and 13.8 MPa. For experiments where the effect of SH content in EVASH was evaluated, a NR–EVA ratio of 80 : 20 wt % was employed. The blends with different NR–EVA ratio were designated as follows: A, B, C, D, E, and F for blends with 0, 20, 40, 60, 80, and 100% by weight of EVA without EVASH and A', B', C', D', E', and F' for blends with 0, 20, 40, 60, 80, and 100% by weight of EVA with 5 wt % of EVASH.

Mechanical Testing

Tensile strength and percent elongation at break were measured at room temperature on a tensile testing machine (Instron, model 1101, TM-M) following ASTM D638-77A. Shore-A2 hardness was measured on a Shore Instrument and Mfg. Co., model A2, following ASTM D2240-64T.

Differential Scanning Calorimetry (DSC)

The glass transition temperatures of the blends were measured on a DuPont-DSC 9900 thermal analyzer. The samples were programmed heated at 20°C/min to 100°C and kept for 5 min at 100°C. The DSC scan was made from –100 to 100°C at 20°C/min.

The glass transition temperature of each sample was taken as the midpoint of the step in the scan.

The peak point temperatures were studied with the help of a Perkin-Elmer DSC7 thermal analyzer. For this study, the samples were programmed and heated at 10°C/min to 200°C, then cooled at 10°C/min to 25°C, and heated again at the same rate for a second time. The peak maximum from the DSC melting thermograms was considered as the melting point.

Microscopy Analysis

The sample was cryogenically fractured and the surface was coated by gold vapor and analyzed on a JEOL 5300 scanning electron microscope (SEM). In other experiments the surface was first etched in *n*-hexane.

RESULTS AND DISCUSSION

The effect of EVASH on mechanical properties of NR–EVA (80 : 20 wt %) blends is presented in Table I, using EVASH with different SH concentration. An improvement on ultimate tensile strength, σ_B , was observed with the addition of EVASH. The SH concentration does not affect significantly this property. Nevertheless, a decreasing on elongation at break, ϵ_B , with SH content was observed. This behavior was also reported for natural rubber–polyethylene (NR–PE) blends containing maleic anhydride modified PE and attributed to better interaction between the two phases.¹⁰

EVASH with higher SH concentration was employed on studies of mechanical properties of NR–EVA blends as a function of EVA content. At higher NR content, the addition of EVASH results on a slight increasing of ultimate tensile strength values, as illustrated in Figure 1. As the proportion of EVA increases, a decreasing on this parameter with EVASH addition is observed. The presence of EVASH results also on an increase of Shore-A2 hardness for most of the NR–EVA blends as shown in Figure 2, while decreases the elongation at break (Fig. 3).

Extraction Experiments

Experiments involving selective extraction of the NR phase were carried out to provide some information about the interaction between NR and EVASH. After treatment of the specimens with *n*-hexane at room temperature, the amount of ex-

Table I Effect of SH Concentration in EVASH on Mechanical Properties of NR-EVA Blend^a

Sample	[SH] (mmol/100 g)	Esterification Degree ^b	σ_B (MPa)	ϵ_B (%)	Hardness Shore-A
1	0	0	0.59	620	22
2	4.56	2	0.85	570	18
3	11.35	5	0.85	560	19
4	22.52	10	0.86	560	20
5	65.38	30	9.86	550	19
6	143.3	70	0.86	550	19
7	195.82	100	0.88	530	19

^a NR-EVA ratio = 80:20 w %; EVASH = 5 wt %; blend and press conditions as in experimental section.

