

# Thermoplastic elastomers from blends of polyethylene and ethylene-propylene-diene rubber: influence of vulcanization technique on phase morphology and vulcanizate properties

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Comparative studies on the dynamic and static vulcanization of blends of polyethylene (PE) and ethylene-propylene-diene monomer rubber (EPDM) are reported. The studies were made using a PE/EPDM blend ratio range of 40/60 to 20/80, over which the occurrence of phase inversion was indicated from torque rheometric studies. The state and rate of sulfur cure were varied by use of different appropriate doses of (a) tetramethylthiuram disulfide-mercaptobenzthiazyl disulfide-sulfur (TMTD-MBTS-S) combination as a conventional curative and (b) TMTD-Si69-S combination as a silane curative system. Of the two curative systems, the conventional system imparted measurably higher cure rates. For a particular blend ratio and for a given crosslink density level established in each case, the tensile strength and elongation at break measured at 298 K were higher for vulcanizates obtained statically compared to those obtained dynamically, while the corresponding modulus values followed the opposite trend. High-temperature tensile properties (at 403 K) and hot elongation and hot set values (at 523 K) for the vulcanizates were also evaluated. The property differences for vulcanizates from static and dynamic curing have been explained in the light of differences in the morphology developed.

(Keywords: PE/EPDM blends; vulcanization; thermoplastic elastomer)

## INTRODUCTION

Thermoplastic elastomers (TPE) based on blends of polyethylene (PE) or polypropylene (PP) with selected grades of polyolefin elastomers have drawn considerable attention in recent years<sup>1-3</sup>. The combination of rubber-like elasticity and thermoplastic processibility of a TPE made by melt mixing of a thermoplastic and an elastomer has been attributed<sup>4</sup> to the prominent existence of co-continuous plastic (hard) and elastic (soft) phases. Energy input during such mixing under shear and the thermal crosslinking of the elastomer component that follows in what is known as dynamic vulcanization, as well as the crosslinking level thus attained in the rubber phase and the interfacial characteristics of each phase are considered to be the major contributing factors in establishing and regulating the co-continuity of the soft and hard phases in a given blend system<sup>5</sup>.

The present paper relates to studies of the vulcanization of blends of polyethylene (PE) and ethylene-propylene-diene monomer rubber (EPDM), and emphasis is given to finding interrelationships between vulcanizate properties and morphologies developed as a function of variations in blend ratio, curative system, vulcanization technique and degree of vulcanization.

## EXPERIMENTAL

### Materials

The polymers used were polyethylene (PE) (grade NCPE 4445 from Neste Polyten AB, Sweden, having density  $915 \text{ kg m}^{-3}$  and melt flow index  $MFI=2.0$ ) and ethylene-propylene-dicyclopentadiene terpolymer (EPDM) (grade Keltan 520 from DSM, Holland, having density  $860 \text{ kg m}^{-3}$  and Mooney viscosity  $ML(1+4)$  of 46 at 398 K). Rubber-grade additives procured from the local market were used, and they were zinc oxide (ZnO), stearic acid, sulfur (S), tetramethylthiuram disulfide (TMTD) and mercaptobenzthiazyl disulfide (MBTS). Si69, i.e. bis(3-triethoxysilylpropyl) tetrasulfide, was obtained from Degussa, Germany.

### Blend preparation and vulcanization

Simple blends of PE and EPDM in different proportions were prepared in a Brabender Plasticorder (model PLE-330) using a cam-type mixing head (N50H) at a temperature of 423 K and a rotor speed of  $50 \text{ rev min}^{-1}$ . Changes in torque with time were recorded. Dynamic vulcanization of the PE/EPDM blends to optimum cure or slightly beyond as indicated by torque developed was carried out using selected curatives and other additives in the Brabender mixer under comparable

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mixing conditions at 423 K for time periods in the range 20–25 min. For static vulcanization, curing agents were mixed with the PE/EPDM blend in the Brabender mixer at a temperature slightly above the melting point of PE (388 K) for 10 min. In each case, the mix was subsequently refined to a sheet of 0.002 m thickness by running through the tight nip of a two-roll mill (0.15 m × 0.3 m) set at a temperature of (a) 388 K for compounds to be vulcanized statically and (b) 428 K for the dynamically vulcanized (TPE) products. The sheets cut into size (0.2 m × 0.2 m) were compression moulded in a steam-heated press at a temperature of 443 K following a sequence of preheating at contact pressure for 10 min followed by pressing at  $9.807 \times 10^5 \text{ N m}^{-2}$  (100 kgf cm<sup>-2</sup>) for 5 min for the dynamically cured (TPE) compound. For static curing, the sequence followed was preheating for 2 min and press curing at 443 K for 25 min under a pressure of  $9.807 \times 10^5 \text{ N m}^{-2}$  (100 kgf cm<sup>-2</sup>).

### Mechanical properties

Tensile properties were studied in a Zwick universal testing machine (model 1445) using dumbbell specimens according to ASTM D415-80. These tests were carried out normally at  $298 \pm 2 \text{ K}$  and selectively at  $403 \pm 2 \text{ K}$  at crosshead speeds of  $0.5 \text{ m min}^{-1}$  and  $0.1 \text{ m min}^{-1}$  respectively. Hot elongation and hot set properties of vulcanizates were determined at 523 K according to BS6899 (1984).

### Scanning electron microscopy

SEM was carried out in a Hitachi SEM model S145A. Samples were prepared by extraction of PE phase from cut surfaces with hot xylene (at 393 K).

