J. nat Rubb. Res., 5(4), 286–295

Factors Affecting the NMR Technique for Estimation of Crosslink Density in Rubber Blends

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

The effects of cure system, polymer molecular weight and restriction of swelling on the NMR spectra of swollen rubber vulcanisates have been investigated using a recently published technique[1]. Within a single polymer type, cis*-polyisoprene or* cis*-polybutadiene, the accelerated-sulphur cure systems produce vulcanisates having the same relationship between the volume fraction of rubber in the equilibrium swollen state (*Vr*) and a measure of line width, H%[1]. Swelling to less than equilibrium uptake results in a higher H%, but the increase is a relatively weak function of degree of swelling and this permits confident use of the technique in the analysis of crosslink distribution in polymer blends.*

For most practical purposes, rubber goods are manufactured from blends of two or more dissimilar polymers. In such blends, the physical properties are determined not only by the properties of the individual component rubbers, but also by the physical structure of the blend. To fully understand the behaviour of the blend, this physical structure must be known. Suitable techniques to determine the blend morphology and filler distribution[2] and the degree of interfacial bonding[3] are well established. Recent papers[1,4] report the first method for directly determining the distribution of crosslinks between the phases of a blend.

This new technique correlates the line widths observed in a continuous-wave ^{1}H-NMR spectrum of a blend vulcanisate to the *Vr* of each phase in chloroform, or to the curative concentration in the individual phases of the blend, by comparison with data from single polymer vulcanisates of the blend components. For practical convenience, the measure of line width is a ratio of signal intensities (H%)[1], and H% is observed to increase smoothly with *Vr* in single polymer vulcanisates. It is believed that the observed line broadening is a consequence of the reduction of mobility of the polymer chain segments effected by the crosslinking network. This results in the incomplete averaging of the magnetic fields of neighbouring atoms, both in the same chain and on adjacent chains, producing local magnetic field inhomogeneities within the sample. The consequent chemical shift anisotropies are responsible for the observed peak broadening; increased crosslinking leads *via* further restriction of chain mobility to increased H% values. Recent work using ^{13}C-NMR spectroscopy to investigate swollen poly (sodium acrylate) gels supports this view[5,6].

For the technique to be useful in the field of polymer blend analysis, the factors affecting H% need to be understood. Various factors may influence H% through their effect on chain segment mobility. Accelerated-sulphur cure systems are known to produce chemical modification of the polymer backbone; these modifications include *cis-trans* isomerisation, the formation of conjugated polyenes and cyclic sulphides, and the addition of pendent groups to the chain[7]. Such modifications may well alter the chain segment mobility. It is possible that the potential equilibrium swelling of the phases of a blend differ due to differences in crosslink density and/or polymer-solvent interaction parameter. The *Vr* of the individual phases attained at equilibrium swelling of the blend may then differ from the

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

Vr that single polymer vulcanisates of similar crosslink density would attain, and this may affect the value of H%.

Many rubbers degrade during mixing[8] and the reduction in molecular weight will decrease the concentration of physically effective crosslinks by reducing the entanglement contribution to the network. Thus *Vr* will be reduced, but the effect on H% is less certain.

This paper aims to investigate the effect of these factors on the NMR spectra obtained from swollen rubber vulcanisates, and thereby explore the applicability of CW-^{1}H NMR spectroscopy to the study of vulcanised rubber blends. To simplify the analyses of the data, only single polymer vulcanisates were used in this study, but the results are applicable to blend systems.

EXPERIMENTAL

The rubbers used in this study were SMR L, SMR CV, SMR 10, *cis*-1,4 polyisoprene (SKI 3 high *cis*-1,4 polyisoprene, Tyre Research Institute, Moscow) and *cis*-1,4 polybutadiene (BR) (Europrene *cis*, 94% *cis*-1,4 polybutadiene, Enichem). Rubber chemicals were standard commercial-grade materials, solvents of AR grade except for the NMR solvents which were of spectroscopic grade [deuterium oxide (99.996 %D), deutero-chloroform and hexamethyldisiloxane (HMDS) Aldrich Chemical Company], and di-isopropylazodicarboxylate (DIAD) which was used as supplied by Aldrich (97%). Cyclo-hexylammonium benzothiazole-2-thiolate (CBM) was prepared according to the published method[9].

Chemical Modification of SMR L

Peroxide-cured vulcanisate: 1.4 g of a peroxide-cured SMR L vulcanisate was allowed to swell to equilibrium in toluene in the dark at 4°C. The toluene was replaced with a cold solution of DIAD in toluene (6 g/litre, the solution strength being chosen to produce a DIAD concentration of 3 g in 100 g rubber; ~1 mol%), and the sample stored for 2 h at 4°C. The sample was removed from the solution and the solvent removed in a current of air for 2 h. It was stored *in vacuo* for 72 h, during which time the azo-ene reaction of DIAD and the rubber olefin group occurred[1,2], before being extracted with methanol using a cold Soxhlet apparatus, and then dried *in vacuo* to constant weight. Infra-red analysis indicated the presence of some main-chain modification, as evinced by carbonyl absorption characteristic of the 'ene' adduct, but at a level too low to quantify (< 1 mol%). A second specimen was similarly treated, omitting the DIAD from the second toluene fraction, to serve as a control vulcanisate.

