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Analysis of Vulcanisate Blends by Swollen State ^{13}C NMR Spectroscopy

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Swollen state ^{13}C spectroscopy has been used to study vulcanised blends of natural rubber/ nitrile butadiene rubber and natural rubber/epoxidised natural rubber both qualitatively and quantitatively. The results obtained show that although the polymers present can be identified and the individual polymers characterised in terms of their co-polymer composition (i.e. the nitrile and epoxide levels determined), the use of this technique to determine the actual blend composition is unsatisfactory. The reasons for the deviations of the results obtained from the true values are discussed.

Proton and ^{13}C NMR spectroscopy are well established techniques[1-3] for the examination of polymers to investigate both their chemical composition and microstructure. Analysis may be carried out in a suitable solvent or in the solid state. The former requires nothing more than that the polymer is soluble whilst the latter is a highly specialised technique requiring modified instrumentation and an extended range of expertise. As a general rule it should also be considered non-quantitative.

In rubber formulation analysis it is obviously useful to be able to determine the chemical composition of the elastomeric phase of a vulcanisate without pyrolysing or otherwise degrading the polymer to make it soluble, or by recourse to the specialised, and hence expensive, solid state NMR technique.

It has already been shown that both ^1H and ^{13}C spectra can provide useful data on the crosslink density of the individual polymers in a swollen blend vulcanisate. The initial work involved the analysis of swollen vulcanised blends[4] using a continuous-wave ^1H NMR spectrometer and has since been extended to FT instruments using both ^1H and ^{13}C NMR spectroscopy[5-7]. It has also been demonstrated that swollen state NMR spectroscopy can be used for the identification and characterisation of some single elastomer vulcanistes[8]. In this paper we demonstrate the application of swollen state ^{13}C NMR spectroscopy to the analysis of blends of natural rubber (NR) with acrylonitrile-butadiene rubber (NBR) and epoxidised natural rubber (ENR) and show the possibilities, and limitations, for both qualiative and quantitative studies of these blends.

EXPERIMENTAL

Single polymer and polymer blend compounds were all prepared using a Banbury internal mixer followed by a final mix on a mill. A Monsanto MDR 2000 E rheometer was used to study the curing behaviour of all of the samples and all samples subjected to NMR analysis were press cured to T_{max} at 150°C as 9" × 9" × 1 mm sheets between milar film.

Strips from the vulcanisates were extracted in hot methanol overnight and dried. 1 mm × 1 mm × 20 mm strips were swollen in deuterochloroform in sealed vials for 24 h. The strips were then cut to size to fit easily into standard

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glass NMR tubes and covered to a constant height with fresh solvent.

All samples of NR, NBR, ENR 50*, NR/NBR and NR/ENR 50 blends of varying crosslink densities were examined by ^{13}C NMR spectroscopy using a General Electric QE300 300 MHz FT-NMR instrument fitted with a dual ^{1}H/^{13}C probe. Raw NBR and ENR 50 were also examined, as solutions in deuterochloroform, by 1H and 13C NMR spectroscopy as control materials. 1H NMR spectra were obtained with 30° pulse, 6 s pulse delay, 16K data size and a sweep width of +/-3000 Hz; ^{13}C NMR spectra were obtained with pulse width 45°, proton decoupling, pulse delay 6 s, 32K data size and a sweep width of +/-10 000 Hz. To determine the effect of possible NOE differences some experiments were also carried out with gated decoupling.

Vulcanisate formulations are shown in *Tables 1* to *6*.

RESULTS AND DISCUSSION

Before attempting to obtain quantitative data from NR/NBR blends it was essential to ensure that valid data can be obtained from the single NBR co-polymer.

Estimation of the Acrylonitrile Content of NBR

Willoughby[9] used the olefinic carbon signals in the ^{13}C NMR spectra of raw NBR to determine the %ACN whilst Gonzalez *et al.*[8] extended these studies to vulcanised NBRs. Estimates of the acrylonitrile content (%ACN) of the raw NBR polymers used in these vulcanisates were obtained by both ^{1}H and ^{13}C NMR spectroscopy. However, in many cases, especially at higher crosslink densities, the overlap of these olefin signals prevented an accurate determination of peak heights; so we propose the use of the methylene signals for this purpose. The various methylene resonances are detailed in *Table 7*, using assignments reported by Katritzky and Wess[10].

