

Effect of Different Curing Systems on Heat Shrinkability and Mechanical Properties of Ethylene Vinyl Acetate/Epoxidized Natural Rubber Blends

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ABSTRACT: Ethylene vinyl acetate (EVA)/epoxidized natural rubber (ENR) blends containing 10 and 30 wt % ENR were prepared by using an internal mixer. Five different types of curing systems were employed: dicumyl peroxide (DCP), sulfur (S), phenolic resin (Ph), DCP + S, and DCP + Ph. DCP could crosslink with both EVA and ENR while S and Ph were curing agents for ENR. The DCP system provided the lowest tensile properties and tear strength because of low crosslinking in ENR phase. Addition of sulfur or phenolic resin increased the mechanical properties due to a better vulcanization of the rubber phase. The mechanical properties of the blends decreased with increasing ENR content. The rubber particle size in the blends containing 30% ENR played a more important

role in the mechanical properties than the blends containing 10% ENR. ENR particle size did not affect heat shrinkability of EVA and a well vulcanized rubber phase was not required for high heat shrinkage. Furthermore, heat shrinkage of the blends slightly changed as the ENR content increased for all curing systems. With regard to the mechanical properties and heat shrinkability, the most appropriate curing system was DCP + Ph and in the case the 10 wt % ENR content produced a more favorable blend. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 38–46, 2011

Key words: blends; shrinkability; ethylene vinyl acetate; epoxidized natural rubber; heat shrink

INTRODUCTION

Ethylene vinyl acetate copolymers (EVA) have been used for many applications due to their vinyl acetate (VA) content. For example, copolymers with a low VA content (<20%) are usually employed as thermoplastics and those with a higher VA content are used as oil-resistance elastomers. Blends of thermoplastic EVA with rubbers have been widely reported, such as EVA with natural rubber (NR),^{1–9} EVA with epoxidized natural rubber (ENR 50, 50 mol % epoxidation),^{10–13} EVA with styrene–butadiene copolymer^{14–16} and EVA with nitrile rubber (NBR).^{17–20} There are many reasons for producing polymer blends, e.g., cost reduction, improvement of certain properties or the generation of new products. It has been reported that the addition of NR to EVA increased the melt elasticity of EVA and those EVA-rich blends provided

an increase in the thermal aging of the blends.⁵ The vulcanizing agents used in those EVA/NR blends were sulfur and dicumyl peroxide (DCP). Compatibility of polymer blends is one of the most important factors controlling the mechanical properties of the blends. The EVA/NR blends are immiscible and incompatible; therefore, compatibilization is required to these blends. Mercaptoacetic acid and sulfhydryl groups have been employed to produce the *in situ* EVA-NR graft copolymer.^{3–5} Although the EVA/ENR blend is immiscible, FTIR analysis of this blend showed a weak dipole–dipole interaction of the epoxy groups with acetate groups.¹⁰ This implies that the EVA/ENR blend may be more compatible than the EVA/NR blend. Furthermore, this assumption has been supported by their chemical structures (being polar polymers). The tensile properties of the EVA/ENR blends were improved by using electron beam irradiation with and without a free radical crosslinking agent to crosslink the polymers.^{12,13}

Heat shrinkable polymers may be referred to as shape-memory polymers.²¹ These polymers could remember their previous shapes. Once they are activated with enough heat energy, they return to their previous shape or its original dimensions. This phenomenon is also referred as “shape memory”, “memory effect,” and “elastic memory”. Factors involving shape memory include chain entanglement,

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crosslinking, crystallization, highly oriented amorphous chains and the formation of a domain structure. The extent of shrinking to the original dimensions can be controlled by many methods, e.g., by heating up to the glass transition temperature and quenching, melting and recrystallization or melting and phase separation. The process of returning to the previous shape requires only a change in physical structure, but not the chemical structure of the polymer molecules. Heat shrinkable polymers have many applications, i.e., toys, containers, sporting goods, packaging materials, pipe-fitting, electric equipment, encapsulation, tight insulating covers, and pipe joints.

Heat shrinkability of EVA has been reported for pure EVA^{22–24} and EVA blended with other polymers, i.e., polyethylene,^{25–27} polyacrylic rubber,²⁸ polyurethane,^{29,30} epichlorohydrin,³¹ chlorosulfonated polyethylene,^{32–34} and carboxylated NBR.^{35,36} EVA was crosslinked by irradiation^{22,23,25,26} and DCP.^{24,27–30,35} Recently, the mechanical properties and heat shrinkability of EVA/ENR blends cured with DCP has been published.³⁷

Although the mechanical properties of EVA/ENR blends have been reported, there have not been any reports on the effects of using different curing systems or different curing agents on the mechanical properties and heat shrinkability of EVA/ENR blends. The goal of the present study was to investigate the effect of different curing systems on the mechanical properties and heat shrinkability of EVA/ENR blends. Five different curing systems with three different curing agents that were classified into either single or binary curing agents have been prepared. The blends used contained 10 and 30 wt % of ENR.