Solution: 110 g of lightly milled SMR L was cut into small pieces and added to a cold solution of DIAD in toluene (3.5 g in 500 ml, 3.2 g/100 g rubber). The solution was kept at 4°C while the rubber absorbed the solvent. The resulting gel was then left in the dark at room temperature for 48 h to complete the modification reaction. The rubber was recovered by adding 1500 ml toluene and then precipitating with methanol. The swollen mass was washed several times with methanol before being dried *in vacuo* to constant weight. Infra-red analysis confirmed the presence of the modification but at a level below 1 mol%. This material was then compounded with 1.2 p.p.h.r. dicumyl peroxide and vulcanised in the usual way.

Compounding (*Tables 1* and *2*) was performed using a BR-size Banbury mixer and/or a two-roll mill, the curatives being added on a two-roll mill.

Samples 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 $CDCl_3$ in an 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 $CHCl_3$ as an internal marker and HMDS as an internal lock was added just prior to acquisition of the spectrum.

TABLE 1. FORMULATIONS OF *CIS*-POLYISOPRENE VULCANISATES

Entry	Type[a]	System	Ratio (w/w)	Sulphur (p.p.h.r.)[b]	Cure Temp (°C)	Time (min)
1	CON	S-CBM	1:16	1.0	70	420
2	CON	S-MBS	5:1	1.5–2.5	140	d
3	CON	S-TMTM	5:2	1.5	150	d
4	SEV	S-MBS	1:1	0.25–2.0	150	d
5	SEV	S-CBS	1:1	1.0	150	d
6	EV	S-MBS	1:15	0.2, 0.4	150	d
7	Novor[11]	Novor 924[c]-ZDMC	10:3	3.35, 6.7	160	d
8	Peroxide	Dicumyl peroxide	-	1–1.8	150	120

Entries 1–6 based on zinc oxide, 5 p.p.h.r.; Stearic acid, 2 p.p.h.r. and Flectol-H, 2 p.p.h.r.
Entry 7 based on zinc oxide, 5 p.p.h.r.; Stearic acid, 1 p.p.h.r.; Flectol-H, 2 p.p.h.r. and Caloxol W5G, 3 p.p.h.r.

[a] CON: conventional, high sulphur; low accelerator ratio
EV: efficient, low sulphur: high accelerator ratio
SEV: semi-EV, intermediate sulphur: accelerator ratio

[b] Concentration of Novor 924 in Entry 7 or dicumyl peroxide in Entry 8

[c] Supplied by Rubber Consultants, Brickendonbury, Hertford, SG13 8NL, UK

[d] Cured to the maximum torque on a Gottfert Elastograph

TABLE 2. FORMULATIONS OF *CIS*-BR VULCANISATES

Entry	Type[a]	System	Ratio (w/w)	Sulphur (p.p.h.r.)[b]	Cure Temp (°C)	Time (min)
1	SEV	S-MBS	1:1	0.4–2.3	150	b
2	Peroxide	Dicumyl peroxide		0.3, 0.6	150	120

Entry 1 formulated as per Entries 1–6 in *Table 1*
SEV: semi-EV, intermediate sulphur: accelerator ratio

[a] Concentration of dicumyl peroxide in Entry 2

[b] Cure time as per *Table 1*

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[10].

The NMR spectra were obtained using a Perkin-Elmer R32 90 MHz continuous-wave spectrometer, interfaced to a BBC micro-computer 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 natural rubber (NR) and BR respectively *(Figure 1)*.

Sub-equilibrium swelling experiments were performed by allowing a rubber sample (0.5 × 15 × 15 mm) to swell in insufficient $CDCl_3$ to allow equilibrium uptake to be reached. A small sliver was cut from the piece and immediately placed in an NMR tube containing D_{20} and a small amount of the sodium salt of 2,2,3,3 tetradeutero-3-trimethylsilylpropionic acid as the internal lock. The remaining swollen sample was accurately weighed and then dried *in vacuo* to allow the degree of swelling, *Vr'*, to be determined. The ^{1}H-NMR spectrum of the sub-equilibrium swollen sample suspended in D_{20} was recorded as above, but combining only twelve transients to minimise solvent loss during the experiment. The olefin peak was observed to move upfield as the *Vr'* of the sample increased, presumably as a consequence of the changing ratio of the solvents D_{20} and $CDCl_3$ in the NMR tube. Account was taken of the movement of the peak when measuring H%, the reference offset used to determine H% was 0.2 p.p.m.

