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*Distribution of Crosslinks between the Phases of Vulcanised NR/*cis*-BR Blends*

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The recently developed NMR method of rubber blend analysis[1,2,3] has been applied to gum vulcanisate blends of natural rubber (NR) and cis*-polybutadiene (BR). Two cure systems have been studied, peroxide and accelerated-sulphur. Although the distribution of crosslinks between the two phases of the blends was different for the two cure systems studied, in neither case was there any significant diffusion of cross-linking agent apparent, both phases achieving similar crosslink levels to those expected in single polymer vulcanisates of equivalent curative loading.*

In the search for the 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[1,2,3] 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], volume fraction of rubber in the swollen state (*Vr*) in chloroform[1] or the crosslink density[2,3] of a single polymer vulcanisate.

McGill and co-workers have reported three methods by which they have determined the distribution of crosslinks between the phases of NR/*cis*-1,4 polybutadiene blends[4,5,6]. Their studies gave contradictory results; two methods generally indicating that the BR was crosslinked preferentially, while the third method suggests that it was the NR. In the instances that the methods agreed in the direction of the crosslink imbalance, this agreement was only qualitative. In this study, blends of natural rubber with a high *cis*-1,4 polybutadiene are examined using the NMR technique to determine the crosslink distribution.

EXPERIMENTAL

The rubbers used in this study were *cis*-1,4 polybutadiene, BR, (*Europrene cis*, 94% *cis*-1,4 polybutadiene, Enichem) and natural rubber (SMR 10). 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 master-

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TABLE 1. MIX FORMULATIONS

Compound	NR 1-NR 10	NR 11-NR 14	BR 1-BR 9	BR10-BR 12	Blends 1	Blends 2	Blends 3	Blends 4
NR	100	100			67	50	33	50
Europrene-cis			100	100	33	50	67	50
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	
Dicup[d]		0.5–1.5		0.3–0.9				0.3–0.9

[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.
[d]98% dicumyl peroxide.

batches mixed in the Banbury. For each polymer two batches were crossblended on the mill prior to finalising. 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)*.

TABLE 2. BANBURY MIX CYCLE[a]

Time	Procedure
Start	Add polymer/polymers
30 s	Add powders
120 s	Sweep
210 s	Dump

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

The accelerated-sulphur vulcanisates were cured to the maximum torque on a Göttfert *Elastograph*, while the peroxide-cured vulcanisates were pre-moulded at 100°C for 20 min before vulcanisation at 150°C for 120 min, which represents about ten half-lives.

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 (~15 × 0.5 × 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 as to 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 was 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[7].

The physical crosslink density (ν) was calculated *(Table 3)* either from the Mooney-Rivlin constant C_1, which was determined from stress-strain measurements[8], or from *Vr* using the Flory-Rehner equation[9]

TABLE 3. CROSSLINK DENSITY OF BR VULCANISATES

Vulcanisate	Vr	χ[a]	v (mol/m^3)
BR 1	0.055	0.297	10.95
BR 2	0.077	0.306	19.1
BR 3	0.114	0.321[b]	36.7[b]
BR 4	0.140	0.330	52.2
BR 5	0.160	0.338	65.1
BR 6	0.171	0.341[b]	73.3[b]
BR 7	0.181	0.346	80.4
BR 8	0.190	0.351[b]	86.5[b]
BR 9	0.196	0.352	92.1

[a] χ values interpolated from *Figure 4*.

[b] Values determined from stress-strain measurements, χ values calculated using the Flory-Rehner equation[9].

$$-(\mathrm{Ln}(1-Vr) + Vr + \chi Vr^2) = 2V_0 v\,(Vr^{1/3})$$

where V_0 = solvent molar volume, 80.7 ml/mol for $CHCl_3$

and v = crosslink density (mol/m^3).

The polymer-solvent interaction parameter (χ) for BR-chloroform was interpolated from *Figure 4*, which depicts the dependence of χ on Vr for BR. The data points derive from the three vulcanisates for which v was determined by stress-strain measurements. A dependence of χ on Vr is often observed[10].

