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Crosslink Distribution in Vulcanised Blends of NR and EPDM

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Blends of NR with EPDM and with a chemically modified EPDM have been investigated using a continuous-wave ^1H NMR spectroscopy technique to determine the crosslink density within the NR phase of the blends. In all cases, the observed crosslink density was higher than in a NR control vulcanisate containing the same level of curatives. The modified EPDM gave blends of superior physical properties, but the modification had little effect on the course of sulphur vulcanisation within the blends.

There is ever increasing technological interest in the use of blends of dissimilar rubbers in order to improve specific vulcanisate properties (e.g. ozone resistance, wear). Unfortunately this can often be at the expense of a reduction in other properties (e.g. modulus, tensile strength) of the compound. In the case of accelerated-sulphur-cured blends of polydiene elastomers with rubbers having a low olefin content [ethylene propylene dienemonomer (EPDM) rubber], the poor strength properties are thought to be a consequence of cure rate incompatibility between the two polymers. The polydiene elastomer is assumed to monopolise the curative chemicals added to the mix, resulting in little if any crosslinking of the EPDM.

There is no data to fully support this thesis in the published literature. A recently published paper[1] described how the crosslink density of the individual components in an incompatible blend can be obtained by analysis of the CW-^1H NMR spectrum of the blend. The spectral line widths are found to increase smoothly with crosslink density. The analysis compares a line width measure for both blend components with data from the single polymer vulcanisates to determine the crosslink densities within the phases of the blend. This paper reports the use of the ^1H NMR spectroscopy technique[1] to study blends of natural rubber (NR) with an EPDM and with a chemically modified EPDM shown by Coran[2] to produce blends with NR possessing superior tensile properties.

EXPERIMENTAL

The rubbers used in this study were SMR L, EPDM [Intolan 155, an ethylidine norbornene (ENB) EPDM, Enichem, described as having a high iodine number which implies a high degree of unsaturation in the context of EPDM] and a modified Intolan 155 produced according to the method of Coran[2] using 2 p.p.h.r. maleic anhydride and 0.2 p.p.h.r. 2,2′ benzothiazole disulphide. Rubber chemicals were standard commercial-grade materials, solvents of AR grade except for the NMR solvents which were of spectroscopic grade, and the maleic anhydride was used as supplied (Koch Light AR).

The olefin content of Intolan 155 was determined by analysis of its solution state ^1H NMR spectrum (General Electric QE 300 MHz), and found to be 0.5 proton% which equates to 2.5 mol% ENB. The ethylene-propylene ratio was determined by infra-red spectroscopy (Perkin Elmer 377)[3] at 6:4 by weight.

Compounding was performed using a BR-size Banbury mixer, a Hampden Shawbury torque rheometer or a two-roll mill, with curatives added on the two-roll mill. The time to reach maximum torque in a Gottfert Elastograph rheometer was used as the cure time.

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Samples for NMR analysis were extracted for 4 h in a hot Soxhlet apparatus with methanol and dried to constant weight *in vacuo* at room temperature. These samples were stored at room temperature *in vacuo* in the dark until required. Small slivers ($\sim 1.5 \times 0.5 \times 3$ mm) were pre-swollen to equilibrium uptake in a minimum of $CDCl_3$ for between 36 h and 60 h in the dark before being cut to fit freely into a 5 mm diameter NMR tube. Fresh $CDCl_3$ doped with $CHCl_3$ as an internal marker and HMDS as an internal lock, was added to cover the sample.

The NMR spectra were obtained using a Perkin-Elmer R24E 90 MHz continuous wave spectrometer interfaced to a BBC microcomputer for computer accumulation of the transients (CAT) to improve the signal to noise ratio. The spectrometer was run at an 80 s sweep of 10 p.p.m. width (11 – 1 p.p.m. downfield of TMS) with between forty and eighty transients combined for each spectrum.

Tensile testing was carried out to *ISO 37* standard.