RESULTS AND DISCUSSION

The possible effect of type of cure system, within the family of accelerated-sulphur systems, on the correlation between H% and *Vr* for polyisoprene vulcanisates is considered in *Figure 2*. The accelerators used include various sulphenamides and a thiuram monosulphide, and a range of accelerator: sulphur ratios was used to produce different network structures[7] *(Table 1)*. The CBM system is known to produce fully polysulphidic networks, typical of a conventional sulphur vulcanisate, but with accelerator-terminated pendent groups as the only type of main-chain modification[9]. The H%–*Vr* data for all of these vulcanisates are found to lie on a smooth curve, as did those for vulcanisates produced using a urethane (Novor) cure system[11]. This important observation is crucial to the successful application of the NMR technique to blend vulcanisates, because the vulcanisation chemistry operating in the individual phases is likely to be different both from each other and from that expected in the single polymers. The H%–*Vr* correlation is independent of the grade of NR used; indeed synthetic high *cis*-1,4 polyisoprene (SKI 3) obeys this same relationship *(Figure 2)*.

When a peroxide-cure system is used, the resulting vulcanisates have H% values significantly lower than their accelerated-sulphur analogues *(Figure 3)*. This difference is not observed in *cis*-BR, for which the semi-EV S/MBS vulcanisates and the dicumyl peroxide vulcanisates share the same H%–*Vr* correlation *(Figure 4)*. This different behaviour of the two polymers may be associated with the methyl group of the polyisoprenes; it cannot be due to non-hydrocarbon materials in the natural rubber since SKI-3, a synthetic high *cis*-1,4 polyisoprene, displays the same response to type of cure system as NR *(Figures 2* and *3)*.

A possible cause of the lower H% values of peroxide-cured NR vulcanisates relative to sulphur-cured vulcanisates of comparable crosslink density is the presence of backbone modifications in the latter vulcanisate type. The only polymer modification expected in the CBM vulcanisate is the addition of pendent groups to the backbone chains[9], and the CBM vulcanisate obeys the H%–*Vr* correlation of the other accelerated-sulphur-cured vulcanisates. Pendent groups would seem to be the functionality introduced during accelerated-sulphur vulcanisation responsible for the greater H% values than were observed for peroxide vulcanisates.

This hypothesis was tested by introducing pendent groups onto the main chains of a peroxide-cured vulcanisate of SMR L using the well established 'ene' reaction of an azodicarboxylate with the olefin group on the polyisoprene chain[12]. The modification was also performed on uncured SMR L rubber which was subsequently vulcanised using dicumyl peroxide. H% values for these pendent-modified, peroxide-cured vulcanisates

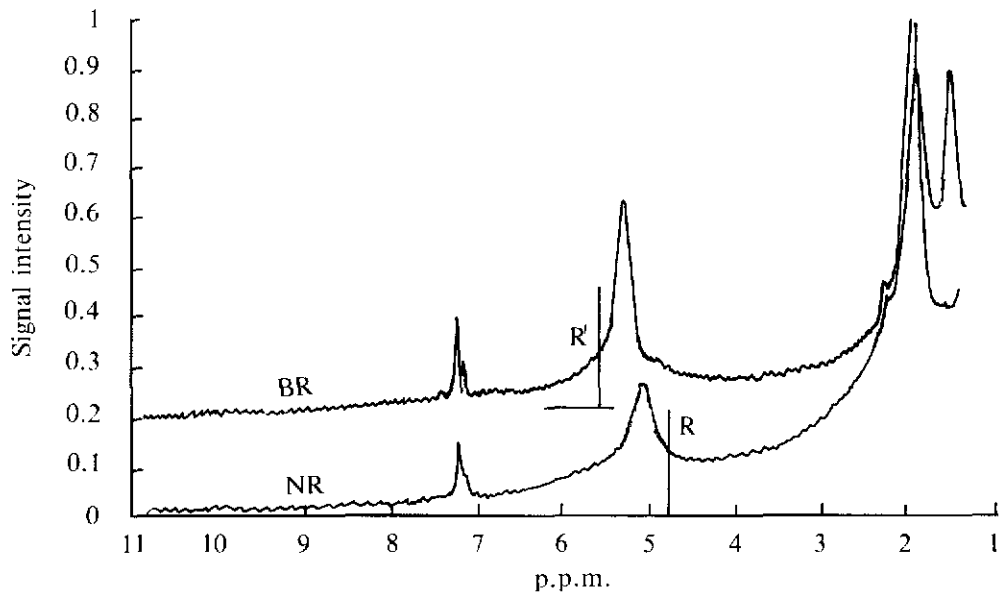

Figure 1. Continuous-wave ^1H NMR spectra of natural rubber (NR) and cis-BR (BR) swollen to equilibrium in deutero-chloroform. The BR spectrum is displaced in intensity for clarity. The reference position used to calculate H% is shown on the side of each olefin peak (R and R' for NR and BR respectively). Both vulcanisates were cured using the semi-EV S/MBS cure system with 0.825 p.p.h.r. sulphur.

