

Mechanical and Aging Properties of Cross-Linked Ethylene Propylene Diene Rubber / Styrene Butadiene Rubber Blends

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ABSTRACT: The mechanical properties and aging characteristics of blends of ethylene propylene diene monomer (EPDM) rubber and styrene butadiene rubber (SBR) were investigated with special reference to the effect of blend ratio and cross-linking systems. Among the blends, the one with 80/20 EPDM/SBR has been found to exhibit the highest tensile, tear, and abrasion properties at ambient temperature. The observed changes in the mechanical properties of the blends have been correlated with the phase morphology, as attested by scanning electron micrographs (SEMs). The effects of three different cure systems, namely, sulfur (S), dicumyl peroxide (DCP), and a mixed system consisting of sulfur and peroxide (mixed) on the blend properties also

were studied. The stress-strain behavior, tensile strength, elongation at break, and tear strength of the blends were found to be better for the mixed system. The influence of fillers such as high-abrasion furnace (HAF) black, general-purpose furnace (GPF) black, silica, and clay on the mechanical properties of 90/10 EPDM/SBR blend was examined. The ozone and water aging studies also were conducted on the sulfur cured blends, to supplement the results from the mechanical properties investigation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2606–2621, 2004

Key words: elastomers; blends; vulcanization; fillers; mechanical properties

INTRODUCTION

Presently, the concept of physically blending two or more existing polymers to obtain new products has been attracting worldwide interest and commercial utilization. The field of polymer science has witnessed the development of new polymers from an endless variety of monomers. However, efforts to modify the existing polymers by various techniques such as block and copolymerization, blending of polymers, etc. were found effective only in the recent past. Polymer blends attract more interest because of the understanding that new molecules are not always required for the preparation of materials with new macroscopic properties and that the blending is more rapid and economical than the development of a new polymer. Furthermore, blends invite more attention because of their improved processing and improved physical properties, in both cured and uncured states. Hence, blending of elastomers is undertaken to improve the technical properties of the original elastomer, to achieve better processing behavior and to lower compound cost.

Interesting studies on polymer blends exist in the literature. For example, the effect of blend ratio on

cross-linking characteristics and dynamic elastic properties of high-density polyethylene/ethylene-propylene diene monomer (HDPE/EPDM) blends was examined by Chandra et al.¹ by a torque rheometer. They found that the cross-link density first increases and then decreases with an increase in EPDM content. Sakr et al.² investigated the effects of carbon black and temperature on the mechanical properties of styrene butadiene rubber (SBR) and natural rubber (NR) at various temperatures. They identified the optimum carbon black concentration as 95 parts per hundred rubber (phr) for unblended samples.

Go and Ha³ studied the dynamic mechanical properties and the morphological behavior of EPDM and butadiene rubber (BR) blends. They found that EPDM and BR are incompatible and the addition of a mixture of aliphatic and aromatic hydrocarbon (AAHC) effectively enhanced the compatibility of both of the elastomers. Chough and Chang⁴ showed the relationship between vulcanization reactivity and chemical structure for NR, BR, and SBR. Their studies reveal that the rate of vulcanization is highest in NR compared with BR and SBR. Amrae et al.⁵ proposed a new method to analyze SBR/BR blends in passenger tire tread compounds by thermogravimetric analysis. The studies on EPDM/silicon rubber blends by Geerts et al.⁶ described the melt mixing of the blends, cross-linking by gamma radiation, and the permeability of the blends

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in methanol vapor. Zaharescu and Mihalcea⁷ studied the degradation effect of EPDM/ethylene-propylene rubber (EPR) blends in different environmental conditions such as oxygen, distilled water, and salt water. The studies showed that in contrast, chloride ions promote degradation of the blends.

Malhotra and Saran⁸ observed the weather resistance of compression molded EPDM/polyvinyl chloride (PVC) blends by accelerated weathering in Xenostst 150 S weatherometer (Atlas Material Testing Solutions, Luchem, The Netherlands) under controlled temperature and relative humidity for 720 h of exposure. Their studies showed that the blends with 50 phr of EPDM had better retention on accelerated weather tests. Mishra and Naik⁹ investigated the internal mixing mastication of ethylene-vinyl acetate (EVA)/EPDM blends at the temperature range of 80–230°C. They found that the extent of degradation of EVA and EPDM was minimum at the temperature ranges of 110–120°C and 150–160°C. Ashalatha et al.¹⁰ worked on the morphological properties of polypropylene (PP)/EPDM/NR blends and they found a double-layered morphological structure in the blends. A conductive rubber composite was developed by Sau et al.¹¹ from different blends of EPDM and Acrylonitrile-butadiene rubber (NBR) containing acetylene black. They found that the conductivity rises with increasing temperature and the activation energy of the conduction increases with a decrease in the loading of conductive fillers.

Younan et al.¹² made an extensive study on the dielectric and mechanical properties of EPDM-chloroprene blends loaded with white and black fillers and with PVC as a compatibilizer. In their studies, the effective blend ratio of EPDM and chloroprene was 50 : 50. They highlighted the improvements in the mechanical properties of the blends with the addition of black and nonblack fillers.

The works by Ghoneim and Ismail¹³ on EPDM/NR blends show that the effective blend ratio for carbon black dispersion is 75 : 25 and that at this blend ratio the mechanical properties and stability against aging are found to be good. The effect of blend ratio on the cross-linking characteristics of EVA and the EPDM copolymer was studied by Mishra et al.¹⁴ by differential scanning calorimetry (DSC) and a torque rheometer. They found that the cure rate increases whereas the optimum cure time and energy consumption for curing decreases with an increase in the EVA / EPDM blend ratio. Phase morphology is an important factor in the determination of properties of polymer blends. Laokijcharoen and Coran¹⁵ worked in this area and they were successful in studying a method for determining phase morphology of unvulcanized NR/HDPE blends. Bandyopadhyay¹⁶ and coworkers studied the dynamic mechanical properties of the blends of NR/EVA in terms of storage modulus and loss tangent. Studies on the dynamic properties, curing

characteristics, etc. in SBR/epoxidized NR (ENR) blends by Ismail and Suzamah¹⁷ and investigations on the highly filled EPDM rubber for the effect of curative systems, grafted rubber, cure rate, temperature, etc. by Markvic¹⁸ and coworkers are some of the recent works in polymer research. Ramesan et al.¹⁹ studied the influence of carbon black on uncompatibilized and compatibilized SBR/NBR blends. Their studies reveal that compatibilized blends show enhanced mechanical properties in the presence of high-abrasion furnace (HAF) black in comparison with uncompatibilized samples. Oliveira and Soares²⁰ investigated the effect of a vulcanizing system on cure and mechanical properties of NBR/EPDM blends. EI Sabbagh²¹ showed that the poor compatibility of NR and EPDM can be enhanced by the addition of compatibilizers such as polybutadiene (BR), chlorinated rubber, PVC, etc. A similar work by Soares et al.²² showed that reactive compatibilization of EPDM-based dissimilar elastomer blends can be performed using mercapto-functionalized copolymers. Studies on SBR/ENR blends by Ismail et al.²³ show that increasing composition of ENR in the blend enhances the mechanical properties and reduces the scorch and cure times. Ghosh²⁴ and Basu were successful in developing filled covulcanizates of elastomer blends comprising of NR and EPDM of commercial importance using a multifunctional rubber additive bis (di isopropyl) thiophosphoryl disulfide (DIPDIS). In another recent work, Soqres et al.²⁵ studied the reactive compatibilization of EPDM-based dissimilar elastomer blends in terms of mechanical properties and swelling degree using mercapto-functionalized copolymers that resulted in an improvement of mechanical properties.

The polymer blends generally termed as polyblends are classified into mechanical, chemical, mechanochemical, solution, and latex polyblends. We focus on the preparation of mechanical polyblends by mill mixing. This method is problem free compared with other methods. High shearing force is applied for the mechanical blending of high molecular weight elastomers, which necessitates the use of mixing mills, internal mixers, etc.

The aim of this work was to prepare and characterize blends of EPDM and SBR with special reference to the effects of blend ratio and cross-linking systems. The cure characteristics, mechanical properties such as tensile strength, tear strength, elongation at break, abrasion resistance, and hardness, have been investigated. The behavior of the blends in water and ozone environment was examined also. The influence of black and nonblack fillers on the blend properties also has been studied. The blends of EPDM and SBR developed by this study could be used in the automobile industry in the form of products such as windscreen channels, glass beadings, tire flaps, tire treads, and for electrical insulation.

TABLE I
Properties of EPDM and SBR Rubbers

Properties	EPDM	SBR
Mooney viscosity : ML1 + 4	55 at 125°C	50 at 100°C
Ethylene / propylene ratio	62/38	—
Diene (%)	4.0	—
Bound styrene (%)	—	23.0
Organic acid content (%)	—	5–7
Density (mg/m ³)	0.86	0.93

EXPERIMENTAL

Materials

The blends in this study were based on EPDM-502 and SBR-1502. EPDM-502 is a commercial product of Herdillia Unimers, Ltd. (Mumbai, India). SBR-1502 is supplied by India Rubber Chemicals (Kottayam, India). The characteristics of these materials are given in Table I. The rubber chemicals such as sulfur (S), dicumyl peroxide (DCP), zinc oxide, stearic acid, mercaptobenzothiazyl disulfide (MBTS), and tetramethyl thiuram disulfide (TMTD) were of commercial grade. The fillers used were HAF and general-purpose furnace (GPF) blacks, silica, and clay.

