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Distribution of Crosslinks between the Phases of Vulcanised Natural Rubber/ cis-*Poly(butadiene) Blends*

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A swollen-state NMR method of rubber blend analysis has been used to study crosslinking in gum vulcanisates for cure times ranging from t_{30} to overcure. Natural rubber (NR), cis-*poly(butadiene) (BR) and NR/BR blend vulcanisates cured with conventional and semi-EV sulphur systems based on three common sulphenamide accelerators were studied. For single polymers, maximum crosslink densities were similar for a given elastomer regardless of accelerator. The crosslink densities attained in the blend phases at maximum crosslinking were close to those expected from single polymer data, but the manner in which this was achieved was rather different from expected from cure behaviour of the single polymers. NR has a shorter scorch time than BR, but results indicate that in blend materials the BR phase begins curing before and at a much faster initial rate than NR. The cure rates are reversed as the cure progresses and the NR phase eventually attains the crosslinking levels expected from single polymer data.*

INTRODUCTION

Crosslink formation in the separate phases of a polymer blend is an important factor contributing to the final properties of the vulcanised material. The solubilities, reactivities, and diffusion rates of the crosslinking agents greatly influence the crosslink levels within each phase. The development of a swollen-state NMR spectroscopy technique[1–4] has allowed the estimation of crosslink densities in the individual phases of vulcanised blends to be determined. The technique is based upon the observation that NMR peak line widths increase smoothly with increasing physical crosslink density (n_{phys}) or other parameters related to this such as curative level or volume fraction of rubber in the equilibrium swollen state (v_r). Line width is measured as the proportion of signal strength at a reference position to that at the peak, and is denoted H%[1]. Previous workers have examined NR/BR blend crosslink densities using DSC and the depression of solvent freezing points within swollen networks[5,6] but the two papers did not give consistent results. More recently Shershnev and co-workers have studied NR/IR blends using the swollen-state NMR technique[7].

'Network visualisation', a transmission electron microscopy (TEM) technique developed recently[8], was used in order to complement the NMR studies. The method involves swelling elastomer networks in styrene

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to equilibrium. The extent to which the network swells is dependent on its crosslink density. The styrene is polymerised and the elastomer component stained with osmium tetroxide for viewing by TEM. The images obtained show a dark mesh structure which is believed to be stained bundles of network chains within a light phase of polystyrene. The average mesh size is related to crosslink density as determined by standard physical crosslink density measurements[8]. A tightly knit mesh structure indicates a high crosslink density and a more open structure indicates a low crosslink density.

In this study the changes in crosslink levels throughout cure, for semi-efficient vulcanisation (semi-EV) sulphenamide accelerator cured natural rubber (NR), *cis*-1,4 poly(butadiene) (BR) and semi-EV and conventionally (CV) cured NR/BR blend vulcanisates with three different sulphenamide accelerators, are examined using the NMR technique.

EXPERIMENTAL

The rubbers used in this study were BR [Europrene Neo-*cis* BR40, 98% *cis*-1,4 poly(butadiene), Enichem] and NR (SMR-CV60). Rubber chemicals were standard commercial grade materials, and solvents were of AR grade except for the NMR solvents which were of spectroscopic grade [chloroform ($CHCl_3$), deuterochloroform ($CDCl_3$) and tetramethylsilane (TMS), Aldrich Chemical Company].

Compounding was performed by mixing single polymers and blends in a BR-size Banbury internal mixer to the formulations in *Table 1* and the conditions in *Table 2*; curatives were then added on a two roll mill, *Table 3*. Cure times were determined using a Monsanto MDR2000E rheometer at 150°C. Cure times are expressed in terms of the time required to attain a specified percentage of torque rise from the minimum torque; thus t_{50} is the time at which 50% of the total increase in torque is achieved. Vulcanisates were prepared to times varying between t_{30} and twice t_{max} by programming the rheometer to cure to the appropriate time and retaining the rheometer disc. To ensure no further curing occurred, the vulcanisate was rapidly removed from the platens and the curing quenched by immersing the disc in iced water.

Vulcanisates were stored in a freezer at –26°C and analyses were performed as soon as practically possible to ensure no further curing.

The equilibrium volume swelling of single polymer vulcanisates in $CHCl_3$ was performed at 23°C; the volume fraction of swollen rubber in the gel, v_r, was calculated by the published method[9].

Physical crosslink densities of the single polymer vulcanisates were calculated from the Mooney-Rivlin constant C_1 determined from stress-strain experiments[10]. Physical crosslink densities in the blends are calculated from H% values determined from NMR spectra.

Small slivers of vulcanisates for NMR analysis were swollen in $CHCl_3$ at 23°C for 24 h. The $CHCl_3$ was refreshed twice to perform a cold extraction in order to remove low molecular weight material. This cold extraction is required because hot extraction of vulcanisates prepared to times before rheometer maximum (pre-t_{max}) would further cure the samples, invalidating analysis. The $CHCl_3$ was then solvent exchanged for $CDCl_3$ containing TMS as an internal lock; remaining $CHCl_3$ served as an internal marker.

TABLE 1. MIX FORMULATIONS

Compound	NR1	BR2	NR/BR3	NR/BR4
SMR-CV60	100	-	50	70
BR	-	100	50	30
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
TMQ[a]	2	2	2	2

[a]Poly-2,2,4-trimethyl-1,2-dihydroquinoline.

TABLE 2. BANBURY MIX CYCLE[a]

Time (min)	Procedure
0	Add polymer/polymers
1	Add powders
2	Sweep
4	Dump

[a]Rotor speed = 116 r.p.m. Water flow rate varied to maintain temperature below 130°C.

^{1}H FT-NMR spectra were obtained using a General Electric QE300 300MHz Fourier-Transform spectrometer fitted with a ^{13}C/^{1}H dual 5 mm probe, Nicolet 1280 processor, and an Oxford Instruments 7 tesla super-conducting magnet, the data acquisition conditions of which have been reported previously[4]. The free induction decays (FIDs) were transferred to an Epson AX3S PC for manual phasing of the transformed FID, and the data were then transferred to a Prime minicomputer for further analysis. Peak widths in the ^{1}H NMR spectra were estimated by the parameter H%, which was determined using the reported method[1], but employing peak reference offsets of –0.2 p.p.m. and +0.1 p.p.m. from the olefin peak positions of NR and BR, respectively. Duplicate, or sometimes triplicate, spectra were obtained from freshly swollen samples.

Vulcanisates were prepared for the 'network visualisation' technique by following the published procedure[8]. Ultra-thin sections of the rubber/polystyrene composite were cut with freshly cleaved glass knives by using an RMC MT-7000 ultramicrotome and RMC CR-21 cryo-preparation unit operating well below the T_g of the BR phase. Specimens were collected on nickel examination grids and stained in osmium tetroxide vapour for two hours prior to examination with a Phillips EM300 TEM operating at 100 kV.

RESULTS AND DISCUSSION

The requirements for the analysis of crosslink density of a binary blend by swollen state NMR are calibration curves which relate n_{phys} to H%, for both single polymer phases of the blend, and those which relate the contributions of one polymer to the signal at the peak (P%H) and reference (R%H) positions of the other polymer to H%[1].

The calibration curves correlating H% with crosslink density from stress-strain measurements, accumulated from numerous single polymer NR and BR gum vulcanisates, are shown in *Figures 1* and *2*. The vulcanisates have base formulations NR1 and BR2, respectively, as given in *Table 1*. Over 40 different accelerated sulphur cure systems

