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Distribution of Crosslinks Between the Phases of Vulcanised ENR 25/cis-BR Blends

P.S. BROWN* AND A.J. TINKER*

The recently developed NMR method of rubber blend analysis[1,4] *has been applied to gum vulcanisate blends of epoxidised natural rubber (ENR) and* cis-*1,4 polybutadiene (BR). It was observed that the degree of crosslinking in each of the two rubbers of the blend was different from that found in the analogous single polymer vulcanisates, the ENR having increased crosslink levels while the BR had reduced crosslink levels. This difference has been quantified in terms of the curative levels required to give vulcanisates of the individual rubbers the same crosslink density as found in that component in the blends.*

In the search for optimum product properties, most rubber goods are manufactured using blends of two or more dissimilar polymers. The physical properties of these blends are determined both by the properties of the individual component rubbers and by the physical structure of the blend. To understand the properties of the blend, the physical structure must be characterised. Recent papers[1,2] report the first method for directly determining the distribution of crosslinks between the phases of a blend, adding to the other well established techniques of blend characterisation.

This new technique compares the line widths observed in a continuous wave ^1H NMR spectrum of the blend with those of the analogous single polymer vulcanisates. Line width is measured as the proportion of signal strength at a reference position on the side of the peak to that at the peak and denoted H%. H% is observed to increase smoothly with curative level[1], the volume fraction of rubber in the swollen state (*Vr*) in chloroform[1] or the crosslink density[2,3] of a single polymer vulcanisate.

In this study, blends of an epoxidised natural rubber with a high *cis*-polybutadiene are examined using the NMR technique.

EXPERIMENTAL

The rubbers used in this study were *cis*-1,4 polybutadiene, BR, (Europrene *cis*, 94% *cis*-1,4 polybutadiene, Enichem) and an epoxidised natural rubber, ENR 25 (25 mol% epoxidised natural rubber, Rubber Research Institute of Malaysia). Rubber chemicals were standard commercial-grade materials, solvents of AR grade except for the NMR solvents which were of spectroscopic grade [deuterochloroform and hexamethyldisiloxane (HMDS) Aldrich Chemical Company].

Compounding *(Table 1)* was performed using a BR-size Banbury internal mixer and/or a two-roll mill, the curatives being added on a two-roll mill. The single polymer vulcanisates were produced from masterbatches mixed in the Banbury. For each polymer, two batches were crossblended on the mill before finalising the blends. The blends were produced either in the Banbury mixer with the curatives added on the two-roll mill or by the crossblending of single polymer masterbatches on the two-roll mill ensuring that the polymers were well blended before the curatives were added. The same cycle was used for all batches mixed in the internal mixer *(Table 2)*.

*Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom

TABLE 1. MIX FORMULATIONS

Compound	Formulation				
	ENR 1-ENR 10	BR 1-BR 8	Blend 1	Blend 2	Blend 3
ENR 25	100		50	80	85.7
Europrene-*cis*		100	50	20	14.3
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
TMQ[a]	2	2	2	2	2
MBS[bc]	0.3-2.3	0.4-2.3	0.5-2.5	0.5-1.9	0.5-1.9
Sulphur[c]	0.3-2.3	0.4-2.3	0.5-2.5	0.5-1.9	0.5-1.9

[a]poly-2,2,4-trimethyl-1,2-dihydroquinoline (e.g. Flectol-H Monsanto)
[b]2-morpholinothiobenzothiazole-2-sulphenamide
[c]Sulphur: MBS ratio = 1:1

TABLE 2. BANBURY MIX CYCLE[a]

Time (s)	Operation
0	Add polymer/polymers
30	Add powders
12	Sweep
210	Dump

[a]Rotor speed = 116 r.p.m. Water as required to keep the temperature below 130°C

Samples of vulcanisate for NMR analysis were extracted for 4 h with methanol in a hot Soxhlet apparatus and dried to constant weight *in vacuo* in the dark until required. Small slivers ($\sim 15 \times 0.5 \times 1$ mm) were allowed to swell in deuterochloroform ($CDCl_3$) in a NMR tube to equilibrium uptake for between 36 h and 60 h in the dark. If necessary, these samples were then trimmed so that they can spin freely in the NMR tube. A small amount of fresh $CDCl_3$ containing chloroform ($CHCl_3$) as an internal marker and HMDS as an internal lock were added just before acquisition of the spectrum.