Blend preparation

The blends of EPDM and SBR with different blend ratios, cross-linking systems, and fillers were prepared on a two-roll mixing mill (diameter, 150 mm; working distance, 250 mm; speed of the slow roll, 24 rpm; gear ratio, 1 : 16). Mastication of each polymer and blending were done separately between hot rolls of the mill at 80°C as per the recipes given in Table II. The different cure systems used in this work were S, DCP, and a mixed system consisting of S and DCP (mixed).

The coding of the blends with different cure systems and fillers is given in Table III. The compounds with the S system are designated as E₀S, E₁₀S, E₂₀S, E₃₀S, etc., where E stands for EPDM rubber and the subscripts indicate the weight percentage of EPDM in the blends. The designation E₀S represents pure SBR vulcanizate. Fillers such as HAF black, GPF black, silica, and clay used in the study have been coded as HB, GB, SI, and CL, respectively, in Table III. The loading has been indicated by prefixes. For instance, 10 HB explains 10 phr of the HAF black loaded system. The compounding time for each blend was maintained for 20–30 min depending on filler loading. Rheometric properties such as optimum cure t_{90} , maximum and minimum torques (MH and ML), and scorch time (TS_2) of the blends were studied by using a Gottfert elastograph "vario" 67 .98 (Buchen, Germany). The vulcanization of the blends was performed on a hydraulic press (platen size, 8' × 8') under a pressure of 30 tonnes and at a temperature of 160°C.

Mechanical properties

Tensile properties of the blends were examined by using an Instron Universal Testing Machine (model 4411; Instron Ltd., Buckinghamshire, UK) at a crosshead speed of 500 mm/min. The tensile tests were conducted according to the ASTM D 412–87 test procedures using dumbbell-shaped test pieces. The measurements were done as per ASTM D 624–81 for tear strength at a crosshead speed of 500 mm/min, using unnicked 90° angle test pieces. Abrasion tests were conducted in a Din Abrader as per DIN 53,516. The hardness (Shore A) of the samples was measured by using a Durometer (Modex India Pvt. Ltd., Mumbai, India) according to ASTM 2240–86.

Aging studies also were conducted on EPDM/SBR blends to determine ozone and water resistance and to

TABLE II
Compounding Recipe

Ingredients (phr) ^a	Sulfur system (S)		Mixed system (S + DCP)	10 HB	20 HB	30 HB	40 HB	40 GB	40 SI	40 CL
	DCP									
Polymer ^b (blends)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zinc oxide	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
MBTS	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
TMTD	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sulfur	2.50	—	—	2.5	2.5	2.5	2.5	2.5	2.5	2.5
DCP	—	4	—	—	—	—	—	—	—	—
S + DCP	—	—	2.0 + 2.0	—	—	—	—	—	—	—
HAF	—	—	—	10.0	20.0	30.0	40.0	—	—	—
GPF	—	—	—	—	—	—	—	40.0	—	—
Silica	—	—	—	—	—	—	—	—	40.0	—
Clay	—	—	—	—	—	—	—	—	—	40.0

^a Parts per hundred of rubber by weight.

^b EPDM / SBR blends of varying composition.

TABLE III
Cure Characteristics of EPDM/SBR Blends

Sample code	Blend ratio	Optimum cure time t_{90} (min)	Scorch time TS_2 (min)	Minimum torque, ML (dNm)	Maximum torque, MH (dNm)	CRI
E ₀ S	SBR100 / EPDM0	4.61	2.70	2.55	15.88	52.36
E ₁₀ S	SBR90 / EPDM10	4.60	2.73	2.73	14.45	53.48
E ₂₀ S	SBR80 / EPDM20	4.62	2.75	2.75	13.19	58.48
E ₃₀ S	SBR70 / EPDM30	4.66	2.74	2.48	12.97	52.63
E ₄₀ S	SBR60 / EPDM40	4.92	2.77	2.63	13.23	46.51
E ₅₀ S	SBR50 / EPDM50	5.40	2.86	2.62	12.52	39.37
E ₆₀ S	SBR40 / EPDM60	5.68	2.83	2.91	12.69	44.44
E ₇₀ S	SBR30 / EPDM70	5.82	3.19	3.33	12.57	38.02
E ₈₀ S	SBR20 / EPDM80	5.90	3.48	3.47	12.85	45.05
E ₉₀ S	SBR10 / EPDM90	5.92	3.65	2.57	13.55	52.63
E ₁₀₀ S	SBR0 / EPDM100	7.40	4.76	2.25	17.00	37.88
E ₀ P	SBR100 / EPDM0	11.20	2.18	0.81	16.69	11.09
E ₂₀ P	SBR80 / EPDM20	12.26	3.17	0.53	13.08	11.00
E ₄₀ P	SBR60 / EPDM40	13.71	3.46	0.38	13.03	08.88
E ₆₀ P	SBR40 / EPDM60	13.80	3.43	0.25	11.96	09.64
E ₈₀ P	SBR20 / EPDM80	13.96	3.88	0.65	11.86	10.19
E ₁₀₀ P	SBR0 / EPDM100	14.96	5.19	1.13	9.57	10.24
E ₀ Mix	SBR100 / EPDM0	4.11	2.44	1.68	16.29	59.88
E ₂₀ Mix	SBR80 / EPDM20	6.22	2.95	1.64	13.14	30.67
E ₄₀ Mix	SBR60 / EPDM40	6.41	3.12	1.51	13.13	43.67
E ₆₀ Mix	SBR40 / EPDM60	8.56	3.13	1.58	12.33	18.42
E ₈₀ Mix	SBR20 / EPDM80	7.73	3.68	2.06	12.36	24.69
E ₁₀₀ Mix	SBR0 / EPDM100	6.90	4.97	1.69	12.28	51.81
E ₉₀ S10 HB	SBR10 / EPDM90 / HAF10	4.86	1.97	1.22	10.93	34.60
E ₉₀ S20 HB	SBR10 / EPDM90 / HAF20	4.84	1.72	1.18	10.69	32.05
E ₉₀ S30 HB	SBR10 / EPDM90 / HAF30	4.53	1.51	1.12	12.20	19.92
E ₉₀ S40 HB	SBR10 / EPDM90 / HAF40	3.59	1.06	1.84	12.40	39.53
E ₉₀ S40 GB	SBR10 / EPDM90 / GPF40	5.03	1.48	1.11	13.03	28.17
E ₉₀ S40 SI	SBR10 / EPDM90 / SI40	7.91	0.99	4.50	13.23	14.45
E ₉₀ S40 CL	SBR10 / EPDM90 / CL40	5.03	1.43	0.76	9.03	27.78

support the observations from mechanical properties analysis. Ozone and water aging studies were conducted as per ASTM D 518 and ASTM D 471-66, respectively.

Morphology

A JEOL JSM-5600 LV Scanning Electron Microscope and Jeol JFC-1200 Fine Coater (Jeol Ltd., Tokyo, Japan) were used for the morphology²⁶⁻²⁸ study of the blends. The nature, size, shape, and phase continuity of the blends E₁₀₀S, E₈₀S, E₆₀S, E₄₀S, E₂₀S, and E₀S have been investigated. The morphology of the blends E₈₀S, E₈₀P, and E₈₀Mix also was studied.

RESULTS AND DISCUSSION

Cure characteristics

The cure characteristics of the EPDM/SBR blends with different vulcanizing systems and fillers are given in Table III. The optimum cure time t_{90} shows a gradual increase with an increase in EPDM content in the blends for all of the cross-linking systems. The optimum cure time t_{90} has been found to be highest for

DCP cured systems compared with S and mixed systems for a given blend ratio. The cure time (t_{90}) of carbon black filled blends have been found to be slightly lower than that of the unfilled ones perhaps because of the adsorption of curatives on the surface of the fillers. In addition, the lesser acidity²⁹ of HAF black increased the rate of cure, which results in the reduction of cure time. A similar result is obtained in GPF blends also. However, the cure time of the silica blends is increased probably because of the tendency of silica to adsorb the accelerators at its surface. Greater acidity of fillers generally retards the cure rate and increases the cure time. Silica and clay are more acidic fillers and hence reduce the cure rate and increase the cure time. The increased HAF black loading in the blends shows that the cure time is lowered from smaller to higher loading.

