

HNBR/EPDM Blends: Covulcanization and Compatibility

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ABSTRACT: The covulcanization characteristics, mechanical properties, compatibility, and hot-air aging resistance of hydrogenated nitrile-butadiene rubber (HNBR)/ethylene-propylene-diene rubber (EPDM) blends cured with either sulfur or dicumyl peroxide (DCP) were studied. The difference between M_H and M_L ($M_H - M_L$), rheometer graphs, selective swelling and a dynamic mechanical analysis of HNBR/EPDM blends confirmed that the peroxide curing system gives better covulcanization characteristics than the sulfur curing system and peroxide exhibited higher crosslink efficiency on EPDM while sulfur showed larger crosslink efficiency on HNBR. Dynamic mechanical analysis and morphology indicated that the compatibility between HNBR and EPDM is limited. Tensile strength and elongation at break of the sulfur-cured blends are greater than those obtained with peroxide and increase with the HNBR fraction. The blends crosslinked with peroxide retain their tensile strength but not their elongation at break after hot air ageing better than blends vulcanized by sulfur. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3054–3060, 2013

KEYWORDS: ageing; compatibilization; crosslinking; rubber

Received 5 December 2012; accepted 13 January 2013; published online 18 February 2013

DOI: 10.1002/app.39014

INTRODUCTION

HNBR is produced by hydrogenation of nitrile rubber with selected catalyst systems in order to provide excellent resistance to thermal and oxidative degradation as well as many aggressive fluids without sacrificing oil and abrasion resistance; however, the application of HNBR elastomers is limited by its cost.^{1–4} To meet the increasing requirements of automotive, aerospace, and other industries for extremely high operating temperatures and extended material service lifetime HNBR can be modified. For example, HNBR has been blended with other elastomers such as EVA,^{5,6} IR,⁷ SBR,⁷ and NBR.⁸ The good heat resistance of EPDM elastomers suggests that as well as being of theoretical interest, blends of these elastomers with HNBR might prove economically valuable.

Peroxides are the crosslinking system of choice for HNBR with a degree of hydrogenation greater than 95% whereas at lower hydrogenation levels blends of HNBR with EPDM can be cross-linked using both peroxide and sulfur cross-linking systems. At HNBR hydrogenation levels (ca. 90%) the sulfur systems are preferred. Generally, curing agents such as sulfur and accelerator tend to be more soluble in unsaturated or polar elastomers and this leads to a migration of these reagents from the less polar, more saturated elastomer and nonuniform crosslinking.^{9,10} To date most research into the covulcanization of dissimilar rubber blends has focused on sulfur curing systems; for example,

Ghosh et al. studied the effect of a multifunctional rubber additive, bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) on the covulcanization of SBR/EPDM, NR/EPDM, and NBR/EPDM blend systems to restrict the curative migration into the more unsaturated rubber. As a result, the cure-rate mismatch problem could at least be ameliorated.^{11–13}

The work described in this article involved two curing systems: dicumyl peroxide (DCP) and a sulfur curing system. The cross-linked HNBR/EPDM blends were analyzed in terms of their rheological parameters and rheometer graphs as well as by selective swelling and dynamic mechanical analysis (DMTA). Additionally, the mechanical properties, compatibility, and hot-air aging resistance of the blends were investigated. It is expected to provide helpful information and data for further researches on HNBR/EPDM blends.

EXPERIMENTAL

Materials and Recipes

HNBR (Therban 3467) with 34 wt % of acrylonitrile (ACN), 5.5% residual double bonds (UML1+4, 100°C, 68) and EPDM (Buna EPG 8850) having a ethylene content (UML1+4, 125°C, 80) were provided by LANXESS Chemical (Leverkusen, Germany). DCP (40%ig) was supplied by AKZO Nobel, the Netherlands. Triallyl isocyanurate (TAIC), tetramethyl thiuram disulfide (TMTD), thio bis benzothiazole (M

Table I. Composition of HNBR/EPDM Blends

Sample designation	HNBR (phr ^a)	EPDM (phr)
H0	0	100
H25	25	75
H50	50	50
H75	75	25
H100	100	0

^a phr, parts per hundred polymer.

were provided by Rhein Chemie (Qingdao, China). Sulfur, ZnO, and stearic acid were supplied by Linyi Haiquan Chemical Industry in China, Jinchangsheng, in China and Gaoxin in China, respectively.