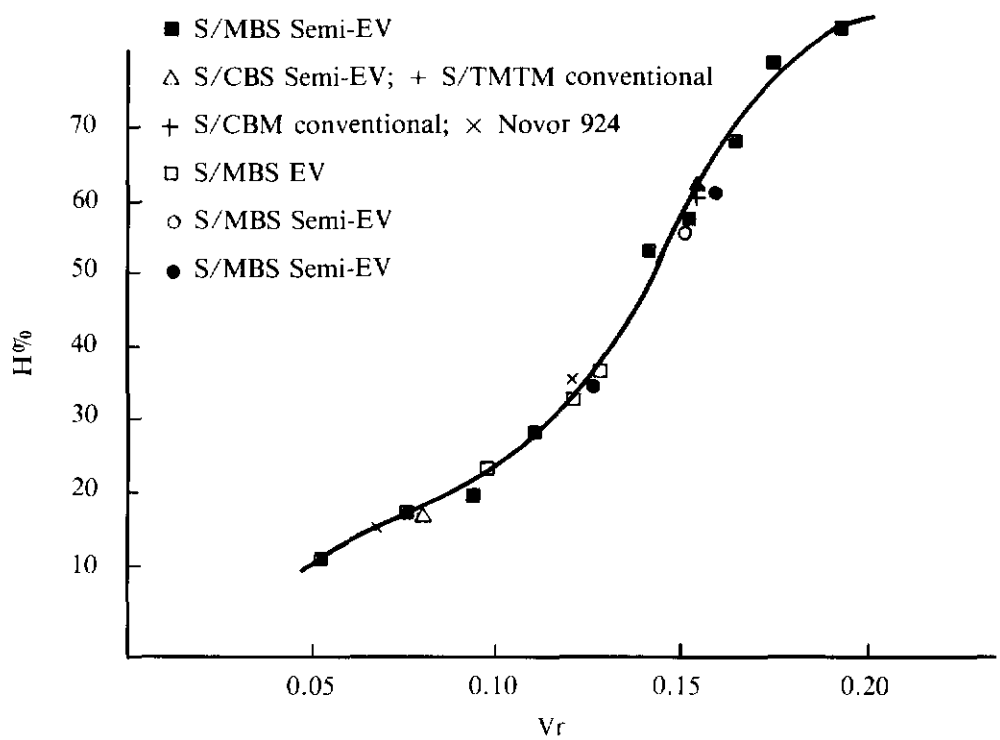

Figure 2. H% versus Vr in chloroform for accelerated sulphur cis-polyisoprene (PI) vulcanisates.

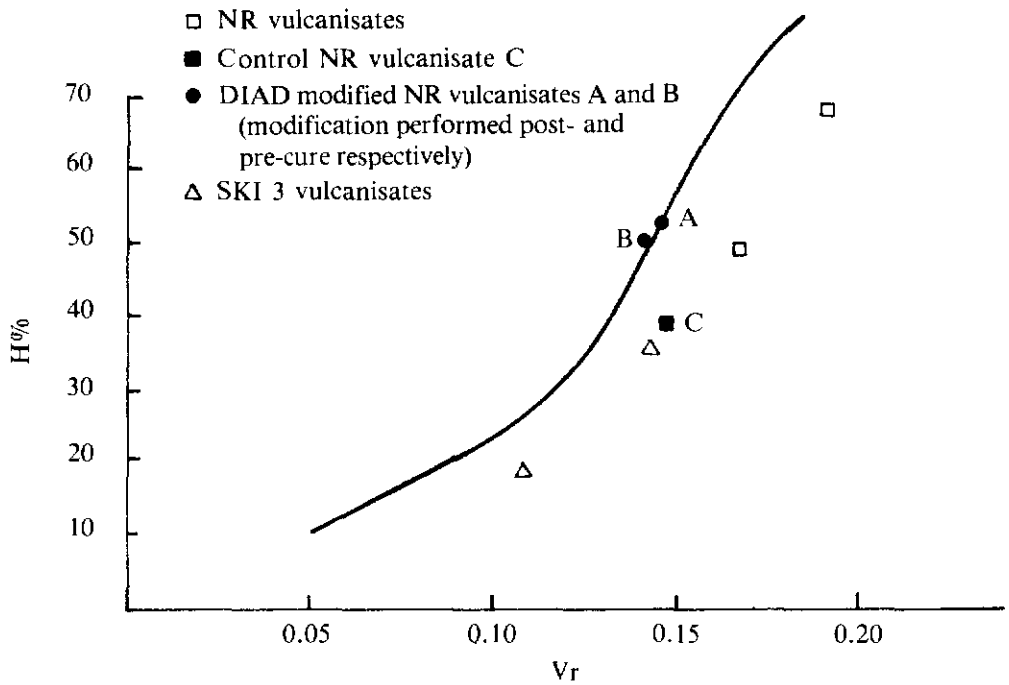

Figure 3. H% versus Vr in chloroform for peroxide-cured PI vulcanisates. The line represents the curve of Figure 2.