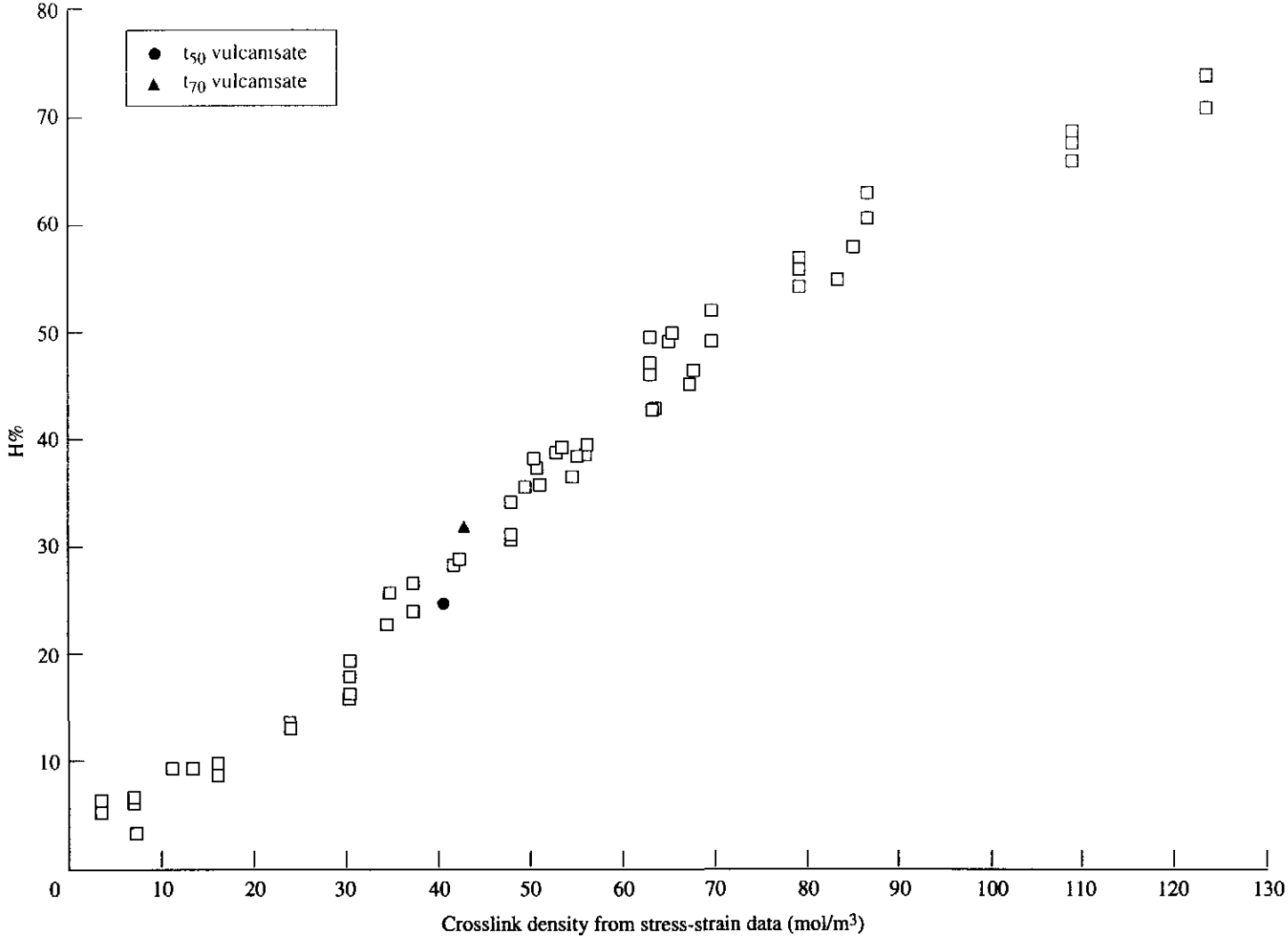

Figure 1. Dependence of H% on crosslink density for single polymer NR vulcanisates.

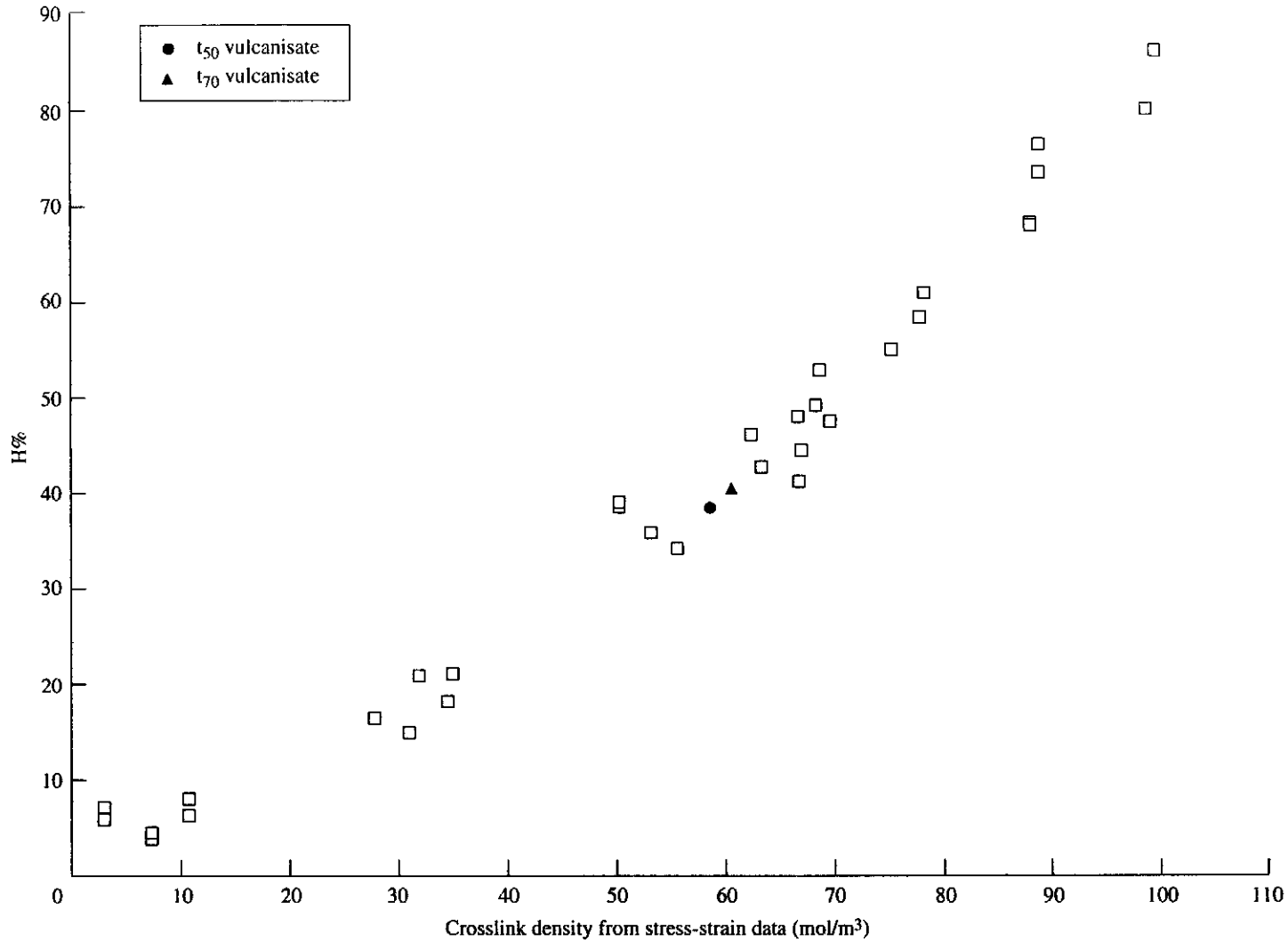

Figure 2. Dependence of H% on crosslink density for single polymer BR vulcanisates.

TABLE 3 CURATIVE LEVELS (p.h.r)

Compound	NR1, BR2, NR/BR3			NR/BR4		
	A	B	C	A	B	C
Sulphur	1.2	1.2	1.2	2.5	2.5	2.5
CBS[a]	1.2	-	-	0.6	-	-
MBS[b]	-	1.2	-	-	0.6	-
TBBS[c]	-	-	1.2	-	-	0.6

[a]N-cyclohexylbenzothiazole-2-sulphenamide

[b]N-oxydiethylenebenzothiazole-2-sulphenamide

[c]N-*t*-butylbenzothiazole-2-sulphenamide

are included which range from conventional through to efficient containing either thiuram or sulphenamide accelerators. *Figures 3* and *4* show the correlation between H% and v_r for NR and BR, respectively. *Figures 1* to *4* show curves with a narrow band of scatter (3–4H%) which correlate physical parameters with H%. These observations are consistent with previous work which showed that H% is independent of the type of accelerated sulphur cure system used[2].

Because NMR peak width, and therefore H%, depends inversely on the mobility of the polymer-chain, there is the possibility that pre-t_{max} vulcanisates may exhibit increased H% values (*i.e.* decreased mobilities) due to accelerator pendant groups which act as crosslink pre-cursors. Pre-crosslink groups would also affect v_r values due to a change in the polymer-solvent interaction parameter (χ), but n_{phys} values calculated from stress-strain measurements should be less affected.

To ensure H% is not significantly affected, stress-strain and H% measurements were performed on NR and BR vulcanisates cured to rheometer t_{50} and t_{70}. Flat sheets 2 mm thick were compression moulded from compounds NR1A and BR2A and then quenched in iced water. Stress-strain and NMR data for these samples are indicated in *Figures 1* and *2* and fit the calibration curves generated from fully cured vulcanisates. This implies that any decreased mobility caused by pendant groups is not sufficient enough to affect the relationship between H% and n_{phys}. Crosslink densities for rheometer disc samples and blends, on which no stress-strain measurements are possible, are therefore calculated from the H% against n_{phys} calibration curves.