The results presented below in *Table 8* show a discrepancy between the measured values and those expected from the manufacturers' specifications at higher levels of acrylonitrile. The figures for the ^{1}H and ^{13}C NMR spectroscopic techniques do, however, show good agreement and suggest that the bales of NBR used in this study may have had a slightly lower than expected acrylonitrile content. This was confirmed by FT-Raman spectroscopy[11] where the lower levels of acrylonitrile were also obtained.

The ^{13}C NMR spectroscopic procedure was then applied to a series of vulcanised NBRs, varying the crosslink density of the samples, the accelerator used and the filler (if any). The results are given in *Table 9*.

This set of experiments confirmed that the method for determining %ACN could be applied to a range of different NBRs, cured with different accelerators, to varying crosslink densities. The use of gated decoupling did not have any significant effect on the results obtained. This is experimentally useful as gated decoupling gives a weaker spectrum and thus longer spectral accumulation times are required to produce acceptable signal/noise ratios.

NR/NBR Blends

Once it had been established that reliable data could be obtained for both raw and vulcanised NBRs it was appropriate to analyse some NR/NBR blends although, with these, the %ACN determination had to be modified

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*ENR 50 is the name given to a modified natural rubber where nominally 50 mole % of the unsaturation is converted to epoxide groups.

TABLE 1. NBR GUM VULCANISATES WITH VARYING CURE AND ACCELERATORS

Mix number	1-1	1-2	1-3	1-4	1-5	1-6
Perbunan 1807 NBR	100	100	100	-	-	-
Breon N41.C80 NBR	-	-	-	100	100	100
TMTD	0.2	2.4	-	0.2	1.4	-
ODIP	-	-	1.9	-	-	1.3
Sulphur	0.5	6.0	1.5	0.4	3.4	1.0
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Flectol pastilles	1.5	1.5	1.5	1.5	1.5	1.5

TABLE 2. CARBON BLACK FILLED NBR N28 AND N34 VULCANISATES

Mix number	2-1	2-2
Krynac 34.5 NBR	100	-
Krynac 27.5 NBR	-	100
N330 Carbon black	30	30
CBS	1.0	1.0
Sulphur	1.5	1.5
Zinc oxide	5	5
Stearic acid	2	2
Flectol pastilles	0.5	0.5

TABLE 3. NBR/NR GUM VULCANISATES

Mix number	3-1	3-2	3-3	3-4	3-5
SMR 10	25	50	75	50	75
Perbunan 1807 NBR	75	50	25	-	-
Breon N41.C80 NBR	-	-	-	50	25
TMTD	0.6	0.6	0.6	0.6	0.6
Sulphur	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Flectol pastilles	0.5	0.5	0.5	0.5	0.5

TABLE 4. BLACK NR/NBR VULCANISATES WITH VARYING POLYMER RATIOS

Mix number	4-1	4-2	4-3	4-4
SMR 10	80	60	40	20
Breon N41.C80 NBR	20	40	60	80
N330 Carbon black	30	30	30	30
CBS	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Flectol pastilles	0.5	0.5	0.5	0.5

TABLE 5. BLACK NR/NBR 50/50 VULCANISATES WITH VARYING CURE

Mix number	5-1	5-2	5-3	5-4	5-5	5-6
Breon N41.C80 NBR	50	50	50	50	50	50
SMR L	50	50	50	50	50	50
N330 Carbon black	30	30	30	30	30	30
CBS	0.4	0.5	0.6	0.8	1.0	1.2
Sulphur	0.6	0.8	1.0	1.2	1.6	1.8
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Flectol pastilles	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 6. BLACK NR/ENR 50 VULCANISATES WITH VARYING POLYMER RATIOS

Mix number	6-1	6-2	6-3	6-4	6-5	6-6	6-7
SMR 10	100	80	60	50	40	20	0
ENR 50	0	20	40	50	60	80	100
N330 Carbon black	30	30	30	30	30	30	30
CBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
Flectol pastilles	0.5	0.5	0.5	0.5	0.5	0.5	0.5

TABLE 7. TRIAD SEQUENCES AND POSITIONS (P.P.M.)

