Effects of Blend Ratio, Crosslinking Systems and Fillers on the Morphology, Curing Behavior, Mechanical Properties, and Failure Mode of Acrylonitrile Butadiene Rubber and Poly(ethylene-*co*-vinyl acetate) Blends

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Received 14 January 1998; accepted 18 August 1998

ABSTRACT: Blends of acrylonitrile butadiene rubber (NBR) and poly(ethylene-co-vinyl acetate) (EVA), with varying proportions of the components, were vulcanized using different crosslinking systems, namely, sulfur (S), dicumyl peroxide (DCP), and a mixed system (S + DCP). Mechanical properties, such as stress–strain behavior, tensile strength, elongation at break, Young's modulus, tensile set, and tear strength, were studied. The mixed system exhibited better mechanical performance than other systems. The tensile and tear fracture surfaces were analyzed under the scanning electron microscope in order to understand the failure mechanism. The variation in properties was correlated with the morphology of the system. The effect of high-abrasion furnace black (HAF), semireinforcing furnace black (SRF), silica, and clay on the mechanical properties and failure mechanism of 50/50 blend of NBR–EVA (N₅₀P) has also been studied. The Kraus equation has been applied to analyze the extent of polymer–filler interaction. Applicability of various theoretical models has been investigated to predict the properties of the blend systems. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2335–2364, 1999

INTRODUCTION

The objective of polymer blending is to achieve commercially viable products having unique properties or low cost.¹ Commercial products have been based on miscible,^{2–4} as well as immiscible, blends.^{5–6} For blends of immiscible polymers, the mechanical response reflects molecular relaxation processes characteristic of each constituent and is also profoundly influenced by blend composition, morphology, and new or modified relaxation processes characteristic of the blend. The morphological arrangement may consist of one phase dispersed in a matrix of the other polymer.

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Contract grant sponsor: Council of Scientific and Industrial Research, New Delhi, India.

Journal of Applied Polymer Science, Vol. 71, 2335–2364 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/142335-30

Materials	Characteristics		Source
Nitrile rubber–(Aparene N553 NS)	Volatile matter (%)	0.130	Gujarat Apar Polymers, Ltd., Mumbai
	Antioxidant (%)	1.400	
	Organic acid (%)	0.250	
	Soap (%)	0.004	
	Mooney viscosity (ML_{1+4} ; 100°C)	40.000	
	Bound acrylonitrile (%)	34.00	
	Intrinsic viscosity (dL, g)	1.527	
Poly(ethylene-co-vinyl acetate)– Pilene 1802	Melt flow index (g/10 min)	2.000	Polyolefins Industries Ltd., Chennai
	Density (g, cc)	0.937	
	Vicat softening point (°C)	59.000	
	Vinyl acetate (%)	18.000	
	Intrinsic viscosity (dL, g)	0.170	

Table I Details of Materials Used

Homogeneity of mixing and cure compatibility are the most pertinent polymeric properties related to polymer blends. Homogeneity at a microscopic level is necessary for optimum performance, but some degree of microheterogeneity is usually desirable to preserve the individual properties of the respective polymer components. Even if true miscibility may not be required, adhesion between polymer phases is necessary for good properties. Shershnev⁷ has summarized the importance of and requirements for covulcanization of the components of elastomer blends. Covulcanization is defined in terms of a single network structure with crosslinked macromolecules of both polymers. Vulcanizates with components having similar curative reactivity generally give better properties than those whose components have large differences in this regard. To select a

Ingredients (phr ^a)	Peroxide System (P)	Sulfur System (S)	Mixed System (M)	10S	10C	10BS	20BS	30BS	10BH	20BH	30BH
Polymer	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zinc oxide		5.0	5.0						_	_	
Stearic acid		1.5	1.5						_	_	
$MBTS^{b}$		1.5	1.5	_	_	_	_	_	_	_	_
Sulfur		1.5	1.5						_	_	
$\mathrm{DCP^{c}}$	4.0		4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Silica				10.0					_	_	
Clay			_		10.0				_	_	
$\mathrm{SRF}^{\mathrm{d}}$		_	_			10.0	20.0	30.0	_	_	
HAF^{e}	—	—	—	—	—	_	_		10.0	20.0	30.0

Table II Compounding Recipe

^a Parts per hundred rubber by weight.

^b Mercaptobenzo thiazyl disulphide.

^c Dicumyl peroxide (40% active).

^d Semireinforcing furnace black.

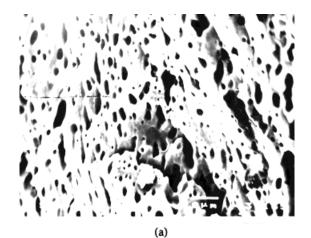
^e High-abrasion furnace black.

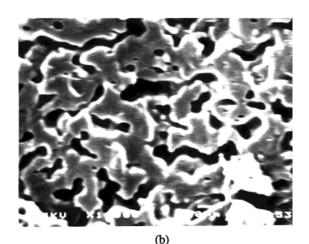
blend ratio and a crosslinking system suitable for a particular application, a clear understanding of the change in properties with blend ratio and crosslinking systems is essential.

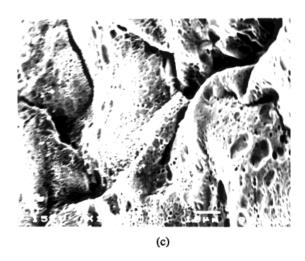
Usually, reinforcement in rubber compounds is achieved by the use of carbon black as well as noncarbon black fillers. Fillers are used to modify the processing characteristics and mechanical properties and also to reduce the cost. They are important to reduce the shrinkage and to increase the modulus and hardness. The reinforcement activity of the filler in blends depends on the affinity of the filler towards the blend components and also on the distribution and dispersion of filler in each phase of the blend. The filler interphase distribution in elastomer blends has been reported by several researchers.⁸⁻¹¹

In the selection of a polymer or a polymer blend for practical applications, one has to consider how the material can resist failure or crack growth under the use conditions. In order to have an insight into the resistance of the material to failure or crack growth, it is essential to carry out the mechanical property measurements. The mode of failure of a material can be investigated using a scanning electron microscope, and the failure pattern can be related to the strength of the material.

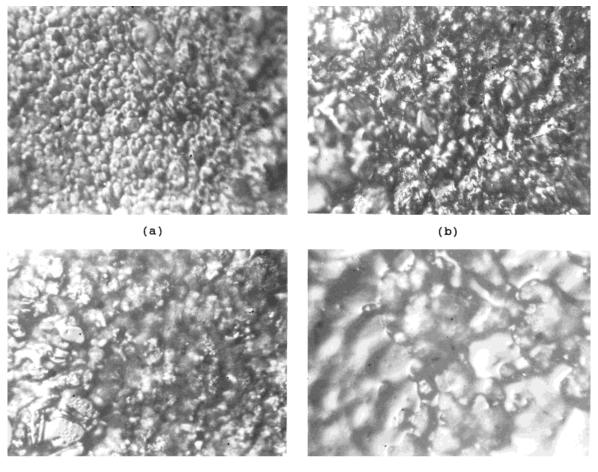
Acrylonitrile butadiene rubbers (NBRs) have excellent oil resistance and abrasion resistance but poor ozone resistance. Poly(ethylene-co-vinyl acetate) (EVA) offers excellent ozone resistance, weather resistance and mechanical properties.¹² The morphology, mechanical properties and viscoelastic behavior,¹³ tearing characteristics and recyclability,¹⁴ and the rheological behavior¹⁵ of NBR-EVA blends have been studied earlier by our research group. The objective of the present work is to study the effect of various crosslinking systems, namely, sulfur, dicumyl peroxide, and a mixed system comprising both sulfur and dicumyl peroxide, the blend ratio, and various fillers on the mechanical properties and failure mechanism of NBR-EVA blends. Dicumyl peroxide has been used for the crosslinking of both NBR and EVA, but sulfur can crosslink only NBR phase and not EVA due to its saturated backbone structure. Hence, a mixed system, containing both peroxide and sulfur, was also selected for the effective curing of both the phases in the blend.