## RESULTS AND DISCUSSION

### Mixing torque behaviour: prediction of the critical blend ratio range showing dual phase continuity

Compositions showing the PE/EPDM blend ratio and the nature and dose of curatives used are described in Table 1. The torque vs. time curves for PE, EPDM and PE/EPDM blends without incorporation of any additive and as obtained from the Brabender Plasticorder at 423 K are shown in Figure 1. It may be seen that the stable torque (i.e. torque value at the plateau region), which is minimum for PE, follows an increasing trend as EPDM content in the blend is increased. Stable torque values of the blends have also been calculated<sup>6</sup> theoretically following the linear additivity rule using the equation:

$$\tau_{\text{blend}} = \phi_{\text{PE}}\tau_{\text{PE}} + \phi_{\text{EPDM}}\tau_{\text{EPDM}} \quad (1)$$

where  $\tau$  and  $\phi$  represent stable torque at a given rotor speed (rev min<sup>-1</sup>) and volume fraction respectively. The theoretically calculated and experimentally obtained stable torque values have been plotted against EPDM volume fraction in Figure 2. The experimental plot deviates negatively from the plot based on the calculated torque values. Maximum deviation between the two plots corresponds to 30/70 (PE/EPDM) blend ratio (Figure 2). In general, dual phase continuity is reported<sup>6</sup> to occur approximately in the composition range at which the experimental plot of stable torque deviates to a maximum from the plot based on the linear additivity rule. Such antagonistic torque behaviour for blends is also known for the polypropylene/ethylene-propylene rubber (PP/EPR) system<sup>6,7</sup>.

The mid-point PE/EPDM blend composition for dual phase continuity is 28/72 (PE/EPDM) as calculated from Sperling's model<sup>7</sup> expressed by the equation:

$$\phi_{\text{PE}}/\phi_{\text{EPDM}} = \tau_{\text{PE}}/\tau_{\text{EPDM}} \quad (2)$$

The calculated values of the parameter ( $\tau_{\text{PE}}/\tau_{\text{EPDM}}$ ) ( $\phi_{\text{EPDM}}/\phi_{\text{PE}}$ ) for the 40/60 PE/EPDM blend at one end and for the 20/80 PE/EPDM blend at the other end deviate differently from unity, and the values are 0.6 and 1.57 respectively. It is indicated<sup>7</sup> from the nature of the deviations from unity of the calculated values that PE forms the continuous phase in the 40/60 PE/EPDM

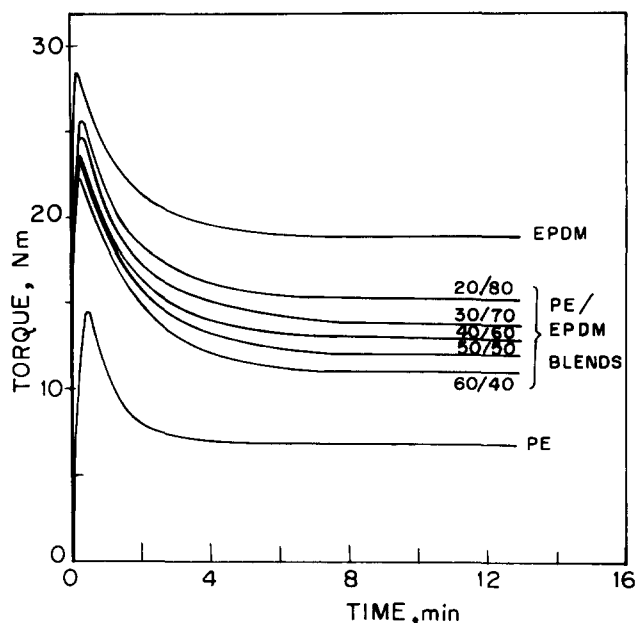
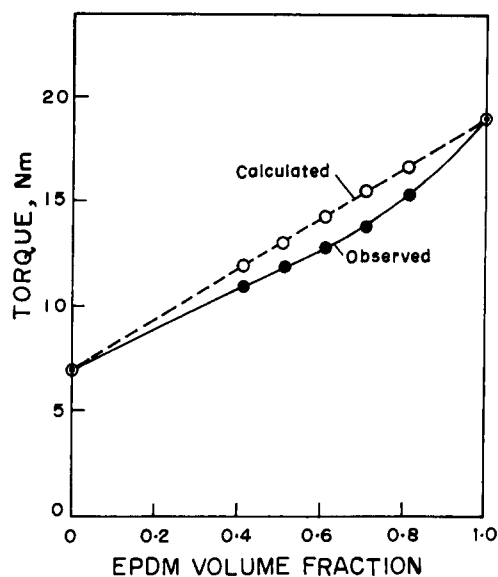


Figure 1 Brabender plots (torque vs. time) at 423 K for PE, EPDM and different PE/EPDM blends

Table 1 Compound recipe showing PE/EPDM blend ratio and doses of additives used (%)

Additives	Compound no. PE/EPDM ratio	(A) Conventional curative system					(B) Silane curative system				
		I 40/60	II 30/70	IIa 30/70	IIb 30/70	III 20/80	IV 40/60	V 30/70	Va 30/70	Vb 30/70	VI 20/80
ZnO		3.0	3.5	3.5	3.5	4.0	3.0	3.5	3.5	3.5	4.0
Stearic acid		0.6	0.7	0.7	0.7	0.8	0.6	0.7	0.7	0.7	0.8
Si69		–	–	–	–	–	2.4	2.8	2.0	1.2	3.2
TMTD		0.6	0.7	0.6	0.5	0.8	1.8	2.1	1.5	0.9	2.4
S		1.2	1.4	1.2	1.0	1.6	0.6	0.7	0.5	0.3	0.8
MBTS		0.3	0.35	0.3	0.25	0.4	–	–	–	–	–



**Figure 2** Plots of stable torque vs. EPDM volume fraction for different PE/EPDM blends

blend whereas EPDM constitutes the continuous phase in the 20/80 PE/EPDM blend. Consequently, phase inversion occurs within this range of composition, thus resulting in dual phase continuity approximately at 30/70 PE/EPDM blend ratio.