^b Amount of 2-mercaptoacetic acid incorporated, based on initial [OH] concentration of hydrolyzed EVA used in esterification reaction (0.229 mol OH/100 g).

tracted NR was determined gravimetrically and plotted against EVA content in the blend, as shown in Figure 4. Sample of NR-EVA blends without EVASH present results as expected for physical blends of polymers. At higher NR content (NR-EVA = 80 : 20 wt %), the sample was completely destroyed after extraction, indicating that EVA phase is dispersed in NR matrix. For NR-EVA ratio of 60 : 40 wt %, nearly 60% of NR phase were extracted while keeping the dimensional stability of specimen. This behavior suggests a morphology near to cocontinuous phases. As expected, increasing the EVA content decreases also the proportion of extracted NR, indicating the presence of NR phase dispersed in EVA matrix. This morphology behavior as a function of NR-EVA ratio was also suggested by Kuriakose et al.¹¹

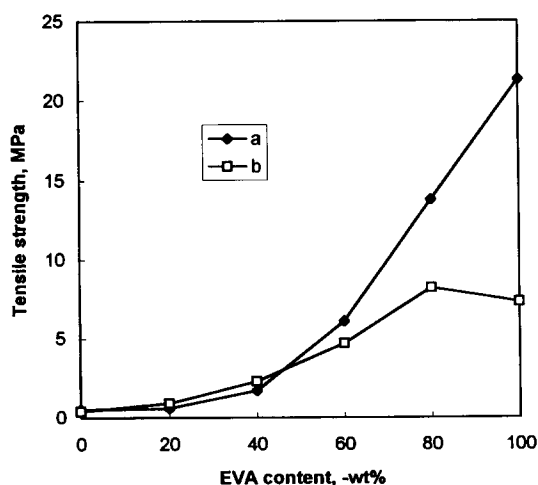


Figure 1 Effect of EVASH on ultimate tensile strength (σ_B) of NR-EVA blends at different compositions: (a) without EVASH and (b) with 5 wt % of EVASH ([SH] = 195.82 mmol/100 g).

Blends containing 5 wt % of EVASH have shown a significant decreasing on the amount of NR-extracted phase, even when only NR and EVASH were blended. These results are a strong indication of NR crosslinking through reaction with EVASH.

Morphology

The morphology of the blends as measured under SEM as shown in Figures 5–7. Figures 5(a) and 5(b) show the micrographs of NR-EVA (60 : 40) blends without and with 5 wt % of EVASH, respectively. No distinguishable domains are observed in both samples. It is possible that at this composition, there is almost a phase cocontinuity as indicated by extraction experiments and suggested by Kuriakose et al.¹¹

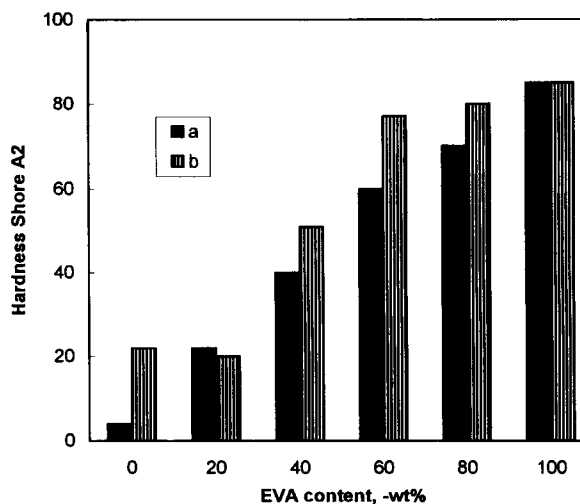


Figure 2 Effect of EVASH on Shore-A2 hardness of NR-EVA blends at different compositions: (a) without EVASH and (b) with 5 wt % of EVASH ([SH] = 195.82 mmol/100 g).

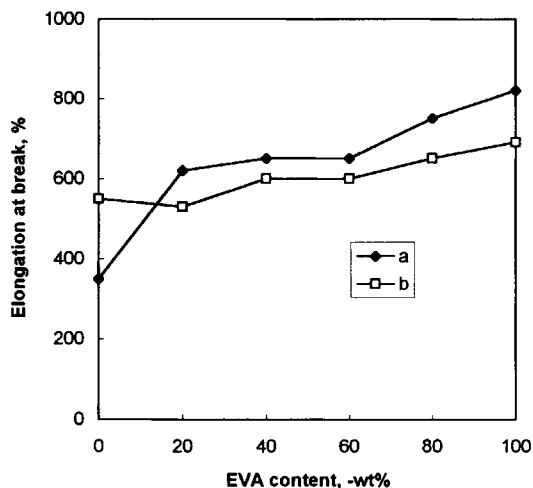


Figure 3 Effect of EVASH on elongation at break (ϵ_B) of NR-EVA blends at different compositions: (a) without EVASH and (b) with 5 wt % of EVASH ([SH] = 195.82 mmol/100 g).

