

Effect of Modifying EPDM on the Crosslink Distribution in NR/EPDM Blends

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The swollen-state FT-NMR spectroscopic method of blend analysis⁷ has been applied to blends of NR with two different EPDMs and chemically modified versions of these EPDMs. The crosslink densities in the EPDM phases of the blends with unmodified EPDM are very low, approximately 10 mol m⁻³. The presence of the chemical modification to the EPDM has a dramatic effect on crosslinking in the EPDM phase, more than doubling it, but only a minor one on that in the NR phase. The overall crosslink density in the blend is, therefore, increased. Despite these changes there remains a large imbalance in the crosslink distribution in favour of the NR phase in both modified blends, yet the reported physical properties are good^{3,4}. This suggests that there may be a threshold value for the crosslink density in the EPDM phase for a blend to achieve good physical properties.

Blends of NR with EPDM have long been recognised as suffering from cure rate incompatibility. This incompatibility arises from the difference in olefin concentration of the two polymers; NR is essentially 100 mol% olefin, whereas EPDM rarely comprises greater than 10% diene monomer by weight (2–3 mol% olefin). Cure rate incompatibility is thought to cause the inferior physical properties of NR/EPDM blends. Early attempts to improve the properties of EPDM/polydiene rubber blends involved changes in the cure system; either limiting the mobility of the cure system and cure intermediates by the use of a large metal counterion (e.g., lead)¹, or by selecting

curatives with a high solubility in the EPDM phase². Several authors have used polymer modification as a route to reduce the cure rate incompatibility^{3–5}. Hopper reacted a potential vulcanisation inhibitor with the EPDM olefin groups, producing PVI groups bound onto the EPDM. He postulated that these groups capture curatives during the early stages of vulcanisation³ thus reducing the access of the NR to the cure system, improving the crosslink distribution and increasing tensile strength by 50% (15.2 MPa to 21.8 MPa). Coran reacted EPDM with maleic anhydride to introduce a potential metal chelating group onto the polymer backbone, thereby improving the physical

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properties of blends with NR⁴, the tensile strength being increased from 14.8 MPa to 23.3 MPa. He postulates that zinc oxide from the sulphur-based cure system of the blend forms ionic crosslinks with these chelating groups on the modified EPDM. Morrissey halogenated the EPDM to increase the number of cure sites⁵.

A previous paper reported the application of a ¹H CW-NMR spectroscopic technique to the study of crosslinking in the NR phase of blends with EPDM and a maleic anhydride modified EPDM⁶. Crosslinking in the EPDM phase could not be determined using this technique. This paper describes the application of the more recently developed technique of swollen-state FT-NMR spectroscopy⁷ to the blends of the type described by both Coran and Hopper. The availability of ¹³C NMR with this revised technique has permitted the study of crosslinking in both phases of the blends.

MATERIALS AND METHODS

The rubbers used in this study were *Nordel 1470* (E.I Dupont), *Intolan 155* (Enichem), and natural rubber (SMR 10, Malaysia). Modified *Intolan 155* was produced according to the method of Coran⁴, whilst the PVI grafted EPDM [N-chlorothio-N-methyl-benzenesulphonamide grafted *Nordel 1470*, 2.9 g bound/100 g rubber (11.5 mmol/100 g)] was kindly supplied by Dr R.J. Hopper of the Goodyear Tire & Rubber Company, Akron, Ohio (USA). Rubber chemicals were standard commercial grade materials, and solvents were of AR grade except for the NMR solvents which were of spectroscopic grade [deuteriochloroform

(CDCl₃) and tetramethylsilane (TMS) Aldrich Chemical Company].

Compounding (*Tables 1 and 2*) was performed by using a BR size Banbury internal mixer or a two roll mill, the curatives being added on a two-roll mill. Test sheets (225 x 225 x 1 mm) were cured at 150°C to t_{max} as determined using Monsanto ODR or MDRE rheometers.

Samples of vulcanisate for NMR analysis were extracted for 4 h with methanol in a hot Soxhlet apparatus, dried to constant weight *in vacuo* and then stored *in vacuo* in the dark until required. Small slivers were swollen in CDCl₃, containing some TMS as an internal reference for 24–48 h before being trimmed so as to spin freely in an NMR tube containing fresh solvent.