Among the S cured blends (unfilled), the scorch time and scorch safety are higher for blends E₉₀S, E₈₀S, and E₇₀S. The minimum torque (ML) values are found to be higher for S cured systems for a given blend ratio than the DCP and mixed systems. The maximum torque (MH), which is a measure of cross-link density, is higher for S and mixed systems than the DCP sys-

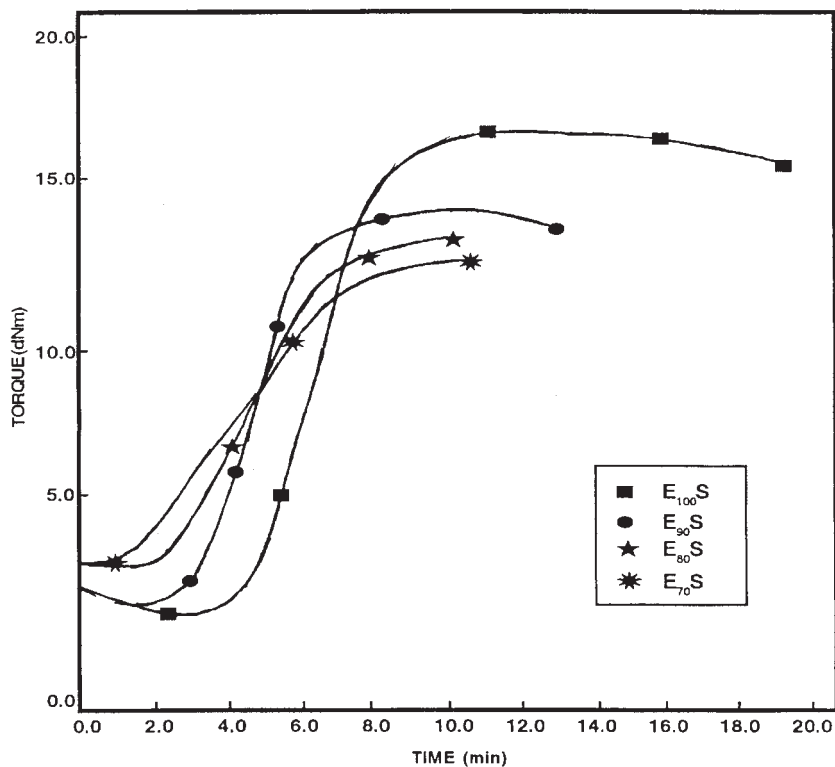


Figure 1 Rheographs of S cured EPDM/SBR blends.

tem. The rheographs of blends E₁₀₀S, E₉₀S, E₈₀S, and E₇₀S are shown in Figure 1. Figure 2 explains the cure characteristics of E₈₀S, E₈₀P, and E₈₀ mix in different

cure systems. Among the filler loaded blends, the scorch safety is higher for GPF black filled blends than the systems filled with clay, HAF black, and silica for

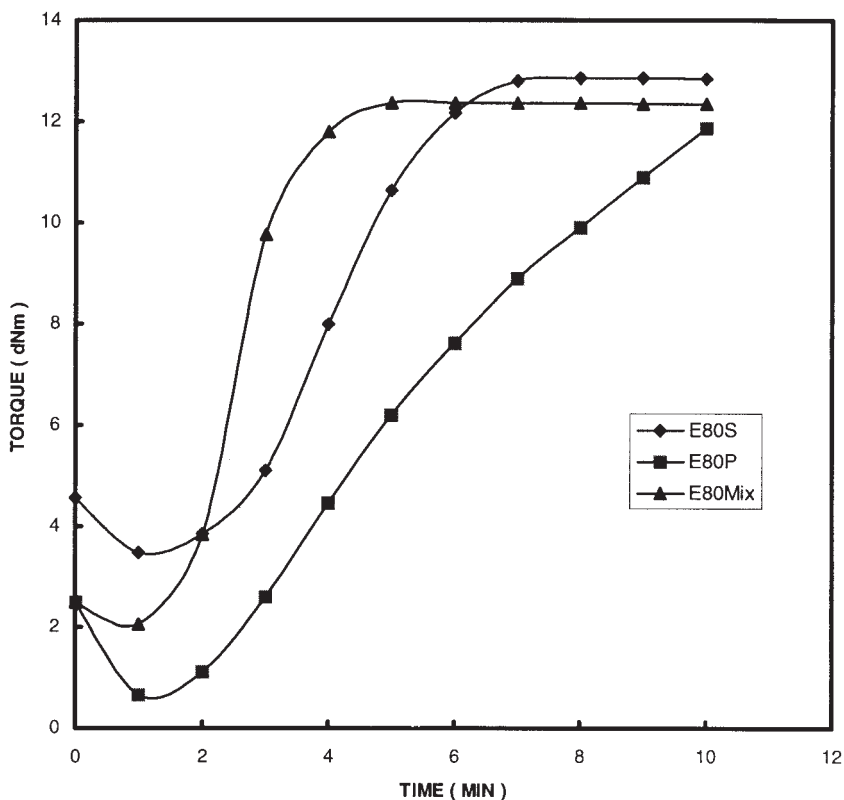


Figure 2 Rheographs of EPDM/SBR blends cured in different cure systems.

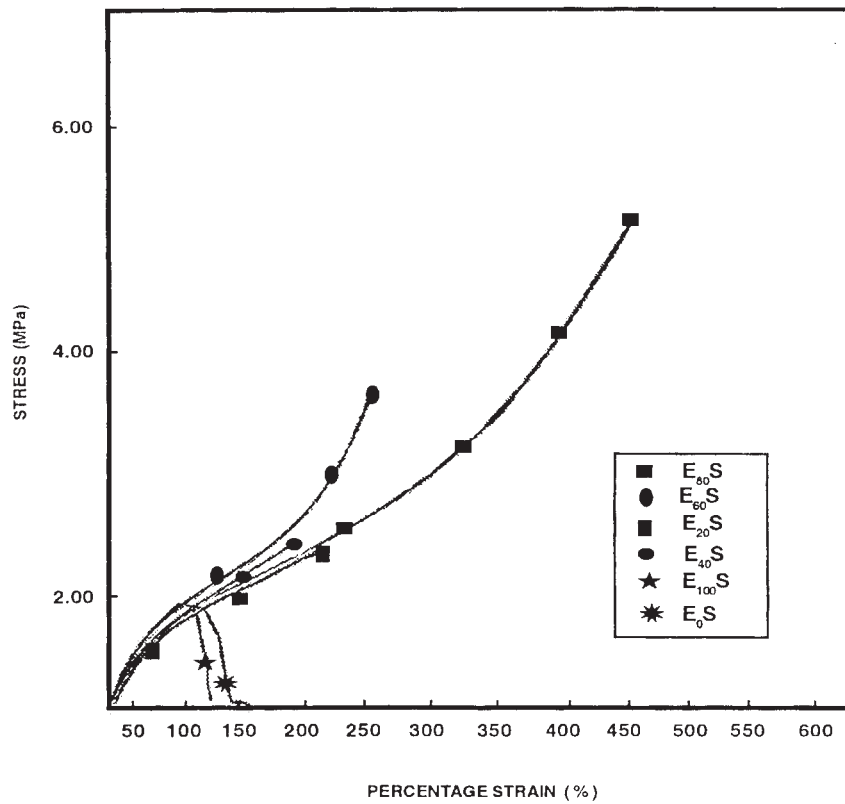


Figure 3 Effect of blend ratio on the stress-strain curves of S cured EPDM/SBR blends.

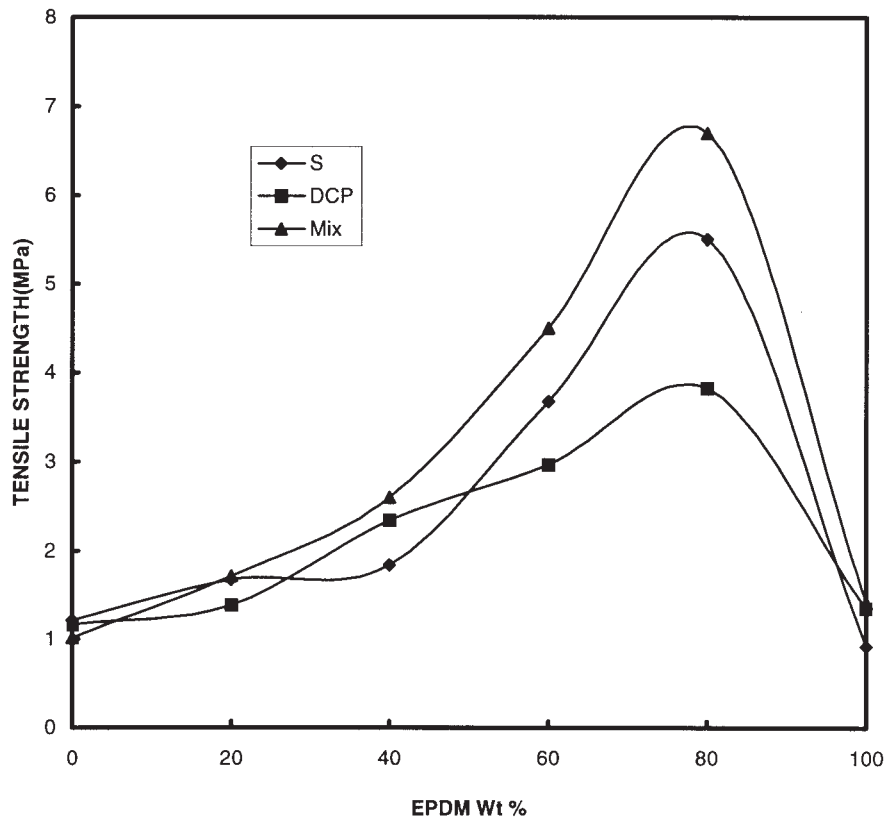


Figure 4 Effect of different cross-linking systems on the tensile strength of EPDM/SBR blends.

a given filler loading. The minimum and maximum torques are higher for silica filled blends compared with HAF black, GPF black, and clay.

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

$$\text{CRI} = 100/t_{90} - t_2 \quad (1)$$

where t_{90} is the cure time and t_2 is the scorch time. The CRI values also are given in Table III. CRI for the present blend systems was found to increase with increased SBR content for all vulcanizing systems. Hence, SBR is the cure-activating component for the systems. A high CRI value shows higher vulcanization rate. For a given blend ratio, the CRI was highest for S systems and lowest for DCP systems. It also is interesting to note that the CRI values decrease with the addition of fillers. The HAF loaded systems have been found to exhibit the highest cure rate.

Mechanical properties

Figure 3 shows the stress-strain curves of S cured (unfilled) EPDM/SBR blends. It is clear from the graphs that as the EPDM content increases, there is an increase in strain with increase in stress. This deformation behavior is caused by the orientation of crystalline regions of EPDM under the applied stress. The stress values are found to be highest in the E₈₀S blend system.