Figures 6(a) and 6(b) show the micrographs of the same blends after surface etching in *n*-hexane. It is important to observe the continuous EVA phase in the NR-EVA sample without EVASH [Fig. 6(a)]. Micrograph of etched surface of NR-EVA-EVASH blend does not show any evidence of extracted phase [Fig. 6(b)]. This observation is in agreement with extraction experiments and suggests that NR phase is bonded to the EVASH.

Good phase dispersion is also observed for NR-EVA (40 : 60) blend with 5 wt % of EVASH, as shown in Figure 7(a). Again no phase separation is observed even after higher magnification (3500 \times) [Fig. 7(b)]. At this composition, Kuriakose et al. observed great NR domains dispersed in the EVA matrix.¹¹

Thermal Analysis

The thermal properties of the homopolymers and the blends were analyzed by DSC. The melting temperature T_m , fractional crystallinities X_c , heats of fusion ΔH , and glass transition temperature T_g of the blends are reported in Table II.

For T_g determination, the analyses were performed on a DuPont 9900 DSC and the thermograms are presented in Figure 8. The T_g values of pure NR and EVA are found to be -56.9 and -28.7°C , respectively. For NR-EVA (80 : 20 wt %) blends, the glass transition temperature of NR was found to be -61.3°C . The addition of EVASH results on a slight increase on T_g (-59.6°C) related to NR phase in pure blend. As observed by other authors,¹¹ there is

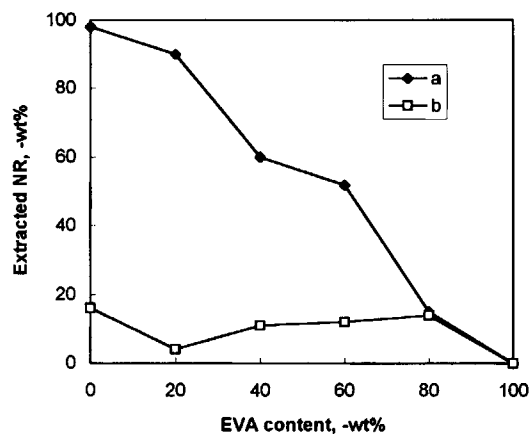


Figure 4 Percent of extracted NR phase as a function of NR-EVA ratio for blends (a) without EVASH and (b) with 5 wt % of EVASH.

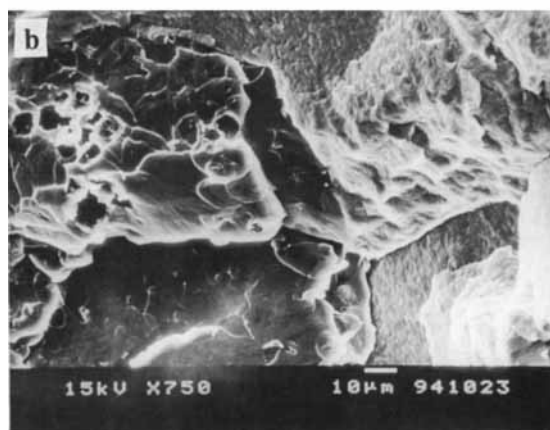
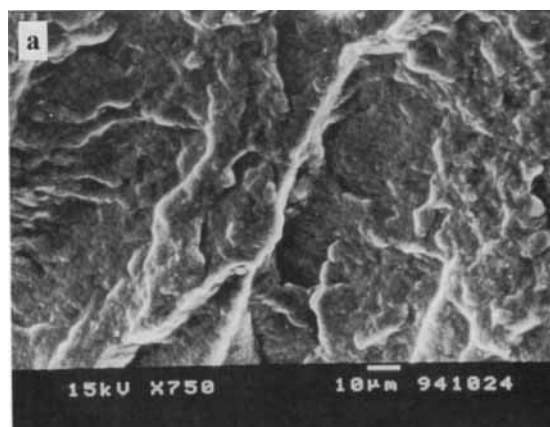


Figure 5 SEM micrographs of NR-EVA (60 : 40 wt %) blends (a) without EVASH and (b) with 5 wt % of EVASH.