FT-NMR spectra were obtained using a General Electric QE300 300 MHz Fourier Transform spectrometer fitted with a ¹³C/¹H dual 5 mm probe, Nicolet 1280 processor and an Oxford Instruments 7 tesla super-conducting magnet. The acquisition conditions are given in *Table 3*. The FIDs were transferred to an Epson AX3S PC for manual phasing of the transformed FID, and the spectrum data were then transferred to a Prime minicomputer for further numerical analysis. Auto phasing was found not to cope well with these spectra which contain predominantly broad signals.

The width of the NR olefin peak in ¹H spectra of the blends was estimated by using the parameter H%⁷, determined at a reference offset of 0.20 p.p.m. The crosslink density within the NR phase was interpolated from H% by using a

TABLE 1 FORMULATIONS I NORDEL SINGLE POLYMER VULCANISATES

Compound	N1	N2	N3	N4	MN1	MN2	MN3	MN4
<i>Nordel 1470</i>	100	100	100	100				
Mod EPDM2 ^a					106.6	106.6	106.6	106.6
Zinc oxide	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Stearic acid	1.75	1.75	1.75	1.75				
<i>Wingstay L</i>	1.00	1.00	1.00	1.00	0.50	0.50	0.50	0.50
Sulphur	0.50	1.00	1.50	2.00	0.50	1.00	1.50	2.00
MBS	0.25	0.50	0.75	1.00	0.25	0.50	0.75	1.00

^a The modified EPDM2 is *Nordel 1470* with 0.5 p.p.h.r. *Wingstay L*, 3.5 p.p.h.r. Stearic acid and 2.9 g grafted sulphonamide

TABLE 2 FORMULATIONS II NR AND NR/EPDM BLENDS

Compound	Blend C1	Blend M1	Blend C2	Blend M2	NR1
SMR L	70	70	50	50	100
<i>Intolan 155</i>	30				
Mod EPDM1 ^a		30			
<i>Nordel 1470</i>			50		
Mod EPDM2				53.30	
Zinc oxide	5.50	5.50	4.00	4.00	4.00
Stearic acid	2.00	2.00	1.75		1.75
<i>Wingstay L</i>			1.00	0.75	1.00
Sulphur	2.00	2.00	2.00	2.00	2.00
MBS	0.50	0.50	1.00	1.00	1.00

^a The modified EPDM1 is *Intolan 155* modified with 2 p.p.h.r. maleic anhydride according to the method of Coran⁴

TABLE 3 NMR ACQUISITION PARAMETERS

Parameter	¹ H	¹³ C
Frequency (MHz)	300.15	75.48
Sweep width (Hz)	6 024	20 000
Data size	16 384	32 768
Pulse width (μs)	3.0	6.0
Pulse width,°	3.0	60
Acquisition time (s)	1.36	0.819
Delay time (s)	10.0	3.0
Temperature (°C)	20 – 22	20 – 22
Spin rate (Hz)	18 – 20	18 – 20
Number of acquisitions	128	15 000, 40 000 ^a

^a 15 000 for single polymer vulcanisates, 40 000 for blends

previously obtained plot of H% against physical crosslink density⁸. The peak widths in ¹³C NMR spectra of blends and single polymer vulcanisates were determined in two ways. Both of the NR olefin signals are single peaks (chemical shifts of 125 p.p.m. and 135 p.p.m.); as there is no overlap with other signals in the spectrum (*Figure 1*) peak width at half peak height ($W_{1/2}$), the conventional NMR measure, can be used as the line breadth measure. The $W_{1/2}$ data were converted to crosslink densities using the correlation presented in reference 7.

The ¹³C NMR signals from the EPDM rubbers are more complicated. There is a considerable number of peaks in a narrow region of the spectra, and thus there is some degree of overlap. In addition, the two signals arising from the aliphatic NR backbone carbon atoms and that form the NR methyl group also lie in this region (*Figure 2*). Two sets of EPDM peaks show both a good variation of peak width with crosslink density and are sufficiently remote from the other signals in the region for easy analysis. These are the two peaks at 37 p.p.m. and the three

peaks at 30 p.p.m. (*Figure 3*). Although the individual peaks within the two groups arise from different carbon atoms on the EPDM molecule, they all broaden with increasing EPDM cross-link density and are analysed as a group. Both sets of signals were analysed in the same way; a line broadening measure, H%, is calculated as the ratio of the signal intensity at the valley positions (a, a') to that of the highest peak in the group (b, b', *Figure 3*), correcting for the baseline intensity. The measurements were taken manually from large scale expansions of the spectrum.