 $\label{eq:stars} \begin{array}{ll} \textbf{Figure 1} & \text{Scanning electron micrographs showing the} \\ \text{morphology of (a) } N_{30} \text{, (b) } N_{50} \text{, and (c) } N_{70} \text{.} \end{array}$



(c)

(d)



(e)

Figure 2 Optical micrographs showing the morphology of (a) $N_{20},$ (b) $N_{40},$ (c) $N_{50},$ (d) $N_{60},$ and (e) $N_{80}.$

Table III Cure Characteristics of NBR-EVA

Systems

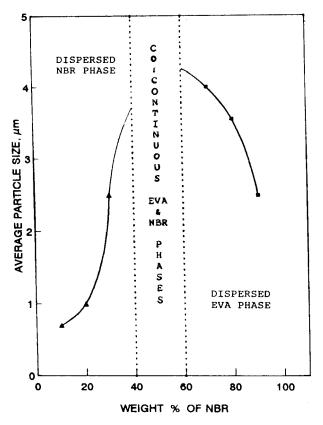


Figure 3 Variation in the average particle size as a function of blend composition.

	Cure	Scorch	Maximum	
Sample	Time	Time	Torque	
Code	(min)	(min)	(dNm)	CRI
N ₀ P	24.0	2.0	80.2	4.5
$N_{30}P$	20.0	3.0	70.1	5.8
$N_{50}P$	18.4	2.5	49.9	6.3
$N_{70}P$	17.2	2.2	35.1	6.7
$N_{100}P$	16.5	2.1	39.2	6.9
$N_{30}S$	32.0	20.0	61.9	8.3
$N_{50}S$	19.0	13.0	51.9	16.7
$N_{70}S$	19.4	11.0	38.1	11.9
$N_{100}S$	14.4	7.2	19.2	13.9
N ₀ M	40.0	18.0	66.4	4.5
$N_{30}M$	34.0	9.4	71.4	4.1
$N_{50}M$	27.0	5.8	52.9	4.7
$N_{70}M$	17.8	5.0	43.5	7.8
$N_{100}M$	18.8	3.6	22.1	6.6
10S	18.6	2.1	82.5	6.1
10C	18.7	1.9	83.1	5.9
10BS	19.1	2.4	83.5	5.9
20BS	19.0	2.2	89.8	5.9
30BS	19.2	2.2	93.2	5.8
10BH	19.4	2.3	84.7	5.8
20BH	19.2	2.1	90.5	5.8
30BH	19.3	2.0	94.9	5.8

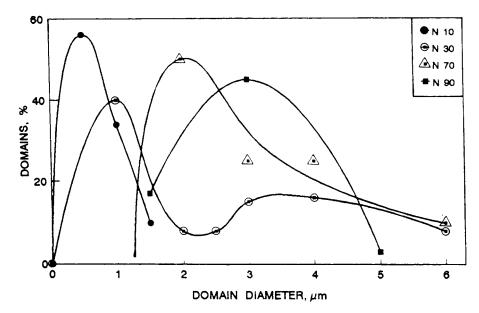


Figure 4 Particle size distribution curve of NBR-EVA blends.

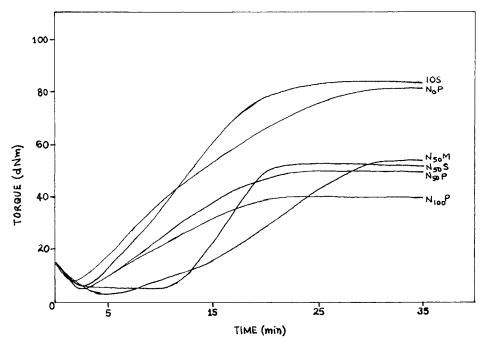


Figure 5 Rheographs of NBR–EVA blends.

Sample Reference	Young's Modulus (MPa)	Tensile Set (%) (After Failure)	Crosslink Density $(\times 10^4)$ gmol cc ⁻¹
N ₀ P	14.8	3.50	3.69
N ₀ M	24.1	4.40	2.88
$N_{30}S$	12.7	1.40	2.62
N ₃₀ P	9.9	2.05	3.02
N ₃₀ M	13.9	1.45	3.11
$N_{50}S$	7.3	0.95	2.27
N ₅₀ P	6.6	0.75	2.18
$N_{50}M$	8.2	0.85	2.31
$N_{70}S$	4.8	0.70	1.67
N ₇₀ P	3.1	1.05	1.44
N ₇₀ M	4.6	0.55	1.89
$N_{100}S$	1.4	0.10	0.77
N ₁₀₀ P	1.9	0.05	1.68
$N_{100}M$	1.5	0.05	0.94
105	9.4	0.55	5.54
10C	8.1	0.40	5.23
10BS	7.9	0.35	5.59
20BS	8.9	0.30	6.73
30BS	9.5	0.20	7.86
10BH	8.3	0.45	6.44
20BH	8.5	0.25	7.52
30BH	9.7	0.20	8.57

Table IVMechanical Properties of Crosslinked and Filled NBR-EVABlends

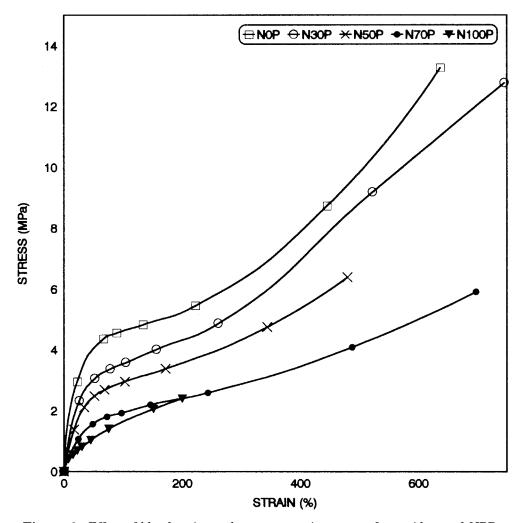


Figure 6 Effect of blend ratio on the stress–strain curves of peroxide-cured NBR–EVA blends.

EXPERIMENTAL

Materials

NBR (Aparene N-553 NS) having 34% bound acrylonitrile content was supplied gratis by Gujarat Apar Polymers Ltd., Mumbai. EVA (Pilene-1802) having 18% vinyl acetate content was procured from Polyolefins Industries Ltd, Chennai. The basic characteristics of NBR and EVA are given in Table I. The rubber chemicals, such as dicumyl peroxide, zinc oxide, stearic acid, mercapto benzothiazyl disulphide (MBTS), sulfur, and fillers such as HAF and SRF, were of commercial grade.

Blend Preparation

The blends of NBR–EVA with different crosslinking systems and blend ratios were prepared on a two-roll mixing mill having a friction ratio of 1 : 1.4. The compounding recipes of the blends are given in Table II. The different crosslinking systems used, namely, peroxide system (DCP), sulfur system (S), and mixed system (DCP + S) are indicated using P, S, and M, respectively. The compounds containing a mixed cure system are designated as N_0M (pure EVA), $N_{30}M$ (30/70 NBR–EVA), $N_{50}M$ (50/50 NBR–EVA), and so on. The subscripts indicate the weight percentage of NBR in the blend. The peroxide-cured 50/50 NBR-EVA blend (N₅₀P) was selected for investigating the effect of fillers. The different fillers used, such as high-abrasion furnace black (HAF), semireinforcing furnace black (SRF), silica and clay are designated as BH, BS, S, and C, respectively. The loading is indicated by prefixing num-

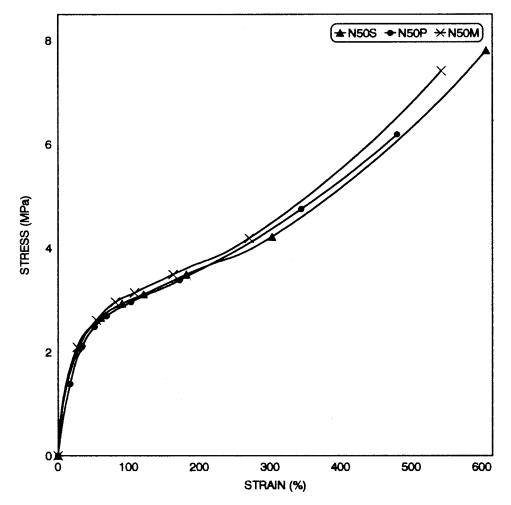


Figure 7 Effect of different crosslinking systems on the stress-strain behavior of 50/50 NBR-EVA blend.

bers. Thus, 10BH indicates the 10-phr HAFloaded system, 20BH indicates the 20-phr HAFloaded system, and so on. The compounded blends were then compression-molded at 160°C for the optimum cure. The samples for tensile and tear tests were punched along the mill grain direction from the molded sheet.