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 NR 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, 2* and *3*). The H%-crosslink density relationship of NR has been reported previously[2], while that of BR is shown in *Figure 5*. Three of the v values of BR were determined from stress-strain measurements[8], the others were calculated from the Flory-Rehner[9] equation as described above.

Ideally the cure system for the single polymer vulcanisates used to produce the various correlations with H% should be identical to that operating in the blends of interest, but this is not essential. It has previously been shown that H% is independent of the particular cure system used, at least within a class of cure system (e.g. accelerated-sulphur)[2]. Thus any differences in the effective accelerator/sulphur ratio resulting from curative diffusion

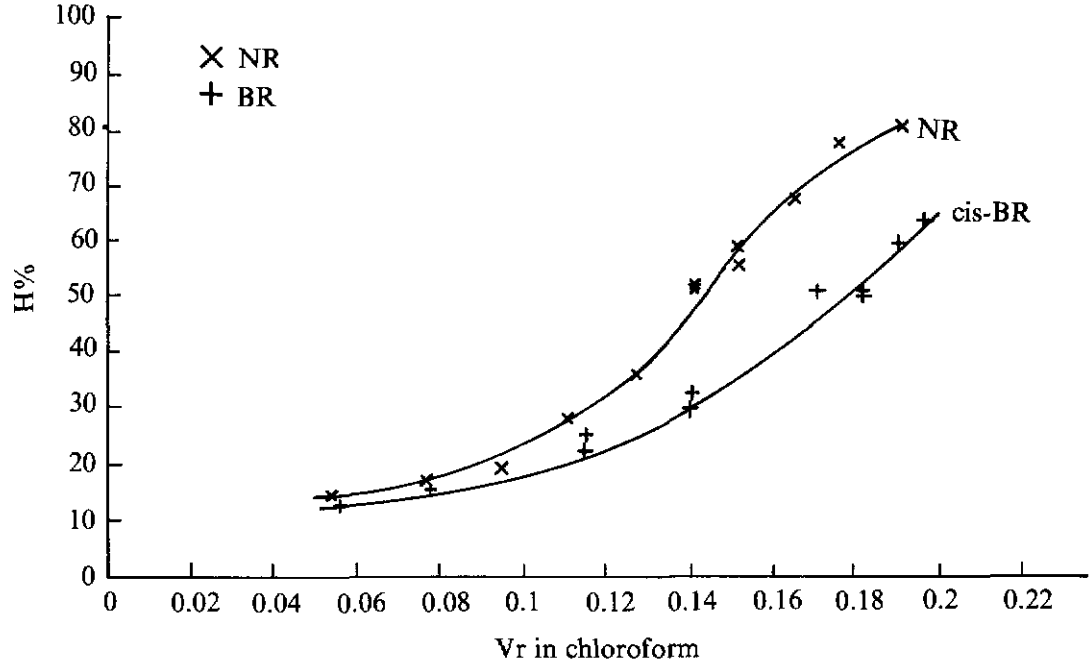

Figure 1. H% versus Vr in chloroform for single polymer vulcanisates.