EXPERIMENTAL

Materials

Polene[®] EVA N8038 (Bangkok, Thailand) with an 18% VA content was used as received. The melt index was 2.0 g/10 min. The ENR used was Epoxyprene[®]50 (Surathane, Thailand) containing 50 mol % of epoxidation. DCP, sulfur, and the phenolic resin (SP1045) (Schenectady, NY) were used as curing agents. Chemicals used for the rubber compounds included stearic acid, zinc oxide, calcium stearate, *N*-cyclohexylbenzothiazole-2-sulfenamide and Wingstay[®]L (Akron, OH).

Blend preparation

The polymer blends were prepared initially by melting the EVA and then ENR was added until a constant torque was obtained. After that a curing agent and other chemicals were added. Blending was achieved using an internal mixer (Brabender[®] Mixer 350E Duisburg, Germany) at 100°C with a rotor speed of 70 rpm. The total

TABLE I
Rubber Compounding Formulations

Chemicals	Loading	
	S	Ph
ENR	100	100
Stearic acid	2	2
ZnO	5	5
Calcium stearate	3	3
CBS	1.5	–
Wingstay L	1	1
Sulfur	0.75	–
Phenolic	–	6

S, sulfur; Ph, phenolic resin; ENR, epoxidized natural rubber; CBS, *N*-cyclohexylbenzothiazole-2-sulfenamide.

time of blending was approximately 7 min. The blend was removed immediately after blending in the mixer and passed once through the two-roll mill to obtain a sheet. There were five curing systems applied to make the blends including DCP, sulfur (S), phenolic resin (Ph), DCP mixed with sulfur (DCP + S), and DCP mixed with phenolic resin (DCP + Ph). DCP, S, and Ph were designated as single curing systems while the DCP + S and DCP + Ph were designated as binary curing systems. In the DCP system, only DCP was added and its concentration was based on the total weight of the polymers (EVA and ENR), referred to per hundred (phr). The concentration of sulfur and phenolic resin in the single curing system was based on the weight of ENR. The rubber compounding formulation is listed in Table I. For the binary curing systems, the DCP content was based on the total weight of the polymers while the sulfur and phenolic resin contents were based on the ENR content. Polymer blends consisted of 10 and 30 wt % of ENR. Compression molded specimens were prepared at 160°C for 10 min to obtain a 2-mm thick sheet.

Testing

Tensile properties, tear resistance and thermal aging resistance were carried out according to ASTM D412C, ASTM D624 (right angle) and ASTM D573, respectively. Eight specimens were used for every sample. The tensile properties and tear resistance were tested at 50 mm/min by using a LLOYD[®]LR10K tensile testing machine (Fareham, England, UK). Thermal aging was conducted at 70°C for 7 days in a Geer oven (Tabai Espec., GPHH-100, Taipei, Taiwan). Changes in tensile properties after thermal aging were calculated based on eq. (1).

$$P = \left[\frac{A - O}{O} \right] \times 100, \quad (1)$$

where *P* is the percentage change in the property, *O* is the original value and *A* is the value after aging.

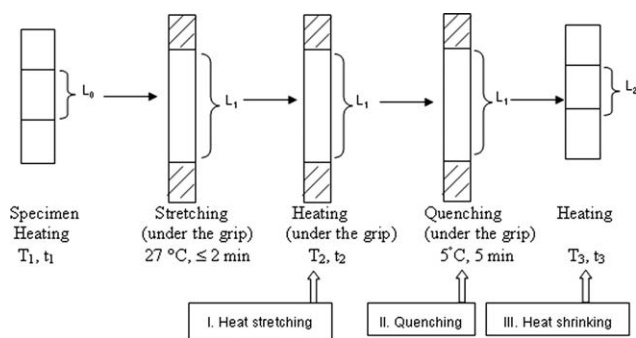


Figure 1 Schematic diagram of the heat shrink test.

Heat shrinkability was tested with various testing conditions. The process of this testing method is illustrated in Figure 1. The heat shrink test consisted of three steps: (I) heat stretching, (II) quenching, and (III) heat shrinking. Rectangular 5 mm × 60 mm specimens were used. The specimens may be heated at a temperature T_1 for a time t_1 prior to stretching. Specimens were stretched slowly at room temperature until they reached the required extension (L_1). The stretched specimens were held in the grips and heated at the temperature T_2 for the time t_2 in the oven (Step I: heat stretching step) and immersed in ice–water at 5°C for 5 min (Step II: quenching step). The specimens were released from the grips and heated again at the temperature T_3 for the time t_3 (Step III: heat shrinking step). The condition of the heat shrink test was indicated as $T_1, t_1/T_2, t_2/T_3, t_3$. There were two conditions of specimen heating (T_1): heating at 100°C for 5 min and no heating. The values of T_1 and t_1 in the second condition were 27°C (room temperature) and 0 min, respectively. The speed of stretching was approximately 70 mm/min. Heat shrinkability was explained in terms of heat shrinkage and an amnesia rating was calculated based on eqs. (2) and (3), respectively:

$$\text{Heat shrinkage (\%)} = \frac{L_1 - L_2}{L_2} \times 100, \quad (2)$$

$$\text{Amnesia rating (\%)} = \frac{L_2 - L_0}{L_0} \times 100, \quad (3)$$

where L_0 is the original length before stretching, L_1 is the length after stretching and L_2 is the length after shrinking. The measurement of L_2 was done at ambient temperature. Three specimens were tested for every sample and the average value was reported.