The equilibrium swelling of each vulcanisate in chloroform was determined for specimens swollen at 23°C in the dark. The swollen vulcanisate was dried *in vacuo* and the volume fraction of rubber in the swollen gel, *Vr*, was calculated with due allowance for the zinc oxide in the vulcanisate[4].

The NMR spectra were obtained using a Perkin-Elmer R32 90 MHz continuous wave spectrometer interfaced to a BBC microcomputer for computer accumulation of the transients to improve the signal to noise ratio. The spectrometer was run at an 80 s sweep of 10 p.p.m. width with between forty and eighty transients combined for each spectrum. H% was evaluated as described previously[1] using reference positions −0.2 p.p.m. and +0.2 p.p.m. from the olefin peak positions of ENR 25 and BR respectively. Duplicate or sometimes triplicate spectra were obtained from freshly swollen samples.

RESULTS AND DISCUSSION

The analysis of a binary polymer blend for the level of crosslinking within each component using the NMR technique[1] is made with reference to the NMR spectra of vulcanisates of the individual polymers in the blend. Thus, two series of single polymer vulcanisates are required to provide the individual H%-*Vr* and H%-curative level relationships (*Figures 1* and *2*). Ideally, the cure system used for these single

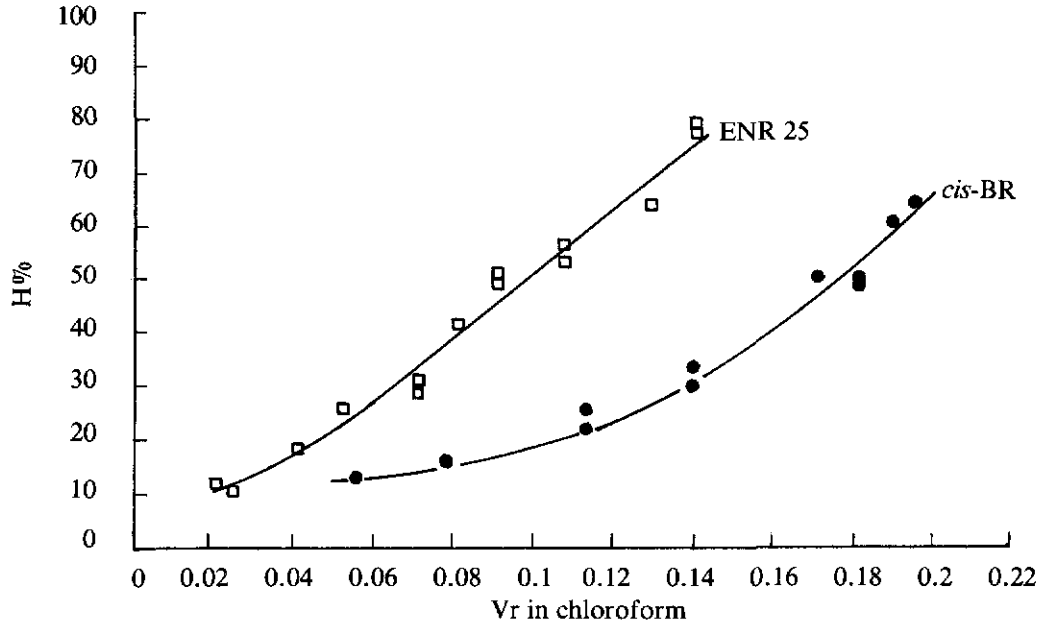

Figure 1. H% versus Vr in chloroform for single polymer vulcanisates.