The composition of the HNBR/EPDM blends is listed in Table I, where H represents HNBR elastomer and the subscript indicates the percentage of HNBR in the blend. The compounding recipes of the blends are given in Table II.

Preparation of HNBR/EPDM Blends

HNBR/EPDM compounds without filler were prepared in a HAAKE (Rheocord90, Germany) operating at 100°C, 60 rpm for 5 min (recipes given in Table II). The curing agents were added on an open two-roll mill of laboratory size (S(X)K-160A, size: 320 × 160 mm², Shanghai Rubber Machinery Factory, China) at room temperature. The rubber compounds were cured at 170°C (Peroxide systems) or, 160°C (Sulfur systems) in an electrically heated, hydraulic press into sheets of 2 mm thickness. All samples were preconditioned at room temperature for 24 h before being tested.

MEASUREMENT AND CHARACTERIZATION

Measurement of Cure Parameters

The cure characteristics of the blends were determined by using MDR 2000 (Alpha Technology, USA) operating at 160°C with a 1° arc, according to the ASTM D 2084-8.

Mechanical Properties

The tensile strength was measured according to ASTM D412-97, using a universal electromechanical tester (Instron 3365, USA)

Table II. Compound Formulations

Ingredient	Quantity(phr)
Sulfur Curing System	
Polymer	100
Zinc oxide	5
Stearic acid	1
Tetra methyl thiuram disulfide(TMTD)	1
Thio bis benzothiazole(M)	0.5
Sulfur	1.5
Peroxide Curing System	
Polymer	100
Dicumyl peroxide(DCP)	3
Triallyl isocyanurate(TAIC)	2

with a crosshead speed of 500 mm/min. Shore A hardness was measured according to ASTM D2240-97 using a hand-held Shore A durometer (LX-A, Shanghai Liuling Instrument Factory, China).

Degree of Equilibrium Swelling

Cured test pieces (cut the sample into thickness less than 1 mm, width is not limited, weight ca. 40–50 mg) were allowed to swell in chlorobenzene or cyclohexane until equilibrium swelling was achieved. After reaching equilibrium, the swollen test pieces were dried under a vacuum to a constant weight. The original (Subscript: uns) and final (Subscript: des) weights were used to calculate the WL (weight loss, soluble material) and CE (crosslinking efficiency) in the network, according to eqs. (1) and (2):

$$cWL = \frac{WL_{uns} - WL_{des}}{WL_{uns}} \times 100\% \quad (1)$$

$$CE = \frac{WL_{des}}{WL_{uns}} \times 100\% \quad (2)$$

Hot-Air Ageing Resistance

Hot-air ageing resistance was measured according to ASTM D573-99. The samples were placed in a hot-air oven at 150°C for 72 h. The retention of mechanical properties was calculated using eq. (3).

$$\text{retention}(\%) = \frac{(\text{mp})_{\text{aged}}}{(\text{mp})_{\text{unaged}}} \times 100 \quad (3)$$

Where mp represents the measured mechanical property.

Dynamic Mechanical Thermal Analysis

The dynamic mechanical properties of the vulcanizates were measured by a dynamic mechanical thermal analyzer (DMTA; Eplexor 500N, GABO) at a heating rate of 2°C/min (from –100°C to 50°C) and a frequency of 1 Hz with 0.01% strain.

Morphology

A small piece of HNBR/EPDM compound sample was heated on a stage at 120°C and then pressed into a film. The specimens

Table III. Cure Characteristics of HNBR/EPDM Blends

Sample code	Scorch time t ₂ (min)	M _H – M _L (Nm)	Optimum cure time t ₉₀ (min)
Sulfur curing system			
H0	2.30	34.03	8.17
H25	1.49	29.41	6.2
H50	0.97	28.96	4.9
H75	0.71	29.09	4.35
H100	0.61	33.09	4.1
Peroxide curing system			
H0	0.46	60.48	12.05
H25	0.51	54.3	10.27
H50	0.56	50.82	10.11
H75	0.62	46.26	10.06
H100	0.73	39.77	10.05