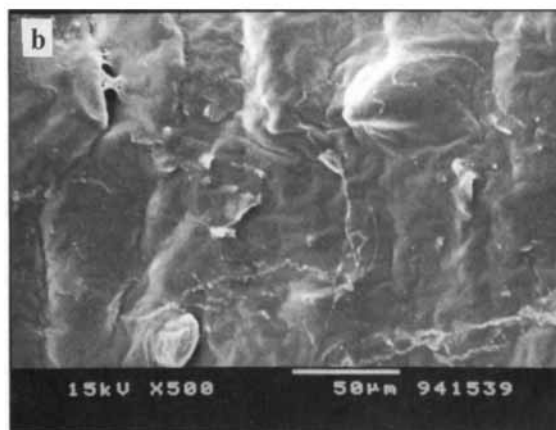
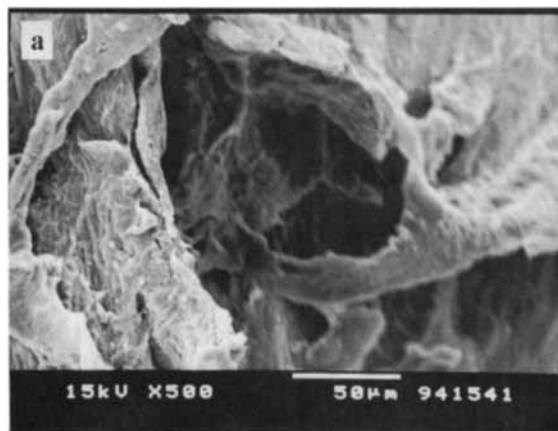


Figure 6 Surface-etched SEM micrographs of NR-EVA (60 : 40 wt %) blends (a) without EVASH and (b) with 5 wt % of EVASH.

no significant shift on T_g values indicating phase incompatibility in these blends.

Figure 9 shows the peak point temperature of the thermograms taken as the melting point (T_m). As observed in Table II, there is no variation on T_m at different blend compositions. Nevertheless, a slight decreasing on T_m with EVASH addition was observed.

The heat of fusion ΔH was also calculated from the area of the melting endotherm. The crystallinity degree of EVA with 18 wt % of vinyl acetate was reported to be 32%.¹¹ Thus, the values of crystallinity degree of EVA in the blends presented in Table II were calculated from the ΔH values by comparison of ΔH and crystallinity degree of EVA reported in the literature.¹¹ The dependence of EVA content on crystallinity degree is illustrated in Figure 10. At

higher NR proportion in NR-EVA blends (80 : 20 and 60 : 40 wt %), there is no significant variation on X_c even with the addition of EVASH. As the EVA proportion in the blend increases (NR-EVA = 40 : 60 and 20 : 80 wt %), a curious behavior is observed. Without EVASH, the crystallinity degree is higher than the theoretical values. The addition of EVASH results in an accentuated decrease on crystallinity degree [Fig. 10(b)].

This behavior may be attributed to the interactions of the components, promoted by EVASH. This effect is observed in EVA-richer blends probably because of higher dispersion and smaller size domain of rubber particles. Considering the higher melt viscosity of NR component related to EVA, the interactions between NR and EVASH contribute to a decreasing of NR phase viscosity with an increase