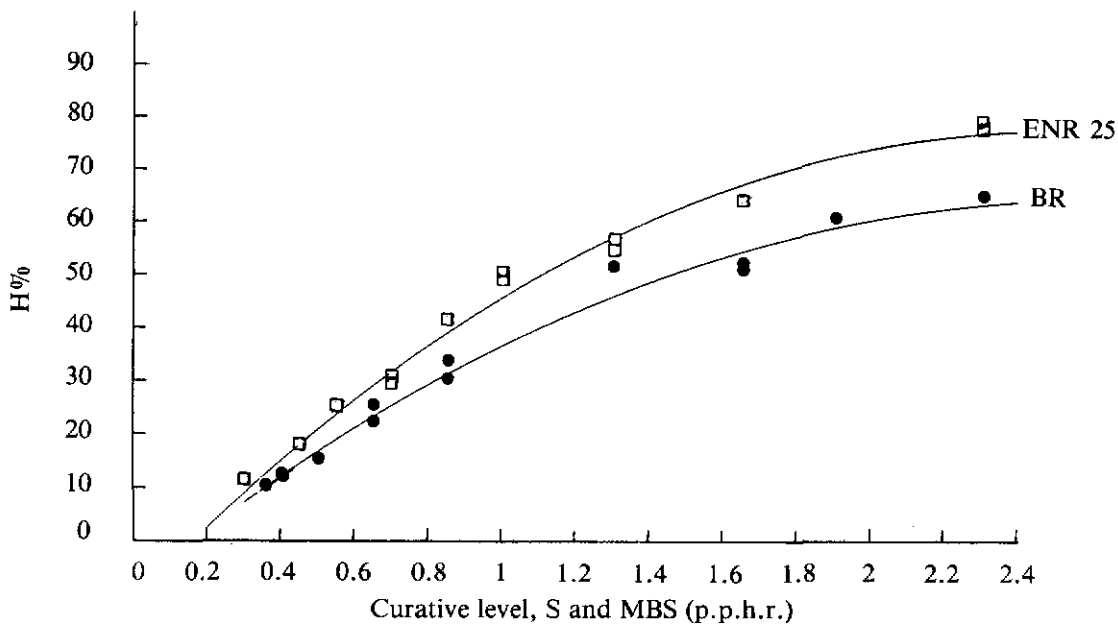

Figure 2. H% versus curative level for single polymer vulcanisates.

polymer vulcanisates should be that used in the blends of interest, however the potential for diffusion of curatives and, more importantly, crosslinking intermediates, means that the cure systems active in each phase of the blend are likely to differ from that of the compounding. It has previously been shown that H% is independent of the particular cure system used, at least within a class of cure systems (e.g. accelerated-sulphur)[2], so that differences in the effective accelerator/sulphur ratio resulting from curative diffusion before and during vulcanisation do not affect the application of the NMR technique. This study used a cure system having a 1:1 ratio of sulphur and N-morpholino-benzothiazole-2-sulphenamide (MBS) compounded at levels ranging from 0.3 p.p.h.r. to 2.3 p.p.h.r. to produce the ten ENR 25, eight BR and twelve blend vulcanisates *(Table 1)*.

The olefin region of the NMR spectra of each of the single polymer vulcanisates was analysed to determine three parameters; H%, P%H and R%H[1]. H%, the measure of peak broadening, is the ratio of the peak intensity at a reference position 0.2 p.p.m. from the peak centre to that at the peak maximum expressed as a percentage, $100Bb/Aa$ *(Figure 3)* and P%H and R%H are the peak overlap terms given by:

$$P\%H = 100\ Pp/Aa$$

$$R\%H = 100\ Rr/Aa$$

where *P* and *R* of *Figure 3* are the peak centre and the reference positions of the second polymer to be used in the blend. P%H and R%H are found to correlate well with H% (*Figures 4* and *5*). In these two figures, the solid curves represent the best fits of the data to first-, second- or third-order polynomial equations in H% as appropriate. These polynomial equations are used in the analysis of the olefin region in the spectra of blend vulcanisates when calculating the corrections for signal overlap to enable determination of H% for each polymer in the blend, as described by Loadman and Tinker[1].