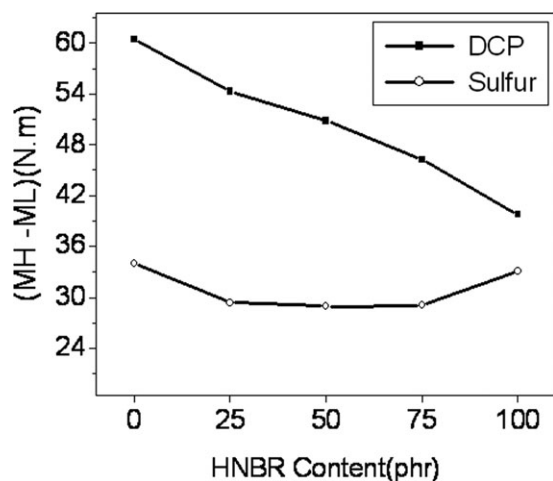


Figure 1. $M_H - M_L$ in HNBR/EPDM blends with two curing systems.

were put on the stage of a phase contrast microscope (BX51, Olympus Corporation, Japan). The micrographs of HNBR/EPDM compounds were obtained at a magnification of $M=200\times$.

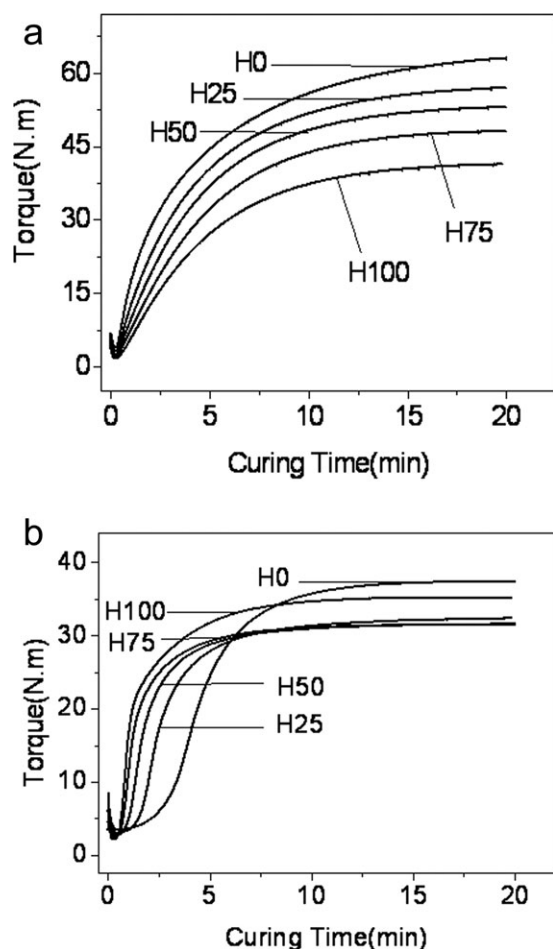


Figure 2. Rheometer curves of HNBR/EPDM blends. (a) Sulfur curing system (b) Peroxide curing system.

RESULTS AND DISCUSSION

Cure Characteristics

Table III shows the cure characteristics of the blends. Scorch time (t_{s2}) is the time taken for the minimum torque value to increase by two units. It is a measure of the premature vulcanization of the material. As shown in Table III, scorch time decreases with increasing HNBR in the blend with sulfur curing system, however, it increases with peroxide curing system as the percentage of HNBR in the blend increases. Optimum cure time decreases with an increase in HNBR content in the blends with both curing systems. These observations indicate that the rate of vulcanization is faster in blends containing more HNBR. Additionally, peroxide-cured HNBR/EPDM blends need a longer time to achieve optimum cure. For the sulfur-cured systems, the values $(M_H - M_L)$ a measurement of crosslink density, especially in unfilled polymer blends, of pure HNBR and EPDM are higher than those of their blends, which are also shown in Figure 1. This suggests that the crosslink density of the HNBR or EPDM phase in the blends is reduced.¹⁴ However, the value $(M_H - M_L)$ for the HNBR/EPDM blends cured with peroxide declines almost linearly with the increase in the percentage of HNBR content, suggesting that the crosslink density of the HNBR and EPDM phases is independent of the HNBR/EPDM blend ratio.