The spectra of single polymer gum vulcanisates were analysed to determine values for the parameters P%H and R%H, which are the terms used to correct for the overlap of peaks in spectra of blend vulcanisates[1]. Multiple linear regression indicates that P%H and R%H are correlated to H% by the following polynomial equations:

for the NR olefin peak at the BR peak and reference positions;

$$P\%H = -2.72 + 0.952H\%$$

$$R\%H = -0.74 + 0.476H\% + 0.0039H\%^2$$

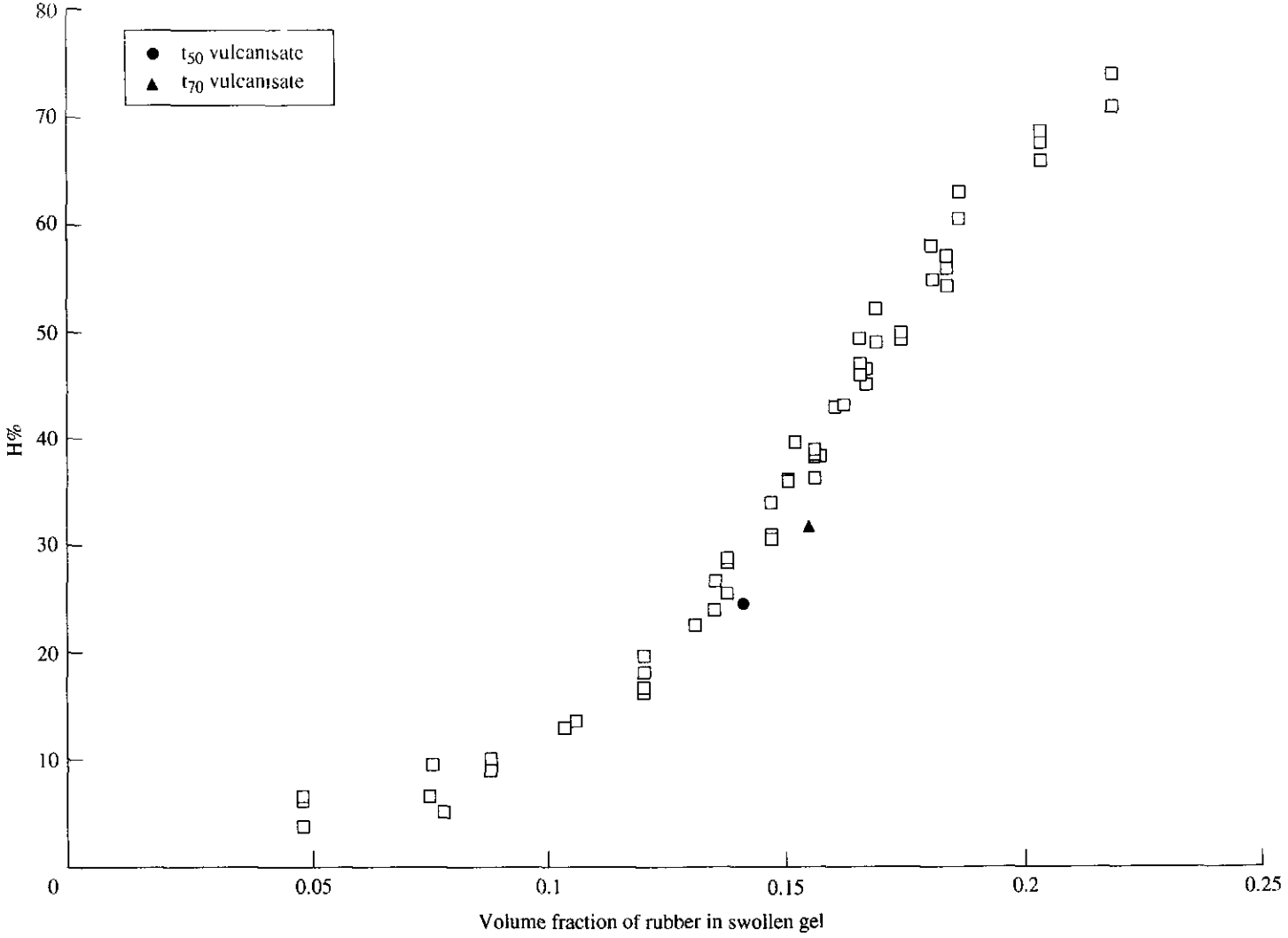

Figure 3. Dependence of H% on v_r for single polymer NR vulcanisates cured to t_{max}.

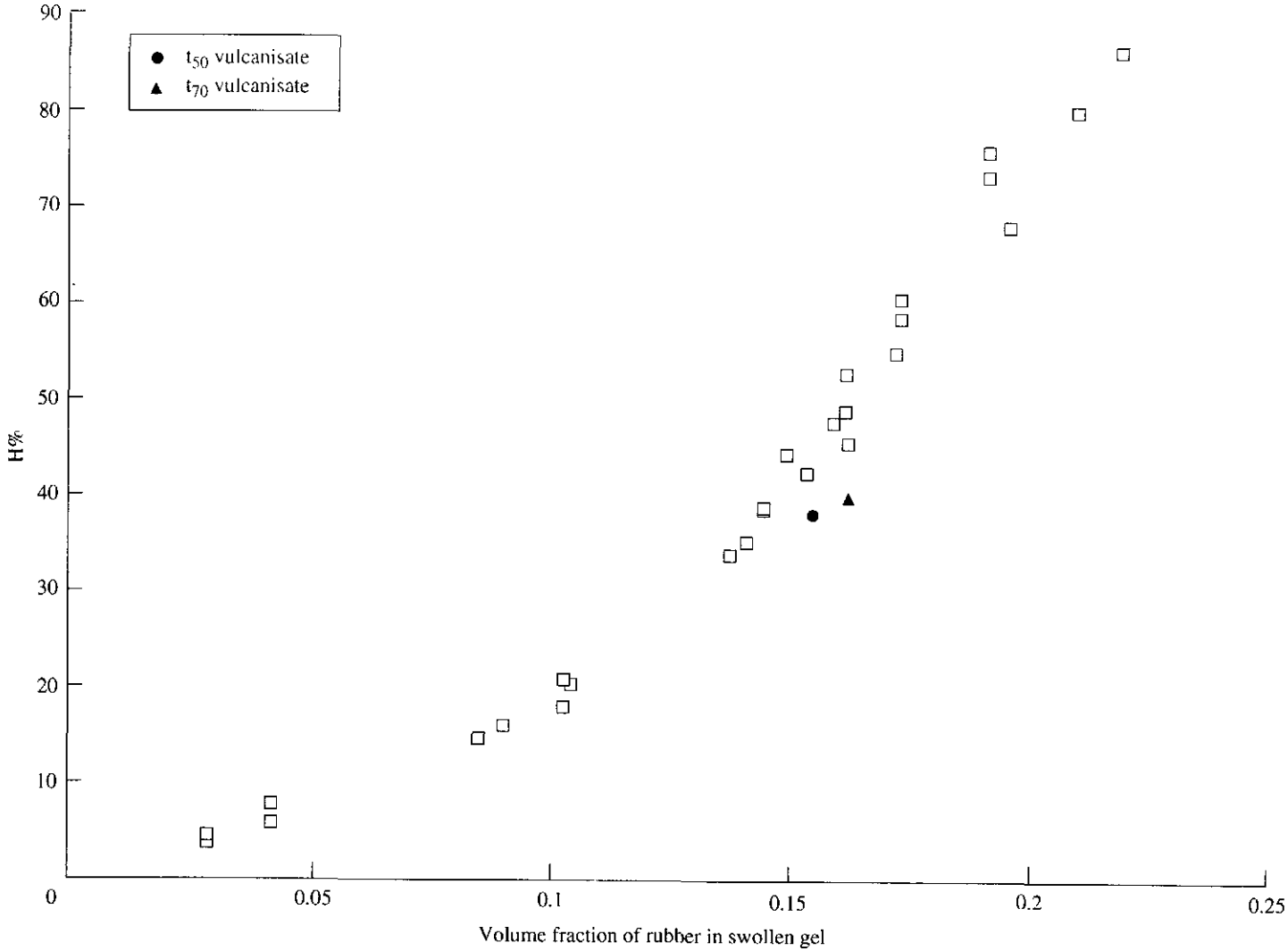

Figure 4. Dependence of H% on v_r for single polymer BR vulcanisates cured to t_{max}.

for the BR olefin peak at the NR peak and reference positions;

$$P\%H = 1.39 + 0.283H\% + 0.00582H\%^2$$

$$R\%H = 0.39 + 0.168H\% + 0.00557H\%^2$$

These equations are used in an iterative procedure to determine the H% values of each phase in blend vulcanisates[1]. H% may then be converted to crosslink density using the appropriate calibration curve.