There is considerable overlap of the olefin signal from these two polymers *(Figure 6)*, the ENR peak maximum being at 5.08 p.p.m. and

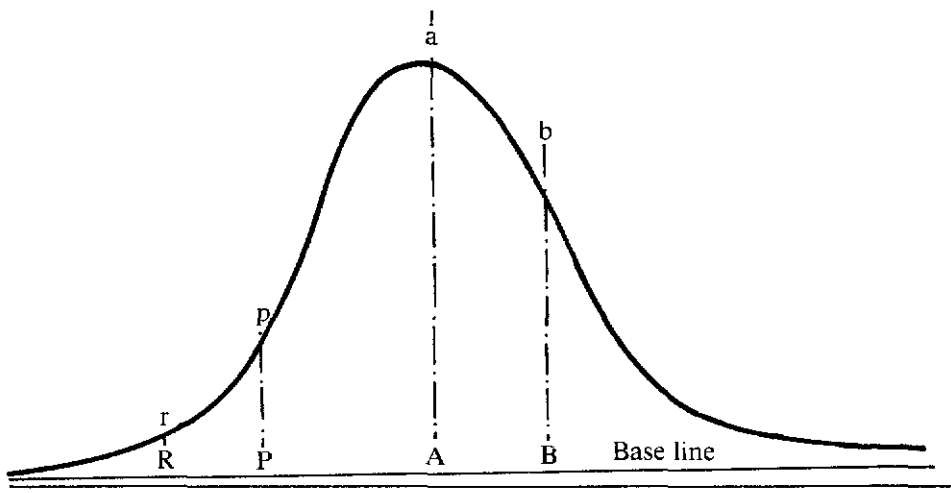

Figure 3. Diagrammatic representation of the determination of P%H, R%H and H%. A and B are the peak centre and reference positions of the polymer whose NMR spectrum is given, P and R are the peak centre and reference positions of the other polymer in the blend to be studied. Aa, Bb, Pp and Rr represent the NMR intensity at the positions A, B, P and R, respectively. H% = Bb/Aa, P%H = Pp/Aa and R%H = Rr/Aa, all expressed as percentages.

