

The Use of EVA-Containing Mercapto Groups in Natural Rubber-EVA Blends. II. The Effect of Curing System on Mechanical and Thermal Properties of the Blends

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SYNOPSIS

Natural rubber (NR)-poly(ethylene-co-vinyl acetate) (EVA) blends have been studied by incorporation of mercapto-modified EVA (EVASH) combined with dicumyl peroxide (DCP) as a curing agent. The mechanical, thermal, and morphological properties of NR-EVA blends as functions of blend composition and compatibilizer and/or curative additions were investigated. An EVASH-DCP combined system leads to the greatest improvement in tensile strength when EVA is dispersed within the NR matrix. Higher performance on Shore A hardness was also achieved with this combined system. For blends characterized by NR domains dispersed in the EVA matrix, the efficiency of pure DCP in improving the tensile strength is higher. Morphological observations and selective extraction experiments indicate the cross-linking of NR phase in both systems. A cross-linking of the EVA phase is also suggested by DCP or an EVASH-DCP combined system, based on the decreasing degree of crystallinity of this phase. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic elastomers are very attractive materials that ideally possess a combination of the service properties of elastomers and the processing properties of thermoplastics.¹⁻⁴ These materials contain rubber domains and resinous thermoplastic domains and may be either block copolymers or blends. In the case of the blend compositions, the soft and hard domains are different polymeric species that must have some kind of interaction between each other if useful properties are required. These interactions may be brought by specific reactions between the rubber and plastic molecules carried out during melt-mixing. This is called reactive compatibilization and is performed by using a chemically modified polymer, normally derived from the thermoplastic component, which acts as a bridge among the two incompatible polymer phases.^{5,6} In addition, improved mechanical properties of thermoplastic

elastomers are also achieved by a method called dynamic vulcanization, which takes place in the elastomeric phase during its melt-mixing with molten plastic.^{2,3,6,7}

Ethylene-vinyl acetate copolymers (EVA) with low vinyl acetate content are thermoplastic and have a pronounced crystallinity degree, due to the ethylene sequences. Their blends with natural rubber (NR) have been studied to develop materials with outstanding aging resistance and good processability.^{8,9}

Recently, mercapto-modified EVA was employed on compatibilization of EVA-NR blends.^{10,11} The mercapto groups located along the EVA backbone react with the NR phase, promoting a better rubber phase dispersion in the EVA matrix. In this paper, we would like to discuss the effect of the curing agent dicumyl peroxide (DCP) on mechanical and thermal properties of NR/EVA blends compatibilized with poly(ethylene-co-vinyl mercaptoacetate) (EVASH). DCP has been employed as curing agent on several reports concerning vulcanization of NR-based thermoplastic elastomer blends.^{8,12,13} Besides its curing performance, DCP may be able to promote a faster

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Table I Effect of DCP Concentration on Mechanical Properties of NR-EVA-EVASH (80 : 20 : 5 phr) Blends

NR (phr)	EVA (phr)	EVASH ^a (phr)	DCP (phr)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Hardness Shore A2
80	20	0	0	0.59	620	22
80	20	5	0	0.88	530	18
80	20	5	0.10	1.81	520	24
80	20	5	0.14	2.81	520	26
80	20	5	0.64	4.46	470	33
80	20	5	0.74	5.41	450	46

^a EVASH with 195.82 mmol SH/100 g.

reaction between mercapto groups situated on EVASH and the NR phase.

EXPERIMENTAL

Materials

Natural rubber (NR) SMR10 grade rubber [(Malaysia) molecular weight = 580,000; specific density = 0.93 g/cm³] was supplied by Irwin, Brazil. An ethylene-vinyl acetate copolymer (EVA), vinyl acetate content = 18 wt %; melt flow index (MFI) = 2.3 g/10 min], was supplied by Petroquímica Triunfo S.A., Brazil. Poly(ethylene-co-vinyl mercaptoacetate) (EVASH) was obtained by esterification of hydrolyzed EVA (EVAL) with mercaptoacetic acid, following the literature procedure.^{10,14} EVAL employed in this synthesis contains 0.229 mol OH/100 g, as calculated from the initial vinyl acetate concentration in EVA (0.209 mol/100 g). For the study presented in this paper, all the hydroxyl groups were esterified. Therefore, the SH concentration on EVASH corresponds to 0.196 mol/100 g.