The differences throughout cure for three different sulphur-sulphenamide combinations were studied in both single polymer and blend vulcanisates for semi-EV cure systems and in blend vulcanisates only for conventional cure systems. The accelerators considered were: N-cyclohexylbenzothiazole-2-sulphenamide (CBS), N-oxydiethylenebenzothiazole-2-sulphenamide (MBS) and N-*t*-butylbenzothiazole-2-sulphenamide (TBBS).

Single Polymers

Dependences of rheometer torque, v_r and n_{phys} (from H%) on cure time for NR vulcanisates are shown in *Table 4* and those for BR in *Table 5*. For both NR and BR, v_r data were found to fit the relationship with H% only at t_{max} (see *Figures 3* and *4*, respectively). This is expected because χ is known to vary with state of cure[11] and thus affects volume swelling. *Figure 5* shows the dependence of crosslink density (from H%) and v_r on cure time for sample NR1A. The figure shows that v_r attains high values at around t_{90} and maintains these high values on overcure, forming a plateau region. This illustrates the point that volume swelling measurements may not be used as a reliable indication of crosslink density under all cure conditions.

The values of n_{phys} (from H%) for the single polymers indicate that NR has shorter scorch times than BR and this confirms rheometric observations. At its maximum crosslink density, BR has crosslinked to a greater extent than NR with equivalent curative levels. Crosslink densities at t_{max} are similar for each single polymer regardless of accelerator and for both polymers the rate of cure is slowest with MBS accelerator as expected[12]. The data also indicate that for both polymers and all accelerators the maximum crosslink density as measured by H% is observed at times shortly prior to t_{max} generally t_{95}. Other workers[13,14] have found vulcanised physical properties, such as tensile strength, are also greater prior to t_{max}. These observations may be due to thermal lag of rheometer equipment, as suggested in reference 13, but may also be due to the method of the assessment of crosslinking. The stress-strain and swollen-state NMR measurements are performed at or close to ambient temperatures, whereas rheometry is performed at elevated temperatures. The possibility of interactions capable of acting as effective crosslinks under one set of conditions, but not the other, arises.

Blend rheometer torque values are influenced by the polymer ratio; a 70:30 NR:BR blend is likely to show torque values more indicative of the continuous phase. The BR phase may be highly cured but not influence the overall torque to a great extent because it is contained in a lower modulus matrix. For this reason rheometer torque values for blend materials may not be used as an indication of the state of cure.

TABLE 4. CROSSLINK DENSITIES OF NR VULCANISATES THROUGH THE CURE

Cure time (min)	Cure state	Torque (dNm)	V_r	H%	n_{phys}[a] (mol/m^3)
		NR1A, S/CBS			
9.0	t_{30}	1.60	0.072	15.9	25.9
9.5	t_{50}	2.95	0.095	21.2	33.1
10.3	t_{70}	4.86	0.126	32.6	47.1
13.0	t_{90}	6.63	0.145	33.7	48.5
15.0	t_{95}	6.95	0.146	34.3	49.2
23.7	t_{max}	7.11	0.146	34.3	49.3
47.4	$2t_{max}$	6.84	0.147	31.1	45.2
		NR1B, S/MBS			
14.3	t_{30}	1.31	0.052	9.0	14.4
15.2	t_{50}	2.31	0.075	18.5	29.5
16.3	t_{70}	4.24	0.101	28.6	42.2
19.7	t_{90}	6.33	0.137	36.6	52.0
22.0	t_{95}	6.80	0.139	41.5	54.0
33.0	t_{max}	7.34	0.152	35.4	50.5
66.0	$2t_{max}$	6.63	0.151	33.1	47.7
		NR1C, S/TBBS			
12.1	t_{30}	3.67	0.096	20.1	32.1
13.6	t_{50}	4.65	0.111	35.7	50.9
16.4	t_{70}	5.87	0.130	35.1	50.1
18.3	t_{90}	6.70	0.141	35.1	50.2
28.8	t_{95}	6.63	0.138	42.5	59.5
57.6	t_{max}	7.01	0.143	37.6	53.2
115.2	$2t_{max}$	6.76	0.145	30.3	44.2

[a]calculated from H% values

TABLE 5 CROSSLINK DENSITIES OF BR VULCANISATES THROUGH THE CURE

Cure time (min)	Cure state	Torque (dNm)	V_r	H%	n_{phys} [a] (mol/m^3)
		BR2A, S/CBS			
30.8	t_{30}	4.20	0.134	-	-
32.1	t_{50}	6.19	0.156	33.4	48.5
33.8	t_{70}	8.17	0.168	43.0	60.5
38.7	t_{90}	10.15	0.169	51.0	69.4
42.0	t_{95}	10.64	0.168	51 4	69 9
55.0	t_{max}	11.14	0.164	45.2	63.3
110.0	$2t_{max}$	-	0.151	42.9	60.8
		BR2B, S/MBS			
50.5	t_{30}	4.25	0.142	-	-
54 4	t_{50}	6 24	0.149	4.2	6 2
59.0	t_{70}	8.23	0.155	17.4	28.6
68.6	t_{90}	10.22	0.164	46.3	64.4
74.0	t_{95}	10.71	0.163	53.2	73.4
91.0	t_{max}	11.21	0.162	51.4	69.9
182.0	$2t_{max}$	-	0.149	43.7	61.6
		BR2C, S/TBBS			
41 0	t_{30}	4.22	0.141	14.0	22.8
44.5	t_{50}	6.22	0.148	26.7	41.3
48.0	t_{70}	8.21	0.154	39.9	48.7
56.5	t_{90}	10.20	0.166	43.5	61.1
63.0	t_{95}	10.70	0.165	52.6	70.7
80.0	t_{max}	11.20	0.167	43.2	61.1
160.0	$2t_{max}$	-	0.154	38.4	55.7

[a]calculated from H% values

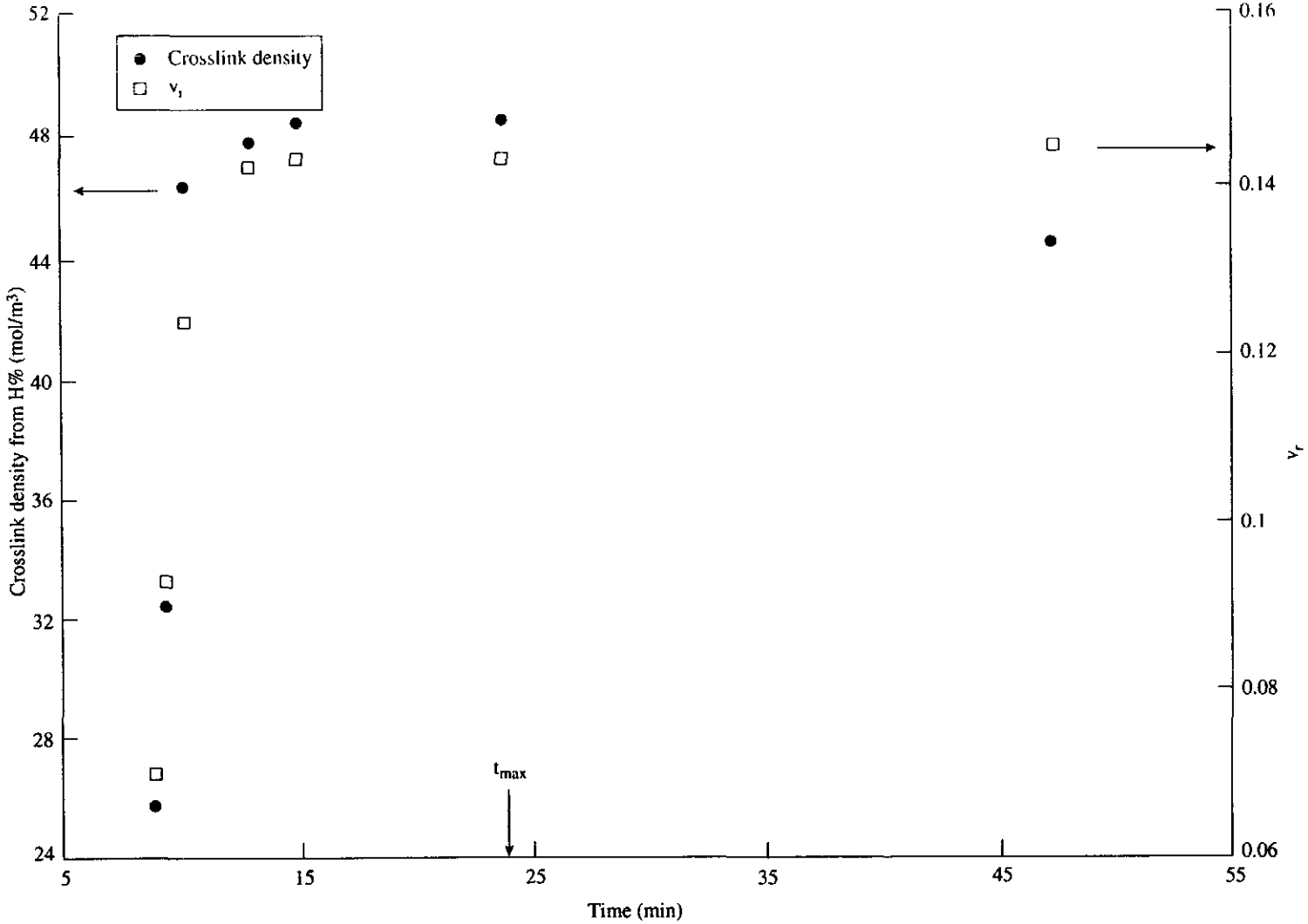

Figure 5. Dependence of crosslink density and v_r for cure time for sample NR1A.