Mechanical Properties

The tensile testing of the samples was done according to the ASTM D412-87 test method using dumbbell-shaped test pieces at a crosshead speed of 500 mm/min using an Instron Universal Testing Machine (Model 1121). The tear test was also done on the Instron UTM according to ASTM D624-81 using unnicked 90°-angle test pieces at a crosshead speed of 500 mm, min. The hardness of the samples was measured as per ASTM D 2240-86 and expressed in shore A units.

Polysulfidic Estimation

Vulcanizate samples, each weighing approximately 0.2 g, were treated with a solution of propane-2-thiol (0.4M) in *n*-heptane for 2 h at room temperature under nitrogen, then the samples were washed with petroleum ether (bp $40-60^{\circ}$ C) and dried. The polysulfidic crosslinks were then obtained by the difference from the values of total crosslink concentration (mea-

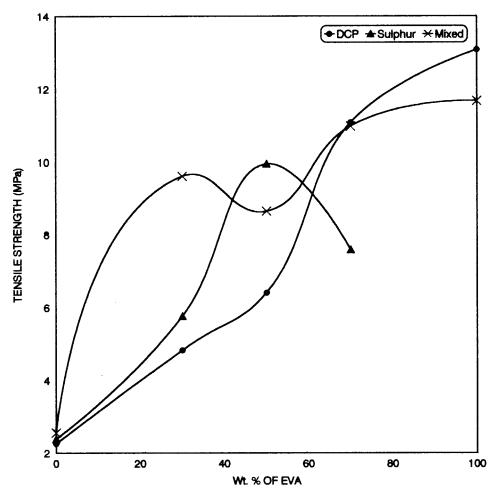


Figure 8 Variation in tensile strength with the weight percentage of EVA.

sured by volume swelling method) before and after the treatment.

Scanning Electron Microscopic Studies

The NBR–EVA blends were cryogenically fractured under liquid nitrogen, and the morphology was studied using a scanning electron microscope. The tensile and tear failure surfaces of the crosslinked and filled systems were also observed by the scanning electron microscope to follow the failure mechanism.

RESULTS AND DISCUSSION

Morphology

The polymer blend properties are strongly influenced by the morphology of the system, and several researchers^{16–19} have related the variations in properties with the blend morphology. The morphology of uncrosslinked NBR-EVA blends is shown in Figure 1. In N₃₀ (30/70 NBR-EVA) and N_{70} (70/30 NBR-EVA), the minor phase is dispersed in the major continuous phase. The N_{50} (50/50 NBR-EVA) shows a co-continuous morphology, where both the phases are continuous. A few optical micrographs of NBR-EVA blends are given in Figure 2. It can be seen that below 40 wt % of NBR, NBR is the dispersed phase, and at the other extreme, below 40 wt % EVA, EVA is the dispersed phase. Between 40 to 60 wt % of NBR, both NBR and EVA exist as continuous phases. The average particle size versus blend compositions is shown in Figure 3. In the EVA-rich blends, NBR is the dispersed phase, and the average particle size of the dispersed domains in-

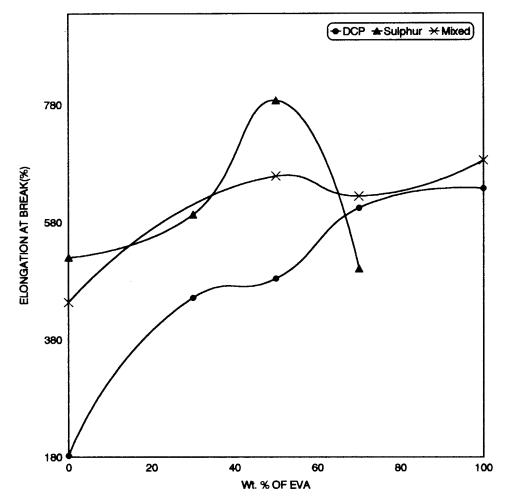


Figure 9 Variation in elongation at break with the weight percentage of EVA.

creases with the increase in NBR content. In NBR-rich blends, the average particle size of the dispersed EVA domains increase with the increase in EVA content. The increase in domain size of NBR or EVA with an increasing proportion of that component is associated with the coalescence of the domains. The particle size distribution curve (Fig. 4) is drawn by measuring 100 particles from the optical micrographs. The blend N_{90} exhibits a broader distribution curve than N_{10} due to the clustering of EVA particles.

Cure Characteristics

The cure characteristics of the crosslinked and filled NBR–EVA blends are given in Table III. The mixed cure system exhibits longest cure time, and the peroxide cure system, in which the cure reaction occurs by free radical mechanism, exhibits the shortest cure time. In all the cure systems, the cure time decreases with the increase in NBR content. The scorch safety is highest for the sulfur cure system and the lowest for the peroxide cure system. Maximum torque, which is a measure of crosslink density, is also given in the table. The maximum torque is higher for EVA (N_0) and EVA-rich blends than the other blend compositions. The filled systems exhibit slightly longer cure times than the unfilled ones $(N_{50}P)$. This is probably due to the adsorption of the curatives on the surface of the fillers. From the table, it is observed that there is not much change in the scorch time compared to the unfilled one. How-

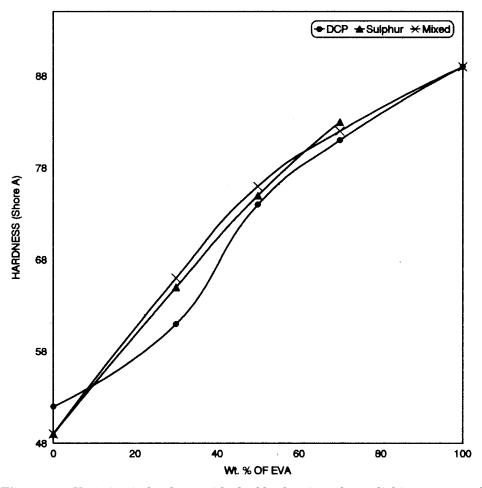


Figure 10 Variation in hardness with the blend ratio and crosslinking systems of NBR-EVA blends.

ever, fillers are found to increase the maximum torque, which is dependent on the level of loading. This is attributed to the increased modulus of the filled vulcanizates. The rheographs of a few mixtures are given in Figure 5, and it can be seen that no compound shows any tendency for reversion.

The cure rate index (CRI) is calculated using the following equation:

$$CRI = 100/t_{90} - t_2 \tag{1}$$

where t_{90} is the cure time, and t_2 is the scorch time. The CRI values are given in Table III. In all the crosslinking systems, the cure rate index increases with the increase in NBR content. Thus, NBR is the cure-activating component in this system. A high CRI value indicates a higher vulca-

nization rate. All the filled systems exhibit nearly the same CRI values.

Effect of Blend Ratio and Curing Systems on the Mechanical Properties

The stress–strain curves of the peroxide crosslinked systems as a function of blend ratio are shown in Figure 6. The deformation characteristics of these blends under an applied stress is clear from the curves. There is an increase in the initial modulus with an increase in the EVA content of the blend. Thus, NBR (N_{100} P) shows the lowest modulus and fails at fairly low stress. As the EVA content in the blend increases, there is an increase in the stress with increasing strain. This is due to the orientation of the crystalline regions of EVA in the direction of stress. The

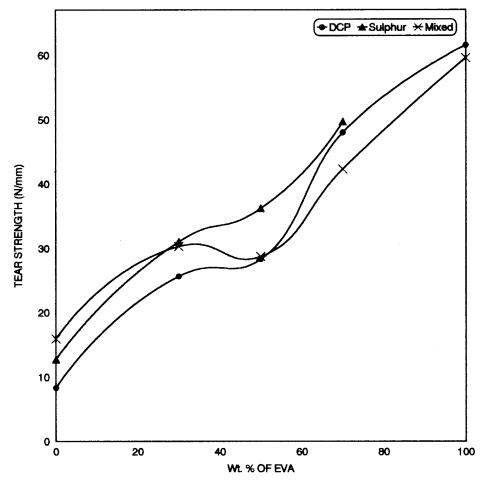


Figure 11 Variation in tear strength with the weight percentage of EVA.

effect of different crosslinking systems, namely, sulphur (S), dicumyl peroxide (P), and the mixed (M) systems on the stress-strain behavior of NBR-EVA blends are given in Figure 7. All the systems show a very similar stress-strain behavior. Also, initial modulus values lie close to each other. However, the peroxide cured system takes the lowest position. This can be explained on the basis of the nature of the crosslinks. The bond lengths for C-C, C-S, and S-S linkages are 1.54, 1.81, and 1.88 A°, respectively; that is, the C—C linkages are short and rigid. Under an applied stress, the rigid C—C linkages break easily compared to the flexible C—S and S—S linkages. The highly flexible and labile linkages are capable of withstanding a higher stress. The polysulfidic estimation was carried out in the case of $N_{50}S$ and

 $N_{50}M,$ and it was found that the polysulfidic crosslinks are 55 and 45%, respectively.