Blend preparation

Blends were prepared in a Berstoff two-roll mill at 130°C and 30 rpm. For blends containing the EVASH/DCP combined system, NR was masticated for 2–3 min. with EVASH and DCP. Then, EVA was blended for 2–3 min until homogenization. For blends performed with DCP as the only curing agent, NR was first blended with EVA during 2–3 min. After this time, the DCP was added and blended for another 3 min. The compounded blends were compression molded at 150°C and 13.8 MPa for 5 min.

Mechanical Testing

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

Differential Scanning Calorimetry

The glass transition temperature of the blends was measured on a DuPont DSC 9900 thermal analyzer at programmed heating of 20°C/min. The DSC scan was made from –100 to 100°C. The melting and crystallization behaviors of EVA phase were studied with the help of a Perkin-Elmer DSC7 thermal analyzer. The samples were programmed heated at 10°C/min. to 200°C, then cooled at 10°C/min. to 25°C and heated again at 10°C/min.

Microscopy Analysis

The compression-molded specimens were cryogenically fractured, and the surface was analyzed on a JEOL 5300 scanning electron microscope. In other experiments, the surface was first etched in *n*-hexane.

RESULTS AND DISCUSSION

Mechanical Properties

The effect of DCP concentration on mechanical properties of NR-EVA (80 : 20 phr) blends is indicated in Table I. The DCP addition increases both ultimate tensile strength, σ_B , and Shore A2 hardness, while decreases the elongation at break, ϵ_B . These

results are proportional to DCP concentration and suggest that this curing agent also acts as an activator during the reactive compatibilization of NR-EVA blends promoted by EVASH. The decreasing on ϵ_B is an indication of curing process and will be confirmed by extraction experiments.

The effect of this curing/compatibilizer system on mechanical properties of NR-EVA blends as a function of blend composition was also investigated. The results concerning the ultimate tensile strength are illustrated in Figure 1. EVASH is able to improve the σ_B of NR-EVA blends only for NR-rich blends, as shown in Figure 1(b). Uncompatibilized blends present higher σ_B values when high EVA proportion is employed. The combined EVASH/DCP system results in an improvement of σ_B for all composition ranges studied [Fig. 1(d)]. The value is, however, inferior to that one found in uncompatibilized blend when NR-EVA proportion corresponds to 20 : 80 phr. The best results for σ_B were achieved when DCP is employed alone [Fig. 1(c)], except for NR-EVA = 80 : 20 phr blends.

The elongation at break decreases with the addition of EVASH and/or DCP, as shown in Figure 2. This behavior is more significant when EVASH-DCP combined system was employed.

The ultimate mechanical properties are related to compatibilization phenomenon. According to literature, an improvement in mechanical properties of thermoplastic-elastomer blends can also be achieved by an appropriated vulcanization of rubber particles within the thermoplastic matrix.^{15,16} In some systems, this process does not require the presence of polymeric compatibilizing agent. Indeed,

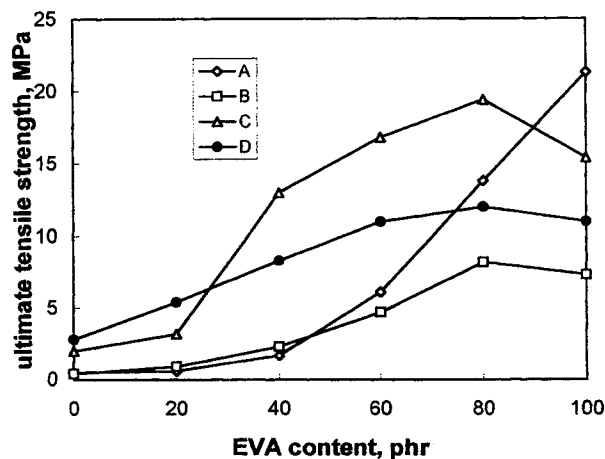


Figure 1 Ultimate tensile strength of NR-EVA blends at different compositions: (a) Without additives and with (b) EVASH (5 phr), (c) DCP (0.7 phr), and (d) EVASH-DCP (0.5 : 0.7 phr).