RESULTS AND DISCUSSION

The modified EPDM when used in blends with NR does improve the tensile properties over those of comparable blends containing Intolan 155, in much the same way as observed by Coran in black filled vulcanisates[2]; thus, the tensile strength increased from 19.7 MPa to 24.3 MPa, and the modulus (M300) from 1.60 MPa to 2.19 MPa *(Table 1)*. If the modified EPDM is mixed with zinc oxide and stearic acid *(Table 2, H)*, a soft, thermoplastic material is produced after heating at 160°C. The modulus of this material is reasonable (M300 = 1.41 MPa), but it rises slowly with extension to give a fairly low tensile strength *(Table 1)*. This material is an ionomer produced by zinc ion crosslinking *via* the pendent succinic acid groups introduced during the modification reaction[2] *(Figure 1)*.

Analysis of the ^1H NMR spectrum of any of the NR-EPDM blends yields information on the crosslinking within the NR phase only. The signals arising from the EDPM protons lie together and overlap with the methyl and methylene signals of the NR, the only remote signal in the spectrum being the NR olefin at a chemical shift of *ca* 5.1 p.p.m. *(Figure 2 Spectrum D)*. Analysis[1] of this signal leads to a measure of line broadness H%. H% increases with increasing crosslink density[1], and H%

TABLE 1. PHYSICAL PROPERTIES

Property	Vulcanisate		
	A	B	C
M300 (MPa)	1.60	2.19	1.41
Tensile strength (MPa)	19.7	24.3	3.27
Extension at break (%)	782	737	595

TABLE 2. FORMULATIONS

Compound	Formulation							
	A	B	C	D	E	F	G	H
SMR	70	70	50	50	100	100	100	–
Intolan 155	30	–	50	–	–	–	–	–
Modified Intolan	–	30	–	50	–	–	–	100
Zinc oxide	5.5	5.5	5.5	5.5	5.0	5.0	5.5	5.5
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Sulphur	2.0	2.0	0.5	0.5	0.5	1.0	2.0	–
MBS[a]	0.5	0.5	0.5	0.5	0.5	1.0	0.5	–

[a]Morpholino benzothiazole-2-sulphenamide

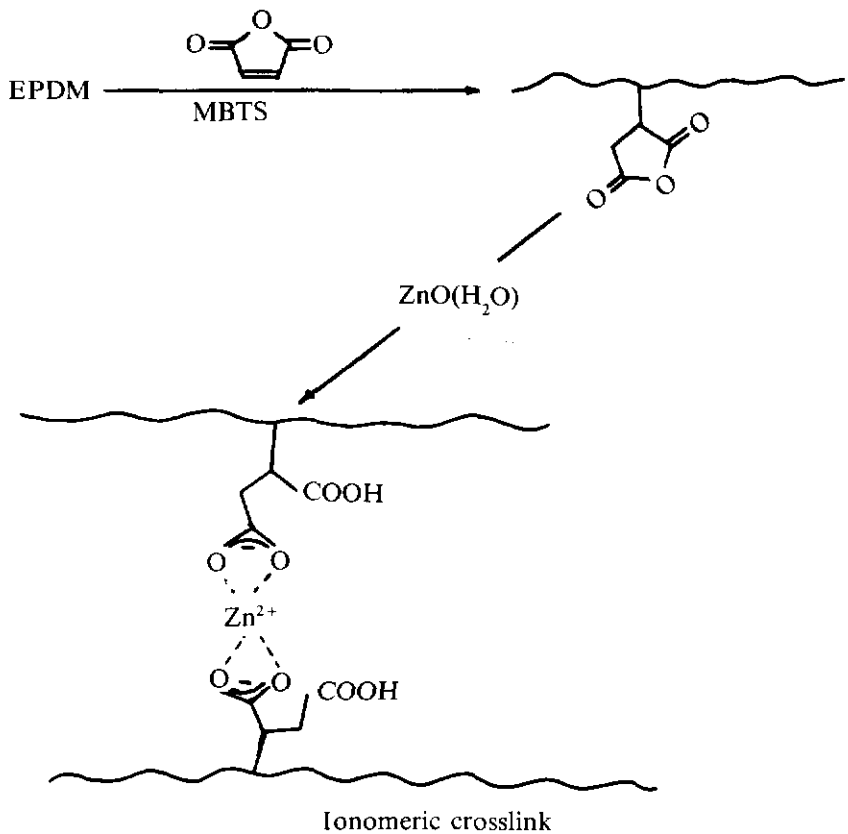

Figure 1. Chemical modification and subsequent ionomer formation in EPDM.