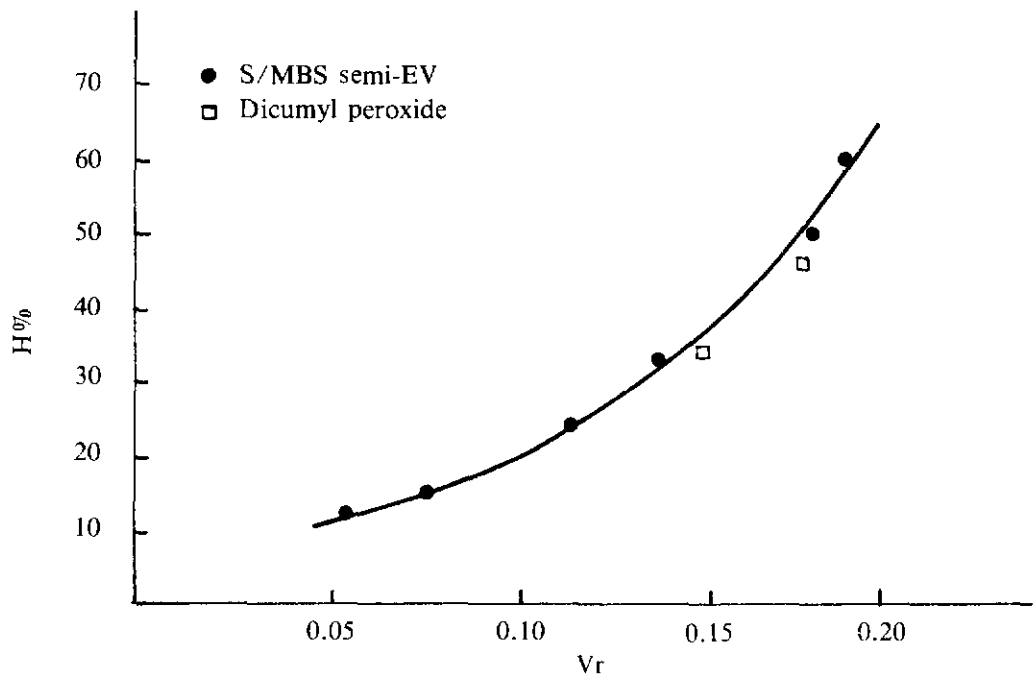

Figure 4. H% versus Vr in chloroform for BR vulcanisates.

(*A* and *B*) are higher than that of an unmodified, peroxide-cured control vulcanisate *(C)* of similar *Vr*, and are in accord with the correlation of H% and *Vr* of the accelerated-sulphur-cured vulcanisates *(Figure 3)*, although this may be coincidental. It would appear, therefore, that pendent groups to the backbone chain could be responsible for the different H%–*Vr* relationships of these two types of NR vulcanisates. A mechanism by which the pendent groups could affect H% is a steric interaction between the pendent group and the methyl groups of the isoprene unit, acting to reduce the mobility of the chain segments in NR. Since *cis*-BR has no such group to form steric interactions with the pendants, accelerator-terminated pendent groups would not be able to exert an effect on H% for vulcanisates of this polymer in accord with observation.

To investigate the effect of the restriction of swelling of one phase of a blend by the other, samples of three of the BR vulcanisates were subjected to the sub-equilibrium technique. BR was chosen as the polymer for this particular study because of the higher intensity of the olefin peak arising, as it does, from two hydrogen atoms for every butadiene repeat unit. This produces spectra with intrinsically higher signal to noise ratios *(Figure 1)*, allowing the number of accumulations combined in each spectrum to be kept small and thereby minimising the loss of deuterochloroform from the swollen samples. On storage, samples showed evidence for solvent loss to the D_{20} suspension medium by the gradual appearance of a haze, presumed to be the sodium salt used to provide a lock signal or to the deuterochloroform precipitating in the D_{20}.