*Effect of blend ratio and curative system on the crosslinking of PE/EPDM blends*

Two sets of curative systems have been used for this study as shown in *Table 1*. In one set, a combination of MBTS, TMTD and S was used as the conventional curative system in the same proportion as used by Coran<sup>1</sup>. In the other set, the curative used was a combination of a sulfur donor silane (Si69), TMTD and S. The doses of the curative components were adjusted (*Table 1*) to give equivalent gel fractions for comparable blends using both the curative systems (*Tables 2 and 3*).

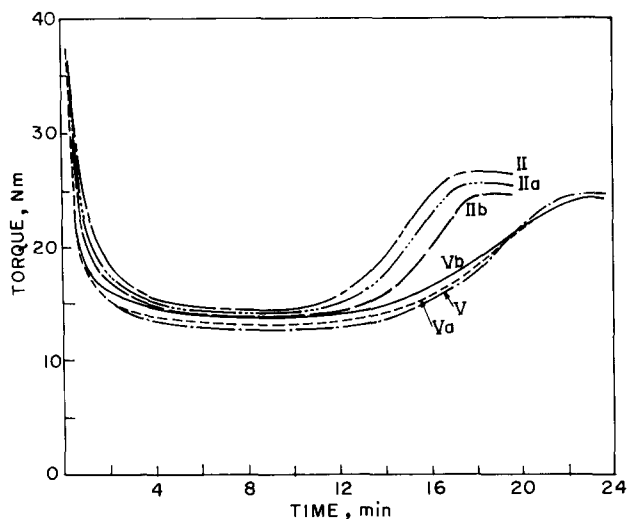
For 30/70 PE/EPDM blend ratio, the degree of crosslinking of the elastomer component was varied to three different extents by varying the amounts of the curative components but keeping their relative doses much the same. Torque-time traces obtained during

**Table 2** Properties of PE/EPDM blend vulcanizates vulcanized statically at three test temperatures

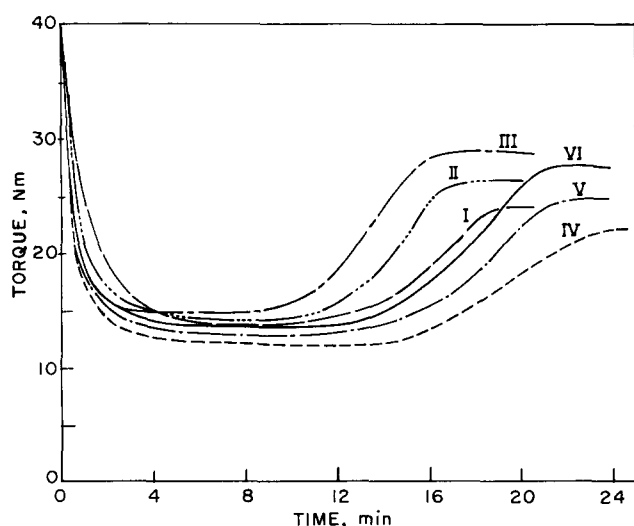
Compound No.	298 K					403 K				523 K	
	Gel content (%)	Modulus, 100% (MPa)	TS (MPa)	EB (%)	Elastic modulus, E (MPa)	TS, $\sigma_{HT}$ (MPa)	EB (%)	Elastic modulus, $E_{HT}$ (MPa)	Crosslink density, $v_c$ (mol m <sup>-3</sup> )	Hot elongation (%)	Hot set (%)
<b>(A) Conventional curative system (TMTD-MBTS-S)</b>											
I	58	2.8	22	700	0.12	0.60	90	0.010	1.01	320	190
II	68	2.6	19	640	0.08	0.75	140	0.015	1.51	195	100
IIa	63	2.5	14.5	670	0.07	0.64	120	0.012	1.20	260	140
IIb	57	2.1	10.0	700	0.06	0.50	110	0.009	0.90	350	200
III	78	1.7	8.5	530	0.03	1.05	120	0.019	1.91	85	38
<b>(B) Silane curative system (TMTD-Si69-S)</b>											
IV	58	3.3	21.0	600	0.14	0.60	95	0.011	1.09	270	160
V	68	2.7	19.0	670	0.07	0.80	100	0.015	1.52	155	80
Va	63	2.5	16.0	680	0.06	0.62	120	0.012	1.20	230	115
Vb	56	2.1	11.0	735	0.05	0.42	120	0.009	0.90	330	180
VI	78	2.2	10.0	500	0.03	1.0	105	0.019	1.94	50	22.5

**Table 3** Properties of PE/EPDM blend vulcanizates vulcanized dynamically at three test temperatures

Compound No.	298 K					403 K				523 K	
	Gel content (%)	Modulus 100% (MPa)	TS (MPa)	EB (%)	Elastic modulus, E (MPa)	TS, $\sigma_{HT}$ (MPa)	EB (%)	Elastic modulus, $E_{HT}$ (MPa)	Crosslink density, $v_c$ (mol m <sup>-3</sup> )	Hot elongation (%)	Hot set (%)
<b>(A) Conventional curative system (TMTD-MBTS-S)</b>											
I	59	4.4	13.0	360	0.18	0.7	105	0.010	1.00	90	33
II	69	3.9	12.0	330	0.09	1.1	120	0.018	1.82	30	6
IIa	63	3.4	11.0	350	0.08	0.9	110	0.016	1.60	55	20
IIb	57	3.2	10.0	375	0.07	0.75	120	0.011	1.10	165	65
III	79	2.7	6.2	280	0.06	1.2	110	0.020	1.97	5	0
<b>(B) Silane curative system (TMTD-Si69-S)</b>											
IV	59	4.3	12.5	350	0.16	0.6	100	0.009	0.90	100	35
V	69	3.7	11.0	350	0.09	1.15	130	0.019	1.87	30	5
Va	64	3.3	10.0	370	0.08	0.95	120	0.017	1.70	50	15
Vb	57	3.0	9.2	400	0.07	0.65	125	0.010	1.00	175	60
VI	79	2.2	6.0	300	0.05	1.25	115	0.020	2.00	10	0