Blend morphology analysis

The blended samples were immersed in liquid nitrogen for 2 h. Then, the freeze fractured surfaces were

etched with methyl ethyl ketone at 80°C for 1 h to dissolve the ENR phase and dried at 60°C for 24 h prior to coating with gold. The morphology of the blends was observed with a scanning electron microscope (JEOL® JSM5800LV, Tokyo, Japan).

RESULTS AND DISCUSSION

Mechanical properties of the blends

The main purpose of this study was to prepare EVA/ENR blends to be used as heat shrinkable products. It has been established that crystallinity and crosslinking are very important because they provide memory points for heat shrinkable polymers. Therefore, it was necessary to crosslink EVA due to its low crystallinity. DCP is an effective crosslinking agent for EVA. Crosslink density affects the mechanical properties of polymers. As a result, the DCP content should be at an appropriate level based on its mechanical properties and heat shrinkability. In the present work, DCP should not be more than 1 phr because DCP is not a good crosslinking agent for ENR. Although DCP is able to crosslink NR and ENR, too much DCP will cause thermal oxidation of NR and ENR during compounding and compression molding. This was evident from the sticky surface of the samples. Two concentrations of DCP were selected in this study: 0.5 and 1 phr. Figure 2 shows the effect of the DCP content on the tensile

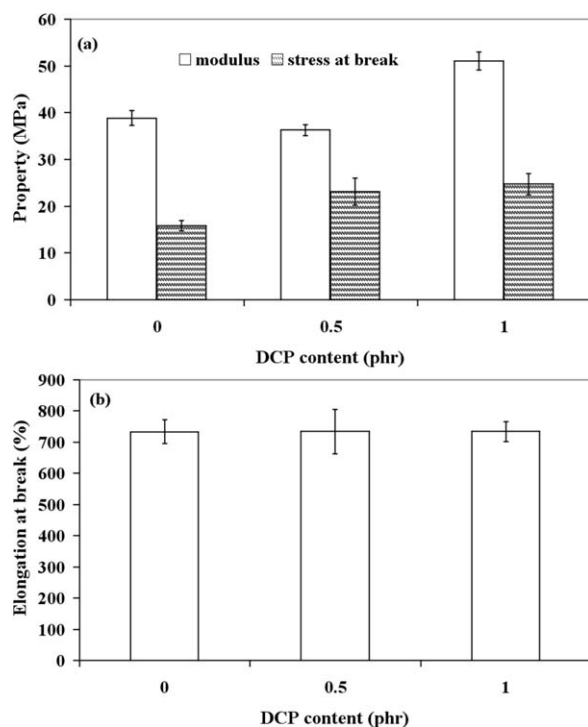


Figure 2 Tensile properties of EVAs containing different DCP contents: (a) Young's modulus and stress at break and (b) elongation at break.

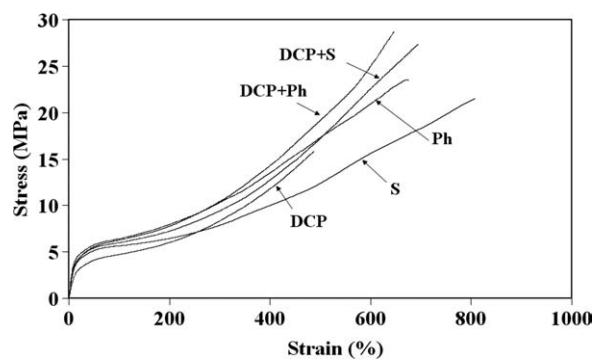


Figure 3 Stress–strain curves of the 10% ENR blends cured with different curing systems.

properties of EVA. The sample containing 1 phr of DCP showed the highest modulus, whereas the tensile strength of the samples containing DCP was similar but certainly higher than the one without DCP. The elongation at break did not change significantly with the DCP content. The degree of crystallinity of EVA determined by differential scanning calorimetry was 12%. After adding DCP and other curing agents, no significant changes in the degree of crystallinity of EVA were detected. Consequently, in the present study, crystallization was not a factor involved in the mechanical properties and heat shrinkability. Generally, crosslinking enhances the modulus and the tensile strength of polymers due to the strong intermolecular bonds. However, little change in the elongation at break was obtained as demonstrated in Figure 2(b). It did indicate that crosslinking played an important role on the modulus and the tensile strength, but not on the elongation at break. The heat shrink test of EVA showed that it was essential to crosslink EVA. Without DCP, low heat shrinkage (64%) was obtained. By adding DCP, the heat shrinkage increased to 74% and 73% for blends containing 0.5 and 1 phr of DCP, respectively. There was no significant difference in the heat shrinkability of EVA due to the different DCP content. This result indicated that optimum crosslinking of EVA had been achieved with regard to heat shrinkage. Furthermore, the blend containing 1 phr of DCP became very sticky after compounding and compression molding. Consequently, 0.5 phr of DCP was selected to crosslink polymers in the present study.