Figure 2 shows the rheometer graphs of sulfur and peroxide crosslinked HNBR/EPDM blends. The initial decrease in torque is due to the softening of the matrix. Torque then increases due to the formation of crosslinks between the macromolecular chains. It can be seen from chart (a) that the cure rate of sulfur-cured pure HNBR is considerably faster than that of pure EPDM. Additionally, the optimum cure and scorch time of HNBR are shorter than those for EPDM. With increasing HNBR content in the blends the curves approach that of pure HNBR. For the peroxide-cured systems the results are similar but (shown in chart (b)) both pure HNBR, EPDM exhibit lower cure rate, longer optimum cure time compared to the sulfur-

Table IV. Swelling Experiment Data with HNBR/EPDM Blends as Function of the Curing System

Sample	WL (%)		WLchl- WLCyc (%)	CE (%)
	Chlorobenzene	Cyclohexane		
Sulfur curing system				
H0	1.92	-	-	98.1
H25	2.43	1.74	0.69	97.6
H50	2.78	2.24	0.54	97.2
H75	3.27	1.96	1.31	96.7
H100	2.95	-	-	97
Peroxide curing system				
H0	1.17	-	-	98.8
H25	1.72	1.53	0.19	98.3
H50	2.31	1.95	0.36	97.7
H75	3.03	1.76	1.27	97
H100	3.39	-	-	96.6

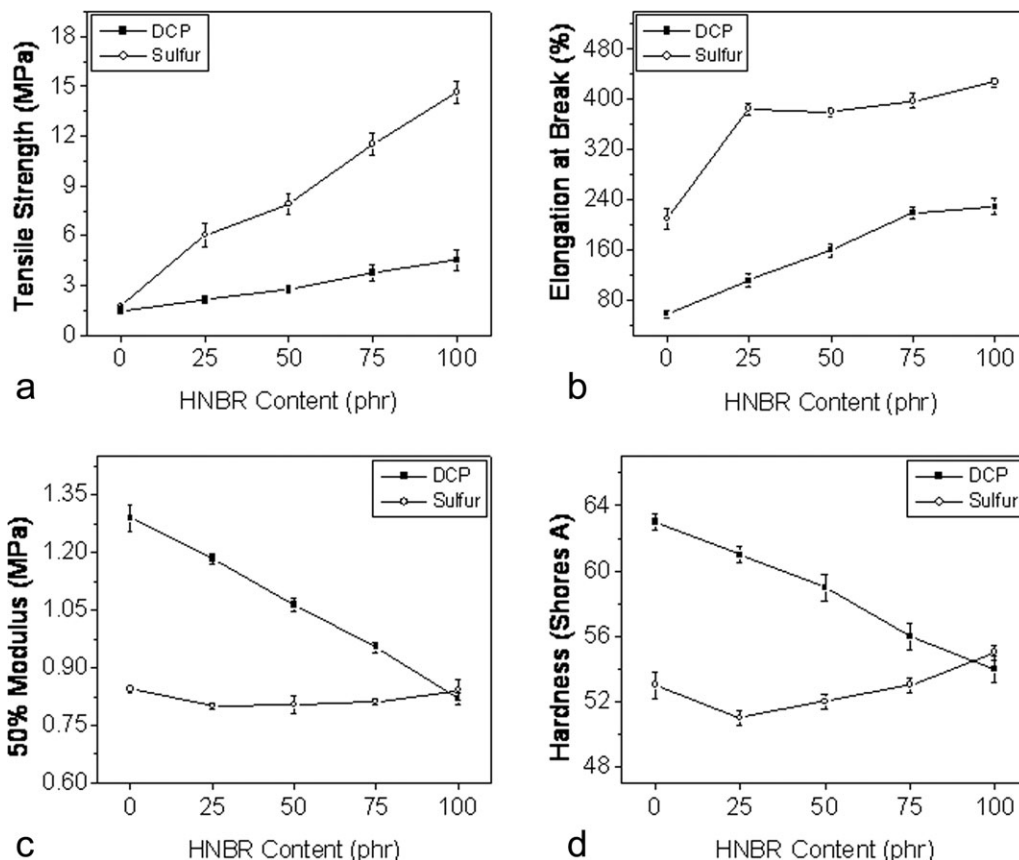


Figure 3. Effects of curing system on the mechanical properties of HNBR/EPDM vulcanizates.

cured systems and EPDM exhibits a faster rate than HNBR. A comparison of chart (a) and (b), suggests that the peroxide cure system should yield improved covulcanization for HNBR/EPDM blends.