**Figure 3** Curing characteristics of PE/EPDM 30/70 blends during dynamic vulcanization using conventional and silane curative systems; curve numbers indicate identity of compounds as in Table 1



**Figure 4** Curing characteristics of different PE/EPDM blends using conventional and silane curative systems during dynamic vulcanization; curve numbers indicate identity of compounds as in Table 1

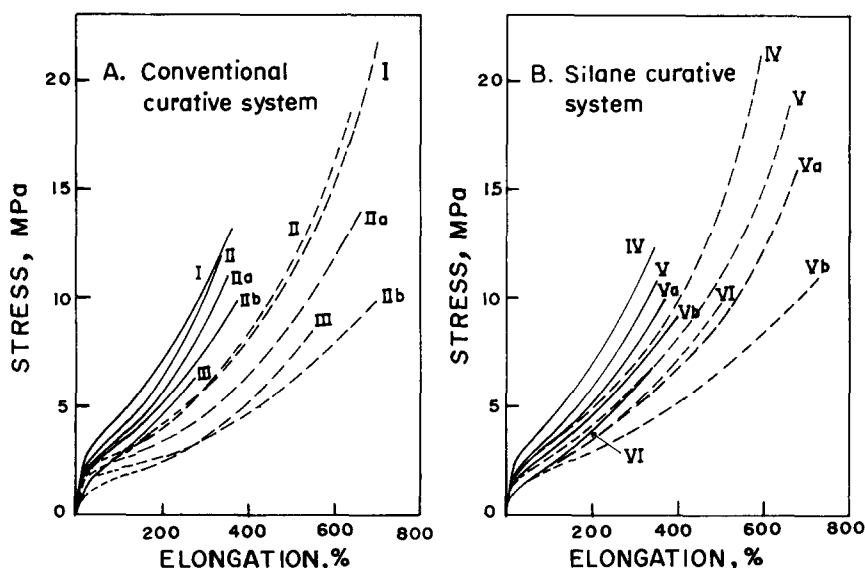
dynamic vulcanization in the Brabender mixer are shown in Figure 3, from which it is apparent that considerably higher cure rates are produced by the conventional curative system (TMTD-MBTS-S) than by the silane curative system (TMTD-Si69-S). In each case, torque rise trends reveal that both degree and rate of cure follow increasing trends with increase in the dose levels of the curative components.

Figure 4 shows the trends of variation of curing behaviour for variation of blend ratio using the two curative systems, keeping a fixed dose level of the respective curatives with respect to EPDM in the blends. Both sulfur cure rate and degree of sulfur cure were found to increase with increasing proportion of the sulfur-curable polymer, i.e. EPDM in the blend. The PE component in the blend remains chemically unaffected during sulfur cure of EPDM component.

#### Variation of properties of blend vulcanizates with blend ratio, vulcanizing technique and degree of vulcanization

The gel content of the blend vulcanizates, their tensile properties measured at ambient (298 K) and at high temperature (403 K) as well as the hot elongation and hot set values measured at 523 K are given in Tables 2 and 3. Stress vs. elongation curves for vulcanizates obtained both dynamically and statically from each of the conventional and silane curative systems at 298 K are illustrated in Figure 5. The plots show that vulcanizates obtained dynamically follow a deformation pattern under stress notably different from those produced by vulcanizates obtained statically.

Figure 5 also shows that the degree of deformation varies significantly with variation in blend ratio and curative dose, i.e. degree of vulcanization. It is apparent from the plots and from data shown in Tables 2 and 3 that, for either curative system and for compounds corresponding to comparable gel content and blend ratio, tensile strength ( $TS$ ) at room temperature ( $\sigma_{RT}$ ) and associated elongation at break ( $EB$ ) values are always higher for statically vulcanized systems compared to those of dynamically vulcanized systems. But the corresponding modulus values follow the opposite trend



**Figure 5** Stress vs. elongation curves for dynamically (—) and statically (---) vulcanized PE/EPDM (40/60, 30/70 and 20/80) blends using (A) conventional curative system and (B) silane curative system. Curve numbers indicate identity of compounds as in Table 1

(Figure 5, Tables 2 and 3). These differences in properties may presumably be attributed to the differences in morphology produced by the two different vulcanization techniques. Similar trends of results were observed by Quin *et al.*<sup>8</sup> for natural rubber/polyethylene (NR/PE) blend system. The above results indicate that PE forms the major if not the sole continuous phase in the PE/EPDM blend vulcanizates obtained statically, while co-continuity of PE and EPDM phases to different degrees results from vulcanization done dynamically. The phase morphology developed is treated separately in the next section.

Whatever the morphology may be, in each case, the relatively hard plastic (PE) phase commonly constituting the continuous phase deforms first on load application. Rapid and large-scale development of stress-induced crystallization on tensile loading in the PE phase appearing as the sole continuous phase in the statically vulcanized blends is likely to result in a relatively high *TS* and *EB*. But dynamic vulcanization of the selected blends resulting in PE/EPDM dual phase continuity is not likely to favour such large-scale inducement of crystallization consequent to stress application in the hard PE phase in view of the presence of the more readily deformable soft EPDM also as a continuous phase. However, for each curative system, *TS* and modulus of the blend vulcanizates decrease on decreasing the content of PE constituting the hard phase. Increasing the content of the hard PE phase in the blend tends to cause tensile rupture at a relatively high elongation. With increasing gel content, i.e. crosslink density, in a blend, *TS* and modulus expectedly increase while *EB* decreases (Tables 2 and 3).

#### High-temperature properties of blend vulcanizates

In order to elucidate the contribution of morphology and network characteristics on tensile strength and elastic modulus, and to find their dependence on vulcanization techniques, it is necessary to examine the said properties at a temperature high enough to permit melting of the hard phase (PE), thus practically nullifying the prominent effect of stress-induced crystallization of the PE phase on tensile loading. So, tensile properties at a temperature (403 K) above the melting point of PE and hot elongation and hot set properties at 523 K (BS6899, 1984) of the different PE/EPDM blend vulcanizates were studied. The results are also given in Tables 2 and 3.