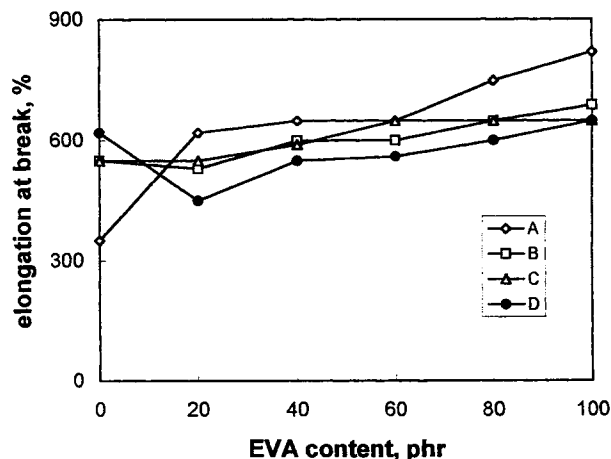


Figure 2 Elongation at break of NR-EVA blends at different compositions: (a) without additives and with (b) EVASH (5 phr), (c) DCP (0.7 phr), and (d) EVASH-DCP (0.5 : 0.7 phr).

the dynamic vulcanization of NR-polyethylene blends leads to an increase in tensile strength when DCP is employed alone.¹³ The addition of modified polyethylene as compatibilizing agent on these NR-PE-DCP blends results in a drop in strength value as well as in elongation at break value.¹³ In other systems, outstanding mechanical properties of thermoplastic-elastomer blends are achieved when the curing agent is employed in the technological compatibilized blends.¹⁷⁻¹⁹

Concerning the compatibilization system used in this work, EVASH promotes chemical bond formation between rubber and plastic molecules during melt-mixing and compression-molding. These chemical interactions were confirmed by extraction experiments of NR phase, previously reported¹⁰ and is responsible for the slight increasing on σ_B for NR-rich blends. DCP is known to be an effective curing agent for both EVA and natural rubber components.⁸ The addition of DCP on NR-EVA-EVASH blends increases the compatibilization ability of EVASH due to its catalytic efficiency in abstracting the hydrogen atom on SH groups situated along the EVASH backbone. DCP also exerts a curing effect in both polymer phases. This compatibilization/curing effect is important when EVA is dispersed in the NR matrix; that is, when the NR/EVA proportion corresponds to = 80 : 20 phr (see Fig. 1). This composition also displays the lowest elongation at break value, as a result of higher cross-linking degree.

NR becomes the dispersed phase when the EVA proportion in the blend is increased. The NR-EVA (60 : 40 phr) blend presents a morphology charac-

terized by the NR dispersed in the EVA matrix.^{8,10} When NR is the dispersed phase, pure DCP is more efficient in improving the tensile strength. This behavior is similar to that one found during curing/compatibilization of NR with polyethylene blends.¹³ The NR/polyethylene composition used by the authors for their studies corresponded to 70 : 30 phr. As discussed in their report, this composition corresponds to phase inversion.¹³ Unfortunately, they did not make a relationship between the effect of compatibilizing/curing combined system as a function of blend composition and phase inversion.¹³

The values of Shore A2 hardness as a function of blend compositions are shown in Figure 3. This property is not significantly affected by interfacial features but it may be related to the cross-linking degree. The values increase with increasing the proportion of the thermoplastic component, as expected. It is also observed an improvement on this property with the addition of EVASH/DCP combined system as a result of a higher cross-linking degree of NR phase.

Extraction Experiments

An idea of cross-linking degree of NR phase is obtained by selective extraction of NR, using *n*-hexane. Figure 4 illustrates the percentage of extracted NR as functions of EVASH and/or DCP addition, as well as of blend composition. The extraction experiments indicate that lower amount of NR can be extracted when EVASH-DCP combined system is used as compatibilizer/curing agent. This feature is,

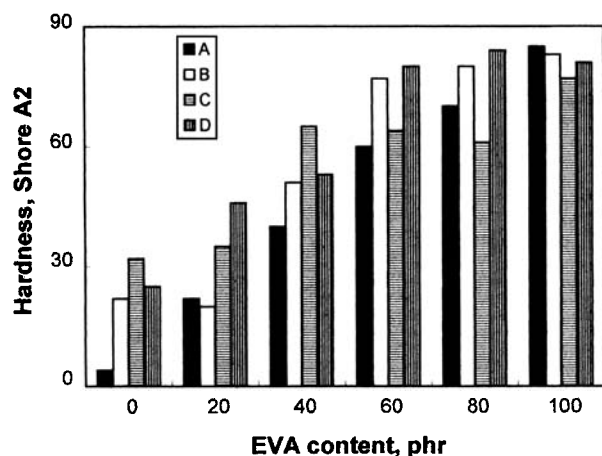


Figure 3 Shore A2 hardness of NR-EVA blends at different compositions: (a) without additives and with (b) EVASH (5 phr), (c) DCP (0.7 phr), and (d) EVASH-DCP (0.5 : 0.7 phr).