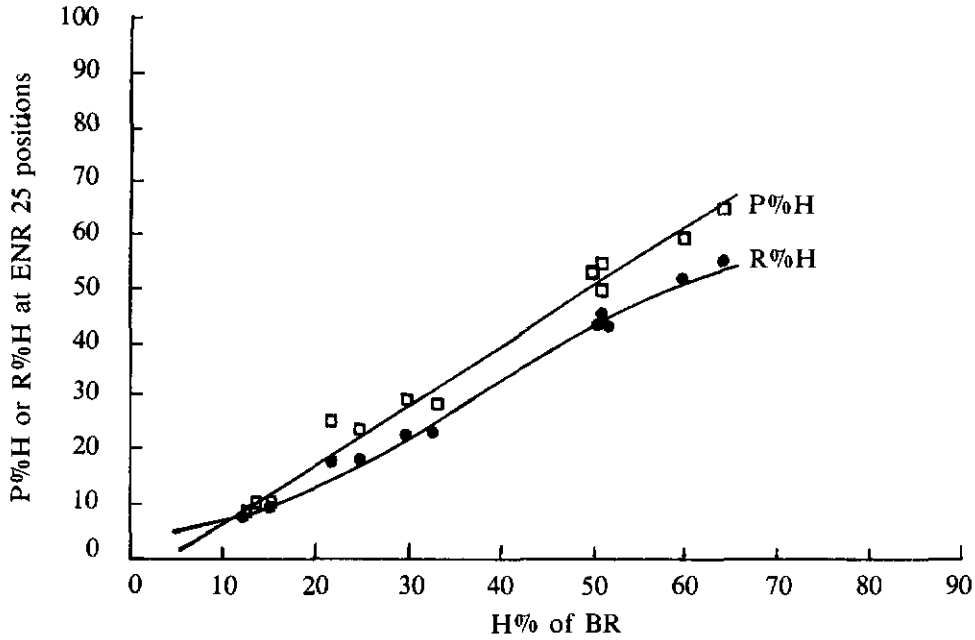

Figure 4. P%H and R%H at the peak and reference positions of ENR 25 in the NMR spectrum of BR versus H% of BR.

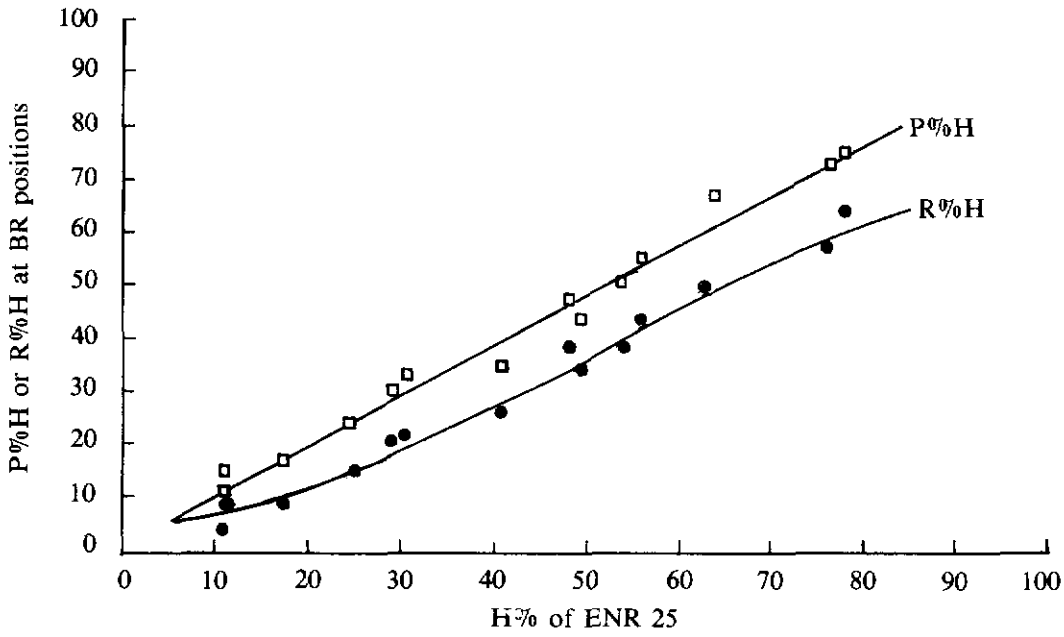

Figure 5. P%H and R%H at the peak and reference positions of BR in the NMR spectrum of ENR 25 versus H% of ENR 25.