Figure 8 shows the variation in tensile strength with the weight percentage of EVA. In the case of peroxide and mixed systems, the tensile strength increases with the increase in EVA content. But in the case of sulfur cured system, there is a drop in tensile strength beyond 50% of EVA content. This is due to the phase inversion in morphology of the system, as observed in Figure 1. Beyond 50% of EVA content, EVA is the continuous phase, which cannot be crosslinked by sulfur. That is, in EVArich blends, the continuous phase remains uncrosslinked when sulfur is the curing agent, hence the drop in tensile strength beyond 50% of EVA content.

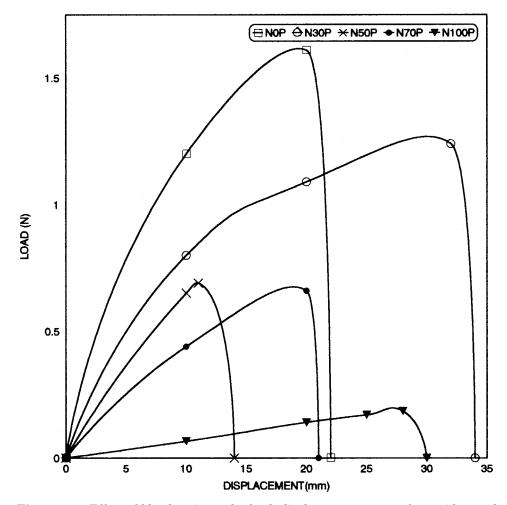


Figure 12 Effect of blend ratio on the load-displacement curves of peroxide-cured NBR-EVA blends.

The crosslink density of the samples was calculated from the tensile measurements using the following equation:

$$v = \frac{F}{2A_0 \rho_p RT \left(\alpha - 1/\alpha^2\right)} \tag{2}$$

where F is the load, A_0 is the cross-sectional area of the sample, ρ_p is the density of the polymer, Ris the gas constant, T is the absolute temperature, and α is the extension ratio.

The values of Young's modulus, crosslink density, and tensile set are given in Table IV. It is seen that the peroxide-cured systems show comparatively lower Young's modulus compared to other curing systems. It is also seen that the Young's modulus values increase with the increasing EVA content in the blend. The peroxidecured systems of the pure components, that is, N_0P and $N_{100}P$, show a higher crosslink density; but in the case of blends, the mixed cured system shows slightly higher crosslink density. The samples with a high crosslink density exhibit lower tensile sets. The set value decreases with increasing NBR content. A low set value is technologically advantageous. The dependency of elongation at break on the weight percentage of EVA is presented in Figure 9. The elongation at break also increases with the increase in EVA content. Figure 10 shows the effect of blend ratio and crosslinking systems on the hardness of NBR-EVA blends. Like other mechanical properties, hardness also increases with the weight percentage of EVA in the blend.

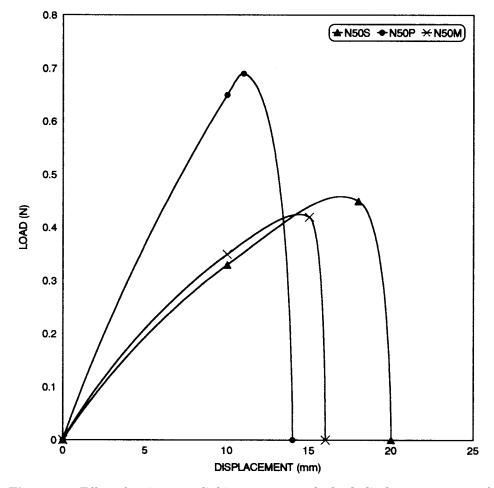
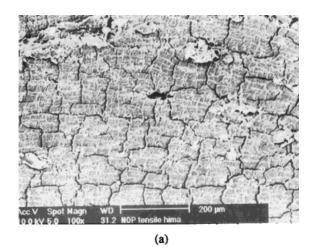


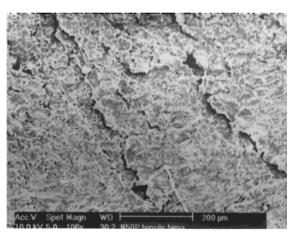
Figure 13 Effect of various crosslinking systems on the load-displacement curves of NBR-EVA blends.

The tear strength is plotted as a function of the weight percentage of EVA in Figure 11. Again, the tear strength increases with increasing EVA content for all the cure systems. The tear curves (load versus displacement) of the crosslinked NBR-EVA blends are given in Figures 12 and 13. The effect of blend ratio on the tear curves is shown in Figure 12. It is seen that EVA requires the highest load for tearing. The tearing force of EVA, that is, N₀P is followed by $N_{30}P$, $N_{50}P$, $N_{70}P$, and, finally, $N_{100}P$; that is, NBR tears with the lowest load. In Figure 13, the tear curves as function of cure systems is given. Here, the peroxide system tears with the lowest load. This is due to the nature of crosslinks, as explained earlier.

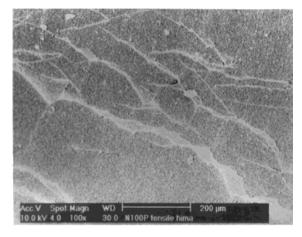
Scanning Electron Microscopic Studies

Scanning electron microscopy has been successfully used by several researchers to follow the failure mechanism in polymer blends.^{20–24} Thetearing behavior and failure mechanism ofuncrosslinked NBR–EVA blends is reported earlier.¹⁴ The scanning electron micrographs of the tensile and tear fracture surfaces of peroxide-cured NBR–EVA blends are shown in Figures 14 and 15, respectively. Figures 14(a)–(c) show the tensile fracture surfaces of N₀P, N₅₀P, and N₁₀₀P, respectively. N₀P shows a fracture surface with full of cracks, which is probably due to the crystallinity of EVA. N₅₀P shows a ductile failure with a rough surface, and that of N₁₀₀P exhibits a smooth failure surface, which is characteristic for rubbers.



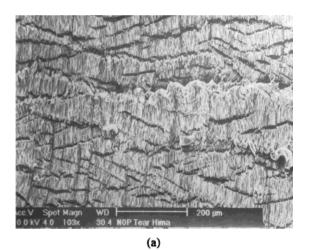


(b)



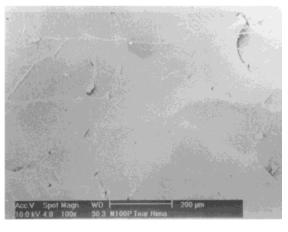
(c)

Figure 14 Scanning electron micrographs showing the tensile fracture surfaces of (a) N_0P , (b) $N_{50}P$, and (c) $N_{100}P$.



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(c)

Figure 15 Scanning electron micrographs showing the tear fracture surfaces of (a) $N_0P,$ (b) $N_{50}P,$ and (c) $N_{100}P.$

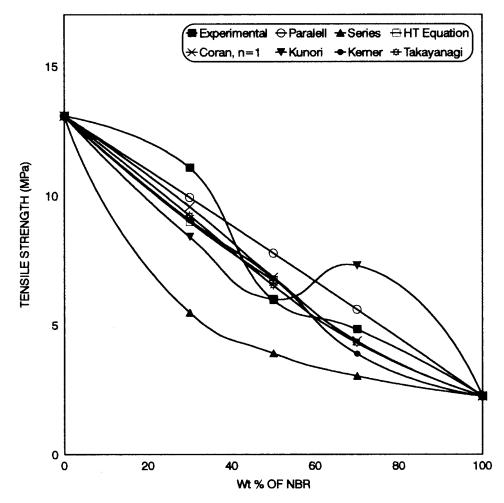


Figure 16 Applicability of various models on the tensile strength of peroxide-cured NBR-EVA blends.