of any of the blends was found to be greater than the H% of the appropriate NR control vulcanisate *(Tables 2* and *3)*. H% can be related to the equilibrium volume swelling of the NR, the concentration of physically effective crosslinks or the curative level employed[4]. All NR vulcanisates employing accelerated-sulphur cure systems have been found to have the same H% *Vr* relationship[5,6] so it is possible to equate each H% value observed in vulcanisates to both the crosslink concentration (ν) and the amount of sulphur required to produce that crosslink density in a reference cure system *(SV)*. The reference system published to-date is sulphur/TMTM (S: TMTM 1:0.4)[4], and both *SV* in terms of this system and ν are given in *Table 3*. *Vulcanisate G*, the NR control vulcanisate for *Blends A* and *B*, is found to have a lower H% value than the blends. The differences represent an increase of 16% and 12% in the crosslink density in the NR phases of *Blends A* and *B* over that in the control. This increase would, for the S/TMTM reference system, represent an increase in curative loading of 22% and 15% respectively.

In NR/NBR blends, the observed uneven crosslink distribution probably arises as a consequence of the solubility parameter difference between the two polymers[4], NBR, the more polar polymer, having a higher concentration of crosslinking intermediates and thus increased crosslink levels. In the NR/EPDM blends, while there are solubility parameter differences possibly favouring NR[2], the major influence on the distribution of crosslinks is probably the concentration of olefin groups in the two polymers (13 530 $molm^{-3}$ for NR *versus* 600 $molm^{-3}$ for the EPDM). The reactivity of the olefin groups of the two polymers is likely

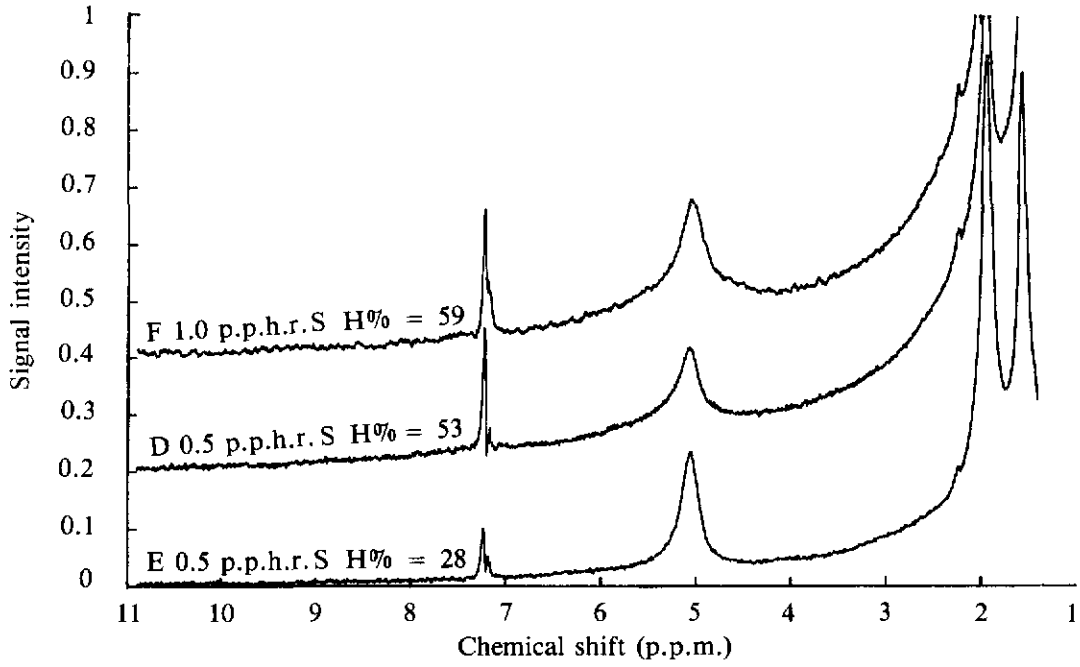

Figure 2. Swollen state ^1H NMR spectrum of Blend D (NR/Mod. EPDM 50:50) and of vulcanisates E and F. The spectra of D and F are offset in intensity for clarity. The signal at 7.2 p.p.m. is the chloroform marker.