The physical crosslink densities in the single polymer EPDM vulcanisates were determined by using stress-strain analyses according to the method of Chapman and Porter⁹.

RESULTS AND DISCUSSION

N-chlorothio-sulphonamide Modified EPDM

Single polymer vulcanisates. Although the control and modified EPDM1 single polymer vulcanisates were similarly com-

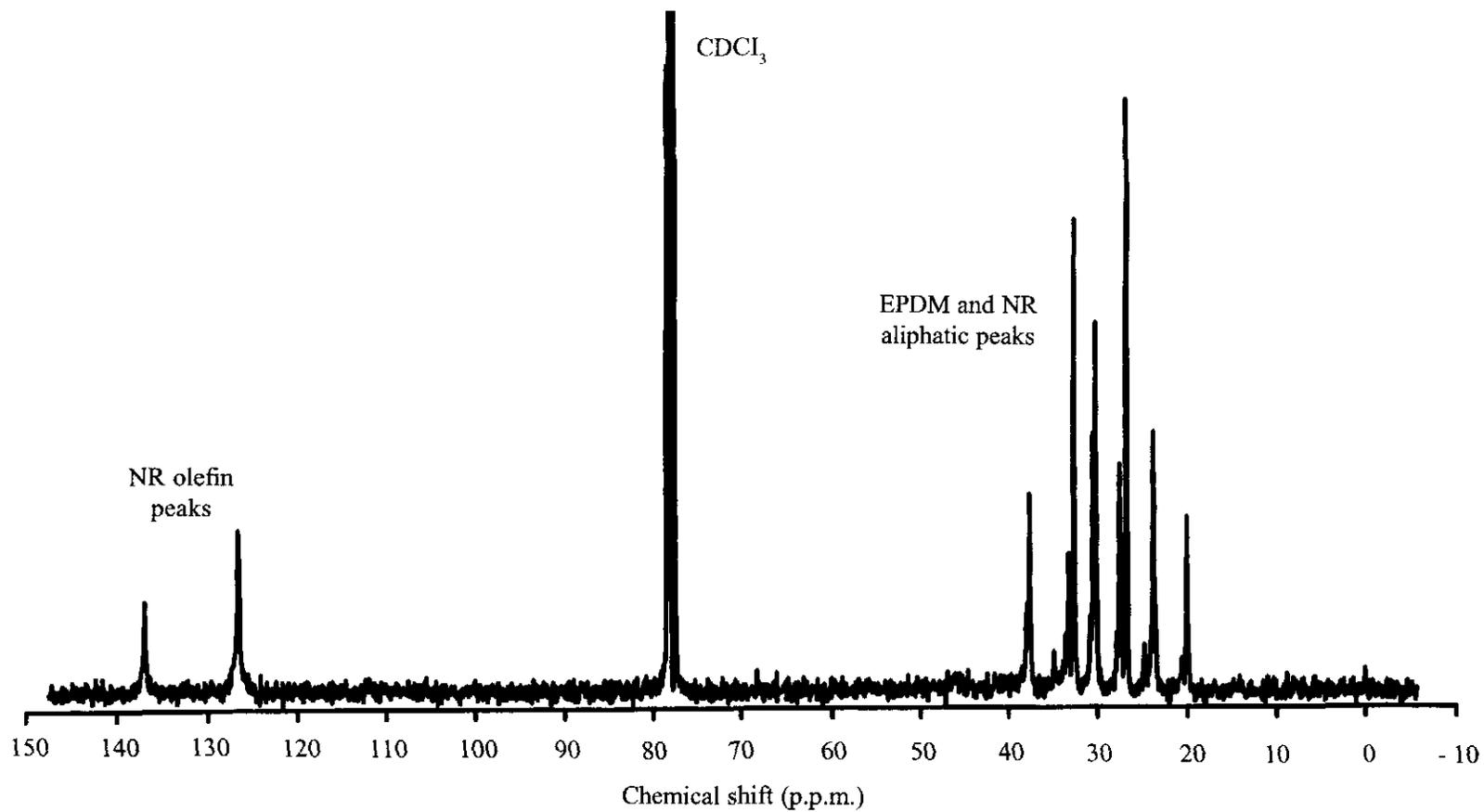


Figure 1. Full ^{13}C NMR spectrum of Blend C1 showing the two distinct regions of elastomer signals. The NR olefin peaks are labelled.