The tear fracture surfaces of peroxide crosslinked NBR-EVA blends is shown in Figure 15. The tear fractograph of N_0P [Fig. 15(a)] shows tear fronts progressing sinusoidally with folds and striations, which is characteristic for tearresistant materials. The spacing between the folds is approximately 25 μ m. Also, it is seen that there are several such sinusoidal tear fronts, which lie close to each other. Sinusoidal tear fronts are also observed in $N_{50}P$ [Fig. 15(b)]. Here, the spacing between the folds is approximately 34 μ m. The increase in the step spacing between the folds indicates the drop in the tear strength of the material. The step spacing was related to the tear strength of polymers by Gent and Pulford.²⁰ They measured the step spacing on the fracture surface and found that strong materials show more closely spaced steps. $N_{100}P$ [Fig. 15(c)] shows a smooth fracture surface characteristic, which is typical for weak materials.

Model Fitting

Applicability of various composite models, such as the parallel model, the series model, the Halpin– Tsai equation, the Coran equation, the Takayanagi model, the Kerner model, and the Kunori model, were checked to predict the mechanical behavior of the blends.

The parallel model (highest upperbound model) is given by the following equation²⁵:

$$M = M_1 \phi_1 + M_2 \phi_2 \tag{3}$$

where M is the mechanical property of the blend, and M_1 and M_2 are the mechanical properties of

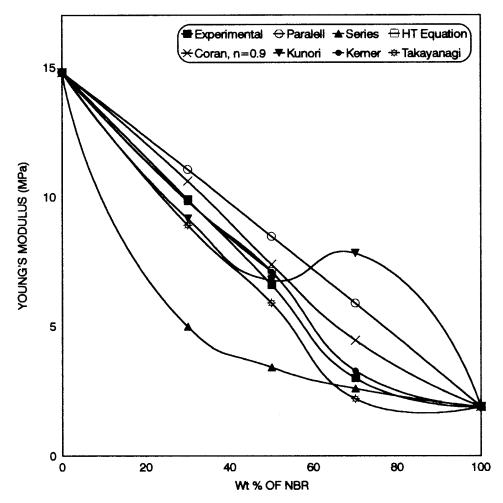


Figure 17 Applicability of various models on the Young's modulus of peroxide-cured NBR–EVA blends.

the components 1 and 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the components 1 and 2, respectively. In this model, the components are considered to be arranged parallel to one another so that the applied stress elongates each of the components by the same amount.

In the lowest lower bound series model, the components are arranged in series with the applied stress. The equation is^{25}

$$1/M = \phi_1/M_1 + \phi_2/M_2 \tag{4}$$

According to the Halpin–Tsai equation,²⁶

$$M_1/M = (1 + \text{AiBi } \phi_2)/(1 - \text{Bi } \phi_2)$$
 (5)

Bi =
$$(M_1/M_2 - 1)/(M_1/M_2 + Ai)$$
 (6)

In this equation, the subscripts 1 and 2 refer to the continuous and dispersed phase, respectively. The constant Ai is defined by the morphology of

Table V	Values	of Negative	Slope	and C f	for
Filled N _i	50P				

Fillers	Negative Slope	С
HAF	0.72	1.44
SRF	0.23	0.94
Silica	0.19	0.90
Clay	0.17	0.88

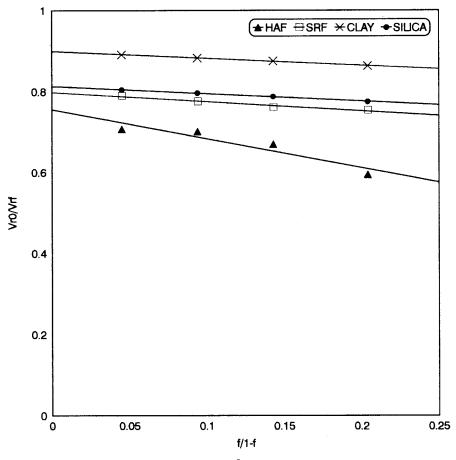


Figure 18 Plots of V^{ro}/V^{rf} versus f/1 - f for N₅₀P.

the system. For elastomer domains dispersed in a hard continuous matrix, Ai = 0.66.

In the Coran model, the mechanical properties are generally in between the parallel model upperbound (MU) and the series model lowerbound (ML).

According Coran's equation,²⁷

$$M = f(MU - ML) + ML$$
(7)

where f can vary between zero and unity. The value of f is a function of phase morphology and is given by

$$f = V_H^n (nV_s + 1) \tag{8}$$

where n contains the aspects of phase morphology, and V_H and V_S are the volume fraction of the hard phase and soft phase, respectively.

According to the Takayanagi model,²⁸

$$M = (1 - \lambda)M_1 + \lambda [(1 - \phi)/M_1 + (\phi/M_2)]^{-1} \quad (9)$$

 M_1 is the property of the matrix phase, M_2 is the property of the dispersed phase, and $\phi\lambda$ is the volume fraction of the dispersed phase and is related to the degree of series parallel coupling. The degree of parallel coupling of the model can be expressed by

% parallel =
$$(\phi(1 - \lambda)/(1 - \phi\lambda) \times 100$$
 (10)

According to the Kerner model,²⁹

$$E_{b} = E_{m} \begin{bmatrix} \phi_{d} E_{d} / [(7 - 5v_{m})E_{m} + (8) \\ -10v_{m})E_{d} + \phi_{m} / 15(1 - v_{m}) \\ \phi_{d} E_{m} / [(7 - 5v_{m})E_{m} + (8) \\ -10v_{m})E_{d} + \phi_{m} / 15(1 - v_{m}) \end{bmatrix}$$
(11)

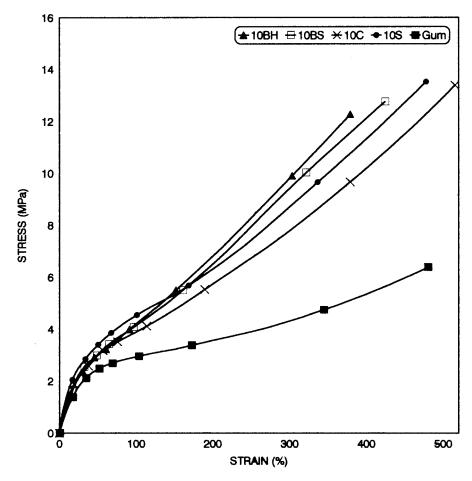


Figure 19 Effect of various fillers on the stress-strain behavior of $N_{50}P$.

where E_b is the blend property, v_m is the poisson's ratio, and ϕ is the volume fraction. The subscripts m, d, and b stand for the matrix, dispersed phase, and blend, respectively.

According to Kunori et al.,³⁰ the tensile failure of a blend is the result of adhesion failing between the blend components. When there is no adhesive force between the blend components, the tensile strength of the blends σ_b may be written as

$$\sigma_b = \sigma_m (1 - A_d) \tag{12}$$

where σ_b and σ_m are the tensile strengths of the blends and the matrix, respectively, and A_d represents the area of fraction occupied by the dispersed phase in transversal cross section. Kunori et al.³⁰ assumed that when a strong adhesive force exists between the blend components, the dispersed phase will contribute to the strength of the blend; therefore, the parallel model may be modified as follows:

$$\sigma_b = \sigma_m (1 - A_d) + \sigma_d A_d \tag{13}$$

If the force propagates mainly through the interface, the above equation may be written as

$$\sigma_b = \sigma_m (1 - \phi_d^{2/3}) + \sigma_d \phi_d^{2/3} \tag{14}$$

and if the force propagates through the matrix, then the equation becomes

$$\sigma_b = \sigma_m (1 - \phi_d) + \sigma_d \phi_d \tag{15}$$

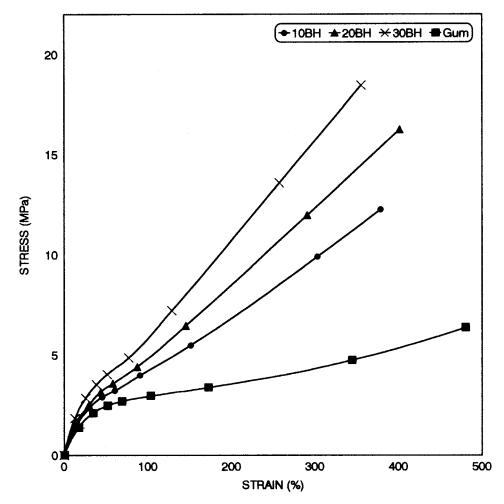


Figure 20 Effect of filler loading on the stress–strain behavior of $N_{\rm 50}P.$