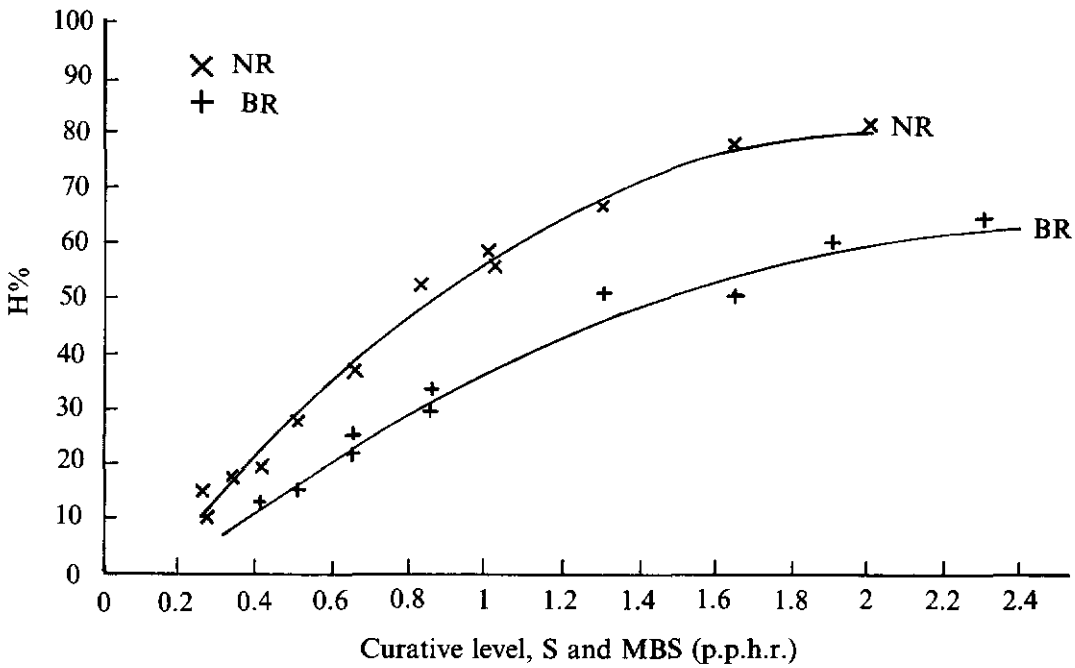

Figure 2. H% versus curative level for single polymer vulcanisates: S/MBS-cured.

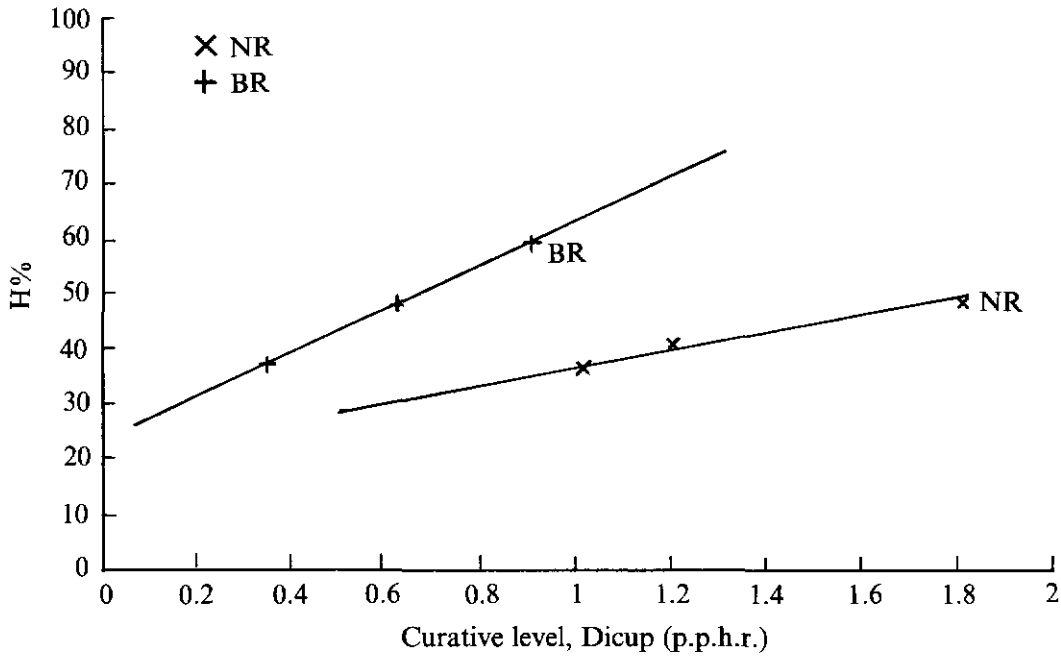

Figure 3. H% versus curative level for single polymer vulcanisates: Peroxide-cured.

before and during vulcanisation do not affect the validity of the correlations and hence the application of the NMR technique. This study considers two cure systems; a 1:1 ratio of sulphur and 2-morpholinobenzothiazole-2-sulphenamide (MBS) compounded at levels ranging from 0.3 p.p.h.r. to 2.3 p.p.h.r. or dicumyl peroxide were used to produce single polymer and blend vulcanisates *(Table 1)*.