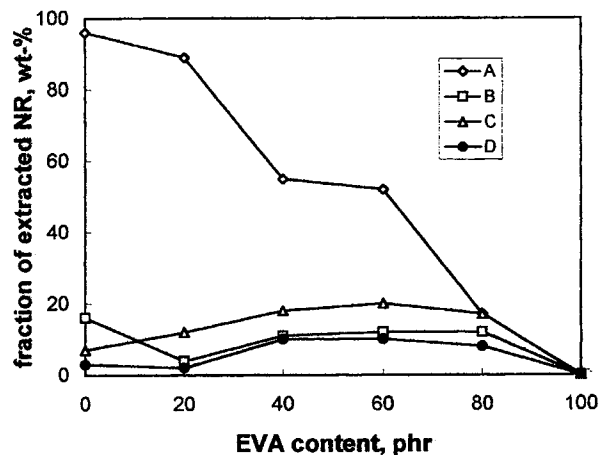


Figure 4 Percent of extracted NR phase as a function of NR-EVA ratio for blends: (a) without additives and with (b) EVASH (5 phr), (c) DCP (0.7 phr), and (d) EVASH/DCP (0.5 : 0.7 phr).

of course, an indication of higher cross-linking degree of this phase.

Morphology

The effect of EVASH addition on the morphology of NR-EVA (60 : 40 phr) blends was discussed in the preceding report.¹⁰ The micrograph of etched surface of NR-EVA/EVASH blend does not show any hole indicating that NR is chemically bonded to EVASH. In this paper, the role of DCP on morphology of such blends was also investigated. Figure 5 presents the micrographs of cryogenically fractured surface of NR/EVA (60 : 40 phr) blends as a function of EVASH-DCP or DCP addition. As in the case of NR-EVA-EVASH compatibilized blends, there is no distinguishable domains in these blends with different curing systems.

The fractured surfaces were submitted to etching with *n*-hexane to remove the NR phase, as illustrated in Figure 6. The blend cured with pure DCP presents some holes, indicating partial extraction of the rubber phase. The etched surface of the blend cured with the EVASH-DCP system does not show any hole at the same magnification, suggesting that the cross-linking efficiency is higher when EVASH-DCP combined system is employed. In addition, this behavior may also indicate that the fracture takes place through the EVA domains, as discussed in several other reports concerning compatibilization of thermoplastic-elastomer blends.²⁰

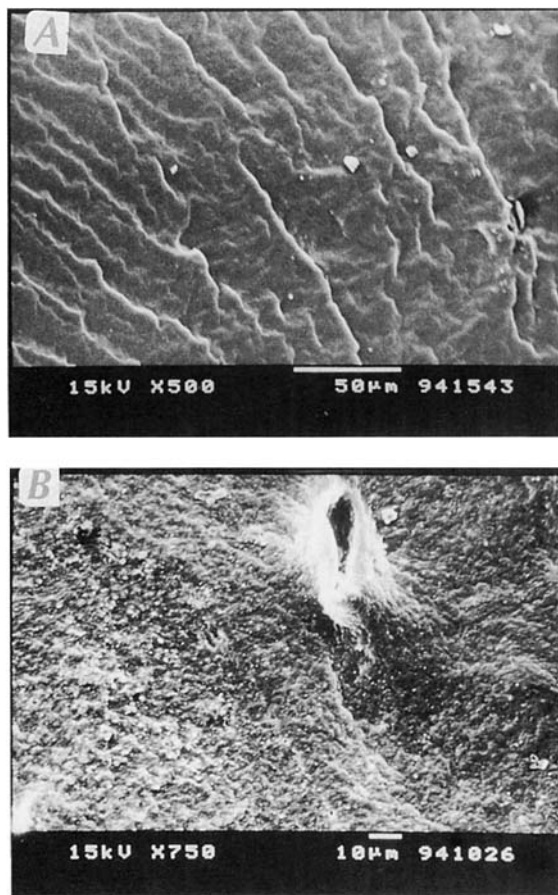


Figure 5 SEM micrographs of NR-EVA (60 : 40 phr) blends with (a) DCP and (b) EVASH-DCP.