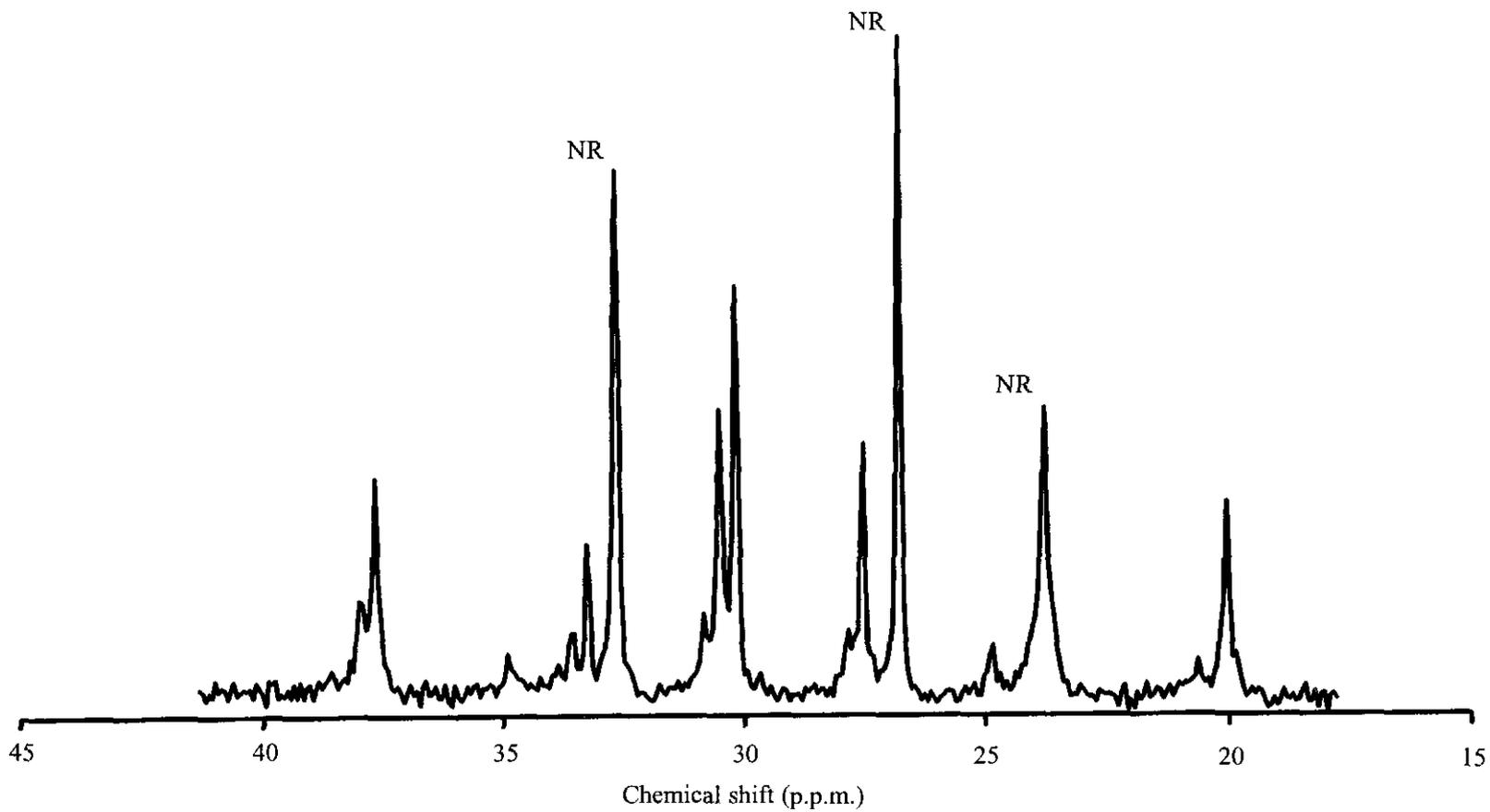


Figure 2. Aliphatic region (20–50 p.p.m.) of the ^{13}C NMR spectrum of Blend C1.