The olefin region of 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, and P%H and R%H are peak overlap terms[1]. P%H and R%H are found to correlate well with H% (*Figures 6* and *7*). In these two figures the solid curves represent the best fit of the data to first-, second- or third-order polynomial equations in H% as found 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[1]. It has previously been reported that peroxide vulcanisates of NR have sharper olefin peaks (lower H%) than accelerated-sulphur vulcanisates at the same physical crosslink density[2], however the P%H- and R%H- H% correlations are the same for both types of vulcanisates (*Figures 6* and *7*). Thus, while different H%-Vr and H%-v correlations are necessary, the same polynomial equations can be used in the analysis of peroxide-cured NR/BR blends.

As was observed for blends of BR with 25 mol% epoxidised NR[11], there is considerable overlap of the olefin signal from these two polymers *(Figure 8)*, the peak maximum being at 5.08 p.p.m. and 5.34 p.p.m. for NR

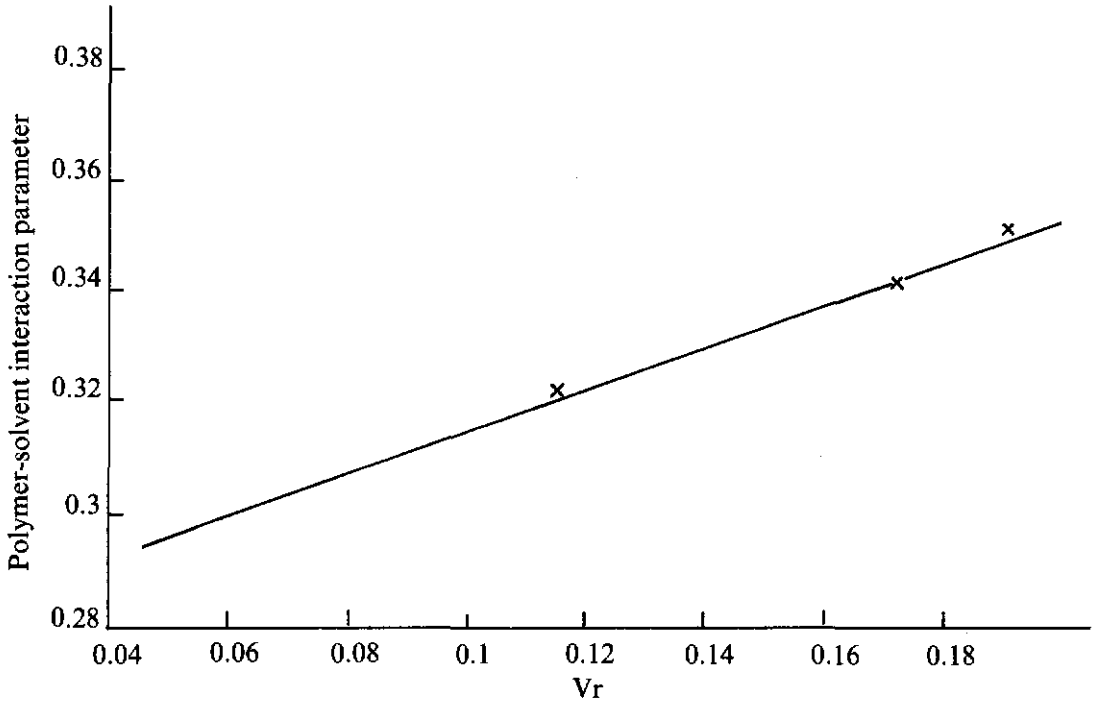

Figure 4. Polymer-solvent interaction parameter (χ) versus Vr for BR.