H% was observed to increase with the *Vr'* of the sub-equilibrium swollen BR vulcanisates *(D, E* and *F, Figure 5)*. The dependence of H% on the *Vr'* of a particular, sub-equilibrium swollen BR vulcanisate was much less than its dependence on *Vr* in a series of equilibrium swollen BR vulcanisates (solid line, *Figure 5*). Consider vulcanisate *D*, which has the lowest crosslink density and was compounded with 0.5 p.p.h.r. sulphur: this had an equilibrium *Vr* of 0.076 and a H% value of 14. The sample of this vulcanisate swollen to the highest degree below equilibrium has a *Vr'* of 0.15 and a H% value of 19. To achieve this *Vr* value at equilibrium swelling, BR requires curatives compounded at a level of 0.9–1.0 p.p.h.r. which would give a H% value of 35. If found for a BR vulcanisate swollen to equilibrium, the observed H% value of 19 would represent a curative level of 0.60–0.65 p.p.h.r. sulphur, which is only slightly higher than that compounded. This departure of swelling from the equilibrium value (*Vr/Vr'* = 0.5) is extremely large in the context of swelling restriction, where *Vr/Vr'* values less than 0.8 are rare[3,4] and is well beyond that expected in practice.

Similar comparisons may be made using the other two vulcanisates. H% therefore appears primarily to be a function of the crosslink density within the sample with a much less dependence on the degree of swelling. This observation demonstrates that for most blend combinations the NMR technique will give crosslink distribution analyses of a quantitative nature.

During compounding, certain polymers suffer reductions in molecular weight as a consequence of the work performed on the mix[8]. For such materials, it is quite likely that the molecular weight of the rubber prior to vulcanisation will vary according to mechanical history. The effect of prolonged milling of a NR mix is shown in *Table 3*. The breakdown was achieved by repeated passing of the mix through the tightest nip setting of a well cooled two-roll mill and represents a level of breakdown far in excess of that likely

TABLE 3. EFFECT OF MN ON H% IN NR

Mix Mn	Vulcanisate	
	H%	Vr
154 000	39.9	0.126
100 000	22.0	0.097

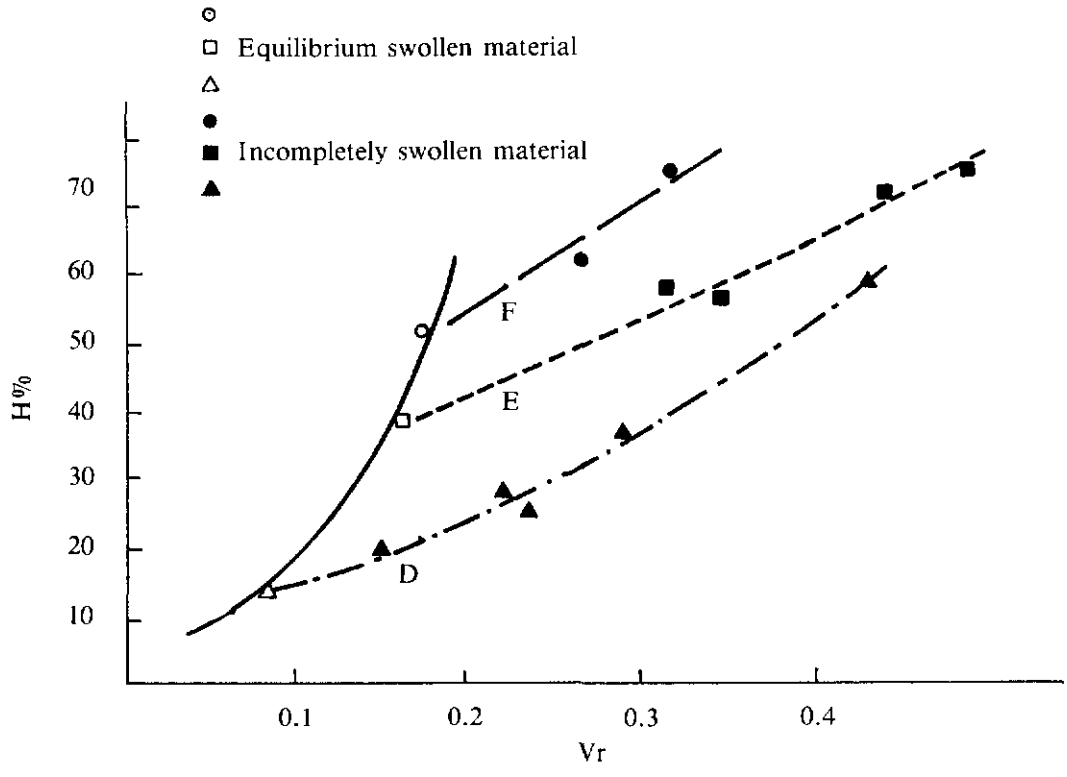

Figure 5. Sub-equilibrium swelling of BR. Solid line represents the curve of Figure 4.