The mechanical properties of the individual polymers and the blends are shown in different figures. The blend E₈₀S (EPDM80/SBR20) shows the highest tensile strength. This could be because of the reinforcement effect of SBR on EPDM matrix. Figure 4 shows the effect of different cure systems, namely, S, DCP, and mixed on the tensile strength of unfilled blends E₈₀S, E₈₀P, and E₈₀Mix. The graphs clearly show that the blends cured by mixed system possess the highest tensile strength. The S cured systems also have better tensile strength but the DCP cured system shows a drop in the tensile strength, probably because of the lesser orientation of crystalline regions of EPDM along the direction of stress.

The cross-linking efficiency of the blends is measured in terms of cross-link density. The cross-link densities of the filled and unfilled blends were calculated from the tensile values using the kinetic theory of elasticity:²⁹

$$V = \sigma/(\lambda^{-1}/\lambda^2)RT \quad (2)$$

where V is the cross-link density (number of cross-links per cc), σ is the modulus, λ is the extension ratio, R is the gas constant, and T is the temperature in absolute scale. The values of Young's modulus and cross-link densities are given in Table IV. It is seen that the cross-link densities of the unfilled blends increase

TABLE IV
Young's Modulus and Cross-Link Density of EPDM / SBR Blends

Sample code	Young's modulus (%)	Cross-link density
E ₀ S	0.10	0.20
E ₁₀ S	1.23	2.81
E ₂₀ S	1.25	2.87
E ₃₀ S	1.24	2.85
E ₄₀ S	1.13	2.58
E ₅₀ S	1.20	2.76
E ₆₀ S	1.28	2.94
E ₇₀ S	1.22	2.79
E ₈₀ S	1.26	2.89
E ₉₀ S	1.19	2.73
E ₁₀₀ S	—	—
E ₀ P	—	—
E ₂₀ P	1.33	3.1
E ₄₀ P	1.22	2.8
E ₆₀ P	1.23	2.8
E ₈₀ P	1.01	2.3
E ₁₀₀ P	0.82	1.9
E ₀ Mix	0.88	2.0
E ₂₀ Mix	0.91	2.1
E ₄₀ Mix	1.21	2.8
E ₆₀ Mix	1.22	2.8
E ₈₀ Mix	1.14	2.6
E ₁₀₀ Mix	0.85	1.9
E ₉₀ S10 HB	1.11	2.5
E ₉₀ S20 HB	1.47	3.3
E ₉₀ S30 HB	1.63	3.7
E ₉₀ S40 HB	3.08	7.1
E ₉₀ S40 GB	1.87	4.3
E ₉₀ S40 SI	2.22	5.1
E ₉₀ S40 CL	1.80	4.1

with increase in EPDM content for all the vulcanizing systems. However, the Young's modulus and cross-link densities are higher in S and mixed cure systems. This may be because of the nature of the cross-links in the blends. The DCP cured systems have rigid C—C linkages, which can be broken easily under an applied stress, whereas in other systems, the flexible C—S and S—S linkages exist and they require more stress to break the bonds. A schematic representation of the network cross-linking is given in Figure 5.

For filled blend systems, the cross-link density increases with an increase in the dosage of fillers. The modulus and cross-link density are higher in E₉₀S 40 HB compared with other blends with a relatively lesser amount of HAF. A similar effect is noticed in blends filled with GPF black, silica, and clay.

The relationship between elongation at break and weight percentage of EPDM for blends cured under S, DCP, and mixed systems is presented in Figure 6. The elongation at break increases with an increase in EPDM content. In blends with cure systems DCP and mixed, the values of elongation at break are lower compared with S cured systems. The dependency of tear strength on the weight percentage of EPDM is shown in Figure 7. The graph shows an increase in

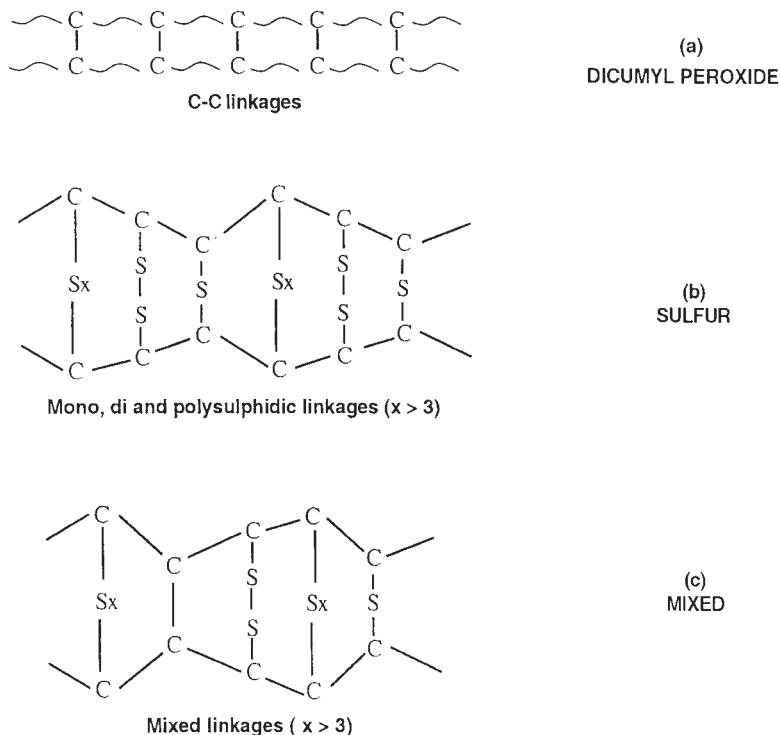


Figure 5 Schematic representation of network cross-linking of EPDM/SBR blends cured under S, DCP, and mixed systems.

tear strength with weight percentage of EPDM. Among the blends cured under various cure systems, the tear strength is highest for mixed systems and it

decreases in S and DCP systems. The tear strengths of filled blends also show the same trend and the tear values increase with an increase in filler dosage. The

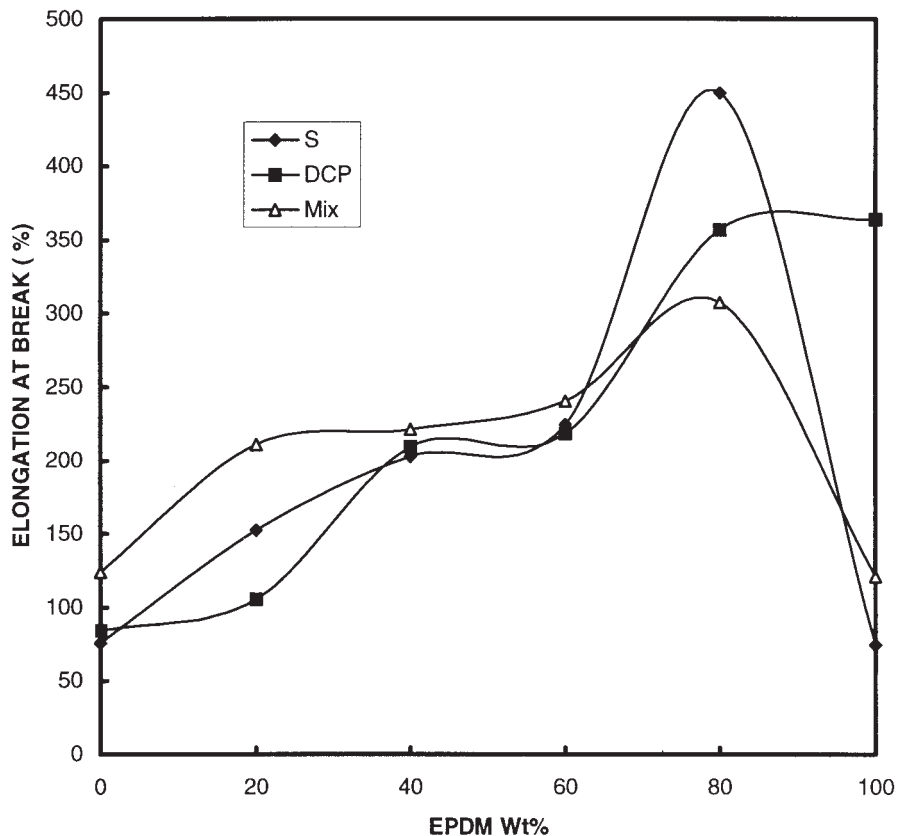


Figure 6 Variation in elongation at break with the weight percentage of EPDM in different cure systems.