To improve crosslinking of ENR, sulfur and phenolic resins were employed. The sulfur and phenolic resin contents were based on the ENR content as demonstrated in Table I and the DCP concentration used was based on the polymer weight (EVA and ENR). Stress – strain curves and tensile properties of the blends containing different curing systems are illustrated in Figures 3 and 4, respectively. The tensile behavior of the blends did not change with dif-

ferent curing systems and all samples showed ductile fracture. The higher ENR content exhibited lower tensile properties. The system containing only DCP displayed the lowest tensile properties in both blends (10% ENR blend and 30% ENR blend). The Ph system yielded the highest modulus and this was slightly higher than the S and the DCP + S systems. The stress at break of the 10% ENR blend tended to change with different curing systems whereas 30% ENR blend tended to fall in the same range. The effect of different curing systems on the elongation at break of the blends was most pronounced in the 10% ENR blend. The S system showed the highest elongation at break. For the blends containing 30% ENR, elongation at break was not significantly different with different curing systems. As stated earlier, DCP is not a good curing agent of ENR.

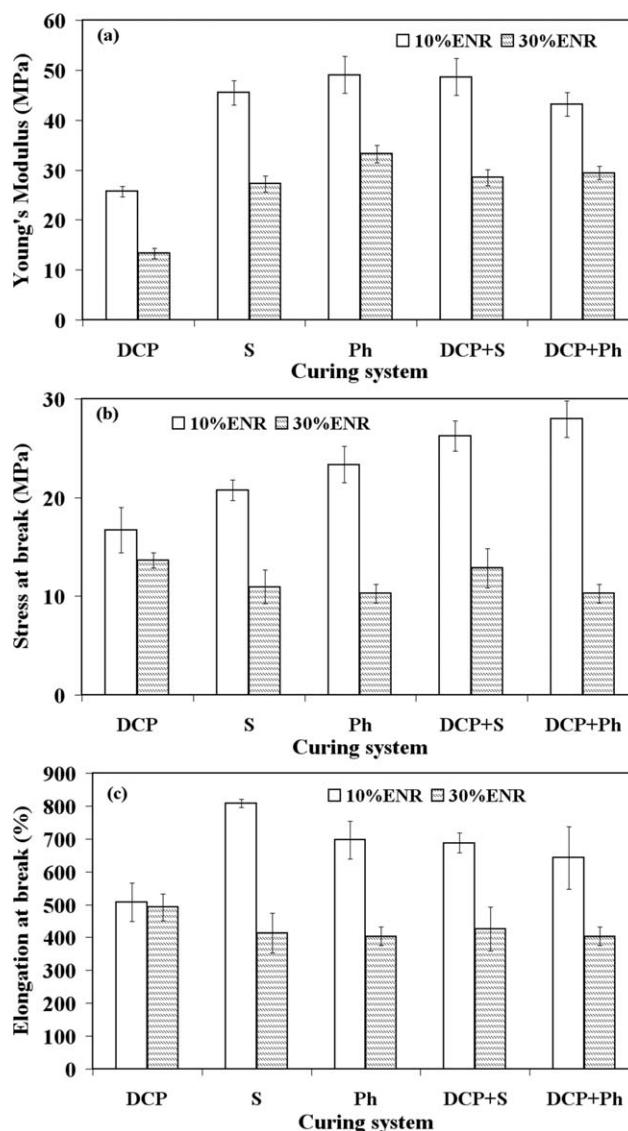


Figure 4 Tensile properties of EVA/ENR blends cured with different curing systems: (a) Young's modulus, (b) stress at break, and (c) elongation at break.

Although the DCP concentration used was sufficient for curing EVA it was very low and not sufficient to vulcanize ENR properly. Based on this preliminary study, ENR containing 0.5 phr of DCP showed very low torque during testing with the moving die rheometer (MDR) and it was unable to be prepared as a normal rubber sheet by compression molding. Hence, the tensile properties of the DCP system were lowest among the blends containing 10% ENR.

There are many parameters that contribute to the mechanical properties and characteristics of polymer blends such as miscibility, blend morphology, interfacial adhesion, size of the dispersed phase, distribution of curing agents, crosslinking, etc. Crosslinking in polymer blends is complex when more than one curing agent is employed or one curing agent can crosslink two polymeric phases. As a result, the distribution of curing agents becomes the important parameter affecting the mechanical properties of the blends. It seemed that crosslinking by DCP was more favorable with EVA than with ENR based on two reasons: the MDR test as stated earlier and the increase in the modulus and the tensile strength as shown in Figure 2(a). The distribution of curing agents in the present blends can be determined indirectly by a standard deviation of the mechanical properties. It was found that the data in Figure 4 and Table II showed small standard deviations. In the case of a poor distribution of curing agents, one may observe large standard deviations in mechanical properties. Furthermore, sulfur and phenolic resin cannot be used as a curing agent for EVA. Therefore, it was expected that a good curative distribution and good crosslinking in each phase would be obtained. Among the three curing agents used, only DCP can crosslink both EVA and ENR. If there was co-crosslinking between EVA and DCP this would increase the interfacial adhesion between EVA and ENR and the mechanical properties of the DCP system should be highest. In contrast, the mechanical properties of the DCP system were not the highest and tended to be the lowest in many samples. This