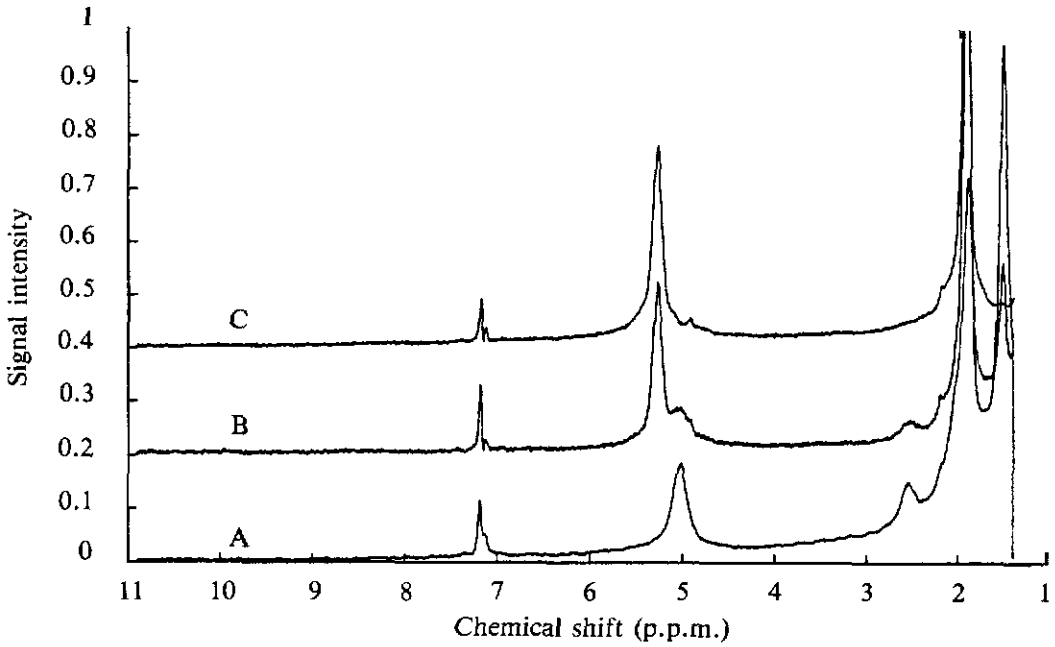

Figure 6. Proton NMR spectra of single polymer vulcanisates of ENR 25 (A) and BR (C) and of a 1:1 (wt/wt) blend (B), all compounded using 0.5 p.p.h.r. sulphur and MBS.

that of BR at 5.34 p.p.m. This close proximity of the peaks in the NMR spectrum of a blend of ENR and BR results in relatively large corrections being applied to the observed intensities to deconvolute these signals. In addition to the problem of peak overlap, the two polymers possess different concentrations of olefinic proton (3.70×10^{-2} molg^{-1} rubber for BR and 1.04×10^{-2} molg^{-1} rubber for ENR 25). As a consequence, the olefin region of the NMR spectrum of the blend is dominated by the BR peak for all but the highest ENR concentrations *(Table 3, Figure 6)* and this in turn restricts the polymer ratios which may be investigated by the technique using proton NMR spectroscopy.

TABLE 3. OLEFINIC PROTON RATIOS[a]

Blend	Blend ratio (wt/wt)	Proton ratio olefin region
1	1:1	1:0.282
2	1:4	1:1.126
3	1:6	1:1.689

[a]All ratios calculated as BR/ENR

A qualitative result may be obtained by comparing the NMR spectrum of a blend vulcanisate with the spectra of its single polymer analogues. *Figure 6* shows the spectrum of blend *1F (Table 4)* together with the spectra of the single polymer ENR and BR vulcanisates also compounded using 0.5 p.p.h.r. sulphur and 0.5 p.p.h.r. accelerator. The ENR olefin signal, chemical shift (δ) 5.05, is obviously broader in the blend vulcanisate (*B*) than in the homopolymer vulcanisate (*A*). This indicates that the ENR has a higher crosslink density in the blend than as the single polymer despite nominally equivalent curative loadings. The BR olefin peaks at δ 5.35 are similar in shape (*B* and *C*), it is therefore not possible to draw any conclusions regarding the crosslinking of this component of the blend. Quantitative analysis of the NMR spectrum of a blend vulcanisate requires the application of the NMR technique[1].