Selective Swelling

In order to quantify the crosslinking of the two phases in the blends the blends were allowed to swell in chlorobenzene and

cyclohexane and the results analyzed according to eq. (1), (2). In chlorobenzene, both HNBR and EPDM phases will swell and dissolve; in cyclohexane, only the EPDM phase is affected. The amount of soluble material from swelling in cyclohexane is related to the fraction of unvulcanized EPDM phase and the weight loss difference (WLchl- WLcyc) is related to the fraction of uncrosslinked HNBR phase. Table IV summarizes the results

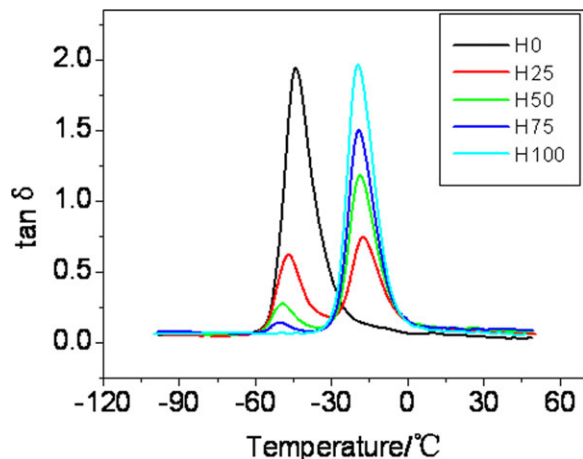


Figure 4. DMA curves of sulfur-cured HNBR/EPDM vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

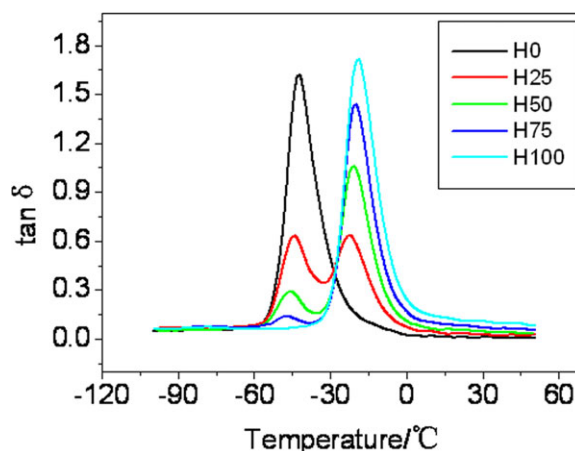


Figure 5. DMA curves of peroxide-cured HNBR/EPDM vulcanizates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