TABLE II
Tear Strength of the 10% and 30% ENR Blends

Curing system	Tear strength (N/mm)	
	10% ENR blend	30% ENR blend
DCP	58.83 ± 1.63	48.56 ± 2.37
S	66.05 ± 2.48	63.42 ± 2.92
Ph	67.89 ± 3.37	57.28 ± 1.28
DCP + S	73.37 ± 4.82	64.96 ± 2.73
DCP + Ph	72.14 ± 2.87	62.25 ± 2.42

ENR, epoxidized natural rubber; DCP, dicumyl peroxide; S, sulfur; Ph, phenolic resin.

indicated that the interfacial adhesion was not affected by the different curing systems.

Theoretically, deformation occurs more in the weaker polymer than in the stronger one. Deformation in the rubber disperse-phase should be easier than the thermoplastic phase during load applying because of its lower modulus compared with the thermoplastic matrix while both phases received same loading. To increase the modulus and the tensile strength of the thermoplastic/rubber blends, the rubber phase must be improved e.g., by crosslinking. By addition of the sulfur and phenolic resin, better vulcanization in the ENR was obtained leading to an improvement in the tensile properties of the blends. It was not necessary to investigate the optimum vulcanization of all curing agents on the ENR and producing a highly cured ENR was not the objective of the present study because it was not useful for heat shrinkability. Furthermore, it was not required to compare the mechanical properties and heat shrinkability between a crosslinked EVA and crosslinked ENR because crosslinked ENR is unable to be the heat shrinkable polymer. Curing in both the EVA and ENR improved the tensile properties as shown in Figure 4 and the effect on heat shrinkability will be described later. In the case of the 30% ENR blends, another parameter i.e., the rubber particle size must be considered. Figure 5 shows the SEM micrographs of the blends cured with phenolic resin.

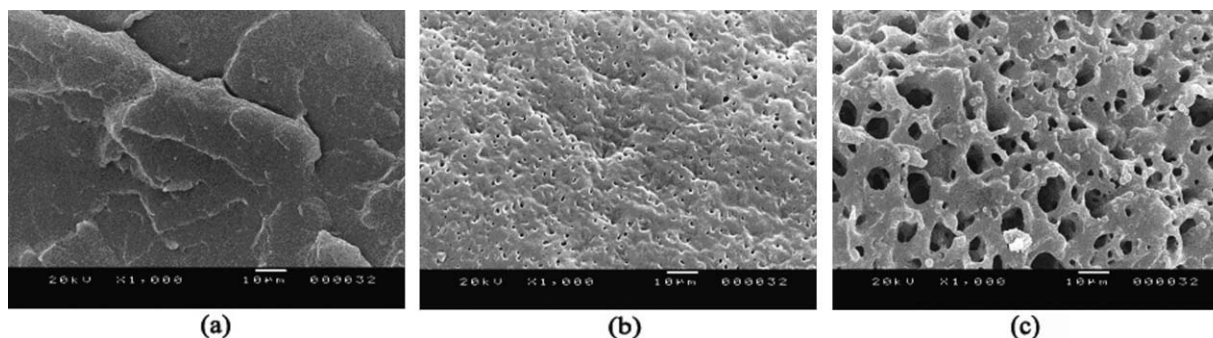


Figure 5 SEM micrographs of the blends cured with phenolic resin: (a) unetched, 10%-ENR blend, (b) etched, 10%-ENR blend, and (c) etched, 30%-ENR blend.

The unetched sample showed a very smooth and non-textured surface. If there was only slight cross-linking in the ENR, solvent etching could be applied to the samples. After etching with MEK, the ENR particles were removed from the fractured surface to produce small holes on the surface. With increased ENR content, the particle size of ENR became much bigger. All different curing systems showed similar blend morphology and similar rubber particle sizes. The average rubber particle size in the blends containing 30% ENR were in the range of 5–10 μm which was an ineffective size for improvement of the mechanical properties. For this reason, the tensile strength and elongation at break showed little effect with the different curing systems. The decrease in tensile properties after increasing the ENR content was attributed to the larger rubber particle size. For the 30% ENR blends, the particle size was the dominant factor in the tensile strength and the elongation at break of all curing systems, the lowest initial modulus in the DCP system resulted from the very low vulcanization in the ENR phase. Although EVA and ENR are immiscible, there was a report by Kannan et al.¹⁰ that mentioned that the EVA/ENR blend showed weak dipole–dipole interactions although no chemical interaction was observed. Furthermore, in the present study, the SEM analysis also demonstrated the compatibility of this blend because no texture was observed in the unetched samples.