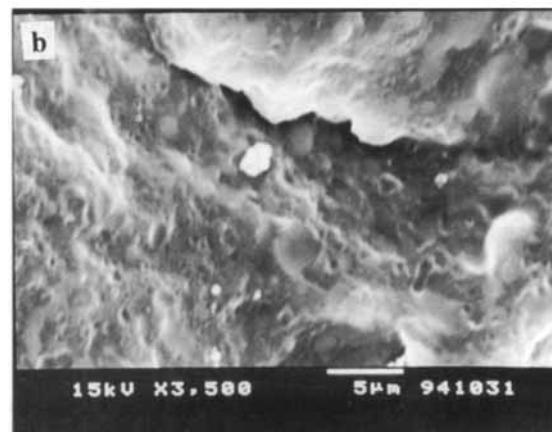
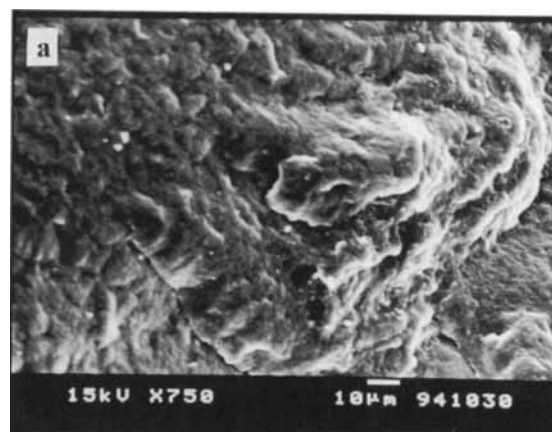


Figure 7 SEM micrographs of NR-EVA-EVASH (40 : 60 : 5 wt %) blend at different magnification: (a) 750 \times and (b) 3500 \times .

Table II Thermal Properties of NR-EVA Blends Containing 5 wt % of EVASH

Properties	Blends without EVASH ^a						Blends with 5 wt % of EVASH ^b					
	A	B	C	D	E	F	A'	B'	C'	D'	E'	F'
Glass transition temperature, T_g (°C) (NR phase)	-57.0	-6.3					-59.5	-59.6				
Peak temperature, T_m (°C)	—	84.1	85.5	85.3	85.3	85.2	—	83.1	84.0	82.7	85.8	84.7
Onset of melting point (°C)	—	65.8	68.6	68.3	68.0	67.3	—	65.6	66.0	64.3	69.4	63.7
Heat of fusion, ΔH , (J/g)	—	7.5	14.3	31.9	40.3	42.2	—	7.5	14.3	20.5	27.1	42.6
Crystallinity (%)	—	5.7	10.8	24.2	30.5	32.0	—	5.7	10.8	15.5	20.5	32

^a NR-EVA = (A) 100 : 0, (B) 80 : 20, (C) 60 : 40; (D) 40 : 60; (E) 20 : 80; (F) 0 : 100 wt %.

^b NR-EVA with 5 wt % of EVASH = (A') 100 : 0, (B') 80 : 20; (C') 60 : 40; (D') 40 : 60; (E') 20 : 80; (F') 0 : 100 wt %.

of segmental diffusion. Therefore, a higher NR dispersion is reached which inhibits the crystal growth in the EVA phase. The effect of EVASH on NR phase viscosity is not significant for blends with higher NR content. A decreasing of overall crystal-

linity was also reported for NR-PE blends containing maleic anhydride modified PE.¹⁰

CONCLUSIONS

The experiments reported here suggest the role of EVASH in promoting a better interfacial adhesion between NR and EVA phases. The SH groups along the EVASH backbone are prone to form free radicals during processing, which react with double bonds of the rubber phase. Therefore, while SH groups are bonded to the NR phase, the EVA backbone of EVASH interacts physically with the EVA phase.