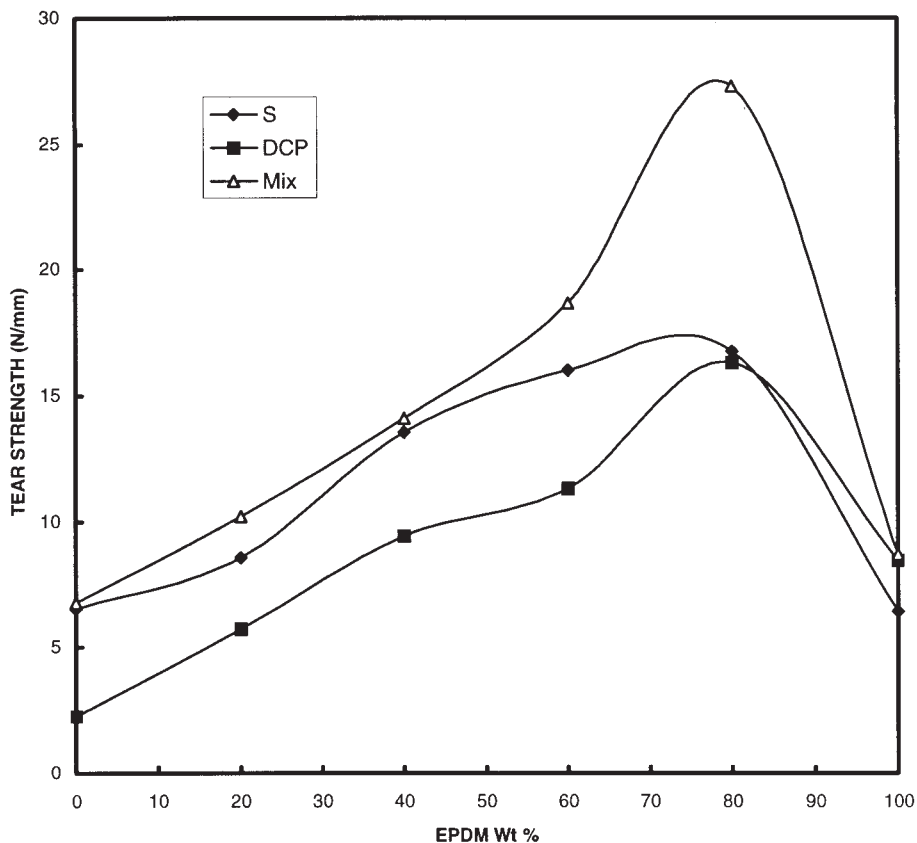


Figure 7 Variation in the tear strength with the weight percentage of EPDM in different cure systems.

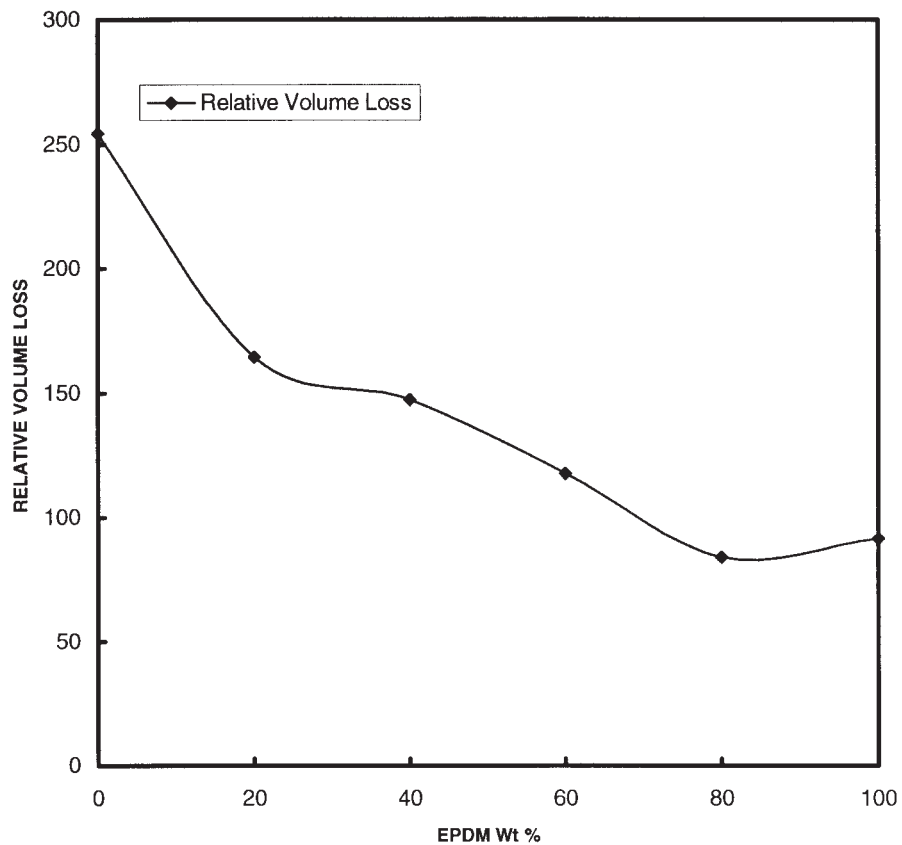


Figure 8 Variation in abrasion resistance with the EPDM/SBR blend ratio in S cured systems.

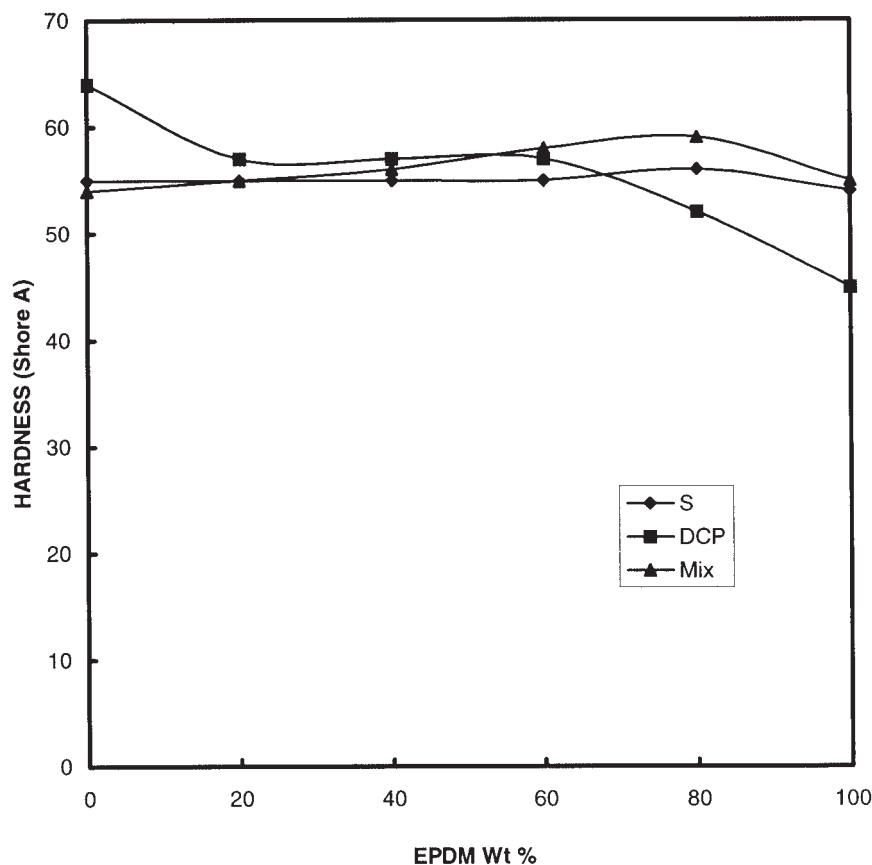


Figure 9 Variation in hardness with the blend ratio and cross-linking system of EPDM/SBR blends.

abrasion resistance in terms of volume loss has been studied for S cured blends. The abrasion loss was found minimum for the blend $E_{80}S$ and, hence, this blend has been identified as the highest abrasion resistant one among the systems investigated. The change in abrasion resistance with weight percentage of EPDM is shown in Figure 8. The abrasion resistance was found to decrease from blend $E_{80}S$ to $E_{20}S$. A marginal increase in the hardness of the blends also was noted with an increase in weight percentage of EPDM in the blend (Figure 9).

Morphology analysis

Figure 10 a explains the scanning electron micrographs (SEMs) of unfractured specimens of EPDM/SBR blends (80/20) cured under S, DCP, and mixed (S + DCP) cure systems. The morphology analysis of the blends shows that the dispersed phase of the blend $E_{80}S$ is a cluster type and the interphase is excellent between the two phases. The phase domains of this blend composition are globular shaped and of uniform size. Effective blend formation via continuous phase formation was noticed in this blend ratio. In the DCP cured EPDM/SBR blend $E_{80}P$, many porosities are seen. The flake-like structure was filled with pores and the molecules were loosely packed. However, the

EPDM/SBR blend $E_{80}Mix$ has shown excellent structural arrangement and the highest mechanical properties. The particles are uniform in size and the needle-like particles were interwoven with the globular structure.

Figure 10 b represents SEMs of tensile fractured specimens of EPDM/SBR blends cured under the S system. To understand the blend morphology, the micrographs of varying compositions, viz., $E_{100}S$, $E_{80}S$, $E_{60}S$, $E_{40}S$, $E_{20}S$, and E_0S , were studied. The blend $E_{100}S$ is pure EPDM cured under S and its flowering structure gives a clear distinction from other blends. In blend $E_{80}S$, it can be noted that the pictures are smooth, and the component elastomers are found homogenized. In blend $E_{60}S$, pullouts were seen; and in blend $E_{40}S$, there is more segmentation, i.e., as the SBR content increases, the uniform dispersion becomes difficult, whereas in blend $E_{20}S$, layer formation was noticed along with cracks. Blend E_0S has shown pullouts at its fractured surface. The depth of the cracks in this sample was increased from the previous sample.