The effect of different curing systems on the tear strength and the thermal aging resistance of the blends are shown in Table II and Figure 6, respectively. The DCP system still showed the lowest tear strength in both blends. The curing system containing two curing agents provided higher tear strength in the 10% ENR blend. The higher ENR content exhibited lower tear strength and tensile properties. It is believed that the better vulcanization in the ENR phase governed the tear strength of the 10% ENR blends whereas the rubber particle size played a role on this property of the 30% ENR blends, as was the case with the tensile properties. Changes in tensile properties after thermal aging relate to chain scission and crosslinking in the molecules. The positive values indicated crosslinking and the negative values indicated chain scission. Both of them are undesirable as no change or only a small change in properties is required. The results in Figure 6 show various trends and it is difficult to draw conclusions. However, the DCP system displayed the highest tendency for changes, particularly changes in the modulus, and the phenolic resin system showed the lowest changes. The thermal aging resistance seemed to be independent of the ENR content. In general, the 10% ENR blend showed higher mechanical properties than the 30% ENR blend, and it was necessary

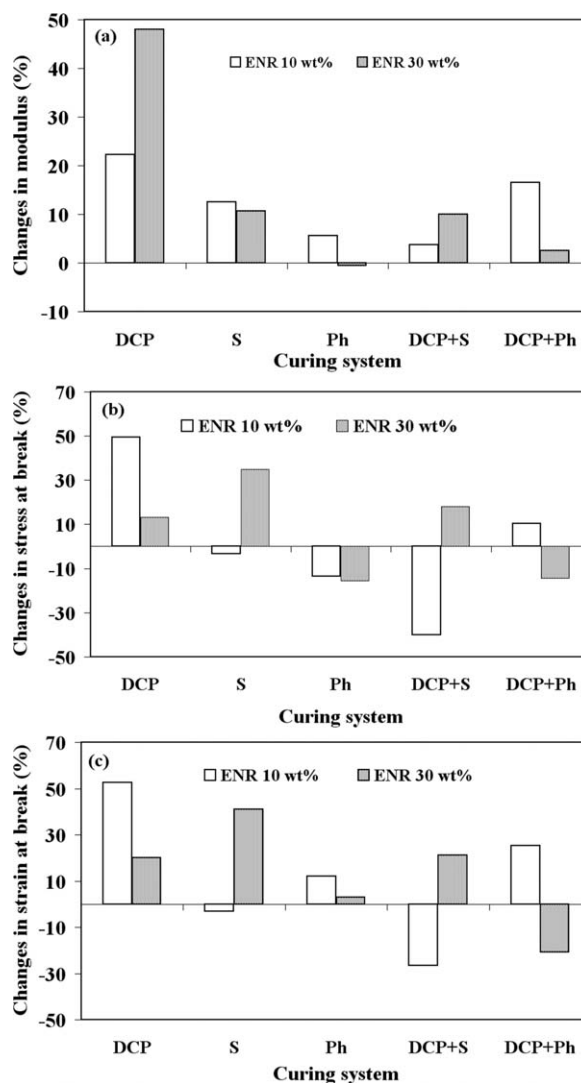


Figure 6 Changes in tensile properties after thermal aging of the 10% and 30%-ENR blends containing different curing systems: (a) changes in modulus, (b) changes in stress at break, and (c) changes in elongation at break.

to vulcanize the ENR phase to improve the mechanical properties. Not only did the curing system have a dominant effect on the mechanical properties of the blends but so did the ENR particle size.

Heat shrinkability of the EVA

Heat shrinkability is a property concerned with changes in the physical performance. Not every polymer is able to show high heat shrinkability. Heat shrinkability depends on molecular architecture, sample preparation, and the heat shrink conditions (application condition). In the present system, the DCP content provided a different molecular architecture. Sample preparation for testing involved the percentage of extension (stretching) as well as the conditions of heat stretching and quenching. The last step in Figure 1 which was heat shrinking

TABLE III
Heat Shrinkage of EVA with and without DCP Stretched at 240%

DCP content (phr)	Testing condition			Heat shrinkage (%)	Amnesia rating (%)
	T_1, t_1	T_2, t_2	T_3, t_3		
0	T_{room}	70, 5	120, 2	64	11
		80, 5		64	16
		90, 5		Broken at step I	Broken at step I
0.5	T_{room}	70, 5	120, 2	70	14
		80, 5		71	14
		90, 5		74	1
		100, 5		74	-2

EVA, ethylene vinyl acetate; DCP, dicumyl peroxide.