		1	50		
		Fill	lers (10 phr Loadii	ng)	
Property	Gum	Silica	Clay	SRF	HAF
Tensile strength (MPa)	5.9	12.2	11.5	11.9	12.9
Elongation at break (%)	458	477	480	424	378
Hardness (Shore A)	74	80	76	76	77
Tear strength (N mm)	24.4	34.1	25.4	32.5	34.9

Table VI Effect of Fillers on the Mechanical Properties of N₅₀P

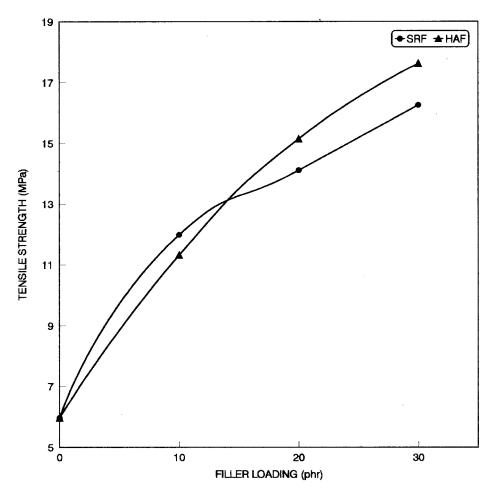


Figure 21 Effect of filler loading on the tensile strength of $N_{50}P$.

The above equation is the same as the parallel model.

Model fitting is presented in Figures 16 and 17. For the tensile strength (Fig. 16), the experimental value of N_{30} lies comparatively closer to the parallel model. As the weight percent of NBR increases, the experimental values deviate from the parallel model and are closer to the Takayanagi's model. In the case of Young's modulus (Fig. 17), the experimental values are in good agreement with the Kerner model.

Effect of Fillers

To study the effect of fillers, the peroxide-cured 50/50 NBR–EVA blend (N_{50} P) was selected. The fillers used are silica, clay, SRF, and HAF. The loading was kept constant, that is, 10 phr, to compare different fillers, and the effect of loading

was studied using SRF and HAF. The reinforcement in blends depends on the filler interphase distribution, that is, the affinity of the filler towards the blend components. It is also affected by the distribution and dispersion of filler in each phase of the blend. Generally, in thermoplastic elastomers, the fillers are preferably located in the rubber phase.³¹

Extent of Reinforcement

The extent of reinforcement is assessed by using the Kraus equation.³² According to this equation,

$$V^{ro}/V^{rf} = 1 - m[f/1 - f]$$
 (16)

where V^{rf} is the volume fraction of rubber in the solvent-swollen filled sample and is given by the following equation:

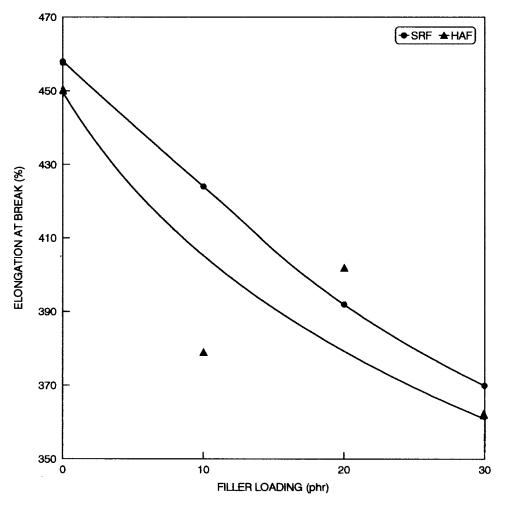


Figure 22 Effect of filler loading on the elongation at break of $N_{50}P$.

$$V^{rf} = \frac{(d - fw)\rho_p^{-1}}{(d - fw)\rho_p^{-1} + A_s\rho_s^{-1}}$$
(17)

where d is the deswollen weight, f is the volume fraction of the filler, w is the initial weight of the sample, ρ_p is the density of the polymer, ρ_s is the density of the solvent, and A_s is the amount of solvent absorbed. For an unfilled system, f = 0. Substituting this in eq. (17), we get the expression for the volume fraction of rubber in the solvent-swollen unfilled sample (V^{ro}) .

$$V^{ro} = \frac{d\rho_p^{-1}}{d\rho_p^{-1} + A_s \rho_s^{-1}}$$
(18)

Since eq. (16) has the general form of an equation for a straight line, a plot of V^{ro}/V^{rf} as a function of f/1 - f should give a straight line, whose slope (m) will be a direct measure of the reinforcing ability of the filler used. According to the theory developed by Kraus³² for highly reinforcing carbon blacks, negative higher slope values indicate better reinforcement. A constant *C*, characteristics of the filler, is also calculated using the following equation:

$$C = \frac{m - V^{r_0} + 1}{3(1 - V^{r_0 1/3})} \tag{19}$$

The Kraus plots for various fillers are shown in Figure 18, and the values of the slope and C are given in Table V. It is observed that the amount of solvent absorbed (A_s) decreases as the filler loading increases. This results in an increase in the

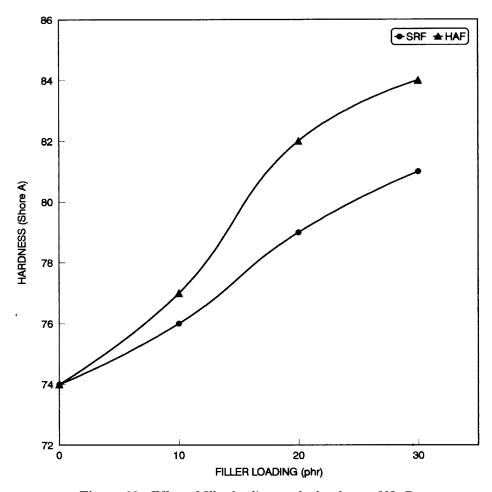


Figure 23 Effect of filler loading on the hardness of $N_{50}P$.

 V^{rf} values (with filler loading) calculated using eq. (17). Since V^{ro} remains constant, the ratio V^{ro}/V^{rf} decreases with the filler loading, resulting in a negative slope (Fig. 18). It is observed that the negative slope values, which is a direct measure of the reinforcing ability of the fillers, decreases in the order of HAF > SRF > silica > clay. This shows that as far as the extent of reinforcement is concerned, HAF is superior to other fillers.

Mechanical Properties

The stress-strain curves of $N_{50}P$ with different fillers at 10 phr loading are compared in Figure 19. For a given strain, filled systems exhibit higher stress than the unfilled polymer blend. A considerable increase of stress with strain is ob-

served beyond the yield stress for the filled systems. Among the different filled systems, the clayfilled system exhibits a low failure stress. This is due to the low reinforcing ability of clay. The stress–strain curves of the HAF-loaded $N_{50}P$ for various loadings are compared in Figure 20. For a given strain, the stress increases with increasing loading. This is due to the better reinforcement at higher loadings.