*TS* measured at a high temperature ( $\sigma_{HT}$ ), i.e. at 403 K, has been plotted in Figure 6 against the corresponding high-temperature elastic modulus ( $E_{HT}$ ) (given by the slope of the stress-strain plot in the Hookian elastic zone, not shown). For both dynamic and static vulcanization, using both the conventional and silane curative systems,  $\sigma_{HT}$  was found to increase linearly with  $E_{HT}$ , so that one may write:

$$\sigma_{HT} \propto E_{HT} \quad (3)$$

Again, elastic modulus ( $E_{HT}$ ) is known to be proportional<sup>9</sup> to molar crosslink density ( $v_c$ );  $v_c$  ( $\text{mol m}^{-3}$ ) may be expressed by the following relationship:

$$v_c = \frac{E_{HT}}{3kTN} \times 10^6 \quad (4)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature (K) and  $N$  is the Avogadro number.

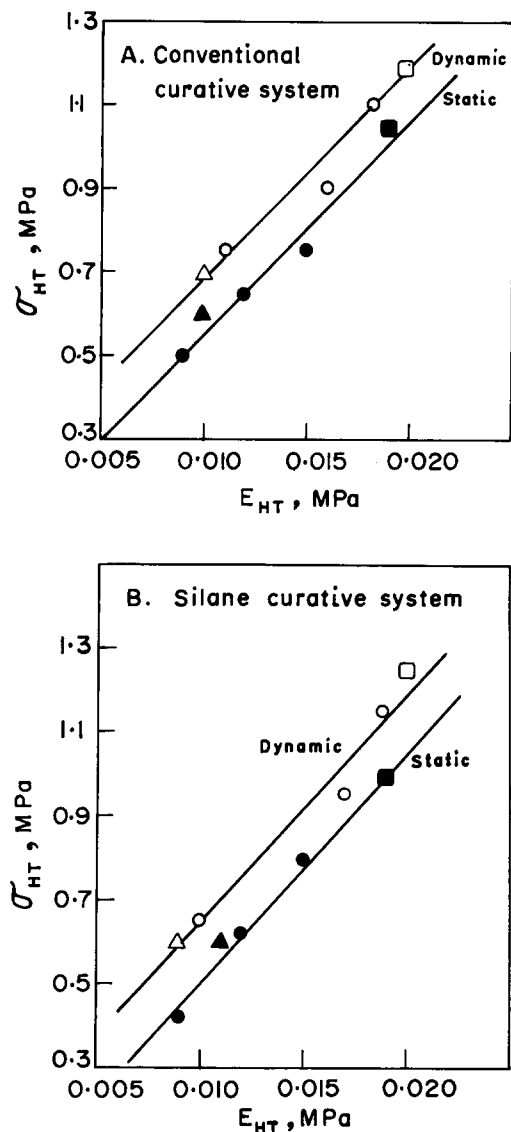


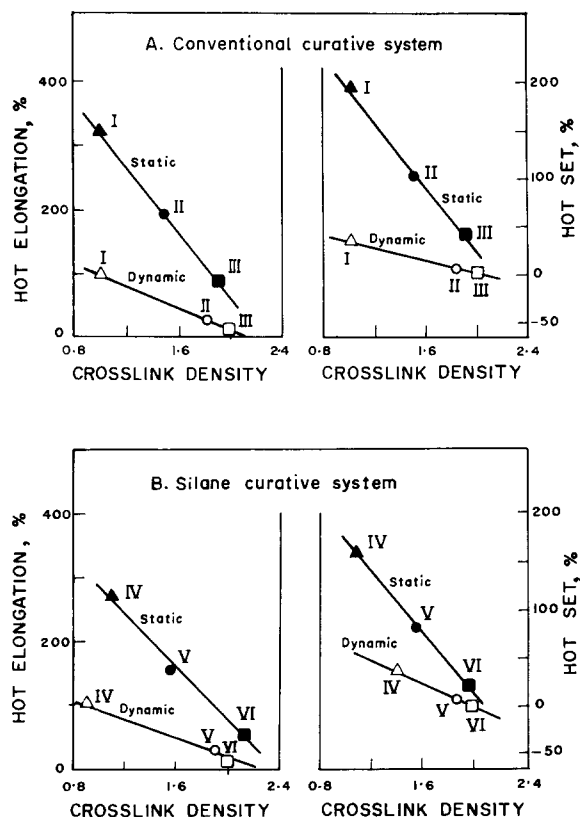
Figure 6 Plots of high-temperature (403 K) strength  $\sigma_{HT}$  vs. high-temperature (403 K) elastic modulus  $E_{HT}$  for PE/EPDM blend vulcanizates. Data given are symbols of plot and blend ratio: ( $\square$ ,  $\blacksquare$ ) 20/80; ( $\circ$ ,  $\bullet$ ) 30/70; and ( $\triangle$ ,  $\blacktriangle$ ) 40/60; open symbols indicate dynamic vulcanization and filled symbols indicate static vulcanization

Considering equations (3) and (4) one may write:

$$\sigma_{HT} \propto v_c \quad (5)$$

It is observed from Figure 6 that, for a given value of  $E_{HT}$ ,  $\sigma_{HT}$  is always higher for a dynamically vulcanized system than for a statically vulcanized system. At any particular value of  $E_{HT}$  and hence for a particular  $v_c$ , the observed difference between the high-temperature strengths,  $\sigma_{HT}(\text{dynamic}) - \sigma_{HT}(\text{static})$ , for the vulcanizates from dynamic and static vulcanizations is likely to have its origin in the difference in their morphologies. Moreover, a set of two approximately parallel lines for each of the two curative systems as given in Figure 6 also indicates that the property difference originating from the morphology difference is by and large intrinsic in nature.