represented the application condition. Table III shows the effect of DCP on the heat shrinkage of EVA under various testing conditions. Without crosslinking, EVA was shrinkable after reheating but its heat shrinkage was lower than EVA containing DCP. By increasing the heat stretching temperature (T_2) to 90°C, the EVA without DCP was unable to proceed. EVA became stronger after crosslinking. The crosslinked EVA could be processed at a higher temperature and heat shrinkage increased slightly with an increase of the heat stretching temperature. The temperature at 90°C was very severe for uncrosslinked EVA because the melting temperature of virgin EVA was 100°C. At 90°C, the molecular movement was high and the molecular flow was more easily achieved in the uncrosslinked molecules than the crosslinked molecules. The heat stretching temperature (T_2) could be separated into two levels: $\leq 80^\circ\text{C}$ and $\geq 90^\circ\text{C}$, and there was little effect on the heat shrinkage at each level. T_2 showed a significant effect on the amnesia rating. The amnesia rating could refer to changes in length after heat shrinking (L_2) compared to the original length before stretching (L_0). A negative value implies that the length after shrinking is shorter than the original length. This reflects the non-equilibrium state of the sample prior to testing. A positive value of the amnesia rating indicates that there was a permanent extension of molecules. After annealing (heat shrinking step, T_3), molecular relaxation took place, resulting in a snapping back of molecules to the equilibrium state. The crosslinked EVA shrank back nearly to the original length when T_2 were 90 and 100°C as shown in Table III. During specimen stretching, molecular orientation was taking place. When the specimen was heated at T_2 , molecular relaxation may occur. Higher temperatures provide more energy for molecular motion leading to more stress relaxation which can be attributed to more chain orientation. This resulted in more driving force to snap back or more heat

shrinkability. The heat shrink test was performed by using three specimens for every sample. It was found that the standard deviation of heat shrinkage and the amnesia rating values of all samples was <1 . There were many parameters in the testing conditions as illustrated in Figure 1. The optimal testing condition should be applied for testing the blends. T_2 at 90°C was selected although T_2 at 90 and 100°C showed similar heat shrinkage as illustrated in Table III. With regard to saving energy and the melting temperature of EVA, 90°C was a better condition. Figure 7 exhibits the effect of heat stretching time (t_2), heat shrinking temperature (T_3) and heat shrinking time (t_3) on the heat shrinkage of crosslinked EVA. Heat shrinkage increased with increasing t_2 and T_3 . In contrast, t_3 showed little effect on the heat shrinkage. T_3 produced the maximum heat shrinkage at 120°C. Consequently, the selected condition of $T_2 t_2 / T_3 t_3$ was 90,5/120,1 in further experiments.

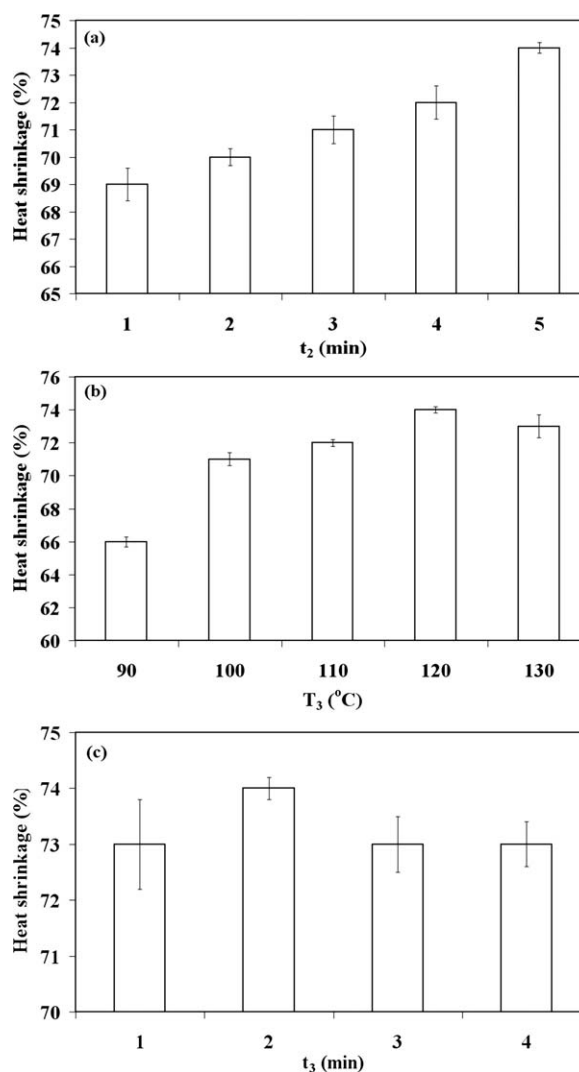


Figure 7 Heat shrinkage of EVA containing 0.5 phr of DCP stretched at 240% tested under various conditions of $T_2 t_2 / T_3 t_3$: (a) 90, t_2 /120,2, (b) 90,5/ T_3 ,2, and (c) 90,5/120, t_3 .

TABLE IV
Heat Shrinkage and Amnesia Ratings of the 10% ENR Blends Tested at $T_{\text{room}}/90,5/120,1$

Curing system	Extension					
	200%		300%		400%	
	HS	AR	HS	AR	HS	AR
DCP	70	-3	77	-1	80	-2
S	Broken at step I					
Ph	Broken at step I					
DCP + S	71	-2	Broken at step I			
DCP + Ph	70	1	75	-1	80	-3

ENR, epoxidized natural rubber; HS, heat shrinkage; AR, amnesia rating; DCP, dicumyl peroxide; S, sulfur; Ph, phenolic resin.