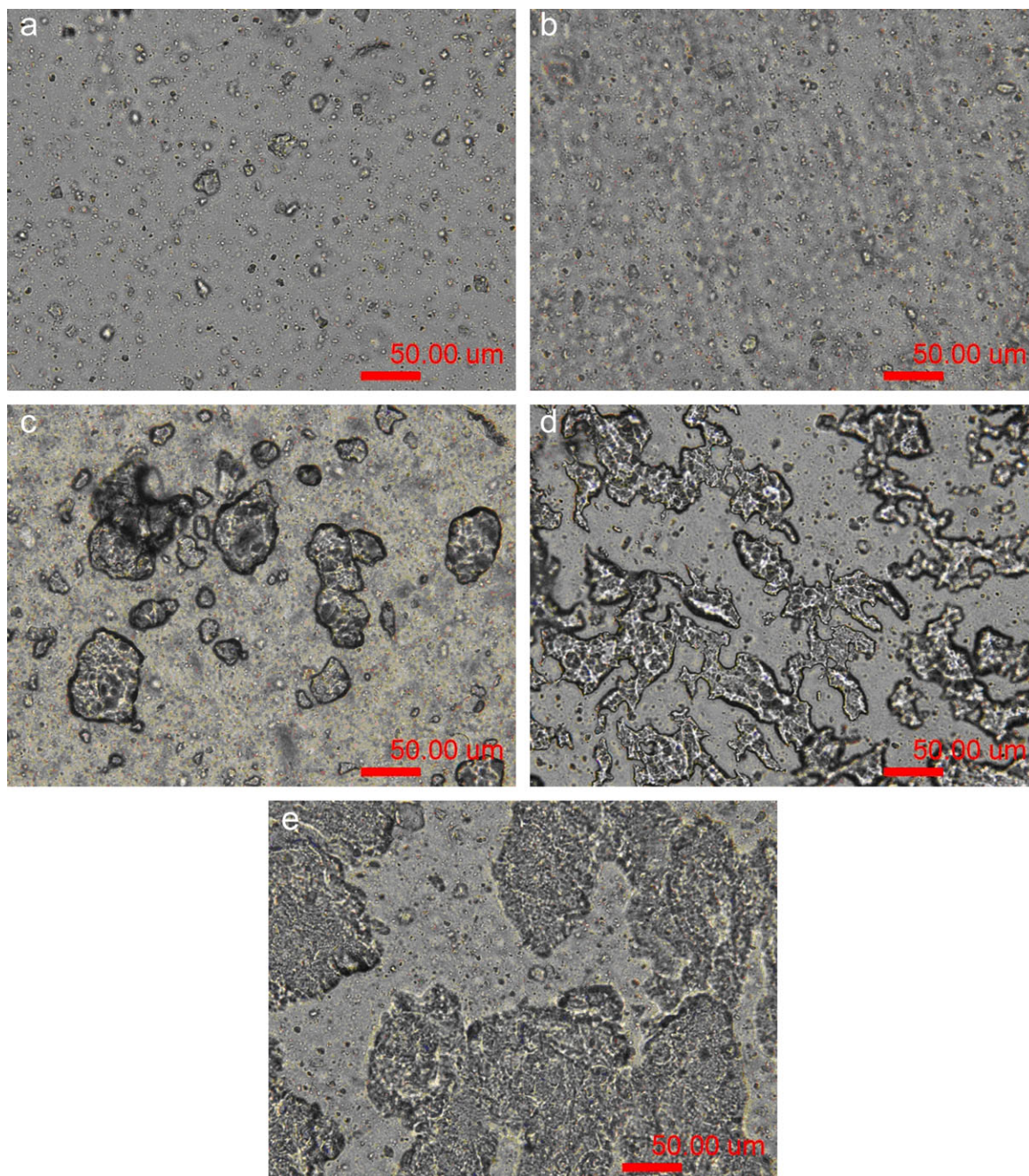


Figure 6. Phase contrast microscopy images of HNBR/EPDM compounds, $M = 200\times$. (a) H0 (b) H100 (c) H25 (d) H50 (e) H75. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the amount of uncrosslinked rubber (WL) as well as crosslink efficiency (CE) for HNBR/EPDM blends. From Table IV it can be seen that, the amount of unvulcanized HNBR phase and EPDM phase were very small for both curing systems and the amount of uncrosslinked HNBR was always less than that of the EPDM. For the sulfur-cured systems there was more unvulcanized material than for the peroxide-cured systems. Additionally, except for the simple HNBR compound, the peroxide cure invariably yielded a greater crosslink efficiency for HNBR whereas the peroxide exhibited a greater crosslink efficiency for

EPDM. The sulfur curing system is more efficient for HNBR. This can be attributed to the better solubility of sulfur and accelerator in HNBR. However, HNBR and EPDM have similar cure rates and cure mechanisms with a peroxide curing system, thus the selectivity is reduced and covulcanization is improved.

Figure 3 presents the mechanical properties of the HNBR/EPDM vulcanizates cured by both sulfur and peroxide curing systems. It can be seen that, as the percentage of HNBR in the blend increases, the tensile strength and elongation at break increases with both curing systems. The hardness and 50%

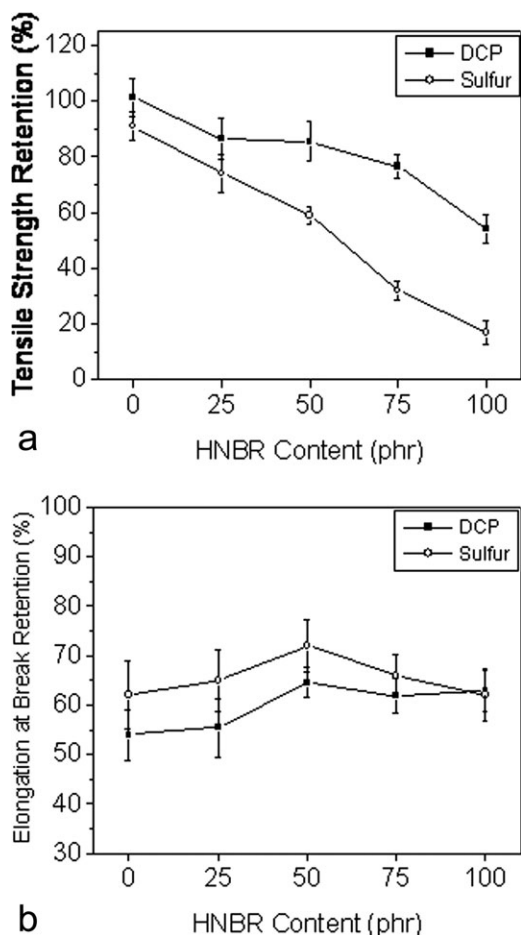


Figure 7. The retention of tensile properties of HNBR/EPDM blends after hot-air aging.

modulus of the blends with peroxide decrease with increasing HNBR while the opposite is true for the sulfur curing system.