to be similar, therefore the rate of crosslinking, and thus the rate of curative utilisation, in the NR phase will be some twenty-two times that in the EPDM phase. This is all the more remarkable since Intolan 155 is described as having a high olefin content. As the NR phase reacts with the crosslinking intermediates their concentration falls, creating a concentration gradient down which crosslinking intermediates formed in the EPDM phase diffuse. Thus, the compounded ingredients are monopolised by the NR components of the blend. In these NR/EPDM blends, the phase sizes were found by phase contrast and differential interference contrast microscopy to be of the order of 1 μ *(Figure 3)* which represents the magnitude of the diffusion distance. Data reported by van Amerongen[7] suggest that the diffusion coefficients *(D)* of the crosslinking agents are likely to be of the order of $10^{-8}cm^2/s$, and the time *(t)* required for the curatives to diffuse X cm is given by:

$$t = (X^2/D) \qquad \ldots 1$$

Use of *Equation 1* gives $t \sim 1$ s. This allows ample time for the diffusion of the crosslinking agents from the EPDM to the NR during the vulcanisation of the blends.

Blends A and *B* have a polymer ratio of 7:3 (NR:EPDM), *Blends C* and *D* have a 1:1 polymer ratio and illustrate the consequences of this migration more clearly. NR control *Vulcanisates E* and *F* represent the extreme cases of : 1) no curative migration *(E)* since the curative level is the same as used in the blends; 2) total curative migration to the NR component *(F)* since the curative level is twice that in the blends. Both *Blends C* and *D* show H% values considerably greater than that of the control *Vulcanisate E,* indeed the high values observed are very close to the H% value of control *Vulcanisate F.* The NMR spectra of *Blend D* and vulcanisates *E* and *F* may be compared in *Figure 2.* When these H% values are related to the crosslink concentrations and to the *SV* values, the effect of curative migration is seen to be much more pronounced in *Blends C* and

TABLE 3. NMR DATA

Item	Vulcanisate						
	A	B	C	D	E	F	G
H%	64	62	56	53	28	59	56
v^a	66.4	64.2	57.3	53.9	25.6	60.7	57.3
SV[b]	2.37	2.23	1.93	1.76	1.0	2.10	1.93

[a]Crosslink density mol/m^3 calculated using Equation 2 of Reference 4.
[b]The amount of sulphur required to give the observed H% value if a S/TMTM (1:0.4) system were used, from Figure 3 of Reference 4.