From the SEMs, it is very clear that effective homogenization of the EPDM/SBR blends would be possible only in blends $E_{80}S$ and $E_{80}Mix$. The mechanical properties measured match the morphologies discussed. A careful examination of the blend morphologies dis-

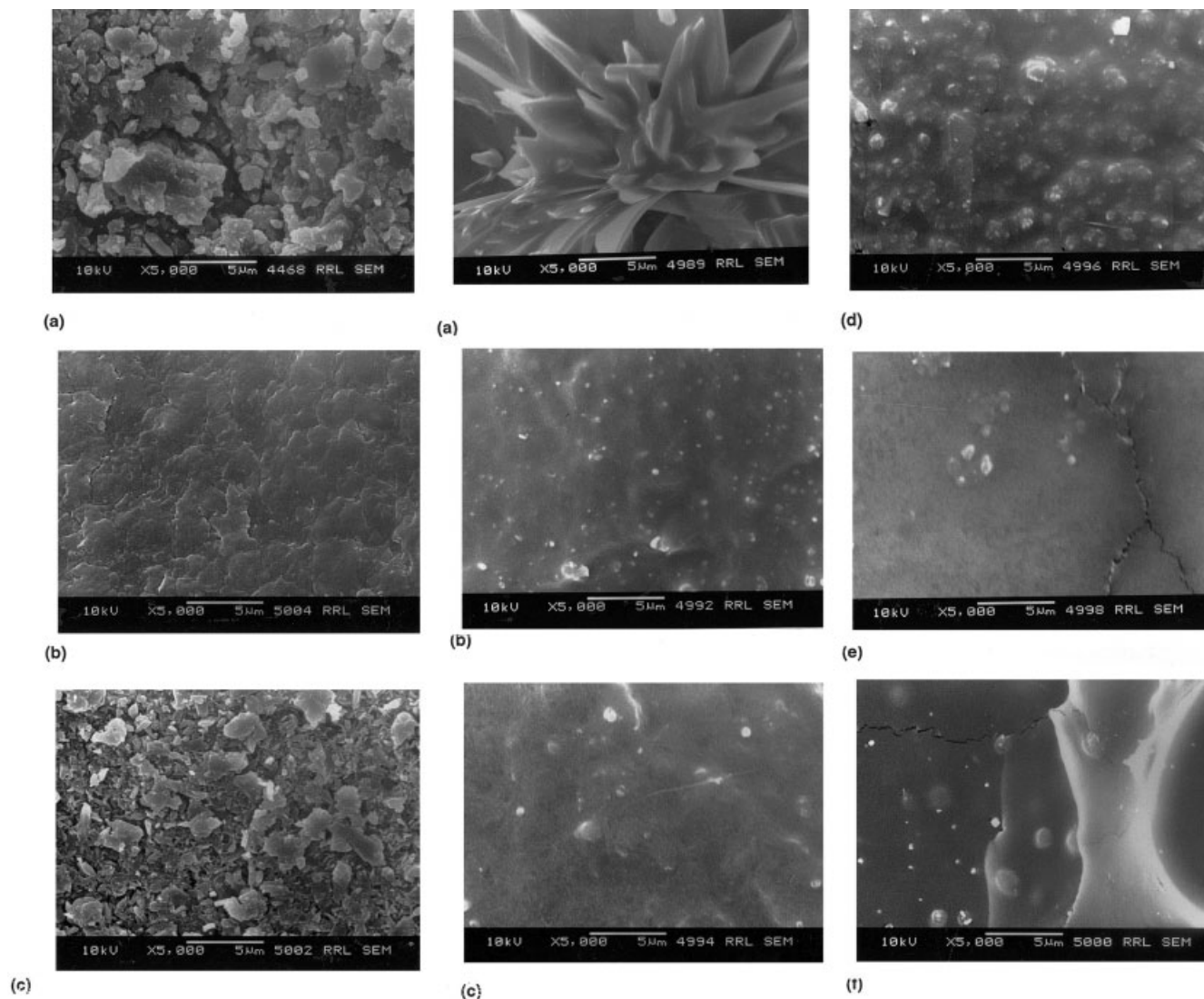


Figure 10 (a) SEM of unfractured specimens of EPDM/SBR blends cured under S, DCP, and mix systems (a) $E_{80}S$, (b) $E_{80}P$, and (c) $E_{80}Mix$. (b) SEM of tensile fractured specimens of S cured EPDM/SBR blends (a) $E_{100}S$, (b) $E_{80}S$, (c) $E_{60}S$, (d) $E_{40}S$, (e) $E_{20}S$, and (f) E_0S .

cussed shows that with increasing concentration of EPDM, the blend morphology becomes better and better and this performance also was reflected in the mechanical properties studied. The SEMs show that the dispersion of SBR in EPDM becomes weak as the SBR content increases. The phenomenon of layer formation, pullouts, and crack formation also were found increased with an increase in SBR composition. On verifying the mechanical properties, it is noted that the blend morphologies of $E_{80}S$, $E_{80}P$, and $E_{80}Mix$ justified the performance.

The mechanical properties such as modulus, tensile strength, elongation at break, tear strength, and hardness of the filled blends were studied also. The elongation at break (Figure 11) and tensile strength (Figure 12) are found highest when the dosage of HAF is 30 phr. The tear strength, modulus, and hardness of the mix at the same dosage of HAF black are moderate.

The tensile properties show a negative trend in HAF black filled blends at a 40-phr level. In the other filled systems at a 40-phr level, clay blends have given the highest elongation at break and the GPF black blends have shown the highest tensile and tear strength values. The hardness of the filled blends at the 40-phr level was compared also and it were found highest for HAF black blends.

To complement the mechanical properties studied, aging studies have been conducted. Compared with EPDM, SBR is highly susceptible to degradation. The degradation of SBR is accelerated by ozone, water, etc. The presence of EPDM in the blends eliminates the degradation behavior of SBR and hence produces useful rubber blends.

The distilled water aging³⁰ properties of S cured EPDM/SBR blends were investigated also and the water uptake at regular intervals of aging is shown in

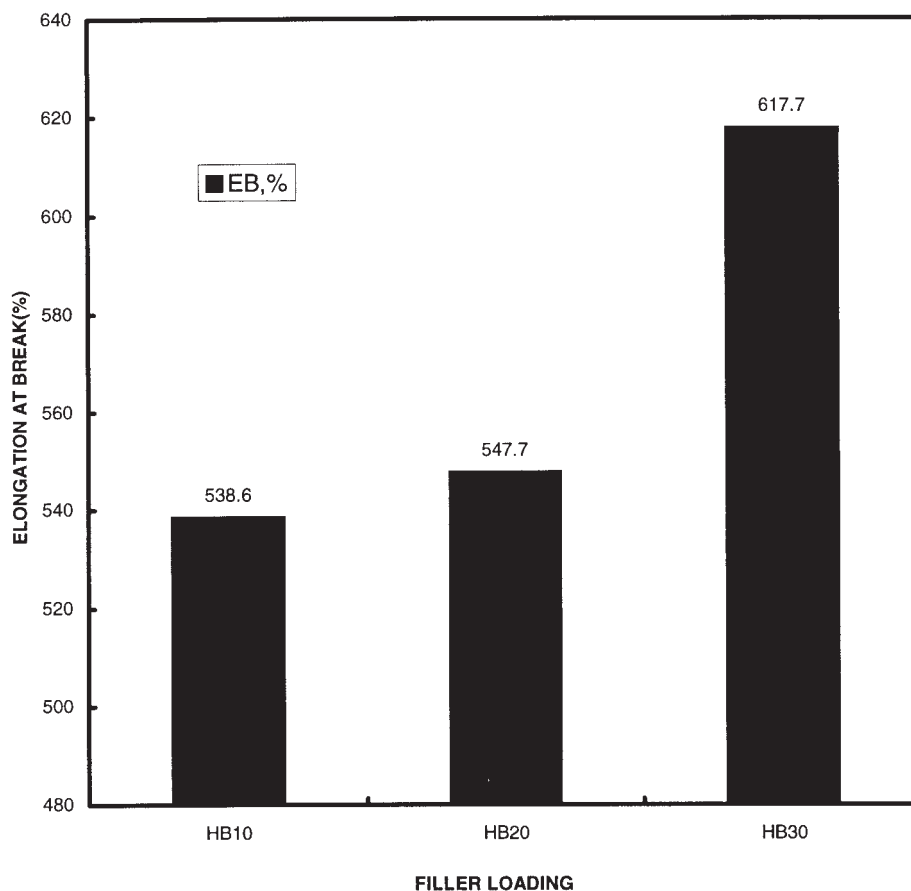


Figure 11 Effect of filler loading (HAF black) on the elongation at break of EPDM/SBR blend $E_{90}S$.

Table V. The water uptake of the blends in four stages after 7 d 14, 21, and 42 d were studied and it was found that the water uptake after 42 d was only 0.63% in the blend $E_{90}S$ (EPDM90/SBR10) and the values increased slightly with an increase in SBR content. Hence, this indicates that the EPDM/SBR blends are highly water resistant.

The studies show that ozone cracks are not developed in EPDM/SBR blends ($E_{100}S$ to $E_{40}S$) after the completion of 120 h of aging. Figure 13 illustrates the crack initiation and the nature of cracks developed in different S cured blends. The optical photomicrographs clearly show that no cracks are formed in the blend compositions $E_{100}S$, $E_{80}S$, $E_{60}S$, and $E_{40}S$ even after completing 120 h of ozone aging but crack initiation started in blend E_0S after 4 h and cracks developed in $E_{20}S$ after 7 h of aging. These two blends are richer in SBR and are susceptible to ozone aging. The ozone cracks developed are deep, wide, and continuous in E_0S and moderate in $E_{20}S$. The ozone aging studies show that the highly ozone-resistant EPDM rubber in different blend ratios has effectively modified the weak SBR from ozone aging. Hence, this proves the suitability of the present blend systems for outdoor applications.