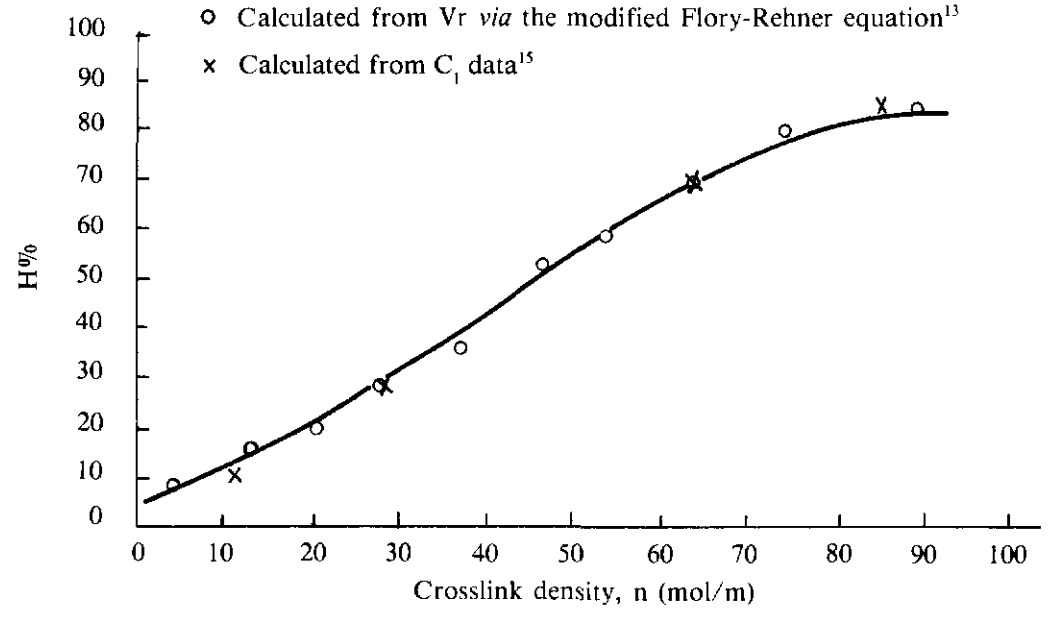

Figure 6. H% versus crosslink density (n_{phys}) for NR vulcanisates. The curve represents the best fit third-order polynomial to the data.

to be encountered during normal mixing. The vulcanisates produced from the original mix and the heavily milled mix have considerably different H% values; however, since *Vr* is also affected by the reduction in molecular weight, the H%–*Vr* relationship is maintained *(cf Figure 2)*. If *Vr* or physical crosslink density is of primary interest, then the NMR technique gives a direct method by which these parameters may be determined. If, however, it is desired to relate the observed H% values to the effective curative levels operating within the phase, the effect of molecular weight must be allowed for in interpreting the results. In either case, the NMR technique is a valuable tool in the analysis of polymer blend vulcanisates.

CONCLUSION

Different accelerator : sulphur ratios, accelerator types and curative levels in NR, produce vulcanisates containing a range of network structures to study using NMR spectroscopy. These studies have shown that the line widths observed in the NMR spectra of equilibrium swollen vulcanisates are primarily a function of the crosslink density, including physical entanglements, within the vulcanisate. Dicumyl peroxide vulcanisates of NR have spectra with lower H% values than accelerated-sulphur vulcanisates of similar crosslink density. This difference is thought to be due to the accelerator-terminated pendent groups present in the sulphur vulcanisates, which may interact with the methyl group on the NR backbone increasing H%. For *cis*-BR a different observation is made: peroxide and accelerated-sulphur vulcanisates follow the same H%–*Vr* correlation. In applying the NMR technique to blend analysis, one H%–*Vr* correlation curve for each polymer will represent the accelerated-sulphur vulcanisates. For some polymers, this correlation curve will also represent the H%–*Vr* relationship of peroxide-cured vulcanisates, but in other polymers, the different H%–*Vr* relationship requires that a separate correlation curve is produced.

H% is influenced by the degree of swelling of the vulcanisate, but this is of secondary importance. Provided that the *Vr* values of the individual phases of the blend are not much greater than the equilibrium values, a condition which in almost all cases will be satisfied, the H% values obtained from the analysis of the NMR spectrum of a blend will accurately reflect the crosslink density within the phases of the blend. Thus, the application of the NMR technique of crosslink density analysis to vulcanised blends in which one phase experiences more degree of restriction of swelling, will still provide quantitative information regarding the distribution of crosslinks between the phases in the blend.

H% is a function of the molecular weight of the polymer prior to vulcanisation, having lower values at lower molecular weights; however, *Vr* is also a function of molecular weight, and the H%–*Vr* correlation is followed by NR vulcanisates produced from the same mix after different periods of mastication. Excessive mastication during the compounding of a rubber blend may thus give misleading results, particularly with respect to the level of curatives active in the phases of the blend. This is most likely to occur when the mechanical histories of the vulcanisates used to create the H%–*Vr*, or H%-curative level correlation curves differ from that of the blend of interest. This problem can be minimised by carefully matching the compounding conditions.