The effect of fillers at 10 phr loading on the mechanical properties of $N_{50}P$ is given in Table VI. It can be observed that the tensile strength, hardness, and tear strength have been increased with the addition of fillers. The propagation of the tear path is obstructed by the filler particles; hence, the increase in tear strength with the addition of fillers. The tensile strength and tear

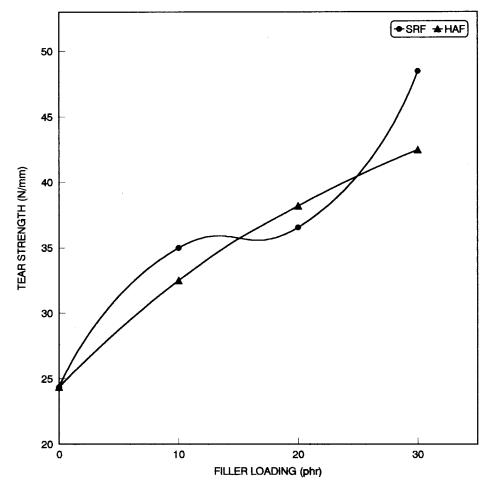


Figure 24 Effect of filler loading on the tear strength of $N_{50}P$.

strength is the highest for the HAF-filled system and the lowest for the clay-filled system. SRFand silica-filled systems show intermediate values. The variation in properties of the different filler systems are in accordance with its reinforcing ability, as established by Kraus analysis. The elongation at break is decreased with the addition of carbon black fillers and is almost unaffected by the addition of white fillers. Here, the reduction in the elongation at break is more predominant for the highly reinforcing HAF black. An improvement in the tensile set is observed on the addition of fillers (Table IV). The high set value of silicaand clay-filled samples is probably due to the lower extent of vulcanization. The tensile set is also improved with loading.

The variation in properties with filler loading is given in Figures 21–24. It can be seen that the tensile strength (Fig. 21), hardness (Fig. 23), and tear strength (Fig. 24) increase with loading for both the HAF- and SRF-filled systems. A reduction is observed in the case of elongation at break with loading (Fig. 22). The load versus displacement curves of filled NBR–EVA blends are shown in Figures 25 and 26. The tearing force is the lowest for the clay-filled system and increases as follows: clay < SRF < silica < HAF (Fig. 25). The tearing force is also in accordance with the reinforcing ability of the fillers (Fig. 18). As the filler loading is increased, the tearing force is also increased (Fig. 26).

Scanning Electron Microscopic Studies

Figures 27(a)–(d) are the tensile fractographs of various filled systems. Figure 27(a) is the silica-filled system. Here, a dewetting of the filler particles is observed. This is because of the poor matrix–filler adhesion. In the clay-filled system [Fig. 27(b)] also, the dewetting phenomena is ob-

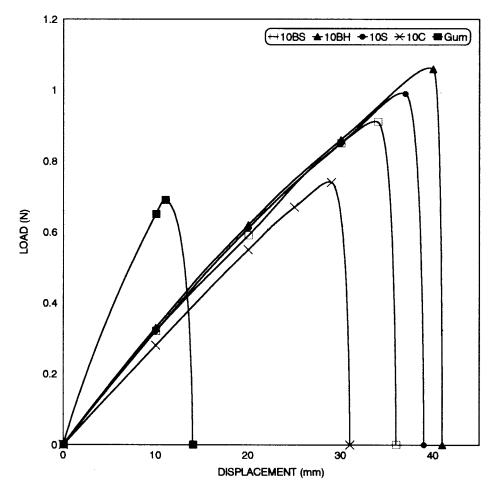


Figure 25 Effect of various fillers on the load-displacement curves of NBR-EVA blends.

served. But the number of filler particles on the surface is less due to the low reinforcing ability of clay, as compared to silica. Coming to the black-filled systems, the dewetting is less predominant in the case of the HAF-filled system [Fig. 27(d)], which is highly reinforcing with fairly good matrix-filler adhesion. Dewetting is also observed in the case of the SRF-filled system [Fig. 27(c)].

The tear fracture surfaces of filled $N_{50}P$ are shown in Figure 28. In the silica-filled system [Fig. 28(a)], crack deviation is observed due to the restriction to crack propagation by filler particles. In Figure 28(b), the clay-filled system also exhibits the crack deviation, but to a lesser extent than the silica-filled system. In the black-filled compounds [Figs. 28(c) and (d)], the fracture surfaces show crack deviation along with parabolic tear lines distributed randomly. The parabolic tear line results from the interaction of main fracture fronts with subsidiary fracture fronts and from the restriction to tear propagation by filler particles.

Model Fitting

The simplest theoretical equation for the reinforcement of a material or the increase in rigidity due to a filler is attributed to Einstein.^{33,34} The Einstein equation, valid only at a low concentration of filler, when there is perfect adhesion between the phases is

$$G = G_1(1 + 2.5\phi_2) \tag{20}$$

where G is the modulus of the filled system, G_1 is the modulus of the unfilled system, and ϕ_2 is the volume fraction of the filler.

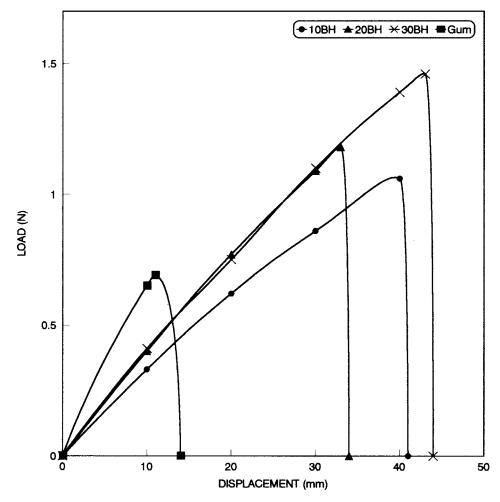


Figure 26 Effect of filler loading on the load-displacement curves of $N_{50}P$.

Einstein's equation implies that the stiffening or reinforcing actions of a filler is independent of the size of the filler particles. This equation shows that the volume occupied by the filler is independent of the size of the filler particles, and it is the volume occupied by the filler, not its weight, that is the important variable. The equation also assumes that filler is very much more rigid than the matrix.

An extension of Einstein's theory, originally developed to explain rubber reinforcement, is due to Guth³⁴ and Smallwood.³³ Their equation for the increase in modulus due to a rigid spherical filler is

$$G = G_1(1 + 2.5\phi_2 + 1.41\phi_2^2) \tag{21}$$

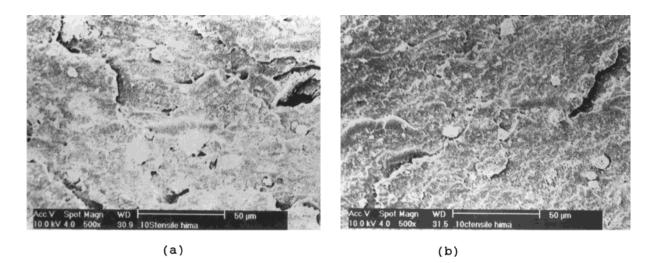
Kerner has developed a mathematical theory to describe the reinforcing action of spherical filler particles. The equation due to Kerner is²⁹

$$G = G_1 \begin{bmatrix} \frac{\phi_2 G_2 / [(7 - 5v_1)G_1 + (8)]}{-10v_1 G_2 + \phi_1 / 15(1 - v_1)} \\ \frac{\phi_2 G_1 / [(7 - 5v_1)G_1 + (8)]}{-10v_1 G_2 + \phi_1 / 15(1 - v_1)} \end{bmatrix}$$
(22)

Many fillers are much more rigid than matrices so that Kerner's equation simplifies to

$$G = G_1 \left\{ 1 + \frac{\phi_2}{\phi_1} \left[\frac{15(1 - v_1)}{8 - 10v_1} \right] \right\}$$
(23)

The model fitting for the HAF-filled system is presented in Figure 29, and it is seen that the



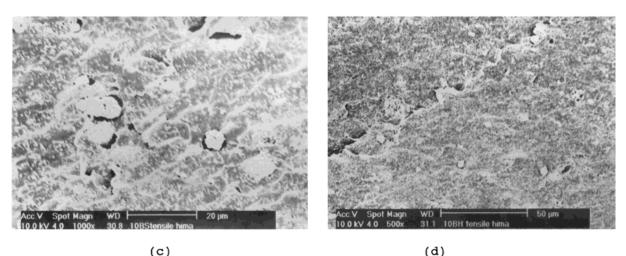
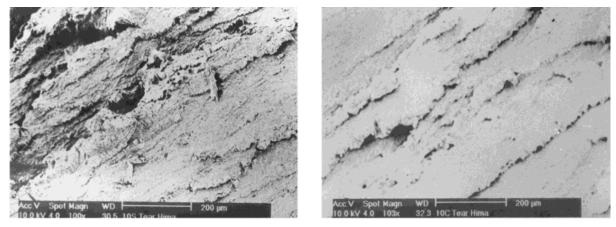


Figure 27 Scanning electron micrographs showing the tensile fracture surfaces of (a) 10 S, (b) 10 C, (c) 10 BS, and (d) 10 BH.

experimental values are higher than theoretically predicted ones for all the filler loadings. This indicates a strong interaction between HAF and the blend system. This is also evident from the scanning electron microscopy photograph [Fig. 27(d)].