Thermal Analysis

As previously reported, the addition of EVASH to NR-EVA blends results in a decrease in the crystallinity of the EVA phase for EVA-richer blends.¹⁰ The thermal properties of these blends as functions of DCP or EVASH-DCP addition were also investigated by DSC. The T_g determinations were performed on a DuPont 9900 DSC, whose thermograms are illustrated in Figure 7. The T_g of pure NR and EVA are -56.9°C and -28.7°C , respectively. For uncompatibilized NR-EVA (80 : 20) blends, the T_g value of NR phase was found to be -61.3°C . As discussed in a previous report¹⁰ and indicated in Figure 7, the addition of EVASH does not cause any substantial shift of this T_g value, as compared to uncompatibilized blend. Nevertheless, a significant shift of T_g toward higher temperatures with the presence of DCP or the DCP-EVASH combined system is noted (Fig. 7). This effect is more pronounced in the last case. Generally, an increase of the T_g value may be related to compatibilization or

to the restriction of the segmental motion of the polymer caused by the cross-links. The T_g of the EVA phase could not be detected in the blends; but, as observed in Table II, the melting point T_m of EVA phase is almost independent on composition or the additive employed. This behavior suggests that the shift on T_g value of NR phase by using DCP or EVASH-DCP may be associated to the cross-linking of this phase.

The melting point temperatures of the NR-EVA blends at various weight fractions of the components and different additives (EVASH, DCP, and EVASH-DCP) are illustrated in Figure 8. The heat of fusion ΔH_m of the EVA phase was calculated from the area of the melting endotherm. The values are proportional to crystallinity degree and are presented in Table II. For comparison, the DSC data of uncompatibilized blends and EVASH compatibilized blends are also shown. The addition of pure DCP results on an accentuated decreasing of ΔH_m of EVA phase. This effect is significant for EVA-richer blends. The presence of EVASH-DCP combined

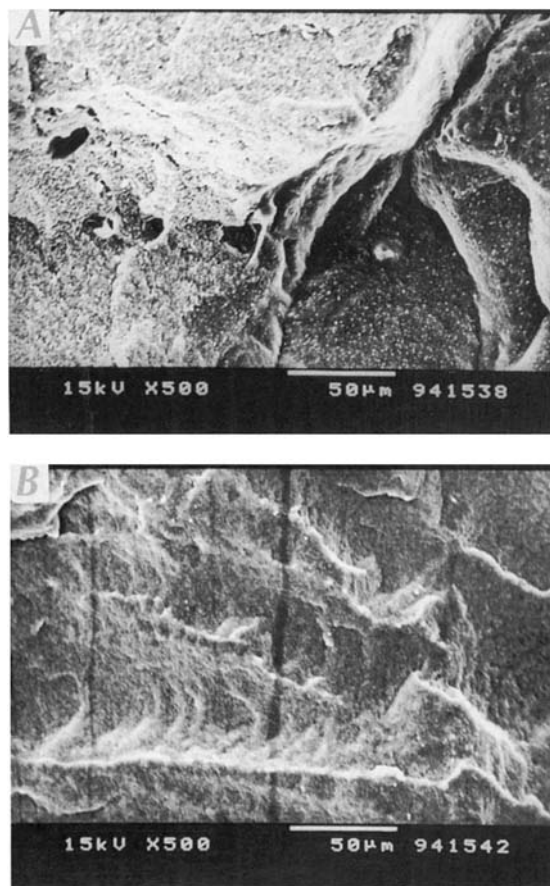


Figure 6 Surface-etched SEM micrographs of NR-EVA (60 : 40 phr) blends with (a) DCP and (b) EVASH-DCP.