Blends

Preferential location of accelerators within the phases of a blend occurs during mixing and their diffusion is rapid at vulcanisation temperatures; diffusion coefficients are in the range 10^{-7} to 10^{-8} cm^2s^{-1} for many curatives[15]. During the curing process the production of vulcanisation intermediates occurs, and these species will also move between the phases of blends in order to maintain their preferred distribution.

Rheometer torque and n_{phys} values (from H%) determined for NR/BR gum blend vulcanisates are shown in *Table 6* for 50:50 NR:BR blends with three differently accelerated semi-EV systems.

For all three systems the data indicate that at early stages in the cure the crosslink density of the BR phase is higher than in the NR phase. As the cure progresses the increasing difference in crosslink density of BR with relation to that in NR, indicates that initially the BR crosslinking rate is greater than the NR. Shortly after t_{50} (or t_{70} in the case of MBS accelerator) the differences in crosslink density begin to decrease, implying the relative crosslinking rates are reversed and NR is now crosslinking more rapidly. At t_{max} there is however still a bias of crosslinks in favour of the BR phase. *Figure 6* shows these effects more clearly for the S/MBS system. Note that the crosslink density value for the BR phase at t_{90} in sample NR/BR3A may be slightly high; the total crosslink density achieved in this blend exceeds that expected from the single polymers. This is not the case for the other systems.

If, in blend systems, no partition of curatives or related species occurs, then rheometer scorch times suggest that in blends the NR phase should be the first phase to cure. As the data indicate however, in blends the BR phase is the first to cure and at a faster rate than it does as a single polymer. The partitioning of sulphur between the phases of NR/BR blends is known to favour the BR phase by a factor of around 1.3 and accelerators also are more soluble in BR[16]. This suggests that diffusion of curatives and vulcanisation intermediates occurring throughout cure has the effect of delaying the onset of cure in the NR and enhancing it in the BR. The maximum crosslink densities attained are, however, close to those achieved in the single polymers. This implies that as the cure progresses there is a further movement of vulcanisation intermediates to redress the balance back to the NR phase with the net effect giving similar levels of crosslinking to the single polymers.

The rheometer scorch times of the 50:50 blends are not presented here but are approximately twice those of the single polymer NR. This suggests that some depletion of the natural activator/accelerator species present in the NR phase has occurred; migrating to the BR phase and shortening the vulcanisation induction period in the BR phase. The methylene carbons adjacent to the olefinic bond in BR are inherently more reactive than those in NR and thus once vulcanisation intermediates are produced they will react quickly with the BR.

Figure 7 shows the change in the ratio of BR:NR crosslinks (50:50 blend) with time for the three different accelerator systems. All three accelerator systems show high initial BR:NR crosslink ratios which decrease as the cure progresses. At maximum cure the BR phase is still more highly crosslinked than the NR phase

TABLE 6 CROSSLINK DENSITIES OF 50:50 NR BR BLEND VULCANISATES THROUGHOUT THE CURE

Cure time (min)	Cure state	Torque (dNm)	NR n_{phys} [a] (mol/m^3)	BR n_{phys} [a] (mol/m^3)	Difference in n_{phys} (mol/m^3)	BR:NR ratio
			NR/BR3A, S/CBS			
18.4	t_{50}	4 72	21.4	57.3	35.9	2.7
19.5	t_{70}	6 39	44.3	65.0	20.7	1.5
23.5	t_{90}	8 08	49.2	77.8[b]	28.6[b]	1.6[b]
26.0	t_{95}	8.50	47.7	64.0	16.3	1.3
37.7	t_{max}	8.92	49.9	61.4	11.5	1.2
75.4	$2t_{max}$	-	47.7	53.8	-	1.1
			NR/BR3B, S/MBS			
32.2	t_{30}	3.03	<1[c]	12 3	11 3	12.3
34.1	t_{50}	4.68	2.0	23.0	21.0	7.6
36 3	t_{70}	6.33	38.4	67.1	28.7	1.7
41.3	t_{90}	7 97	52.4	78.4	26.0	1 5
44.2	t_{95}	8.38	50.4	71.4	21.0	1 4
57.9	t_{max}	8.81	48.0	65.9	17.9	1.3
115.8	$2t_{max}$	-	55.9	47.8	-	0.9
			NR/BR3C, S/TBBS			
23.1	t_{30}	2 83	26.4	51.8	25.4	2.0
24 1	t_{50}	4.42	31.6	64.7	33.1	2.0
25.7	t_{70}	6.00	40.0	65.9	25.9	1.6
29.7	t_{90}	7.58	48.3	68.3	20.0	1.4
32.1	t_{95}	7.97	56.1	62.0	5.9	1.1
43.7	t_{max}	8.37	46.4	56.3	9.9	1.2
87.4	$2t_{max}$	-	53.7	42.0	-	0.8

[a]Calculated from H% values

[b]BR n_{phys} value possibly in error, see text

[c]Beyond range of calibration curve

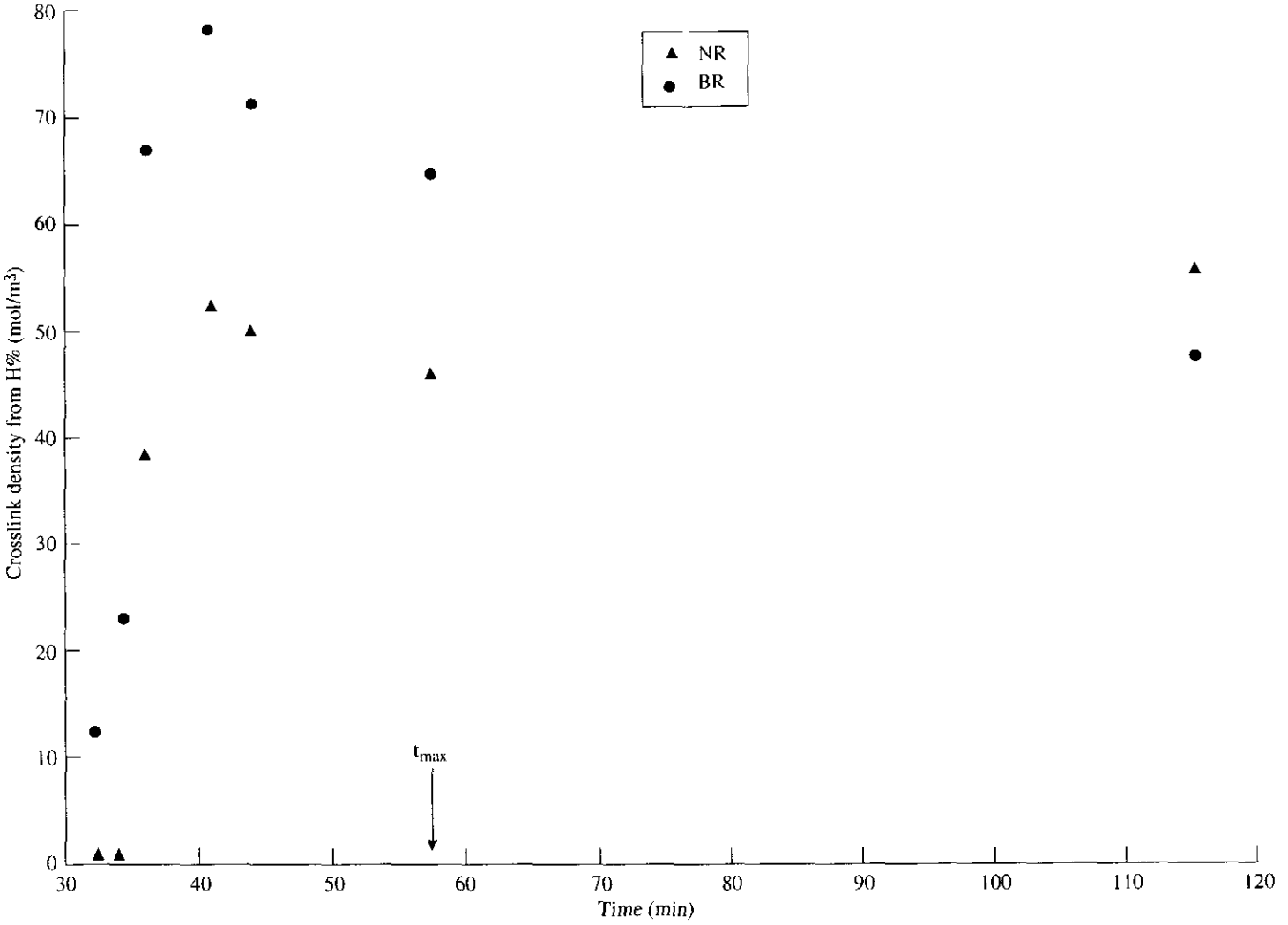

Figure 6. Dependence of crosslink density on cure time for both phases of sample NR/BR3B (50:50 blend, S/MBS cured).