The morphological patterns and hence the physical properties pattern of the PE/EPDM blend vulcanizates from both dynamic and static cures do not apparently vary much with variation in the curative system. However, these patterns depend intrinsically on the



**Figure 7** Plots of hot elongation and hot set vs. molar crosslink density  $v_c$  ( $\text{mol m}^{-3}$ ) for PE/EPDM blends vulcanized using (A) conventional and (B) silane curative systems. Data given are symbols of plot and PE/EPDM blend ratio: ( $\square$ ,  $\blacksquare$ ) 20/80; ( $\circ$ ,  $\bullet$ ) 30/70; and ( $\triangle$ ,  $\blacktriangle$ ) 40/60. Open symbols indicate dynamic vulcanization and filled symbols indicate static vulcanization in each case

vulcanization technique (static or dynamic) employed and on the blend ratio selected. The curative dose used or crosslink density established are also important controlling factors in this respect.

In Figures 7 and 8 the hot elongation and hot set values of the two sets of vulcanizates given by each curative system have been plotted against  $v_c$  values ( $\text{mol m}^{-3}$ ) calculated from the experimental  $E_{HT}$  values using equation (4). It is revealed that hot elongation and hot set values decrease linearly with increase in crosslink density ( $v_c$ ). Figure 7 shows the effect of blend ratio variation and Figure 8 shows the effect of variation of curative dose for a given blend ratio (30/70 PE/EPDM). However, the severity of the falling trends is much higher for static vulcanization than for dynamic vulcanization, as can be well appreciated by comparing the slopes of the respective plots in Figures 7 and 8. But what is more important is that, for a particular value of  $v_c$  and blend ratio, hot elongation and hot set values are all the way much lower for blends vulcanized dynamically. Only some of the blends (compounds Nos. II, III, V, Va, VI) vulcanized dynamically meet the full requirements of the relevant high-temperature property specification (BS6899, 1984) set for elastomeric cable insulation (i.e. hot elongation  $\leq 175\%$ , hot set  $\leq 15\%$ ), and vulcanizates obtained statically fail to pass the specification (Tables 2 and 3). It is indicated that, for a comparable crosslink density, the morphology of the vulcanizates obtained dynamically is favourably poised compared to the morphology of those obtained statically to enable the former to bear higher stress level at a high temperature.

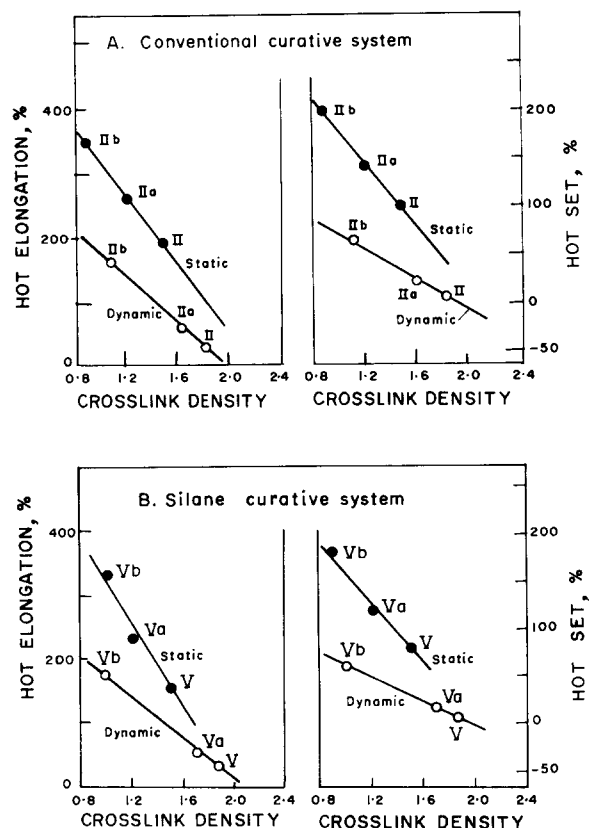
The net result is that the vulcanizates obtained dynamically show substantially lower creep (low hot elongation) and relatively high elasticity response (i.e. low hot set) at the specified high temperature.

### Morphology

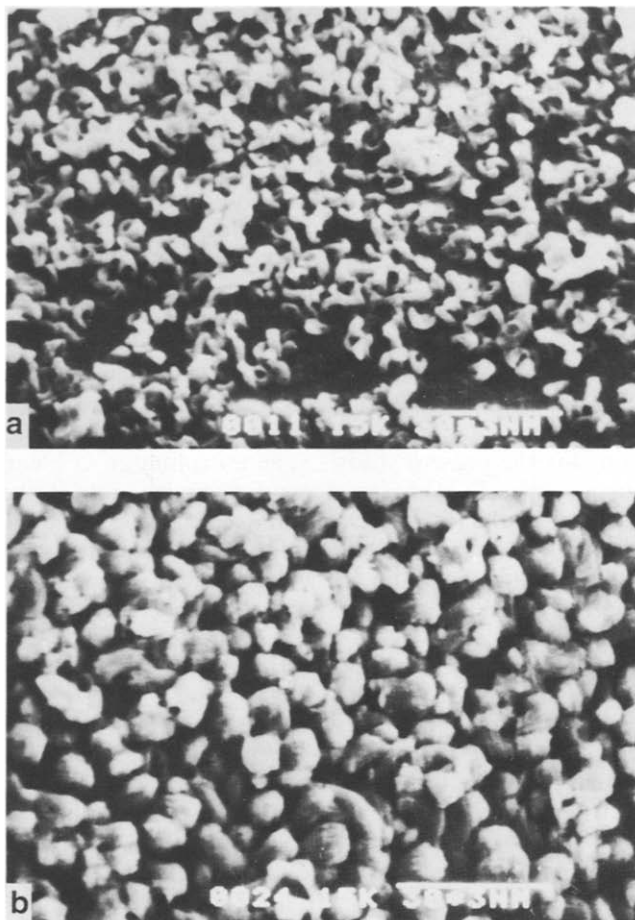
The continuous phase morphology of melts of unvulcanized PE/EPDM blends is likely to suffer major changes on cooling to ambient temperature in view of the associated crystallization of large fragments of the hard PE phase, much like the changes observed by Ho *et al.*<sup>6</sup> and Kresgi<sup>4</sup> for the PE/EPR blend system.