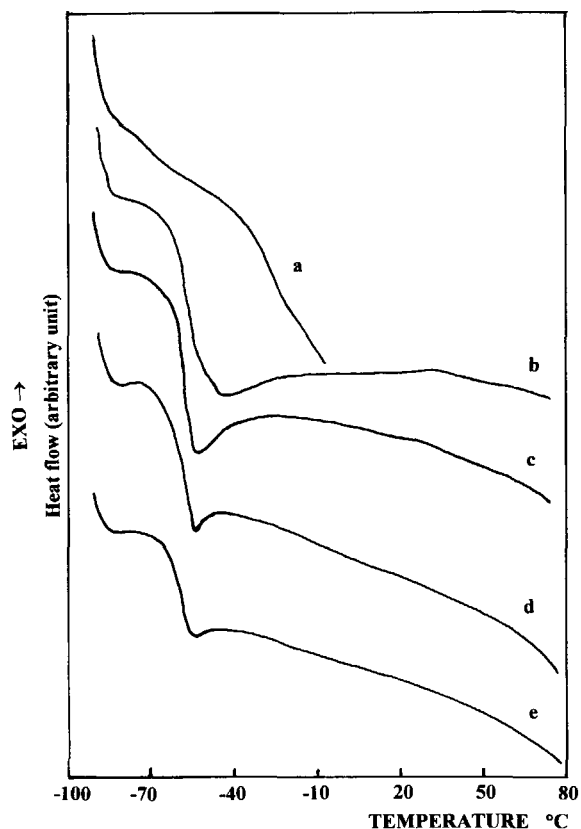


Figure 8 DSC thermograms of (a) EVA (b) NR, (c) NR-EVASH (80 : 20 wt %) blend, (d) NR-EVA (80 : 20 wt %) blend, and (e) NR-EVA-EVASH (80 : 20 : 5 wt %) blend, taken under low temperature.

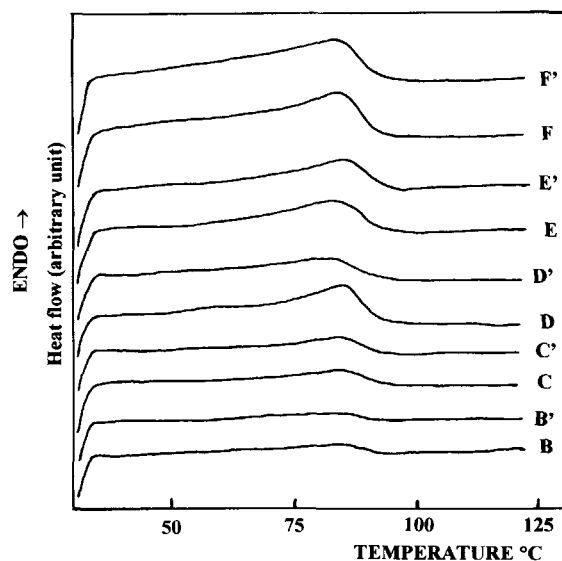


Figure 9 Peak point temperature of NR-EVA blends, obtained from DSC thermograms. Blend composition in experimental section.

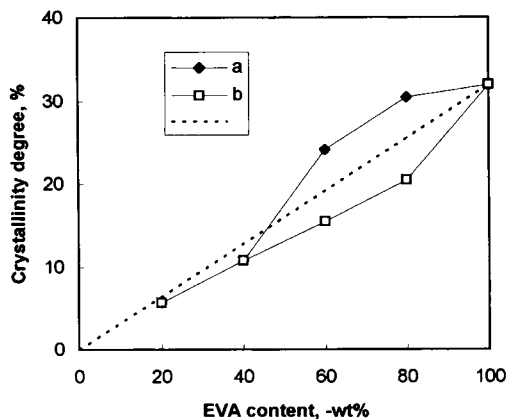


Figure 10 Effect of EVASH addition on crystallinity degree of NR-EVA blends with different compositions. (a) NR-EVA blends, (b) NR-EVA-EVASH blends and (· · ·) theoretical dependence of crystallinity degree on EVA content.

This interaction is responsible for better phase dispersion and decreasing of phase extracted in NR-EVA-EVASH blends and may explain the hardness improvement in most of the studied blends. The best results for hardness and ultimate tensile strength were achieved for NR-EVA ratio of 60 : 40 probably due to the proximity of phase inversion at this composition.

For EVA-richer blends, the addition of EVASH results on a decreasing of ultimate tensile strength. As observed in DSC studies, there is a decrease on the crystallinity degree with EVASH addition, for blends with high EVA content. It is stated that ultimate tensile strength of semicrystalline polymers depends also on crystallinity degree. Thus, the behavior found in EVA-richer blends may be explained by the decreasing on crystallinity. Additional studies on the effectiveness of NR-EVASH interaction by solid state ^{13}C -NMR techniques will be presented in a subsequent work.

It is important to emphasize that a crosslinked system was obtained without the addition of free radical promoters. The addition of vulcanization accelerators increases the crosslinking efficiency of EVASH, as will be reported sooner.

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