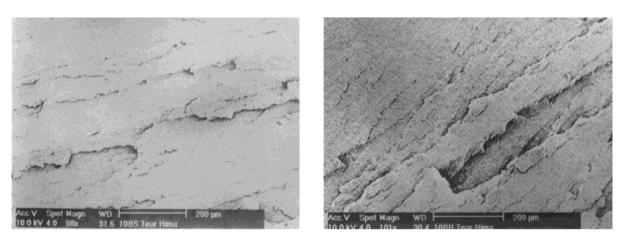
CONCLUSION

The morphology, curing behavior, mechanical properties, and failure mode of NBR–EVA blends have been studied with special references to blend ratio, crosslinking systems, and fillers. From the cure characteristics, it was observed that the peroxide cure system shows the shortest cure time. Better scorch safety was exhibited by the sulfurcured system. The deformation characteristics of NBR-EVA blends is clear from the stress-strain curves. In the EVA-rich blends, there is an increase in stress with increasing strain, which is due to the orientation of crystalline region of EVA in the direction of stress. The effects of different crosslinking systems on the stress-strain behavior have been explained on the basis of the nature of crosslinks formed during vulcanization. The mechanical properties, such as tensile strength, elongation at break, Young's modulus, tear strength, and hardness, increase with an increase



(a)

(b)





(d)

Figure 28 Scanning electron micrographs showing the tear fracture surfaces of (a) 10 S, (b) 10 C, (c) 10 BS, and (d) 10 BH.

in the EVA content. But in the case of sulfurcured system, there is a drop in tensile strength and elongation at break beyond 50% of EVA. This is due to the fact that at a high concentration of EVA, it tends to be the continuous phase, which cannot be crosslinked by sulfur. The extent of reinforcement was determined using the Kraus equation, and it was found that the reinforcing ability of the fillers is in the order of HAF > SRF> silica > clay. The mechanical properties of the filled systems were in good agreement with its reinforcing ability, as established by Kraus equation. The tensile and tear failure surfaces was observed under a scanning electron microscope to follow the failure mechanism. The N₀P exhibits a cracked tensile fracture surface due to its crystallinity and $N_{100}P$ exhibits a smooth fracture surface, which is characteristic for rubbers. In the

tensile fracture surfaces of all the filled systems except HAF, a dewetting phenomenon was observed, which is associated with the poor matrixfiller adhesion. In the HAF-filled system, the dewetting is less predominant because of its better reinforcing ability. The tear fractograph of N_0P shows tear fronts with fold and striations, characteristic for tear-resistant materials. N₁₀₀P exhibits a smooth tear fracture surface. In the filled systems, crack deviation is observed due to the restrictions to crack propagation by fillers. Applicability of various theoretical models to predict the properties of the unfilled and filled blends was also checked. It was found that the Young's modulus of the blends can be predicted using the Kerner model. For the filled systems, the experimental values are higher than the theoretically predicted ones.

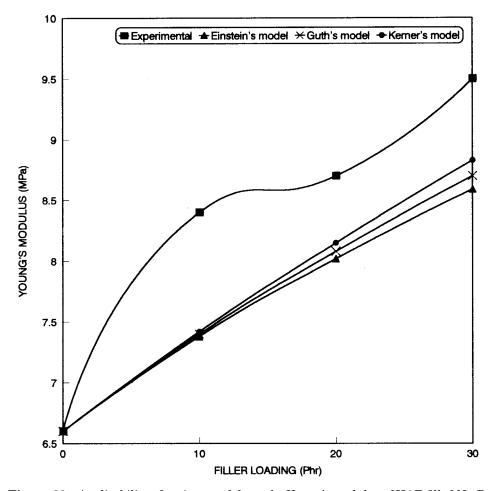


Figure 29 Applicability of various models on the Young's modulus of HAF-filled $N_{50}P$.

The authors thank Mr. G. Balasubramanian and Mr. S. Balasubramani Iyer for their help in performing the mechanical measurements. One of the authors (H.V.) is grateful to the Council of Scientific and Industrial Research, New Delhi, India, for financial support.

REFERENCES

- Paul, D. R.; Newman, S. Polymer Blends, Vol. I, Academic Press: New York, 1978; p 1.
- 2. Hay, A. S. Polym Eng Sci 1976, 16, 1.
- 3. Nishi, T.; Wang, T. T. Macromolecules 1976, 8, 909.
- 4. Imken, R. L.; Paul, D. R.; Barlow Polym Eng Sci
- 1976, 16, 593.
 Walters, M. H.; Keyte, D. N. Rubber Chem Technol 1965, 38, 62.
- Bauer, R. F.; Dudley, E. A. Rubber Chem Technol 1977, 50, 35.

- Shershnev, V. A. Rubber Chem Technol 1982, 55, 537.
- Callan, J. E.; Hess, W. M.; Scott, C. E. Rubber Chem Technol 1971, 44, 814.
- 9. Chappuis, M. M.; Polley, M. H.; Schulz, R. A. Rubber Chem Technol 1955, 28, 253.
- Hess, W. M.; Vegvari, P. C.; Swor, R. A. Rubber Chem Technol 1985, 58, 350.
- Hess, W. M.; Swor, R. A.; Vegvari, P. C. Kautsch Gummi Kunstst 1985, 38, 1114.
- Koshy, A. T. Ph.D. Thesis, Mahatma Gandhi University, 1991 (submitted).
- Varghese, H.; Bhagawan, S. S.; Rao, S. S.; Thomas, S. Eur Polym J 1995, 31, 957.
- Varghese, H.; Bhagawan, S. S.; Prabhakaran, N.; Thomas, S. Mater Lett 1995, 24, 333.
- Varghese, H.; Anand, J. S.; Ramamurthy, K.; Janardhan, R.; Bhagawan, S. S.; Thomas, S. Polym Plast Technol Eng to appear.

- Cimmino, S.; Dorazio, L.; Greco, R.; Maglio, G.; Malinconico, M.; Mancarella, C.; Martuscelli, E.; Palumbo, R.; Ragosta, G. Polym Eng Sci 1984, 24, 48.
- 17. Greco, R.; Mancarella, C.; Martuscelli, E.; Ragosta, G.; Jinghua, Yin Polymer 1987, 28, 1929.
- 18. Choi, G. D.; Kim, S. H.; Jo, W. H. Polym J 1996, 28, 527.
- Bagheri, R.; Pearson, R. A. J Mater Sci 1996, 31, 3945.
- Gent, A. N.; Pulford, C. T. R. J Mater Sci 1984, 19, 3612.
- 21. Kuriakose, B.; De, S. K. J Mater Sci 1985, 20, 1864.
- Bhagawan, S. S.; Tripathy, D. K.; De, S. K. J Mater Sci 1987, 6, 157.
- Thomas, S.; Kuriakose, B.; Gupta, B. R.; De, S. K. J Mater Sci 1986, 21, 711.
- 24. Thomas, S.; Gupta, B. R.; De, S. K. J Vinyl Technol 1987, 9, 71.

- 25. Thomas, S.; George, A. Eur Polym J 1992, 28, 1451.
- 26. Nielson, L. E. Rheol Acta 1974, 13, 86.
- Coran, A. Y. Hand Book of Elastomers, New Development & Technology; Bhowmick, A. K.; Stephens, H. L., Eds; Marcel Dekker: New York, 1998; p 249.
- Holsto-Miettiner, R. M.; Seppala, J. Y.; Ikkala, O. T.; Reima, I. T. Polym Eng Sci 1994, 34, 395.
- Kerner, E. H. Proc Phys Soc, London 1956, 69B, 808.
- Kunori, T.; Geil, P. H. J Macromol 1960, 218, 36.
- Walker, B. M.; Rader, C. P., Eds; Handbook of Thermoplastic Elastomers; Van Nostrand Reinhold Company: New York, 1988.
- 32. Kraus, G. J Appl Polym Sci 1963, 7, 861.
- 33. Smallwood, H. M. J Appl Phys 1944, 15, 758.
- 34. Guth, E. J Appl Phys 1945, 16, 20.