Differences in morphological characteristics of PE/EPDM blend vulcanizates consequent to adoption of different vulcanization techniques are prime considerations for the present studies. The morphology of blend vulcanizates is likely to depend primarily on (i) the blend ratio and (ii) the vulcanization technique (dynamic or static) adopted. It is therefore interesting to examine the morphology of the PE/EPDM blend vulcanizates prepared by employing static and dynamic vulcanization techniques and to try to understand and interpret the differences in their properties in the light of morphological differences.

As the EPDM phase is vulcanized dynamically under high shear, the viscosity of the rubber phase initially increases markedly, resulting in an effect that starts playing a role in disturbing the continuity of the phases. When the crosslink density of the EPDM phase increases sufficiently, the relatively immobilized rubber particles



**Figure 8** Plots of hot elongation and hot set vs. molar crosslink density  $v_c$  ( $\text{mol m}^{-3}$ ) for 30/70 PE/EPDM blends vulcanized using (A) conventional and (B) silane curative systems. Compound numbers given near each plot are the same as in Table 1. Curative levels are in the order (A) II > IIa > IIb and (B) V > Va > Vb; open symbols refer to dynamic vulcanization and filled symbols to static vulcanization

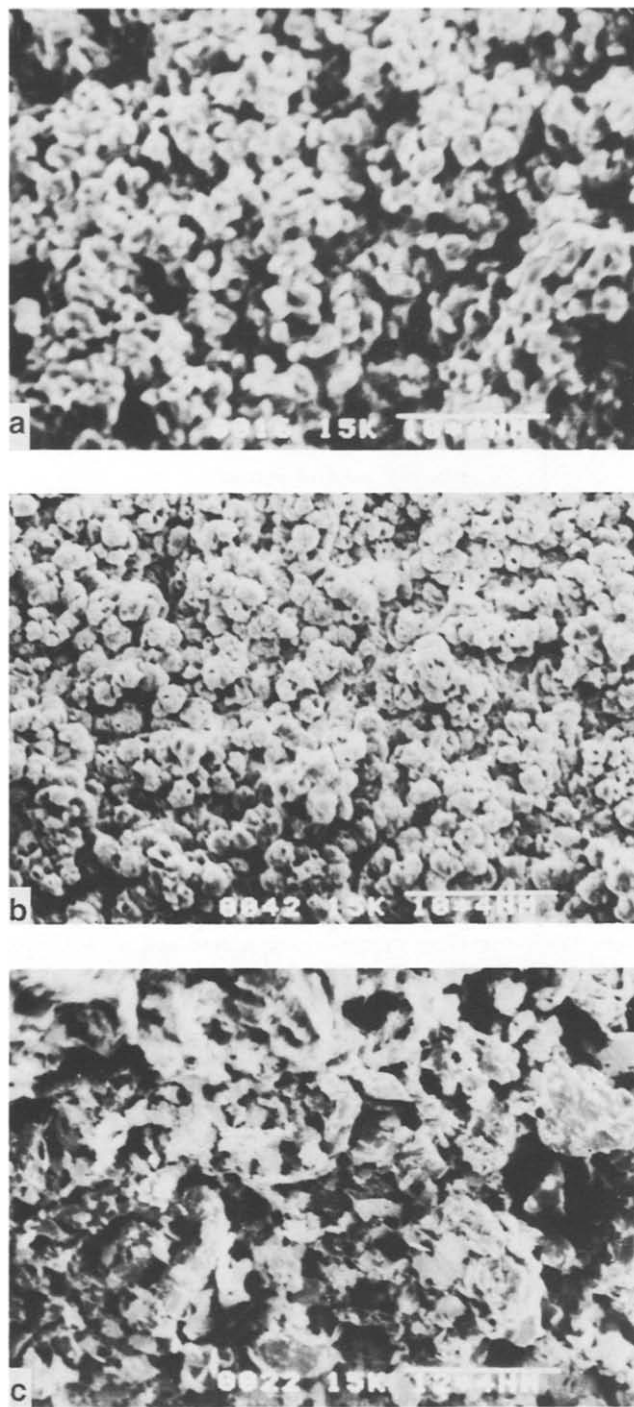


**Figure 9** SEM micrographs of (a) 50/50 and (b) 40/60 PE/EPDM blend vulcanizates cured dynamically at 423 K using silane curative system

break up to lower sizes under the prevalent shear level and become dispersed in the continuous PE phase. Thus, the degree of vulcanization attained, the PE/EPDM blend ratio selected and the shear level applied in the dynamic process together will ultimately decide the size and shape of the broken, dispersed vulcanized EPDM particles, their state of dispersion or distribution in the continuous PE matrix and hence the overall morphology.