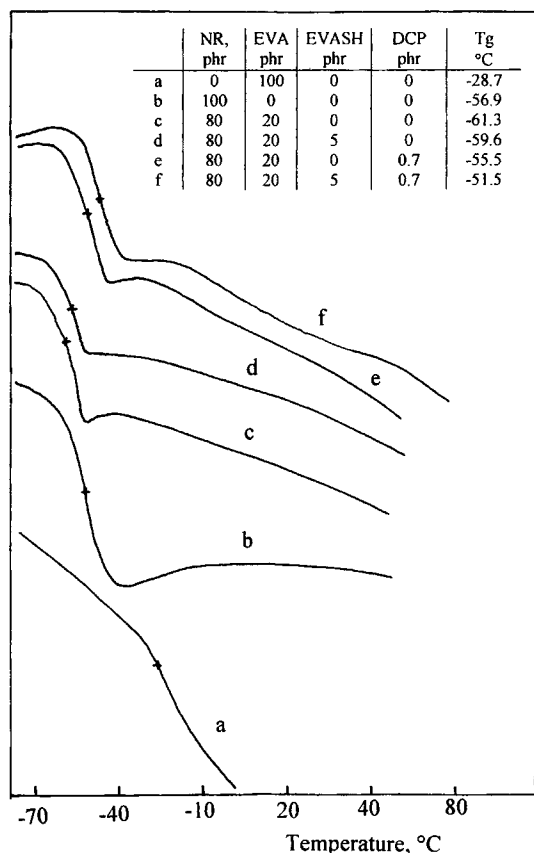


Figure 7 DSC thermograms of NR-EVA (80 : 20 phr) blends as a function of different additives, taken under low temperature (T_g of the NR phase are indicated).

system results on a further decreasing on this property.

The interactions of EVASH, DCP or EVASH-DCP systems with the blend components, NR and EVA, are different. These features may explain the

different behavior on crystallinity of EVA phase shown in Table II and Figure 8. Pure EVASH is believed to form a chemical bond with NR. As the EVASH backbone is similar in chemical structure to EVA phase, it is able to act as an interfacial agent between both components. These interactions contribute to a better dispersion of NR domains within the EVA matrix, which inhibit the crystal growth in EVA phase. Therefore, the presence of EVASH causes a decrease in crystallinity of EVA-richer blends. As this property is not affected when EVASH is blended with pure EVA, one may assume that the physical entanglement between the EVA component and this compatibilizing agent is not enough to disturb the crystallization behavior of EVA.

When DCP is employed as the cross-linking system in NR-EVA blends, there is a decrease in ΔH_m of the EVA phase in all composition ranges, including pure EVA. DCP is a curing agent which may cross-link both the NR and the EVA phase.⁸ The results observed with this curing agent suggest a cross-linking of EVA phase together with NR.

The influence of EVASH-DCP combined system on the crystallinity of the EVA phase is more significant. It is important to remember the different addition order of DCP in our compatibilized system. Blends compounded with the EVASH-DCP combined system were performed by adding DCP to NR-EVASH mixed blend and before the addition of EVA. Thus, the cross-linking efficiency of DCP in the EVA phase may not be so important as that one expected in pure DCP-cured system when the curing agent was added after all components were well-blended. The higher drop on ΔH_m observed EVASH-DCP system may be attributed to the compatibilization effect associated to the cross-linking phenomenon.

Table II Thermal Properties of NR-EVA Blends^a

NR (phr)	EVA (phr)	Without Additive			With EVASH ^b (5 phr)		With DCP (0.74 phr)		With EVASH/DCP (5 : 0.74 phr)	
		T_m (°C)	ΔH_m (J/g)		T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)
			Theor.	Exp.						
80	20	84.0	8.4	7.5	83.1	7.5	84.7	4.3	84.8	4.7
60	40	85.5	16.9	14.3	84.0	14.3	84.5	7.9	84.7	4.5
40	60	85.3	25.3	31.9	82.7	20.5	84.3	10.3	84.7	6.3
20	80	85.3	33.8	40.3	85.8	27.1	83.0	14.7	84.6	7.5
0	100	85.2	42.2	42.2	84.7	42.6	85.9	15.1	85.8	17.6

^a Melting behavior of EVA phase; T_m = melting temperature; ΔH_m = heat of fusion.

^b EVASH with 195.82 mmol SH/100 g.