Model fitting

The mechanical behavior of the EPDM/SBR blends was modeled using various composite models such as parallel, series, and the Halpin-Tsai equation. The parallel model (highest upper-bound model) is given by the equation³¹

$$M = M_1\phi_1 + M_2\phi_2 \quad (3)$$

where M is the mechanical property of the blend and M_1 and M_2 are the mechanical properties of components 1 and 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of components 1 and 2, respectively. In the parallel 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. The arrangement of the components in the blend is in a series with the applied stress in the lowest-bound series model. The equation³² used is

$$1/M = \phi_1M_1 + \phi_2M_2 \quad (4)$$

The equation, according to Halpin-Tsai is

$$M_1/M = (1 + A_iB_i\phi_2)/1 - B_i\phi_2 \quad (5)$$

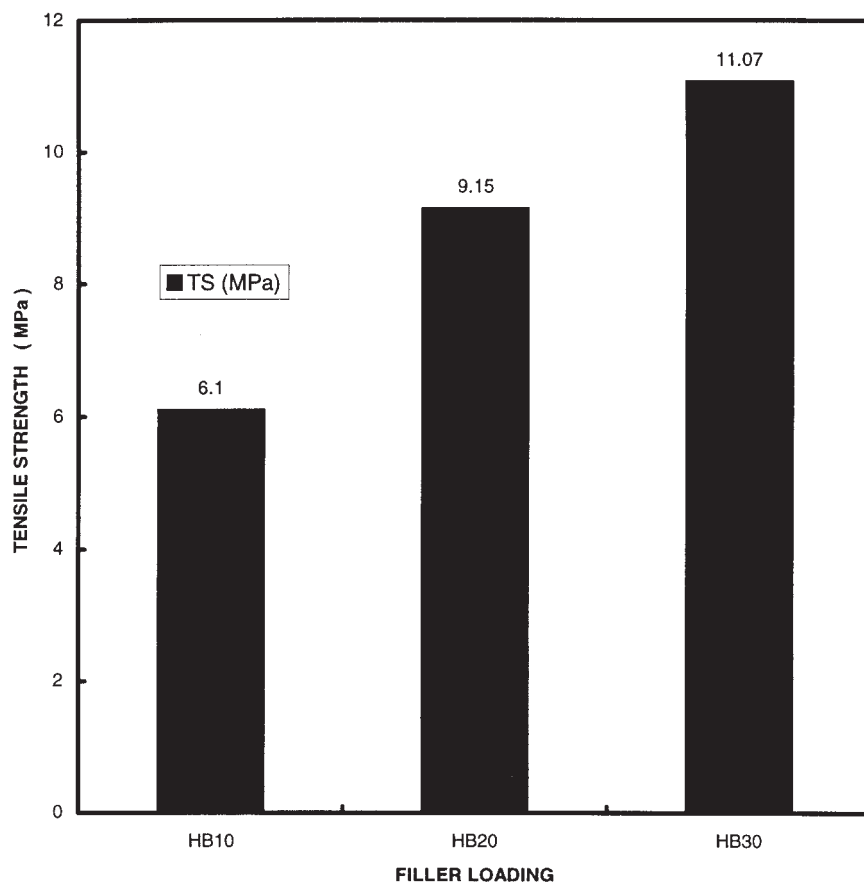


Figure 12 Effect of filler loading (HAF black) on the tensile strength of EPDM / SBR blend E₉₀S.

where B_i is given as

$$B_i = (M_1/M_2 - 1)/M_1/M + A_i \quad (6)$$

In this equation, subscripts 1 and 2 represent the continuous and dispersed phase, respectively. The value of A_i for elastomer domains dispersed in a hard continuous matrix is 0.66. The experimental results are compared with the theoretical models in Figures 14

TABLE V
Distilled Water Aging on EPDM / SBR Blend
Vulcanizates at Ambient Temperature

Samples	Water uptake (%)			
	After 7 d	After 14 d	After 21 d	After 42 d
E ₁₀₀ S	+0.07	+0.25	+0.331	+0.44
E ₉₀ S	+0.36	+0.44	+0.495	+0.63
E ₈₀ S	+0.48	+0.70	+0.726	+1.12
E ₇₀ S	+0.53	+0.87	+0.881	+1.15
E ₆₀ S	+0.48	+0.87	+0.938	+1.32
E ₅₀ S	+0.77	+1.17	+1.367	+1.86
E ₄₀ S	+0.99	+1.31	+1.549	+2.23
E ₃₀ S	+0.93	+1.40	+1.587	+2.23
E ₂₀ S	+1.63	+2.09	+2.499	+3.05
E ₁₀ S	+1.99	+2.54	+2.874	+3.19
E ₀ S	+2.09	+2.58	+2.898	+3.26

and 15. The graphs show that for tensile strength (Figure 14), the experimental value of E₉₀S lies relatively close to the parallel model as the weight percentage of EPDM increases.

CONCLUSION

The effects of blend ratio, cure systems, and fillers on the mechanical properties of EPDM/SBR blends were investigated. The morphology studies of the blends show the existence of excellent interphase between EPDM and SBR in the blend ratio 80 : 20. The properties such as elongation at break, tensile strength, tear strength, abrasion resistance, and hardness increase with an increase in EPDM content. Among the different vulcanizing systems, the tensile and tear strengths were higher for mixed systems compared with the S and DCP systems. The elongation at break was higher for S cured blends unlike in the other two systems, perhaps because of the more orientation of crystalline regions of EPDM in the direction of stress. There is a visible decrease in the elongation at break in both DCP and mixed cured blends. The abrasion resistance of the S cured blends was examined and it was found that the properties increased with EPDM content and the values were highest for E₈₀S. The results of the

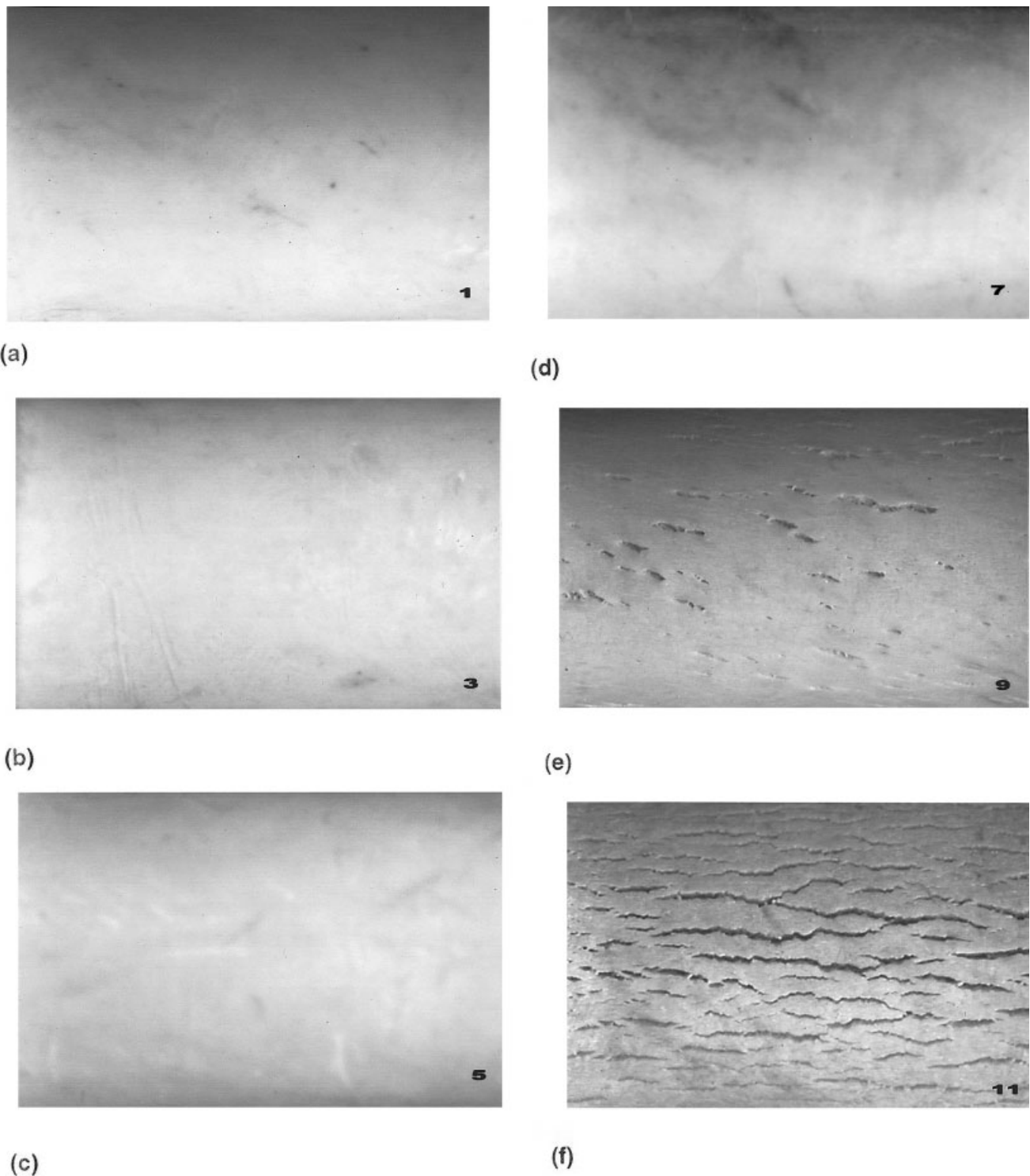


Figure 13 Optical photomicrographs of ozone exposed (120 h) EPDM/SBR blends in different blend ratios: (a) $E_{100}S$, (b) $E_{80}S$, (c) $E_{60}S$, (d) $E_{40}S$, (e) $E_{20}S$, and (f) E_0S .