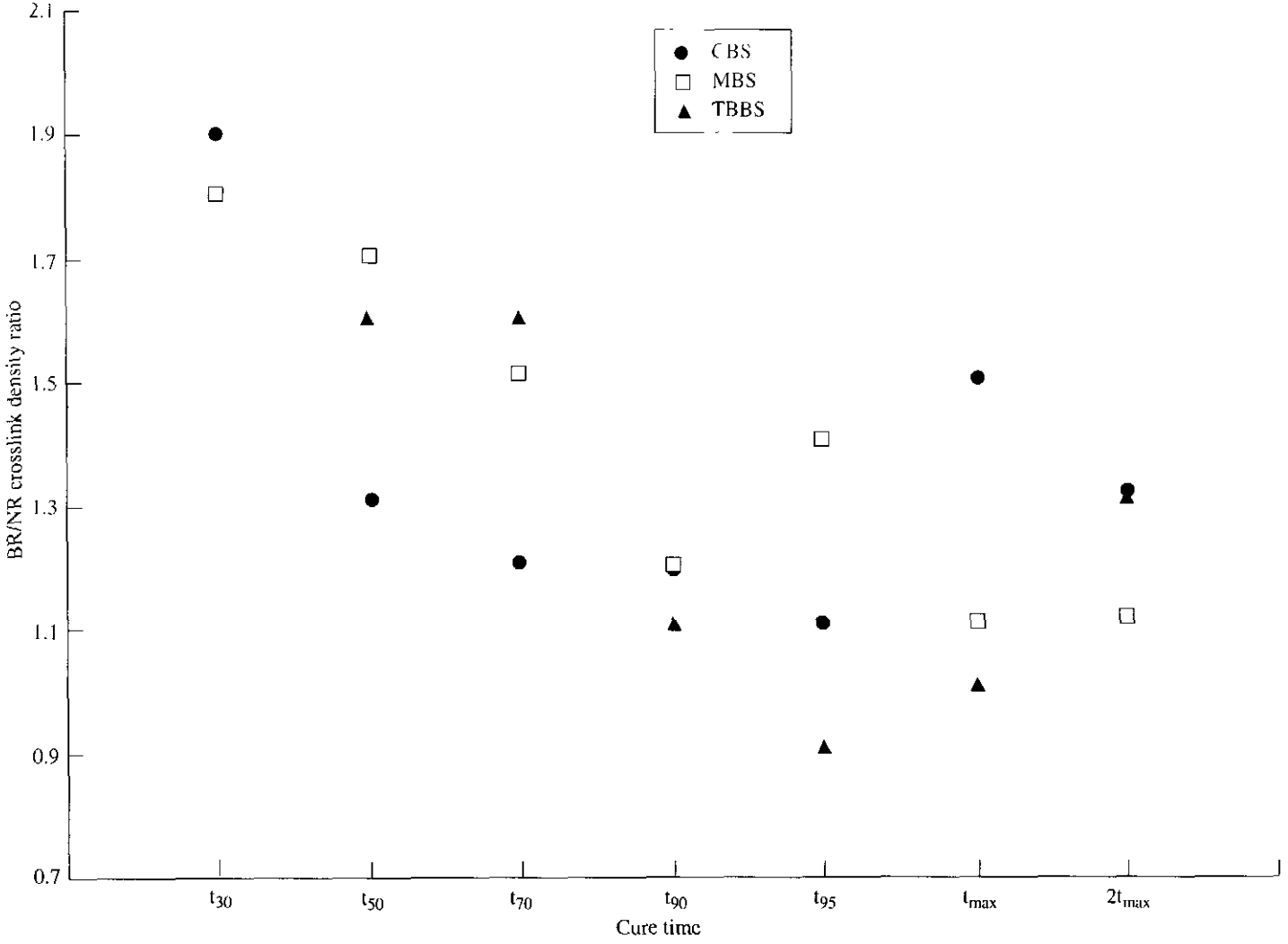

Figure 7. Variation of BR:NR crosslink density ratio on cure time for NR:BR 50:50 blends.

and the crosslink densities are very similar to those found for the single polymers with identical cure systems. McGill and co-workers used DSC either alone[5] or in combination with solvent swelling[6] to investigate 50:50 NR:BR and IR:BR blends and also found a higher crosslink density in the BR phase compared to that in the NR or IR phase.

Data for blends with a higher NR content (70:30) and vulcanised with conventional sulphur cure systems are presented in *Table 7*. *Figure 8* shows the variation of crosslink density (from H%) within the phases throughout the cure for the S/MBS system. The observations are similar to those for the 50:50 blend; crosslink densities are higher in the BR than the NR phase at maximum cure, and higher crosslink densities are attained in the BR at an early stage. One slight difference is that the BR:NR crosslink ratios are generally lower for 70:30 blends. This is seen more clearly by comparing *Figures 7* (50:50 blends) and *9* (70:30 blends) which depict the change in crosslink ratio with time. The difference may be due to the lower levels of accelerators in the 70:30 blends and this supports the suggestion that the partition of accelerator species in favour of BR is an important factor.

Shersnhev[7] and co-workers have investigated 70:30 polyisoprene(IR):BR blends by using the swollen-state NMR technique to study crosslink formation throughout the cure. Higher crosslink densities were reported for the BR phase of fully cured materials than in this work. The workers did not find that BR is the first phase to start curing in the blend system. This may be due to the differences between NR and IR. IR does not contain the natural activator/ accelerators that are present in NR and thus movement of such species to enhance the BR crosslinking may not occur.

In order to verify that BR is the more highly crosslinked phase at short cure times a cured sample was studied[8] using 'network visualisation'. *Figure 10* is a micrograph of a swollen/polymerised stained section from sample NR/BR4A cured to t_{30}. The dark mesh structure is stained polymer network and the light region the unstained polystyrene. The micrograph shows quite clearly that there is a large difference in the mesh structure of the two phases. Morphologically NR:BR 70:30 blends are comprised of discrete regions of BR within a continuous NR phase and when swollen, the BR phase will remain as discrete regions. *Figure 11* indicates that the discrete regions have the more tightly knit mesh. A tightly knit mesh structure indicates a high crosslink density and a more open structure indicates a low crosslink density, therefore the BR phase has the greater crosslink density. Thus the microscopy technique supports the NMR evidence in favour of a highly crosslinked BR phase in NR/BR blends at early stages of cure.

CONCLUSIONS

Swollen-state NMR spectroscopy may be used to assess NR, BR and NR/BR blend crosslink density formation throughout cure for different sulphur-accelerator cure systems.

Single polymer NMR data indicate maximum crosslink densities are achieved slightly prior to t_{max} as determined by rheometry. This is in agreement with other workers who have shown physical properties to peak shortly before t_{max}[13,14].