Compared with HNBR/EPDM blends using peroxide as cure agent, the blends vulcanized by sulfur possess much higher tensile strengths and elongations at break. This can be explained by the lower crosslink density of these blends (see Table III and Figure 1) and that the crosslinks are mainly polysulfidic, endowing the crosslinks with a greater ability to adjust to external force.^{15,16} However, the crosslink density of the vulcanizates prepared with peroxide is too high; the length of segments between two crosslinking points is very short making the chains of the vulcanizates stiff and reducing both the tensile strength and the elongation at break.

Dynamic Mechanical Thermal Analysis

The loss $\tan \delta$ as a function of temperature for HNBR/EPDM blends vulcanized with sulfur and peroxide, measured by dynamic mechanical thermal analyses, is plotted in Figures 4 and 5. From these we can see that the damping peak related to the glass transition of the HNBR phase appears at around -10°C whereas that related to the glass transition of the EPDM phase appears in the range of -50°C to -40°C . The loss peaks of HNBR, EPDM increase and decrease with increasing HNBR percentage in HNBR/EPDM vulcanizates in both curing sys-

tems. From Figure 4 (sulfur cure) it can be seen that the loss peaks of the blends corresponding to the HNBR phase remain at the same temperature, whereas the loss peaks of the EPDM phase shift to lower temperature suggesting that with increasing HNBR in the blend the crosslink density of the EPDM phase decreases. With the peroxide cure (Figure 5) the loss peaks of both the HNBR and EPDM phases shift to lower temperature suggesting that the crosslink density of both the HNBR and EPDM phases decreases in the blends.

That for all compositions there are two damping peaks (Figures 4 and 5) confirms that these blends are composed of two distinct phases and that the compatibility is very limited; as might be expected from the difference in their polarity.

An examination of the $M_H - M_L$ data leads to the conclusion that improved covulcanization can be achieved with peroxide when compared with the sulfur systems used in this work.

Morphology

The micrographs of unvulcanized HNBR/EPDM blends are shown in Figure 6. Since the refractive index of EPDM is smaller than that of HNBR the region in the micrographs corresponding to EPDM phase is lighter than that of the HNBR phase. As shown in Figure 6, the darker HNBR phase is separated from the EPDM continuous phase, and the HNBR domains increase with the proportion of HNBR in the blend corroborating the incompatibility of these two polymers.

Hot-Air Ageing Resistance

The retention of tensile strength and elongation at break of the blends after thermal aging in an air oven at 150°C for 72 h is shown in Figure 7. The retention of tensile strength of the blends decreases with increasing HNBR with both curing systems. The blends vulcanized by peroxide display better retention of tensile strength but lower retention of elongation at break compared with the blends vulcanized by sulfur.

CONCLUSIONS

Curing parameters showed scorch time and optimum cure time decrease and crosslink density increases with increasing HNBR in the blends cured with sulfur. Scorch time increases, while the optimum cure time and crosslink density decrease with increasing HNBR content in blends cured with peroxide. Peroxide-cured blends have longer optimum cure times and higher crosslink density compared with those of the blends cured by sulfur.

The value ($M_H - M_L$), the rheometer graphs, selective swelling and dynamic mechanical analyses of HNBR/EPDM blends confirm that the peroxide curing system leads to improved covulcanization and peroxide exhibited higher crosslink efficiency on EPDM while sulfur showed higher speed and larger crosslink efficiency on HNBR. In particular, the dynamic mechanical analysis and morphology indicated that the compatibility between HNBR and EPDM is very limited.

With both curing systems, tensile strength and elongation at break increase with HNBR content in the blend. The tensile strength and elongation at break of the blends cured with sulfur are greater than those cured with peroxide. The blends cured with peroxide exhibit a better retention of tensile strength but

worse retention of elongation at break compared with the blends vulcanized by sulfur.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support of Lanxess Deutschland GmbH and Shandong Science and Technology Program for Universities (J12LA14) without which the work presented here would not have been possible.

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