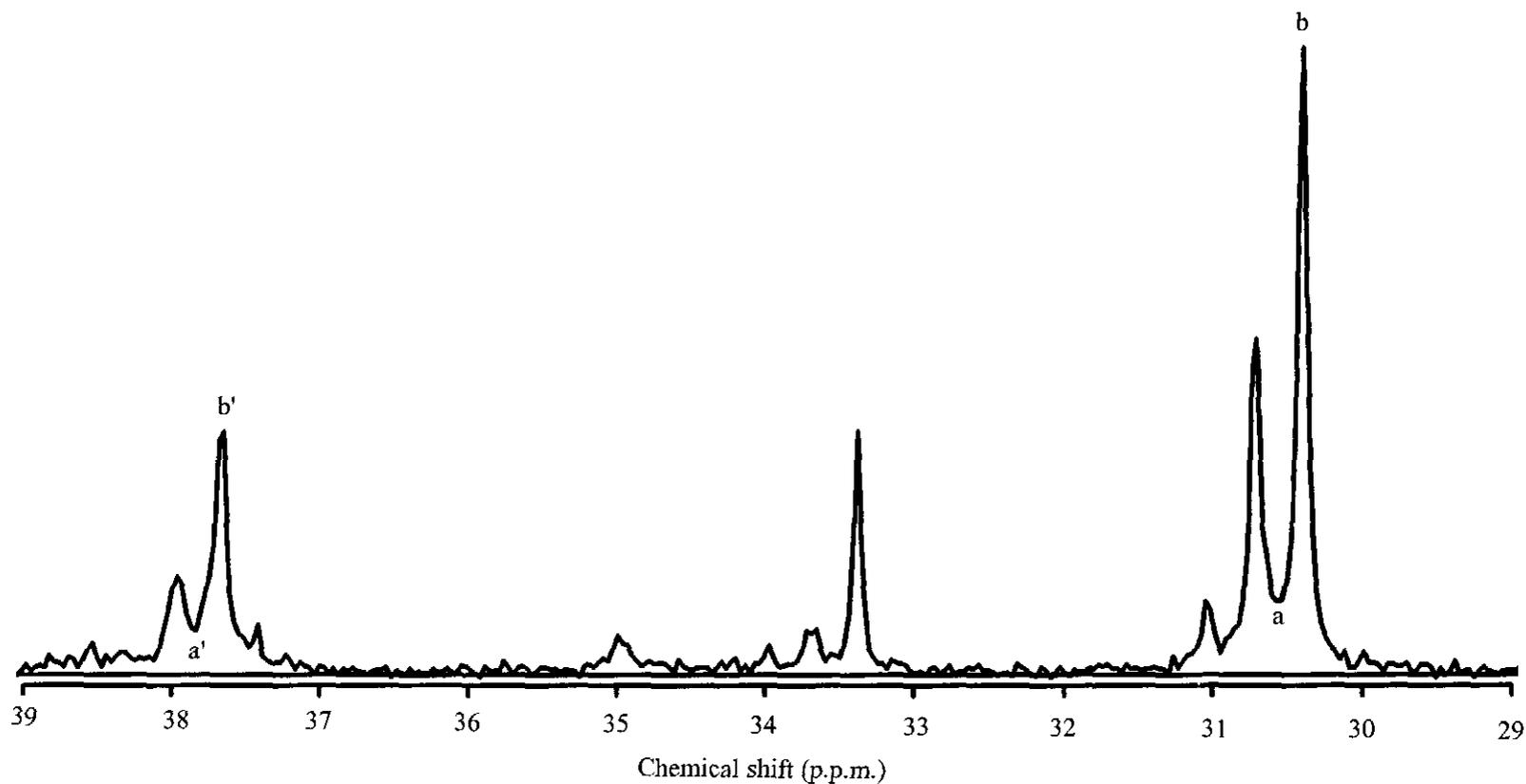


Figure 3. Expanded section of the ^{13}C NMR spectrum of single polymer vulcanisate N1 showing the triplet and doublet peaks at 30 and 37 p.p.m. together with the reference points used to determine the H% values (a and b and a' and b'). Note the similarity of the peaks with those of the Intolan 155 blend in Figure 2.