The authors acknowledge that *Vr* is not an ideal measure of crosslink density since the polymer-solvent interaction parameter χ may well vary with degree of network modification as well as with crosslink density. *Figure 6* shows how H% varies with the crosslink concentration, n_{phys} (n), in NR vulcanisates. The data is based mainly on n values calculated from volume swelling data *via* the modified *Florey-Rehner equation*[13] *using the* χ *value* for NR/chloroform of Bristow and Watson[14]. Also included in this figure are n values calculated from C_1 data derived from stress-strain measurements[15], these values being in reasonable agreement with the volume swelling derived data. There are four samples where n is obtained both *via Vr* data and *via* C_1 data. At the extremes of crosslink density, the data

do not agree as well as at the intermediate crosslink densities, but the agreement is sufficiently good to allow *Vr* to be used as the measure of crosslink density within this system. Further work relating H% to crosslink density is being carried out, and will be reported in a future publication.

ACKNOWLEDGEMENT

The authors wish to thank the Board of the Malaysian Rubber Producers' Research Association for permission to publish this work.

Date of receipt: March 1990
Date of acceptance: August 1990

REFERENCES

1. LOADMAN, M.J.R. AND TINKER, A.J. (1989) The Application of Swollen State CW-^{1}H NMR Spectroscopy to the Estimation of the Extent of Crosslinking in Vulcanized Polymer Blends. *Rubb. Chem. Technol.*, **62**, 234.

2. HESS, W.M., SCOTT, C.E. AND CALLAN, J.E. (1967) Carbon Black Distribution in Elastomer Blends. *Rubb. Chem. Technol.*, **40**, 371.

3. ZAPP, R.L. (1973) Chlorobutyl Covulcanization and Interfacial Elastomer Bonding. *Rubb. Chem. Technol.*, **46**, 251.

4. TINKER, A.J. (1989) Crosslink Distribution and Interfacial Adhesion and Vulcanized blends of NR and NBR. Paper 117 presented at a Meeting of the Rubber Division, American Chemical Society, Detroit, Michigan, USA. October 17-20 1989. *Rubb. Chem. Technol.* (in press).

5. NEPPEL, A., EATON, D.R., HUNKELER, D. AND HAMIELIC, A.E. (1988) Effect of Crosslinking on the ^{13}C Nuclear Magnetic Resonance Spectra of Super Absorbent Poly (sodium acylates). *Polymer*, **29**, 1338.

6. BAIN, A.D., EATON, D.R., HAMIELEC, A.E., MLEKUZ, M. AND SAYER, B.G. (1989) Line Broadening in the Carbon-13 NMR Spectra of Cross-linked Polymers. *Macromol.*, **22**, 3561.

7. BATEMAN, L., MOORE, C.G., PORTER, M. AND SAVILLE, B. (1963) Chemistry of Vulcanization, *The Chemistry and Physics of Rubber-like Substances. (Bateman, L.ed.)*. London: Maclaren and Sons Ltd.

8. BRISTOW, G.M. AND WATSON, W.F. (1963) Mastication and Mechanochemical Reactions of Polymers, *The Chemistry and Physics of Rubber-like Substances. (Bateman, L.ed.)*. London: Maclaren and Sons Ltd.

9. BROWN, P.S., PORTER, M. AND THOMAS, A.G. (1985) Influence of Crosslink Structure on Properties in Crystallizing and Non-crystallizing Polyisoprenes. *Proc. Int. Rubb. Conf. 1985 Kuala Lumpur*, **2**, 20.

10. ELLIS, B. AND WELDING, G.N (1964) Estimation, from Swelling, of the Structural Contribution of Chemical Reactions to the Vulcanization of Natural Rubber: Part 2. Estimation of Equilibrium Degree of Swelling. *Rubb. Chem. Technol.*, **37**, 571.

11. BAKER, C.S.L. (1988) Non-sulphur Vulcanization, *Natural Rubber Science and Technology (Roberts, A.D. ed.)*. Oxford: Oxford University Press.

12. PORTER M. (1978) Recent Chemical Developments with Natural Rubber. *Plast. Rubb.: Materials and Applications*, **3**, 32.

13. FLORY, P.J. (1950) Statistical Mechanics of Swelling of Network Structures. *J. Chem. Phys.*, **18**, 108.

14. BRISTOW, G.M. AND WATSON, W.F. (1958) Viscosity-equilibrium Swelling Correlations for Natural Rubber. *Trans. Faraday Soc.*, **54**, 1567.

15. CHAPMAN, A.V. AND PORTER, M. (1988) Sulphur Vulcanization Chemistry (Method 1), *Natural Rubber Science and Technology (Roberts, A.D. ed.)*. Oxford: Oxford University Press.