Heat shrinkability of the blends

The heat shrinkage and amnesia rating of the blends containing different curing systems are displayed in Tables IV–VI. The blends without DCP were broken during heat stretching although the extension was low (200%). Keep in mind that the S and Ph systems produced no crosslinking in the EVA matrix. The addition of sulfur or phenolic resin did not increase the heat shrinkage of crosslinked EVA, compared with the DCP system. Furthermore, in some cases the addition of sulfur lowered the heat shrinkability of the blends such as some samples of the DCP + S system in Tables IV and VI were broken during testing. These results were different from those of the mechanical properties. It appeared that the binary curing systems did not improve heat shrinkability but they did increase the mechanical properties of the blends. Fortunately, the DCP + Ph system provided similar heat shrinkage to the DCP system and this binary system also provided better mechanical properties than the DCP system. Therefore, in the present study, the DCP + Ph system was the most suitable curing system for the EVA/ENR blend.

Moreover, the amnesia rating of the DCP + Ph system was lower than that of the DCP system in the 10% ENR blends as shown in Tables IV and V. This substantiated the conclusion, in this study, that the DCP + Ph curing system was the best.

The effect of specimen heating prior to stretching (T_1) is shown in Tables IV and V. Without specimen heating ($T_1 = \text{room temperature}, 27^\circ\text{C}$), the maximum extension was 400%. After heating the specimen at 100°C for 5 min, the specimen could be stretched up to 500% causing higher heat shrinkage. The effect of the ENR content on heat shrinkage could be deduced by comparisons among the Tables III–VI. Without ENR, the heat shrinkage of EVA was 74% at 240% extension. There was little change in heat shrinkage observed at low extension (200–300%) caused by the addition of ENR (Tables IV–VI). However, the addition of ENR increased the extensibility of EVA during heat stretching.³⁷ This was attributed to a higher extension and heat shrinkage suggesting that there was a high interfacial adhesion between EVA and ENR which resulted from the dipole–dipole interaction between EVA and ENR¹⁰ as stated previously. The present study showed that the particle size of ENR had a minimal effect on the heat shrinkability of EVA although some rubber particles were as large as 10 μm . The rubber particles did not hinder the molecular orientation of EVA and crosslinking of the rubber particles was not crucial for an increase in the heat shrinkage of the blends. Another parameter reported in Tables IV–VI was the percentage of extension. Obviously, heat shrinkage increased with increasing extension. A higher extension provided more orientation leading to a greater driving force of retraction or snapping back. In other words, more orientation provided more internal stress or more nonequilibrium in the specimens. Once the molecules received enough heat energy, molecular retraction to the equilibrium state would occur immediately.

TABLE V
Heat Shrinkage and Amnesia Ratings of the 10% ENR Blends Tested at $100,5/90,5/120,1$

Curing system	Extension							
	200%		300%		400%		500%	
	HS	AR	HS	AR	HS	AR	HS	AR
DCP	65	9	74	8	78	14	83	5
S	Broken at step I							
Ph	Broken at step I							
DCP + S	68	-1	75	4	80	5	84	-1
DCP + Ph	67	2	76	-1	80	2	84	-2

ENR, epoxidized natural rubber; HS, heat shrinkage; AR, amnesia rating; DCP, dicumyl peroxide; S, sulfur; Ph, phenolic resin.

TABLE VI
Heat Shrinkage and Amnesia Ratings of the 30% ENR Blends Tested at 100,5/90,5/120,1

Curing system	Extension							
	200%		300%		400%		500%	
	HS	AR	HS	AR	HS	AR	HS	AR
DCP	69	-12	76	-7	80	-6	83	-3
S	Broken at step I							
Ph								
DCP + S	68	-7	75	-6	78	1	Broken at step I	
DCP + Ph	65	3	73	9	78	10	81	9

ENR, epoxidized natural rubber; HS, heat shrinkage; AR, amnesia rating; DCP, dicumyl peroxide; S, sulfur; Ph, phenolic resin.

CONCLUSIONS

The effects of different curatives on the mechanical properties and heat shrinkability in EVA/ENR blends were reported. The binary curing systems provided better mechanical properties than the single curing systems and had different effects on the heat shrinkability of the blends. The best curing system in the present study was DCP mixed with phenolic resin. It was essential to crosslink EVA for high heat shrinkage and vulcanized ENR was desired for its high mechanical properties. The rubber content, rubber particle size, and degree of vulcanization of the rubber phase had no significant effects on the heat shrinkability of EVA. The 10% ENR blend was more favorable because the 30% ENR blend consisted of very large ENR particles that lead to lower tensile properties. The effect of the rubber content on the tensile properties produced different results between the blends that contained 10% and those with 30% of ENR. It is believed that the tensile properties of the 10%-ENR blend were controlled by rubber vulcanization, higher vulcanization of the ENR produced higher tensile properties of the blend. On the other hand, the tensile properties of the 30%-ENR blend were controlled by the ENR particle size. This blend composition provided very large sizes of the ENR phase, thus the tensile properties did not change significantly after adding sulfur and phenolic resin.

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