TABLE 4 NORDEL SINGLE POLYMER DATA

Vulcanisate	C1 (kPa)	$\frac{1}{2}Mc$ (mol m ³)	H% (30)	H% (37)
N1	16.7	6.7	10.1	15.5
N2	60.8	24.7	39.9	45.5
N3	82.4	33.4	55.0	60.0
N4	91.3	37.0	62.0	64.0
MN1	82.4	33.4	58.1	62.9
MN2	107.9	43.8	62.5	68.9
MN3	121.6	49.4	67.7	72.0
MN4	125.6	51.0	72.0	81.0

pounded, (Table 4) their crosslink densities were very different. The values obtained with the control vulcanisates ranged from 6.7 to 37 mol m³, those using the modified material from 33.4 to 51 mol m³ (Table 5). This increase of crosslinking in the presence of the modification was also reflected in the NMR spectra of the modified EPDM vulcanisates which were considerably broader. The two H% values (37 ppm and 30 ppm) were quite similar for both EPDMs, and H% was found to increase smoothly with crosslink density. These data appear to lie on a common curve, indicating that the modification does not greatly interfere with the analysis (Figure 4). This curve was used to interpolate the crosslink densities in the EPDM phases of the blends with NR (Table 6).

NR/EPDM blends ¹H NMR spectroscopy of the blends can only give information regarding the NR phase. H% was found to be similar in both blends, with that in the modified blend having a slightly lower value (Table 5). The difference is similar to the scatter expected in the NMR measurements, so it may not be significant,

but it is equivalent to a fall of about 5% in the crosslink density in the NR phase (85 to 81 mol m³). A similar small reduction in the NR crosslink density was observed in the ¹³C NMR spectra of the blends, 95 to 92 mol m⁻³. These values are a little higher than those determined from ¹H NMR spectroscopy, but not so great as to cause concern over the reliability of the technique. That both methods indicate that the modification effects a small reduction in the NR crosslink density suggests that it is a real observation and not just scatter in the data.

In both blends, the crosslink density in the NR phase is considerably higher than in the single polymer analogue (NR1 in Table 5). These increases in crosslinking in the NR phases of the blends (25–30 mol m³) represent a considerable capture of the curatives by that phase, even in the presence of the vulcanisation inhibitor bound to the EPDM.

Despite the minimal effect on crosslinking in the NR phase, this modification does cause a considerable increase in the crosslink density in the EPDM phase of