TABLE 4. BLEND ANALYSIS RESULTS

Blend	Polymer[a] ratio	S (p.p.h.r.)	ENR		BR		S_{ENR}/S_{BR}
			H%	S_{ENR}[b]	H%	S_{BR}[b]	
1A	1:1	0.5	16.6	0.45	9.5	0.3	1.50
1B	1:1	1.0	51.3	1.1	18.6	0.6	1.83
1C	1:1	1.5	62.7	1.55	38.6	1.0	1.55
1D	1:1	2.0	72.2	2.05	52.2	1.4	1.46
1E	1:1	2.5	83.6	>2.5	55.3	1.55	>1.6
1F	1:1	0.5	32.8	0.7	13.7	0.45	1.55
1G	1:1	0.9	38.6	0.8	27.1	0.75	1.07
1H	1:1	1.4	70.9	1.95	43.1	1.1	1.77
1I	1:1	1.9	83.2	>2.5	57.9	1.7	>1.5
2A	4:1	0.5	21.2	0.5	13.5	0.45	1.11
2B	4:1	0.9	43.2	0.95	20.5	0.65	1.46
2C	4:1	1.4	55.2	1.25	31.0	0.8	1.56
2D	4:1	1.9	80.9	2.45	52.7	1.4	1.75
3A	6:1	0.5	31.6	0.65	13.0	0.45	1.44
3B	6:1	0.5	56.4	1.3	37.5	0.95	1.36
3C	6:1	1.4	64.9	1.6	36.6	0.95	1.68
3D	6:1	1.9	85.0	>2.5	60.5	1.8	>1.4

[a]By weight ENR 25:BR

[b]S_{ENR} and S_{BR} determined from the calculated H% values by reference to *Figure 2*. Note the calibration stops at 2.5 p.p.h.r. S which in ENR 25 gives a H% value of 82.

Vulcanisates from the three blend systems *(Table 1)* were analysed using the procedure of Loadman and Tinker[1] to give H% values for the two component polymers. These H% values were translated into equivalent curative levels by reference to *Figure 2* and the data presented as a function of total curative level in the blend in *Figure 7*. These data show that the notional curative levels effective in the blend components are not the same with that in the ENR 25 being higher than that in the BR by approximately 50% *(Table 4)*. The degree of scatter in these results is quite large and probably arises from a combination of effects. The proximity of the two signals, as mentioned above, results in relatively large P%H and R%H correction terms being applied to the observed signal intensities at the two peak and two reference positions. Furthermore, the uneven crosslink density, biased as it is towards the ENR component of the blend, renders the ENR signal considerably broader than and consequently much lower in intensity than the BR olefin peak. The nett effect is to cause relatively large corrections to be applied to the signal at the ENR peak and reference positions during the iterative deconvolution calculations. Thus, any errors in the polynomial fits of the P%H – and R%H – H% relationships are of substantial consequence when the blend spectra are analysed, resulting in the increased scatter observed. When the NMR technique is applied to blends of NR and a butadiene-acrylonitrile copolymer (NBR), for which the olefin