Blend NMR data indicate that, in the two phase system, BR initially crosslinks more rapidly than NR for all cure systems and this

TABLE 7. CROSSLINK DENSITIES OF 70:30 NR:BR BLEND VULCANISATES *THROUGHOUT THE CURE*

Cure time (min)	Cure state	Torque (dNm)	NR n_{phys}[a] (mol/m^3)	BR n_{phys}[a] (mol/m^3)	Difference in n_{phys} (mol/m^3)	BR:NR ratio
			NR/BR4A, S/CBS			
9.7	t_{30}	3.19	19.2	37.1	17.9	1.9
10.8	t_{50}	4.78	30.3	40.1	9.8	1.3
12.2	t_{70}	6.35	39.1	46.7	7.6	1.2
15.4	t_{90}	7.93	50.4	59.6	9.2	1.2
17.2	t_{95}	8.33	59.3	63.9	4.6	1.1
23.8	t_{max}	8.73	50.5	73.6	23.1	1.5
47.5	$2t_{max}$	7.95	45.4	60.3	-	1.3
			NR/BR4B, S/MBS			
10.4	t_{30}	3.18	10.7	19.5	8.8	1.9
12.0	t_{50}	4.71	21.9	36.7	14.8	1.7
13.8	t_{70}	6.24	36.1	55.3	19.2	1.5
17.2	t_{90}	7.77	50.9	63.4	12.5	1.2
19.1	t_{95}	8.15	51.5	70.2	18.7	1.4
26.3	t_{max}	8.53	55.0	62.2	7.2	1.1
52.6	$2t_{max}$	7.75	48.4	51.8	-	1.1
			NR/BR4C, S/TBBS			
11.6	t_{30}	3.01	<1[b]	7.3	6.3	7.3
13.0	t_{50}	4.43	17.9	28.7	10.8	1.6
15.0	t_{70}	5.85	32.5	53.4	20.9	1.6
18.9	t_{90}	7.27	45.7	48.6	2.9	1.1
21.2	t_{95}	7.62	55.5	51.8	-3.7	0.9
29.6	t_{max}	7.98	50.9	48.4	-2.5	1.0
59.1	$2t_{max}$	7.13	38.1	51.2	-	1.3

[a]Calculated from H% values

[b]Beyond range of calibration curve

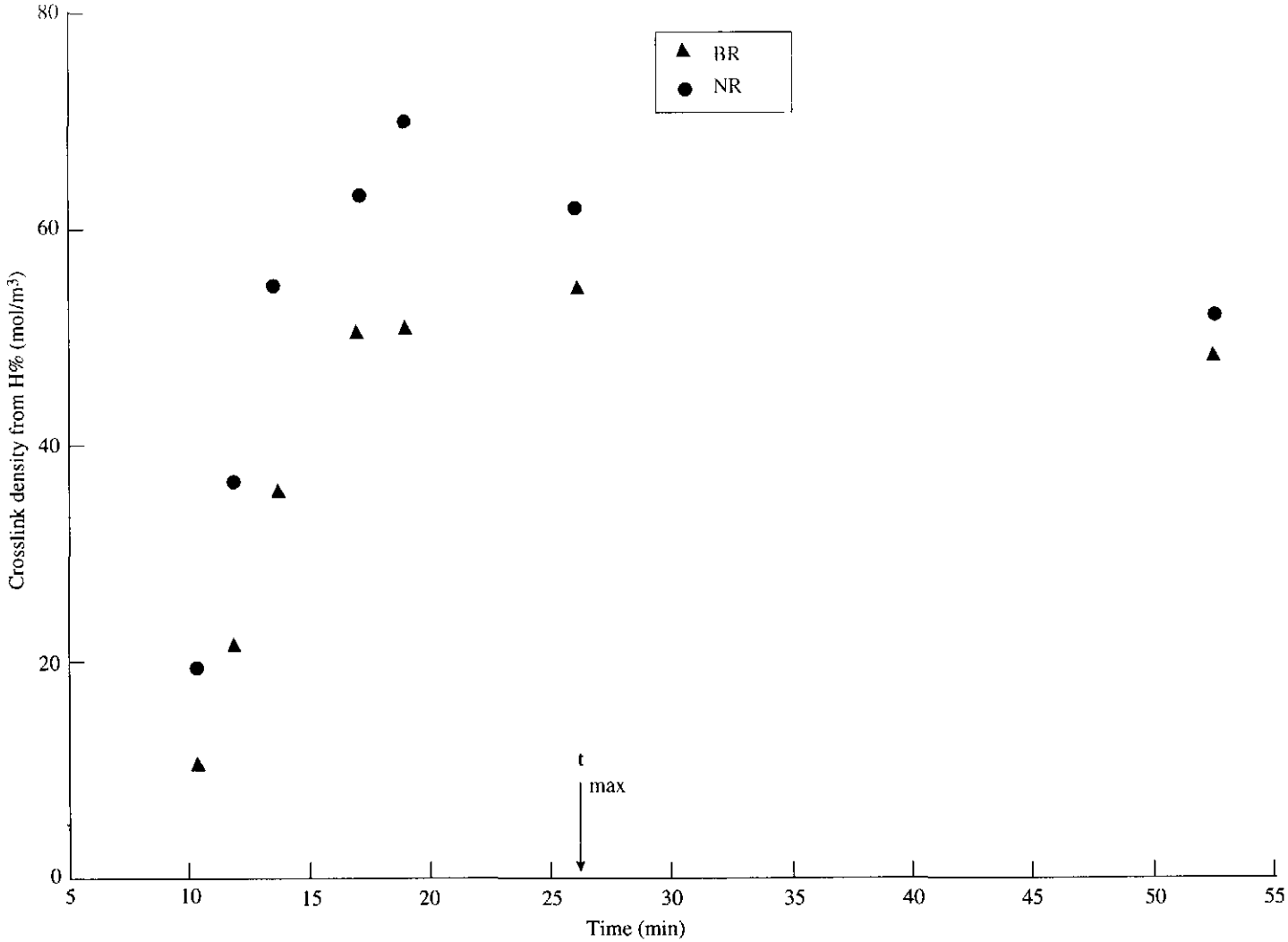

Figure 8. Dependence of crosslink density on cure time for both phases of sample NR/BR4B (70:30 blend S/MBS cured).

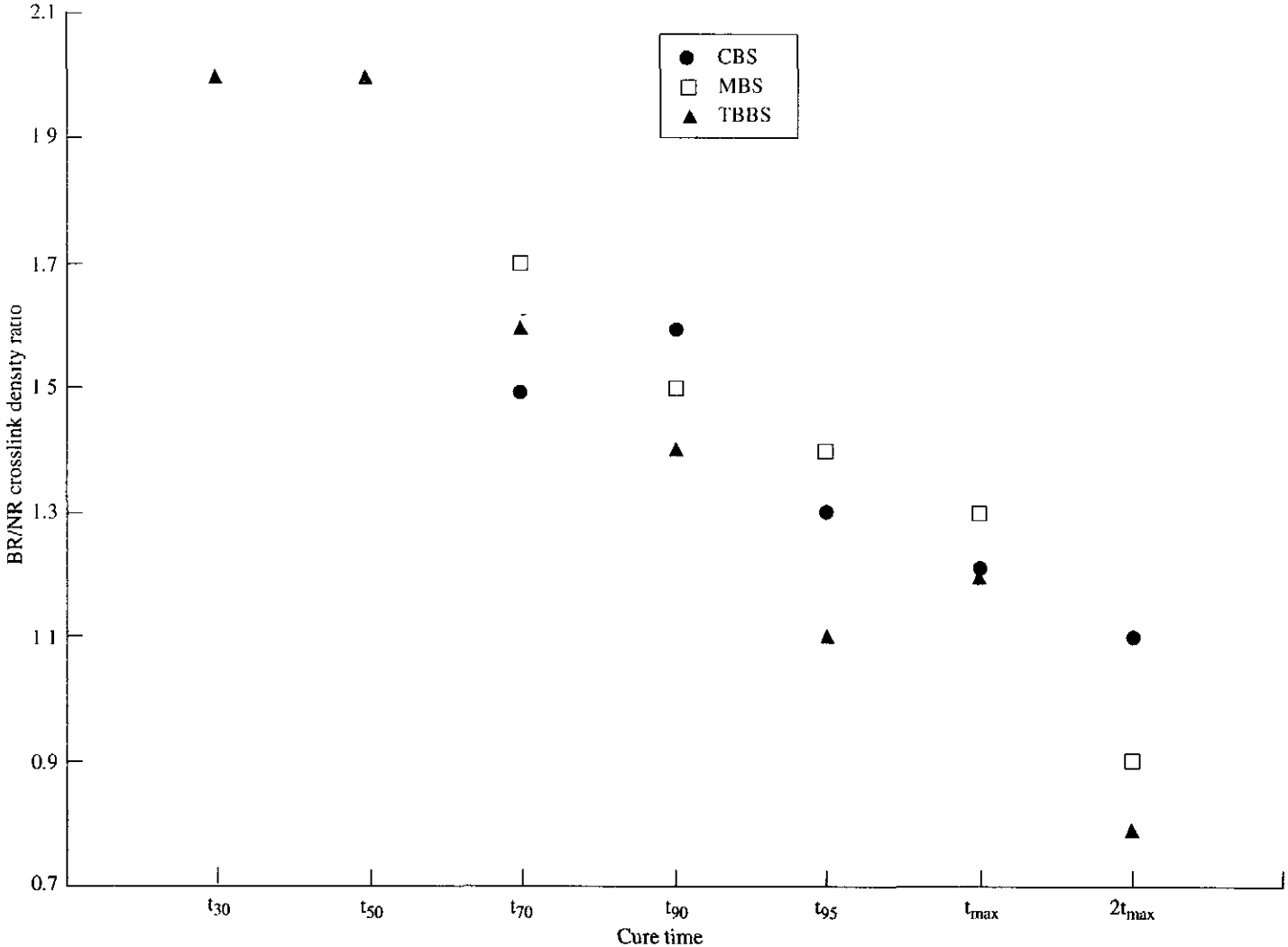

Figure 9. Variation of BR:NR crosslink density ratio on cure time for NR:BR 70:30 blends.