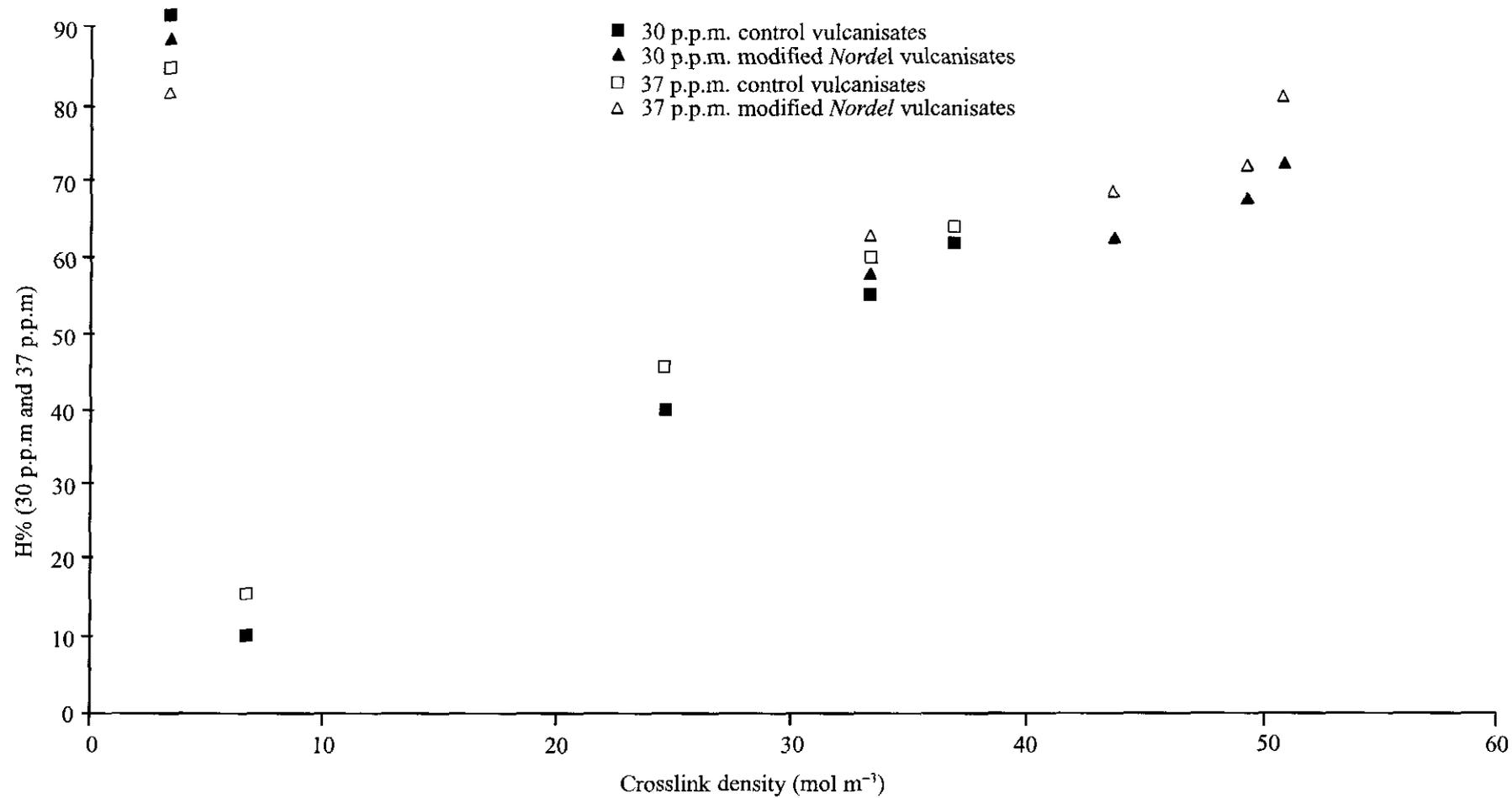


Figure 4. H% (¹³C spectra 30 p.p.m. peaks) versus crosslink density for single polymer Nordel Vulcanisates.

TABLE 5 N-CHLOROTHIO-SULPHONAMIDE EPDM BLEND DATA

	Blend C2	Blend M2	NR1
EPDM H% (30 p.p.m.)	10.9	42	
EPDM H% (37 p.p.m.)	15.2	46.2	
EPDM $\frac{1}{2}$ Mc, mol m ⁻³ (30, 37 p.p.m.)	7.0, 6.5	26.3, 25.0	
NR H% (¹ H NMR)	84	81	70
NR $\frac{1}{2}$ Mc, mol m ³ (¹ H NMR)	85	82	57
NR W _z , Hz (¹³ C NMR)	57, 57	54, 54	35, 35
NR $\frac{1}{2}$ Mc, mol m ⁻³ (¹³ C NMR)	95	92	65

the blend, raising it by a factor of 3.5 (Table 5). The modification is present at about 11 mmol/100 g in the EPDM³, or 5.5 mmol of modification in the blend, whilst 1 g of MBS is 4.4 mmol of the accelerator. If all of the compounded accelerator is preferentially captured by the polymer-bound PVI and a crosslink in the EPDM is produced upon its release, a crosslink density of about 90 mol m⁻³ would result. That level is not observed, however crosslinking in the EPDM does increase by about 18 mol m³ to a level of 26 mol m⁻³, a significant improvement over that in the control. This indicates that only 20–30% of the polymer bound PVI is acting in the manner suggested by Hopper³.

It is interesting to note that the crosslink density in the EPDM phase of control blend C2 is comparable to that in the single polymer EPDM vulcanisate N1, but the crosslink density in the EPDM phase of the modified blend M2 is lower than that observed in the single polymer vulcanisate MN1, the modified EPDM analogue of vulcanisate N1. Thus it appears that additional crosslinking, which the modification produces in the single polymer EPDM vulcanisates, is reduced

upon blending with NR. The crosslink density determined for the NR phase of blend M2 shows that this phase is still capturing a significant proportion of the curatives even in the presence of the PVI bound to the EPDM. The reduced effect of the PVI modifier in boosting crosslinking in the EPDM phase in the blend is a consequence of the curative capture by the NR phase.