Triad sequences	Number of ACN units	Total number of units	Ratio of ACN units to total units	Methylene carbon shift (ppm)
BAB, BBA, ABB, ABA	5	12	0.42	30.0
BAB, BBA, ABA, ABB	5	12	0.42	31.3
BBB	0	3	0	32.6
BAB, ABB, ABA	4	9	0.44	35.2

% ACN = 0.42 × 30.0 ppm integral + 0.42 × 31.3 ppm integral + 0.44 × 35.2 p.p.m. integral/total methylene integral

TABLE 8. RAW NBR ANALYSIS

Description	Manufacturers' %ACN	^{1}H NMR %ACN	^{13}C NMR %ACN
Perbunan N1807 NS	18	17.7	19.1
Krynac N27.5	27.5	27.9	28.2
Krynac N34.5	34.5	32.0	32.4
Breon N41.C80	41	38.9	38.1

TABLE 9. NBR SINGLE POLYMER VULCANISATES; %ACN *VS* DATA OBTAINED FROM THE RAW ELASTOMERS

Description	%ACN raw NBR[a]	%ACN vulcanised NBR
N18 gum vulcanisate (mix 1-1)	18.4	19.5
N18 gum vulcanisate, gated decoupling (mix 1-1)	18.4	19.1
N18 gum vulcanisate, medium crosslink density (mix 1-3)	18.4	20.1
N41 gum vulcanisate (mix 1-4)	38.5	38.0
N41 gum vulcanisate, gated decoupling (mix 1-4)	38.5	38.5
N41 gum vulcanisate, high crosslink density (mix 1-5)	38.5	38.0
N41 gum vulcanisate, medium crosslink density (mix 1-6)	38.5	37.0
N34 black filled vulcanisate (mix 2-1)	32.2	32.6
N28 black filled vulcanisate (mix 2-2)	28.5	28.0

[a] The average of determinations by ^{1}H and ^{13}C NMR spectroscopy

due to the presence of the methylene and methyl carbon signals from the NR. The NR (polyisoprene) has methylene signals at 32.2 p.p.m., 26.4 p.p.m. and a methyl carbon signal at 23.3 p.p.m. As the 32.2 p.p.m. isoprene methylene overlaps with the 32.6 p.p.m. NBR methylene a correction must be made for the presence of this peak. Examination of both raw and vulcanised NR indicates that the area of the 32.2 p.p.m. peak is equivalent to that of the NR 26.4 p.p.m. methylene. Thus the area of the 32.6 p.p.m. signal which is derived from the NBR methylene may be determined by subtracting the integrated peak area of the NR signal at 26.4 p.p.m. from the total 32 p.p.m. envelope. The %ACN is then determined as above.

From the NR and NBR methylene carbon integrals the weight % NR is calculated using the following scheme:

(A) Amount of NR = 26.4 p.p.m. NR integral × 2 × molecular weight of the isoprene unit (68)

(B) Amount of NBR = total NBR methylene integral × [%ACN × molecular weight of acrylonitrile (53) + %butadiene × molecular weight of butadiene (58)].

Thus weight % NR = results from (A) × 100/[results from (A) + results from (B)]. *(The multiplication factor of '× 2' in (A) is to take into account that each NBR unit has two methylene carbons for every isoprene carbon measured.)*

This method was used to examine a range of NBR vulcanisates and the results from these analyses are given in *Table 10.*

It can be seen from *Table 10* that there is good agreement in determination of the %ACN content of each sample but poor correlation in the NR/NBR ratio determination. Analysis of a raw NR/NBR 50/50 blend, prepared by an identical mixing process but without subsequent vulcanisation showed a ratio of 52/48, suggesting that the problem results from the vulcanisation stage.