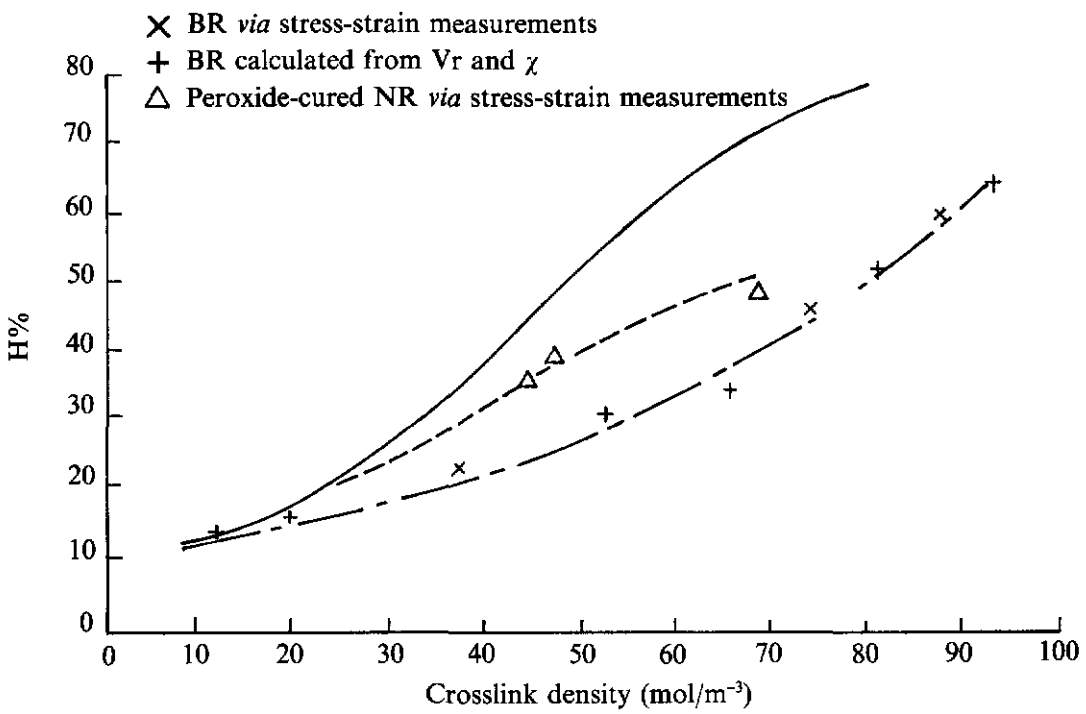

Figure 5. H% versus crosslink density. The solid curve is that of accelerated-sulphur NR, taken from Reference 2.

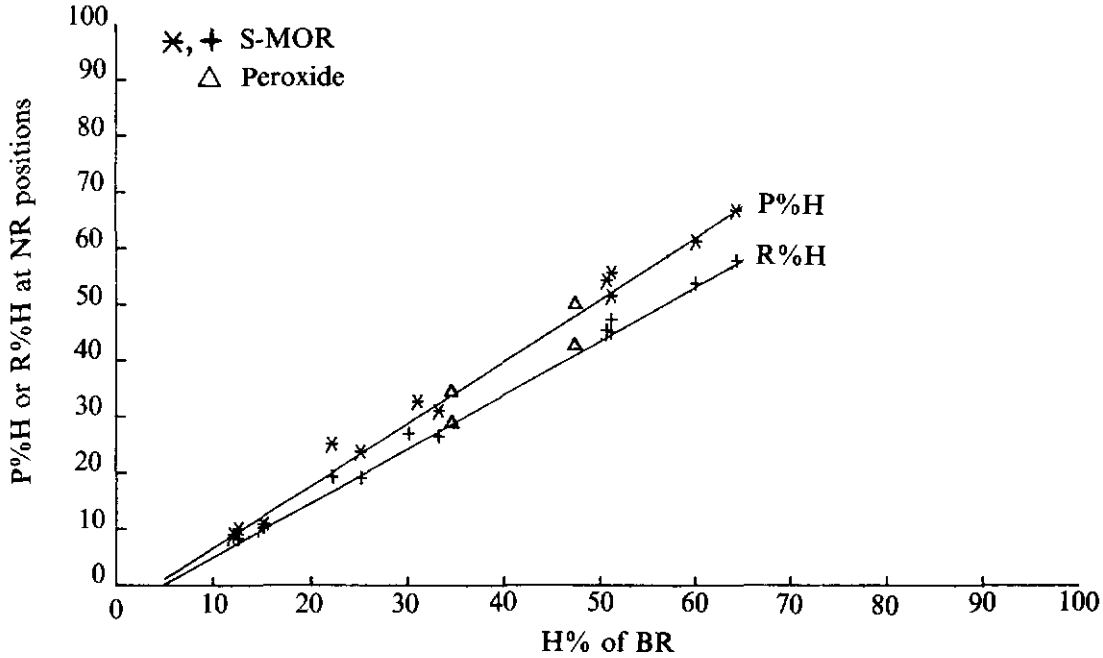

Figure 6. P%H and R%H at the peak and reference positions of NR in the NMR spectrum of BR versus H% of BR.