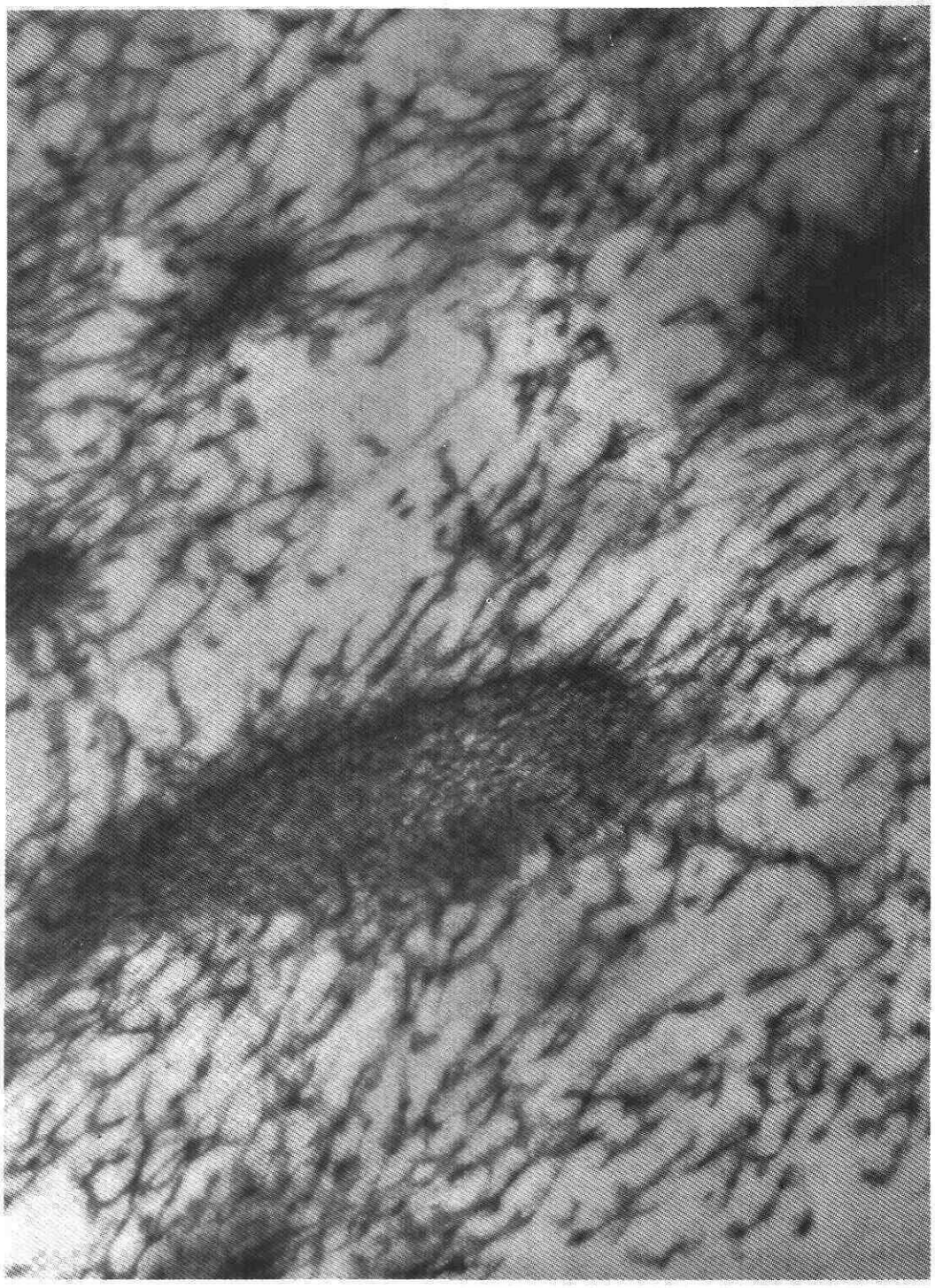

Figure 10. TEM micrograph of a swollen/polymerised t_{30} sample of NR/BR4A indicating the network density is different for the two phases.

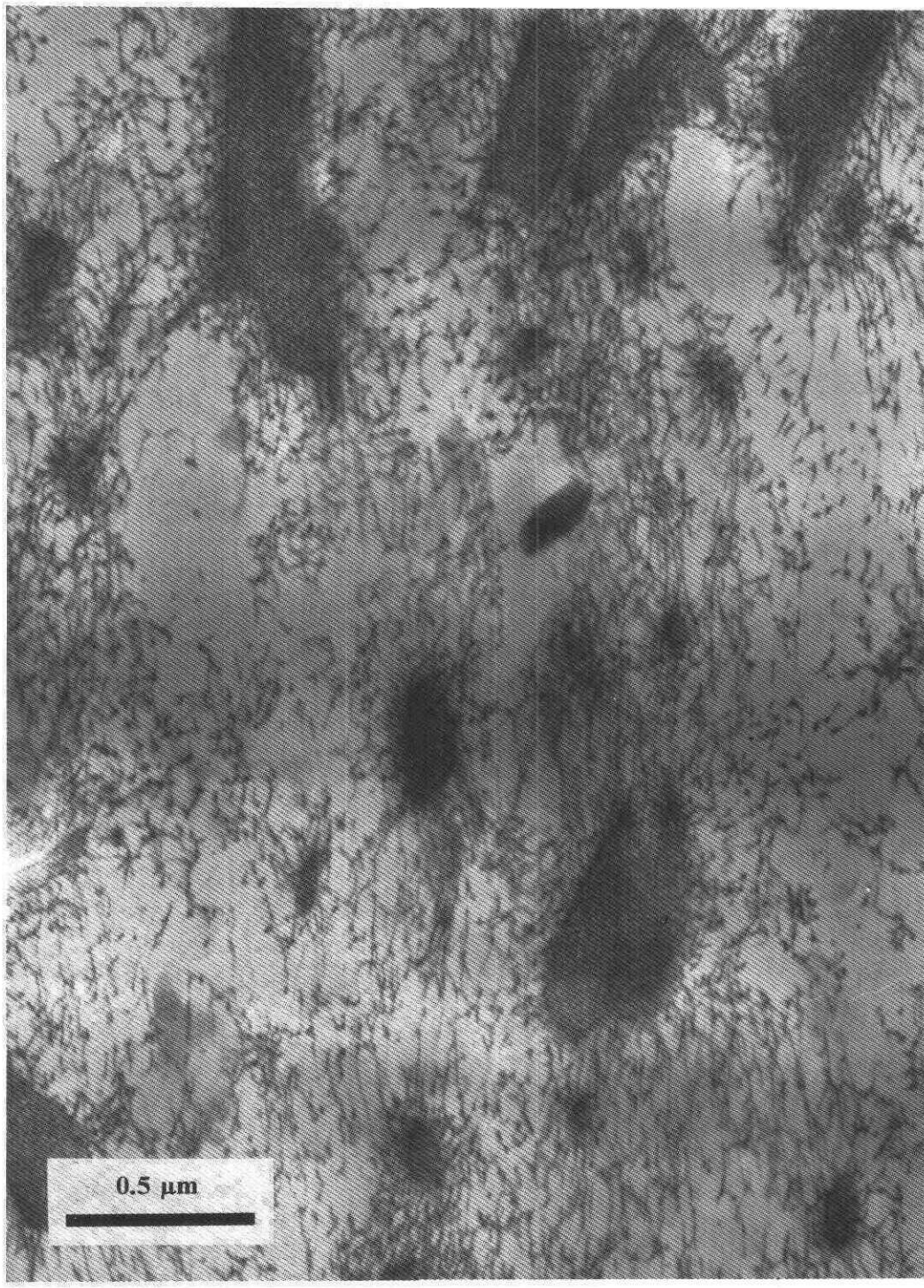

Figure 11. TEM micrograph of a swollen/polymerised t_{30} sample of NR/BR4A showing the morphology of the 70:30 blend.

has been confirmed by the 'network visualisation' technique. This may be due in part to increased partitioning of sulphur and accelerators in favour of the BR, but also to natural activators/solubilisers present in NR diffusing into the BR phase. Reducing the level of accelerator in the blends decreases the initial difference in crosslink density and supports the suggestion of curative migration. As the cure progresses in the blends the NR phase cures more rapidly than the BR and the initial large differences in crosslink density are reduced. At maximum cure BR is still the more highly crosslinked phase. Where comparison is possible the crosslink densities in the blend at maximum cure are comparable to those indicated by single polymers.

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