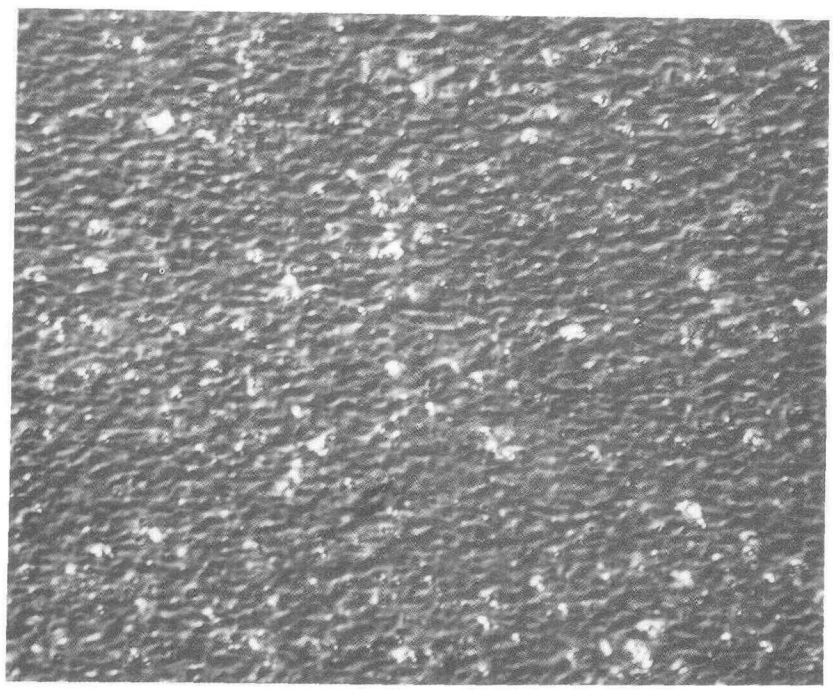

Figure 3. Differential interference contrast light micrograph of Blend A (NR/EPDM 70:30). Field of view 72 × 58 μm. White flecks are zinc oxide particles.

D than in *Blends A* and *B*. The crosslink concentrations in the NR phases of *Blends C* and *D* are actually more than double that in the control *Vulcanisate E*. They are, however, still lower than that in control *Vulcanisate F*. The *SV* values indicate that the NR components of the blends are utilising 84% - 92% of the curatives in the compound, this means that about 80% of the curatives initially located in the EPDM phase are diffusing to the NR phase during vulcanisation.

The higher level of crosslinking attained in the NR phase of an NR/EPDM blend may be undesirable - it can reach levels at which properties in a single polymer vulcanisate would be expected to decline. This should be considered in formulating such blend compounds, and thought should be given to reducing the level of curatives. In order to achieve the degree of crosslinking expected from the level of curatives used, *i.e.* the level that would be obtained in the absence of diffusion of crosslinking agents,

the diffusion of curatives from the EPDM must be considered. If ϕ is the weight fraction of NR in the blend then the proportion of the compounded curatives diffusing from the EPDM is given by the product of this 80% factor and the weight fraction of EPDM [0.8 $(1-\phi)$]. This material increases the proportion of the curatives used by the NR phase by 0.8 $(1-\phi)/\phi$. The increase can be allowed for in compounding if the curative levels are adjusted by a factor of α where:

$$\alpha = 1/\{1 + [0.8\ (1-\phi)/\phi]\}. \qquad \ldots 2$$

This latter factor may vary with cure system, and should merely be used as a rough guide to the curative levels required. Furthermore, the optimum degree of crosslinking of the NR phase for good physical properties of the blend may lie at a somewhat higher level, due to the near absence of crosslinking in the EPDM phase. Further investigation is required in order to resolve these issues.

At both polymer ratios, the chemical modification of the EPDM results in a small reduction in the observed crosslink levels in the NR phase of the blend, but this is probably too small a reduction to account for the improvement in tensile properties in terms of increased sulphur crosslinking of the EPDM phase. The ionomeric network in the modified EPDM must be responsible for the improvements observed.

CONCLUSIONS

The analysis of swollen rubber vulcanisates, both homopolymer and blends, using ^{1}H NMR spectroscopy has demonstrated the effect of diffusion of crosslinking agents from EPDM to NR during the vulcanisation process. Such diffusion results in elevated crosslink levels in the NR. The magnitude of the effect has been quantified both in terms of the increase in crosslink density within the NR phase (some 14% for a 70:30 NR:EPDM blend, greater than 100% in a 1:1 blend), and in terms of the level of curatives required to produce that amount of crosslinking in a pure NR gum vulcanisate. This latter analysis shows that the NR phase utilises some 80% of the curatives that are expected to reside in the EPDM component. It is recommended that this factor should be allowed for in compounding such blends, indeed in any blend of polydiene elastomer with an elastomer of low unsaturation. Given such monopolisation of chemicals by one phase, the poor tensile properties of such blends are easily understood.

The use of chemically modified EPDM in NR-EPDM blends results, as reported by Coran[2], in materials of superior tensile properties. The effect of this modification on the vulcanisation chemistry appears to be minimal, at least in terms of the crosslink density observed in the NR component of the blends.

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