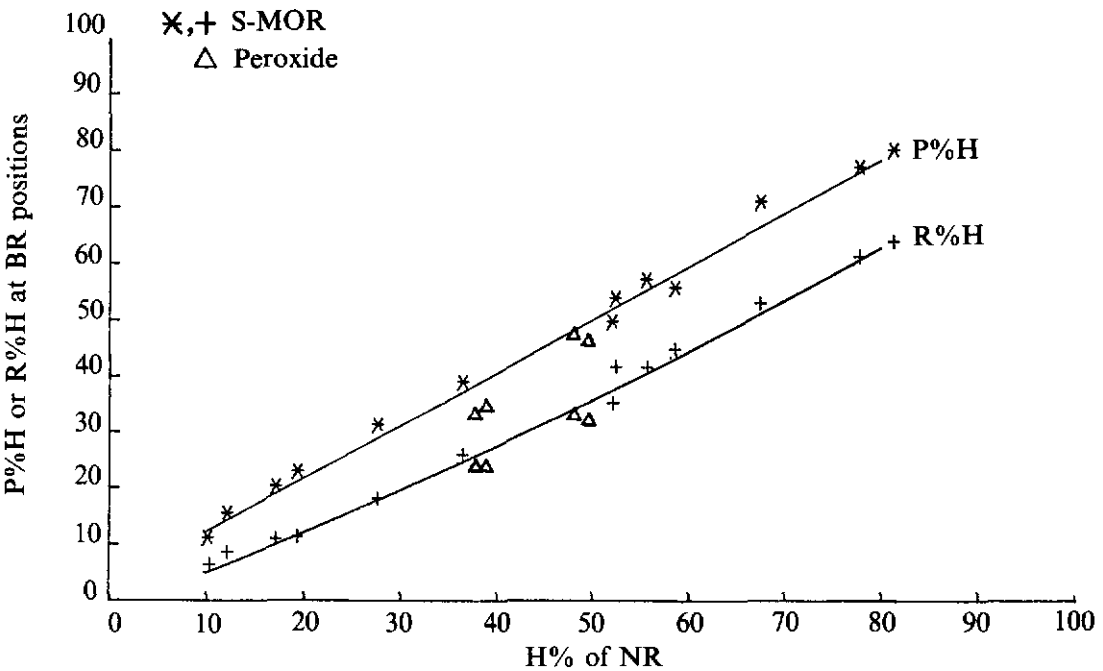

Figure 7. P%H and R%H at the peak and reference positions of BR in the NMR spectrum of NR versus H% of NR.