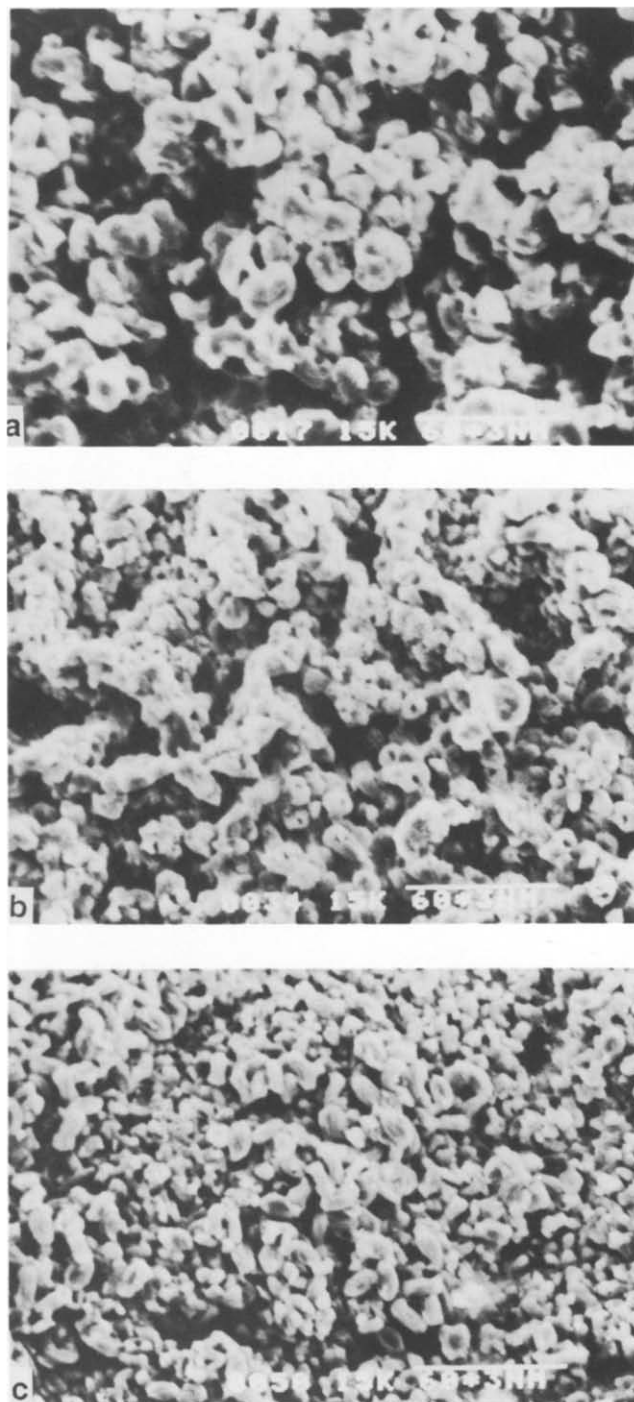
The phase morphologies of the 50/50 and 40/60 PE/EPDM blends vulcanized dynamically using the selected silane curative system are shown in *Figures 9a* and *9b*, respectively. It is apparent from the two micrographs that vulcanized EPDM particles (white specks) are uniformly distributed in the PE matrix (dark background). Under otherwise comparable conditions, vulcanized EPDM particles are relatively large in size for the blend having higher weight proportion of EPDM, and the EPDM phase remains dispersed as discrete domains in the continuous PE phase. This is probably due to the fact that the amount of EPDM in these blends falls short of what is required for deriving a co-continuous phase morphology.

The morphologies of 30/70 PE/EPDM blends made by dynamic and static vulcanization are shown in *Figure 10*. Micrographs (a) and (b) correspond to 30/70 PE/EPDM blends vulcanized dynamically using conventional and silane curative systems, respectively, whereas micrograph (c) is for the said blend vulcanized



**Figure 10** SEM micrographs of 30/70 PE/EPDM blend vulcanizates. Data given for each micrograph are vulcanization technique and curative system used: (a) dynamic, TMTD-MBTS-S; (b) dynamic, TMTD-Si69-S; (c) static, TMTD-Si69-S

statically using the silane curative system. The difference in morphology between dynamically and statically vulcanized blends is apparent from the micrographs in *Figures 10b* and *10c*. In both the dynamically vulcanized blends, micrographs (a) and (b), tiny hollow globular or doughnut-like particles of vulcanized EPDM appear, largely interlinked with one another and fairly uniformly dispersed in the PE matrix, thus effectively forming a co-continuous phase morphology. Fine fibrils or strings of PE passing through the EPDM particles help in holding and clustering them together in three dimensions and in development of a co-continuous phase morphology.



**Figure 11** SEM micrographs of 30/70 PE/EPDM blends vulcanized dynamically using conventional curative system. Data given for each micrograph are compound number as in Table 1: (a) IIb, (b) IIa and (c) II; curative doses are in the order II > IIa > IIb

In the case of statically vulcanized blend (Figure 10c), layered and flaky clusters of coarse vulcanized EPDM particles of irregular sizes and shapes remain relatively non-uniformly distributed in the PE matrix. The morphology of the blends becomes favourably modified

to a greater uniformity during dynamic vulcanization under high-shear action. There is, however, little or limited scope for such modification during static vulcanization simply under a fixed low compression in a closed mould. The morphology difference for vulcanizates obtained dynamically and statically explains well the differences in their mechanical properties at ambient and high temperatures as given in Tables 2 and 3 and as discussed in the preceding section.

#### *Effect of degree of vulcanization on morphology*

The change in morphology with degree of vulcanization of the dynamically vulcanized 30/70 PE/EPDM blends is shown in Figure 11. When the degree of vulcanization is relatively low (giving low gel content), the domain size of the vulcanized EPDM particles is relatively high (Figure 11a). As the sites of crosslinking spread, leading to higher degree of vulcanization with higher level of curatives, the number of vulcanized EPDM particles increases, thus decreasing their particle size and rendering their distribution progressively finer and more uniform (Figures 11b and 11c).

## CONCLUSIONS

Significant or subtle morphological differences seen to develop under different sets of conditions for dynamic and static vulcanization of PE/EPDM blends appear to be primarily consequential in regulating the mechanical and physical properties of the blend vulcanizates.

For comparable blend compositions and curative dose levels permitting high crosslink densities, dynamic cure imparts thermoplastic processibility and favours the development of a uniform, co-continuous phase morphology. Establishment of dual phase continuity contributes to improved balance in room-temperature and high-temperature strength, modulus, elongation and set properties very much needed to meet demands of elastomeric cable insulation. Dual phase continuity favourably permits ready and direct stress transfer on load application through each continuous phase component.

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