Blends with Maleic Anhydride Modified EPDM

The crosslink densities in the NR components of NR/maleic anhydride modified EPDM blend and its control blend were reported in an earlier publication⁶. The NR was found to have a crosslink density considerably higher than expected from the compounding. The observed level was equivalent to that expected if 80–90% of the curatives in the blend were utilised by this polymer alone, *i.e.* equivalent to a single polymer NR vulcanisate compounded with almost twice the level of curatives used in the blend. The maleic acid modification of the EPDM had only a minor effect on the crosslinking in the NR phase⁶. In this current study, the use of ¹³C NMR

TABLE 6. MALEIC ANHYDRIDE EPDM BLEND DATA

	Blend C1	Blend M1
EPDM H% (30, 37 p.p.m.)	17.9, 21.4	43.3, 45.6
EPDM crosslink density, mol m ⁻³ (30, 37 p.p.m.)	11.4, 10.5	26.4, 24.7
NR $W_{1/2}$, Hz (125, 135 p.p.m.)	30, 30	24, 24
NR crosslink density, mol m ⁻³	61	52
NR crosslink density by ¹ H NMR ⁶ , mol m ⁻³	56	53

spectroscopy allows the study of crosslinking in the EPDM phase. In the absence of a series of single polymer *Intolan 155* vulcanisates to create the necessary crosslink density H% correlation plot, a fully quantitative analysis of the data is not possible. However, the similarity in the ethylene:propylene ratio of the two EPDMs means that the crosslink density-H% correlation produced for *Nordel 1470* should be applicable to these blends without too great an error, thus the analysis of crosslinking in the EPDM phase can be qualitative or even semi quantitative.

The peak width data are given in *Table 6*. The data for the NR olefin peaks are in agreement with the earlier ¹H data in that there is a small reduction in peak width in the presence of the modification ($W_{1/2}$ falls from 30 to 24 Hz). The EPDM multiple peaks at 30 and 37 p.p.m. both show considerable increases in H%, the values roughly doubling (*Table 6*).

The ¹³C NMR peak width data confirm the finding of the earlier study; the NR crosslink density is only slightly reduced (from 61 to 52 mol m⁻³). These data are in remarkably good agreement with the earlier ¹H results (*Table 6*), again suggesting that the reduction is real. While it is strictly incorrect to use the crosslink density/H% correlations produced for the other EPDM in

this study to estimate the EPDM crosslink density in these blends, its use will provide a reasonable estimate of the crosslink density in the EPDM phase. Such an analysis suggests that the EPDM crosslink density in the modified blend is about two and a half times that in the control blend (25 mol m⁻³, up from 11 mol m⁻³). It is worth noting that this value is similar to that found in the blends with N-chlorothio-sulphonamide modified EPDM.

CONCLUSIONS

These two different approaches to solving the problem of cure incompatibility between NR and EPDM elastomers result in broadly similar changes in the crosslink distribution. The poor properties of the control blends are certainly a consequence of the very low crosslink density in the EPDM phases of these blends. Both modifications cause a significant increase in the crosslink density within the EPDM phase without causing a great change in the NR phase of the blend, yet in both cases the crosslink distributions still show a marked bias in favour of the NR phases. The improved physical properties that arise from these modifications^{3,4,6} are probably due to a combination of effects. The increase in overall crosslink density and the reduction in the difference

in the moduli of the two phases must contribute to the improvement. Reducing the imbalance of crosslinking may also lead to improved interfacial crosslinking¹⁰ which would have a marked effect on ultimate properties.

The NMR results show that it is not necessary to create an even crosslink distribution in the blends to produce good physical properties. Merely to have a sufficient level of crosslinking in the EPDM phase of the blend 20-25 mol m⁻³ would appear to be enough for this blend system. This is an important result. It is unlikely that any simple process could be found to effect even crosslinking in these blends, however, a crosslink concentration of 25 mol m⁻³ in the EPDM only requires a two to three fold increase, an achievable target. There may also be implications for other blend systems, although the optimum crosslink density in the softer phase may not be that found in these studies.

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