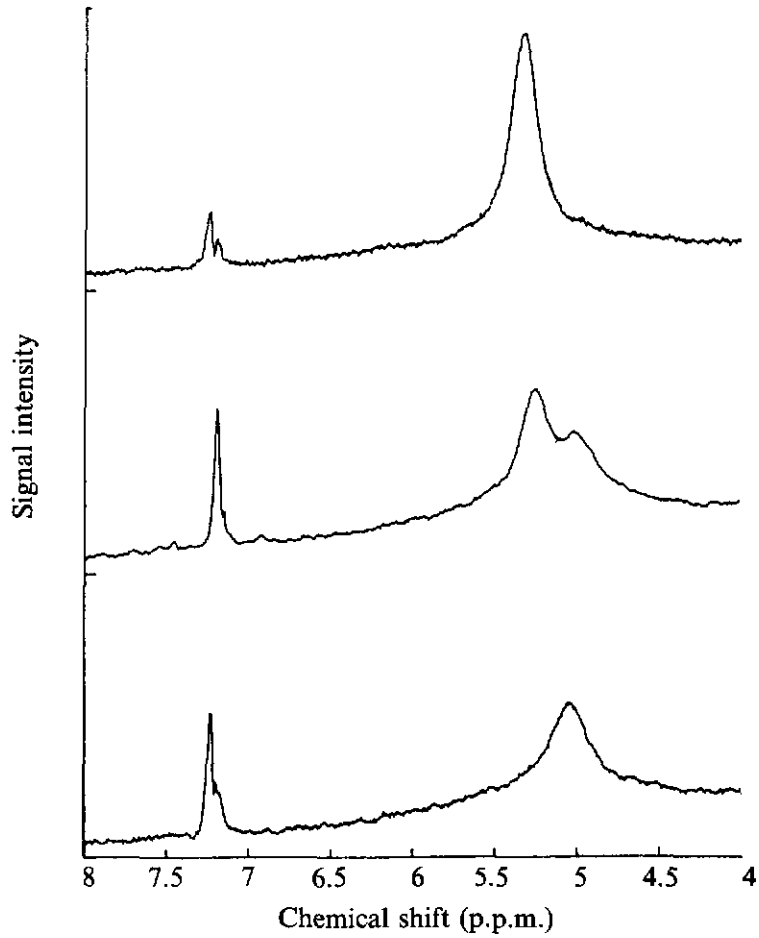

Figure 8. Proton NMR spectra of single polymer vulcanisates of NR (A) and BR (C) and of a 1:1 (wt/wt) blend (B) of similar compounding, showing the olefin region only.

and BR respectively. This close proximity of the peaks in the NMR spectrum of a blend of NR and BR results in relatively large corrections being applied to the observed intensities in order to deconvolute these signals.

Vulcanisates from the four blend systems *(Table 1)* were analysed to give H% values for the two component polymers. These H% values were translated into equivalent curative levels (S_{NR} or S_{BR}) by reference to *Figures 2* and *3*, and these data are presented in *Table 4*. Crosslink densities obtained by reference to *Figure 5* and *Figure 6* of Brown and Tinker[2] are presented in *Table 5*.

There appears to be one rogue result *(Blend 2A)* in *Table 4*, with the other S/MBS-cured blends having S_{NR}/S_{BR} values around 1. The average S_{NR}/S_{BR} value (excluding *Blend 2A*) is 1.05, indicating that the cure system in the blend is operating in each phase such that the net result is that total crosslinking in each phase is much the same as that in the analogous single polymer vulcanisates. The distribution of crosslinks *(Table 5)* shows that the BR

TABLE 4. BLEND ANALYSIS RESULTS

Blend	Polymer ratio[a]	S (p.p.h.r.)	NR		BR		S_{NR}/S_{BR}
			H%	S_{NR}[b]	H%	S_{BR}[b]	
1A	2:1	0.6	46.3	0.74	26.6	0.74	1.000
1B	2:1	0.9	52 5	0.85	27.4	0.76	1.118
1C	2:1	1.4	73 6	1.46	47.8	1.20	1.217
1D	2:1	1.9	75.5	1 60	55.0	1.55	1.032
2A	1:1	0.6	22 5	0.44	30.0	0.80	0.550
2B	1:1	0.9	60.5	1.02	36.4	0.91	1.13
2C	1:1	1.4	74.0	1.51	54.0	1.49	1.013
2D	1:1	1.9	87.0	2+[c]	74.0	2+[c]	
3A	1:2	0.6	40.5	0.65	22.8	0.66	0.985
3B	1:2	0.9	61.2	1.04	39.3	0.98	1.061
3C	1:2	1.4	69.4	1.33	56.3	1.63	0.816
3D	1:2	1.9	85.9	2+[c]	66.9	2+[c]	
4A[d]	1:1	0.3	14.6	c	34.6	0.3	
4B[d]	1:1	0.6	26.2	~0.4	53.1	0.6	
4C[d]	1:1	0.9	36.8	0.95	62.7	~0.9	

[a]By weight NR:BR

[b]Equivalent sulphur values, S_{NR} and S_{BR}, determined from the calculated H% values by reference to *Figure 2*. Note the calibration stops at 2.0 p.p.h.r. S.

[c]H% value lies outside the calibration range.