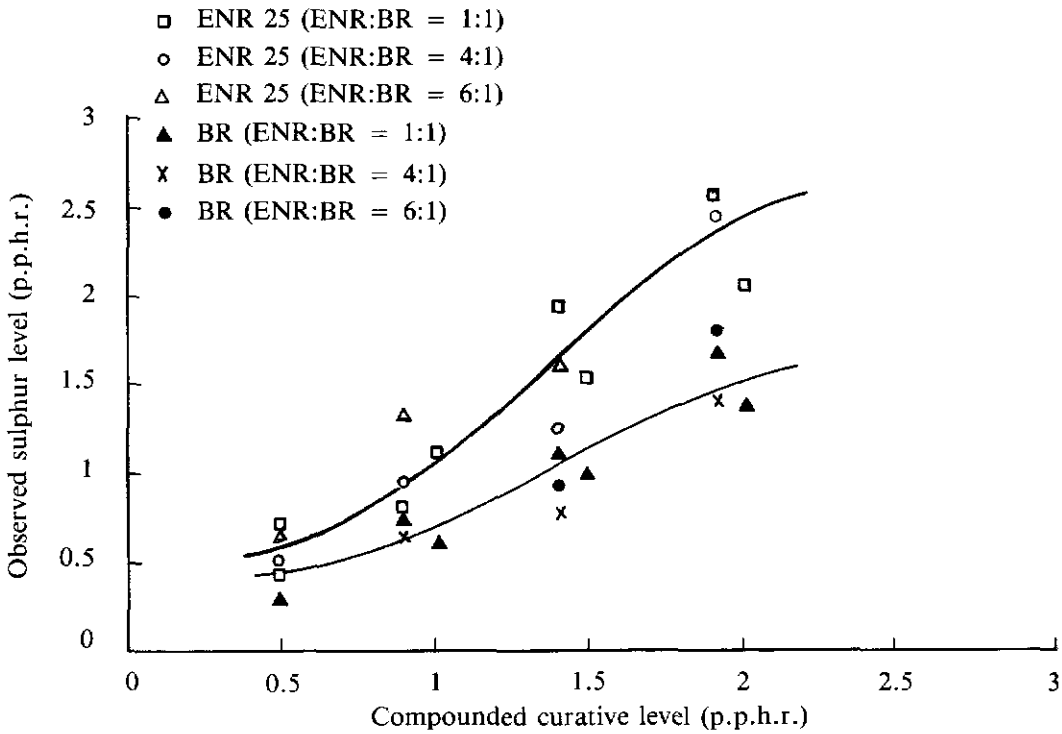

Figure 7. Effective sulphur level observed in each phase versus the compounded sulphur level in the ENR 25/BR blend for blend ratios of 1:1, 4:1 and 6:1 (ENR:BR)

signals are more separated, the H% and derived crosslinking data show much less scatter[3].

The uneven curative utilisation indicated by these results probably reflects the partitioning of the actual crosslinking agents between the two polymers in the blend. This partitioning is achieved by the diffusion of crosslinking agents (CLA) from the BR to the ENR phase before and during vulcanisation. Such effects of CLA diffusion have been observed previously in blends of natural rubber (NR) with an ethylene-propylenediene rubber (EPDM)[5] and in blends of NR with NBR[3]. In the former blend, the CLA diffusion is driven by the more rapid utilisation of materials by the NR phase because of the higher concentration of olefin group in NR. However in the latter blend, this is not so, the observed crosslink densities show that the CLA diffusion has been away from the polymer of highest olefin concentration. Similarly here, the ENR has utilised more of the curative during the blend vulcanisation. The presence of the oxirane group in ENR should make this polymer more polar than BR, indeed the solubility parameters of these polymers confirm this thesis [17.09 $(MPa)^{1/2}$ for BR[6], 17.4 $(MPA)^{1/2}$ for ENR 25[7]]. The compounds involved in vulcanisation chemistry are generally quite polar in nature[8] and might therefore be expected to have a higher solubility in the ENR phase than in the BR phase of the blend. Consequent partition of the CLA between the rubbers would lead to the observed crosslink distribution. Similar arguments apply to the results obtained by Tinker[3].

It must be noted that the chemical nature of the CLA is dependent on the crosslinking system used. The distribution of CLA between the polymers in a blend is therefore dependent not only on the polymers in the blend but also on the vulcanising ingredients in the compound

and possibly on the relative proportions of these ingredients. Thus, the results of the blend analyses reported herein are specific to this particular cure system when used in these two polymers. A change in just one component may, by changing the distribution of the CLA in the blend, alter the distribution of crosslinks between the polymers — a change which would be detected by the application of the NMR technique of polymer blend analysis.

CONCLUSIONS

Blends of ENR 25 with BR having three different polymer ratios have been studied using swollen state NMR spectroscopy[1]. The crosslink densities within each component of each blend have been expressed in terms of the curative concentrations required to produce that crosslink density in a single polymer vulcanisate. In all cases, this nominal curative level was higher for the ENR 25 component, typically by as much as 50%. This uneven utilisation of the curatives is caused by the more polar nature of the ENR polymer, containing as it does 25 mol% epoxidation of the olefin groups of NR, resulting in increased concentrations of the crosslinking agents within the ENR phase at the expense of the BR phase.

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