ozone aging studies show that the weak SBR could be modified with EPDM against ozone aging. The studies also show that water resistance is excellent in EPDM/SBR blends. The mechanical properties of the filled EPDM/SBR blends in a selected ratio $E_{90}S$ were studied. Among the different fillers, the blends filled with

HAF black gave the highest tensile and tear strengths, elongation at break, etc. at the 30-phr level. A comparison of filler performance of EPDM/SBR blends at the 40-phr level shows that elongation at break is highest for clay; tensile and tear strengths are highest for GPF black; and hardness is highest for HAF black. HAF

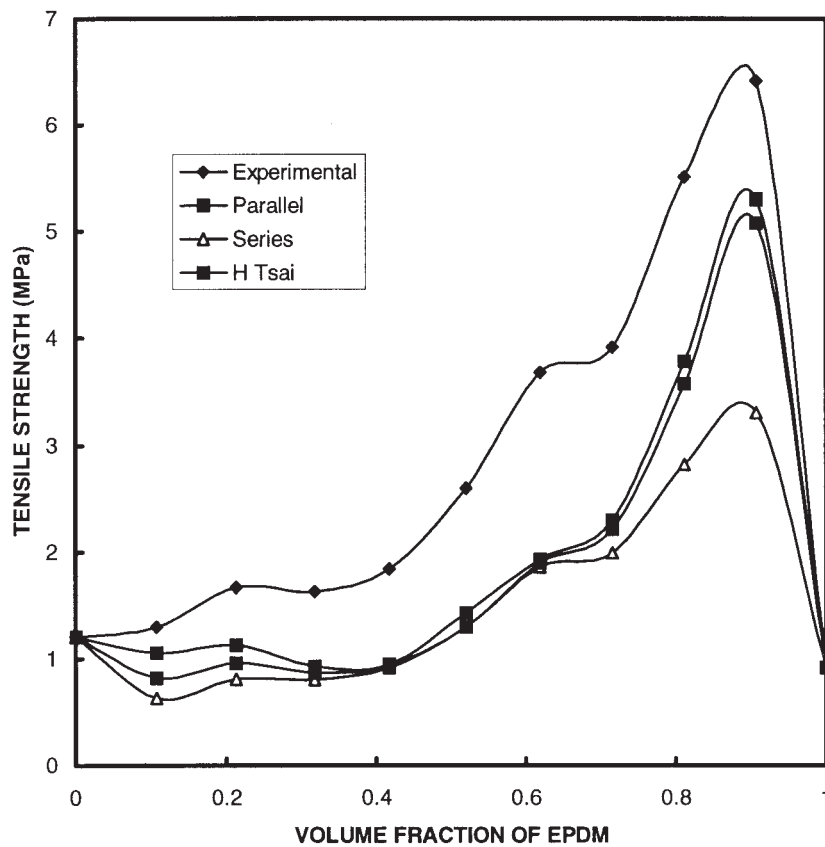


Figure 14 Applicability of various models on the tensile strength of S cured EPDM/SBR blends.

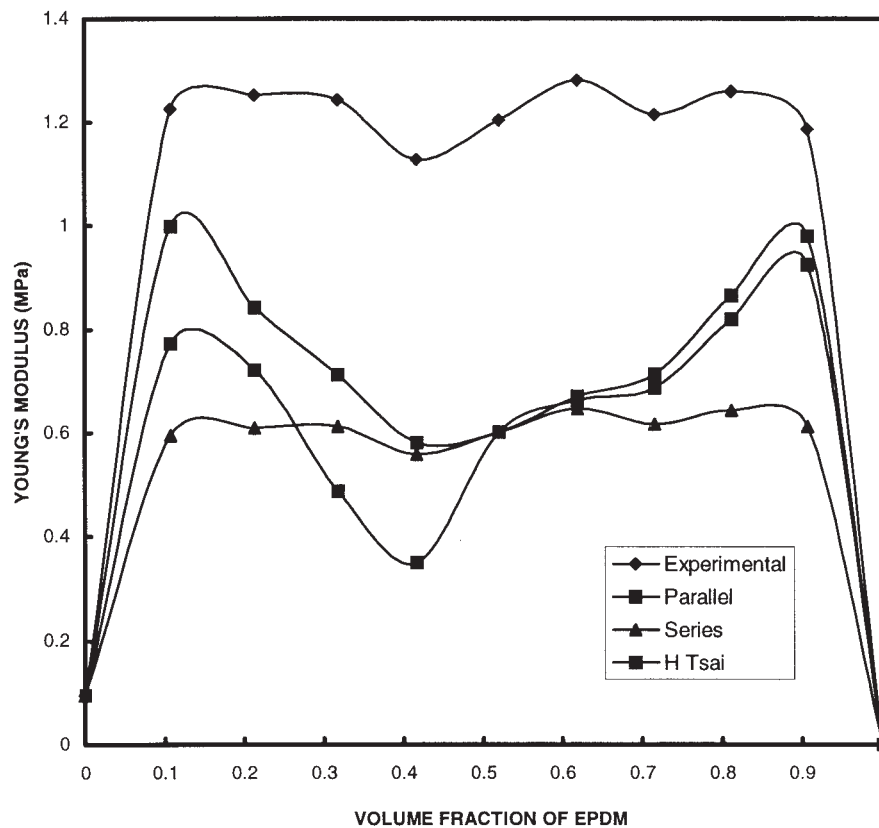


Figure 15 Applicability of various models on the Young's modulus of S cured EPDM/SBR blends.

black shows better tensile properties due to its excellent reinforcing power. The effect of filler in the EPDM/ SBR blend based on tensile properties at the 30-phr level is given in the order of HAF black > GPF black > clay > silica.

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References

- Chandra, R.; Mishra, S.; Parida, T. R. *Polym Int* 1995, 37, 141.
- Sakr, E. M.; Zayed, H. A.; El Mawla, S. A.; Kenawy, M.; Nagy, M. R. *Czechoslovak J Phys* 1995, 45, 275.
- Go, J. H.; Ha, C. S. *J Appl Polym Sci* 1996, 62, 509.
- Chough, S. H.; Chang, D. H. *J Appl Polym Sci* 1996, 61, 449.
- Amraee, I. A.; Katbab, A. A.; Aghafarajollah, S. *Rubber Chem Technol* 1996, 69, 130.
- Geerts, Y.; Gillard, S.; Genskens, G. *Eur Polym Mater* 1996, 32, 143.
- Zaharescu, T.; Mihalcea, I. *Polym Degrad Stab* 1995, 50, 39.
- Malhotra, V. P.; Saran, V. *J Appl Polym Sci* 1997, 56, 45.
- Mishra, S.; Naik, J. B. *Polym Plast Technol Eng* 1997, 36, 231.
- Ashalatha, P. V.; George, K. E.; Francis, D. J. *J Elast Plast* 1997, 29, 92.
- Sau, K. P.; Chaki, T. K.; Khastgir, D. *J Mater Sci* 1997, 32, 5717.
- Younan, A. F.; Abd-el-Messieh, S. L.; Gasser, A. A. *J Appl Polym Sci* 1998, 70, 2061.
- Ghoneim, A. M.; Ismail, M. N. *Polym Plast Technol Eng* 1999, 38, 979.
- Mishra, S.; Baweja, B.; Chandra, R. *J Appl Polym Sci* 1999, 74, 2756.
- Laokijcharoen, P.; Coran, A. Y. *Rubber Chem Technol* 1998, 71, 966.
- Bandyopadhyay, G. G.; Bhagawan, S. S.; Ninan, K. N.; Thomas, S. *J Appl Polym Sci* 1999, 72, 165.
- Ismail, H.; Suzamah, S. *Polym Test* 2000, 19, 879.
- Markovic, M. G.; Choudhary, N. R.; Dimopoulos, M.; Matison, J. G.; Dutta, N. K.; Bhattacharya, A. K. *Polym Eng Sci* 2000, 40, 1065.
- Ramesan, M. T.; Premalatha, C. K.; Alex, R. *Plast Rubber Comp* 2001, 30, 355.
- Oliveira, M. G.; Soares, B. G. *Polym Polym Comp* 2001, 9, 459.
- El Sabbagh, S. H. *Polym Test* 2003, 22, 93.
- Soares, B. G.; Sirgueira, A. S.; Oliveira, M. G.; Almeida, M. S. M. *Kaut Gummi Kunstst* 2002, 55, 454.
- Ismail, H.; Suzaimah, S.; Hainezam, H. M. *J Elast Plast* 2002, 34, 119.
- Ghosh, A. K.; Basu, D. K. *J Appl Polym Sci* 2002, 84, 1001.
- Soqres, B. G.; Sirgueira, A. S.; Oliveira, M. G.; Almeida, M. S. M. *Macromol Symp* 2002, 189, 45.
- Varghese, H.; Bhagavan, S. S.; Thomas, S. *J Appl Polym Sci* 1999, 71, 2335.
- Mathew, A. P.; Packirisamy, S.; Thomas, S. *J Appl Polym Sci* 2000, 78, 2327.
- George, S. C.; Ninan, K. N.; Groenineckx, G.; Thomas, S. *J Appl Polym Sci* 2000, 78, 1280.
- Blow, C. M., Hepburn, C., Eds. In *Rubber Technology and Manufacture*, 2nd ed.; Butterworths: London, 1981; pp 290, 299.
- Sulekha, P. B.; Joseph, R.; Madhusoodanan, K. N.; Thomas, K. T. *Polym Degrad Stab* 2002, 77, 403.
- Thomas, S.; George, A. *Eur Polym Mater* 1992, 28, 1451.
- Nielson, L. E. *Rheol Acta* 1974, 13, 86.