[d]For the peroxide-cured blends the data are in p.p.h.r. Dicup equivalent determined from *Figure 3*.

phase has a slightly higher crosslink density than the NR phase. The average v_{NR}/v_{BR} ratio is 0.9, again excluding *Blend 2A*. It should be noted that the S_{NR}/S_{BR} data indicates that a small amount of diffusion of the curative towards the NR may have taken place, hence the bias of crosslinking towards the BR phase is slightly lower than might be expected.

The scatter in these results is quite large and probably arises from a combination of effects. The close proximity of the two signals, as mentioned above, results in considerable overlap in the blend spectrum. This results in relatively large corrections being applied during the deconvolution process. Any errors in the polynomial fits of the P%H- and R%H- H% relationships are thus of substantial consequence when the blend spectra are analysed, resulting in the increased scatter observed. A large degree of scatter was also observed when blends of BR with 25 mol% epoxidised NR were studied[11]; the olefin peaks of these polymers also overlap considerably. When the NMR technique is applied to blends for which the olefin peak overlap is less, such as is the case for blends of NR and a butadiene-acrylonitrile copolymer, the H% and derived crosslinking data show much less scatter[3].

For peroxide vulcanisates of a NR/BR blend, the H% value observed in each phase is similar to that found in the single polymer vulcanisates *(Table 4)*. With this vulcanisation system, the crosslink yield in BR is expected to be higher than that in NR due to the greater crosslinking efficiency of peroxide cures in BR[12]. Since the H% values found in the blend agree with the analogous

TABLE 5. CROSSLINK DENSITIES IN EACH PHASE

Blend	ν_{NR} (mol/m^3)	ν_{BR} (mol/m^3)	ν_{NR}/ν_{BR}
1A	41.3	44.0	0.939
1B	46.0	45.3	1.016
1C	64.3	70.3	0.915
1D	66.7	75.7	0.881
2A	22.4	50.0	0.449
2B	52.4	59.2	0.885
2C	65.0	75.1	0.865
2D	79+[a]	92+[a]	
3A	36.9	36.4	1.013
3B	53.0	62.7	0.846
3C	60.3	76.7	0.785
3D	79+[a]	92+[a]	
4A	14.7[b]	61.6	0.239
4B	28.1	81.4	0.345
4C	41.9	89.7	0.467

[a]H% value lies outside the calibration range, thus a lower limit on the crosslink density is quoted.

[b]Although the H% value of the NR phase in this blend was below those of the peroxide vulcanisates of NR, a crosslink density is quoted by reference to the accelerated-sulphur H%-ν correlation. At this low crosslink density the two H%-ν curves are very close *(Figure 5)*.

single polymer vulcanisates, the peroxide cure system appears to be functioning in each phase as if the other phase were not present. This would be expected in the absence of any preferential partitioning of the peroxide, and the similarity in polarity of the two polymers would not favour this. These differing crosslinking efficiencies give rise to an uneven distribution of crosslinks in the blend *(Table 5)*. The change in ν_{NR}/ν_{BR} from 0.23 to 0.46 as the level of peroxide used increases, arises from a reduction of efficiency in the BR phase rather than an increase in the NR phase. Peroxide curing of BR proceeds *via* a radical chain mechanism[12] with a chain termination step. Increased peroxide loading in the blend results in an increase in the concentration of radicals in both phases. In the NR phase, which has no such chain mechanism, a corresponding increase in crosslink density is observed. In the BR phase the probability of the chain termination reaction occurring is higher, this reduces the overall chain propagation length, and thus the crosslinking efficiency falls.

CONCLUSION

Blends of NR with a high *cis*-1,4 polybutadiene have been examined, using NMR spectroscopy, to determine the distribution of crosslinks between the two polymers in the blend. These blends were vulcanised using either dicumyl peroxide or a semi-EV S/MBS cure system. Both cure systems appear to have operated evenly in that neither polymer has significant additional crosslinking above that which would be expected in single polymer vulcanisates. The crosslink density in the BR phase is found to be approximately 10% higher than that in the NR phase of the accelerated-sulphur cured blends, and is considerably more so in the peroxide-cured blends. It must be stressed that these results may be peculiar to the specific polymers and curatives investigated herein.

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