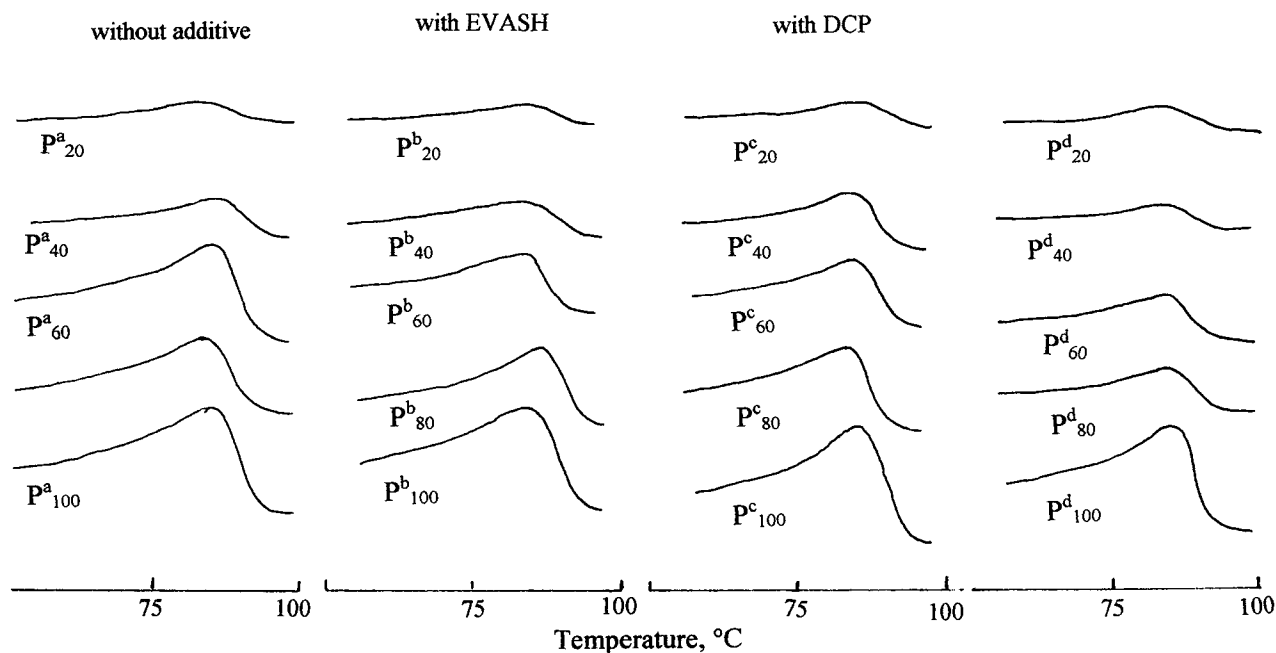


Figure 8 Melting endotherm of NR-EVA blends as functions of blend composition and curing/compatibilizer systems. (The number in subscript corresponds to the EVA proportion in blends; the superscripts a, b, c, and d indicate the blends without additives, with EVASH (5 phr), with DCP (0.7 phr), and EVASH-DCP (5 : 0.7 phr), respectively).

CONCLUSIONS

The addition of DCP to NR-EVA blends compatibilized with EVASH increases both ultimate tensile strength and Shore A2 hardness, while it decreases the elongation at break. These results indicate an effective cross-linking of the rubber phase and are confirmed by selective extraction of NR phase and by electronic microscopy. The decrease in crystallinity degree of the EVA phase as indicated by DSC thermal analysis, suggests that a cross-linking phenomenon also takes place in this phase. When the curing process involves pure DCP, the tensile strength values of the blends are improved for EVA-richer blends, but the magnitude of cross-linking of the rubber phase is not as high as with the EVASH-DCP combined system. This behavior may be attributed to the different addition order of the curing agent DCP in these compounded blends. As indicated in the Experimental Section, blends cured with pure DCP were compounded by following the dynamic vulcanization technique.³⁻⁷ This process involves the addition of the curing agent after all components are well-mixed. Concerning the EVASH-DCP combined system, the curing agent DCP was added just after NR was masticated with EVASH and before EVA addition. This procedure was employed to improve the reactive compatibilization

between SH groups in EVASH and the NR phase and does not characterize a real dynamic compatibilization. The cross-linking of the natural rubber phase as a result of the addition of EVASH-DCP or DCP can be analyzed by the shift in the glass transition temperature of the natural rubber phase towards higher temperatures. The addition of EVASH, DCP, or EVASH-DCP into NR-EVA blends decreases the ΔH_m of the EVA phase and, consequently, the crystallinity degree. As pure EVASH is not able to cross-link the EVA phase, the decreasing on crystallinity observed with EVASH addition may be explained by the better dispersion of NR within the EVA phase as a result of compatibilization. DCP is only a curing agent. The decreasing on crystallinity of the EVA phase with the DCP addition is attributed to the ability of this additive in reacting with both EVA and NR components. The lowest values of ΔH_m of the EVA phase observed with the addition of EVASH-DCP combined system suggest a combination of compatibilization/curing process.

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