It has previously been concluded that the overall measured NMR signal area derived from a single polymer vulcanisate analysed by the swollen state procedure reduced with increasing crosslink density[12], a result that would be expected since it is in line with decreasing chain mobility. It has also been shown[5] that the NBR phase of a NR/NBR blend vulcanisate has a higher crosslink density than does the NR unless special care is taken in selecting an appropriate mix of accelerators and one thus might reasonably expect a proportionally greater reduction in the signal from the elastomer with the higher crosslink density. As the overall curative level increases, this would be expected to enhance the effect. A set of 50/50 NR/NBR blends was therefore prepared with increasing crosslink density *(Table 5)* to determine if the increase in curative level, and thus crosslink density, would affect the calculated value of the NR/NBR ratios. These were obtained using the above technique and the results are given in *Table 11.*

There is an obvious trend within this set of results indicating that the level of NBR found in the NR/NBR blend decreases with the overall increasing crosslink density. Thus when there is a higher level of curative used, the difference in the level of crosslinking between the two phases increases and the results deviate further from that of the known mix. Obviously any other change in the cure system which has the potential to modify the crosslink ratio and absolute levels will also have an effect on the apparent polymer blend ratio when measured by this procedure. This factor, whilst confirming the earlier work on crosslink

TABLE 10. RESULTS FROM ANALYSIS OF NR/NBR RATIO AND %ACN

Mix number	NR/NBR ratio as mixed	NR/NBR ratio determined	%ACN determined in raw rubber[a]	%ACN determined in vulcanisate
3-1	25/75	42/58	18.4	17.6
3-2	50/50	53/47	18.4	18.5
3-3	75/25	95/05	18.4	18.1
3-4	50/50	78/22	38.5	40.5
3-5	75/25	95/05	38.5	40.0
4-1[b]	80/20	91/09	38.5	39.1
4-2[b]	60/40	81/19	38.5	39.4
4-3[b]	40/60	58/42	38.5	39.8
4-4[b]	20/80	32/68	38.5	39.1

[a]Average of determinations by ^{1}H and ^{13}C NMR spectroscopy
[b]Carbon black filled vulcanisates

TABLE 11. QUANTIFICATION OF NR/NBR BLENDS OF INCREASING CROSSLINK DENSITY

Mix number	NR/NBR ratio mixed	NR/NBR ratio calculated	%ACN raw rubber[a]	%ACN calculated
5-1	50/50	58/42	38.5	36.4
5-2	50/50	63/37	38.5	38.0
5-3	50/50	66/34	38.5	37.8
5-4	50/50	68/32	38.5	37.6
5-5	50/50	73/27	38.5	36.8
5-6	50/50	74/26	38.5	39.3

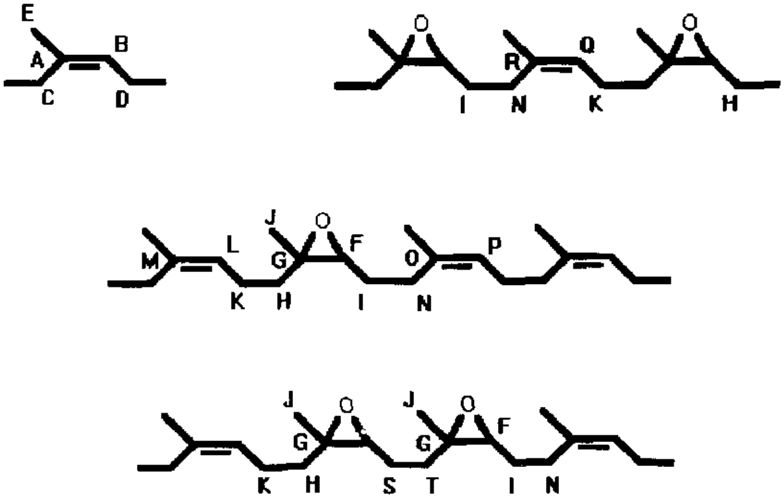
[a]Average of determinations by ^{1}H and ^{13}C NMR spectroscopy

density determinations[5], limits the use of solvent swollen ^{13}C NMR spectroscopy to the determination of the %ACN of the NBR in a NR/NBR blend although this, in itself, is valuable information which is otherwise difficult to obtain.

NR/ENR Blends

As with the study of NR/NBR blends, the examination and quantification of NR/ENR blends was approached by first attempting to obtain a reliable method for the determination of epoxide content in ENR vulcanisates by solvent swollen ^{13}C NMR spectroscopy. The estimation of the epoxide content of raw ENR by ^{13}C NMR has been demonstrated by Davey and Loadman[13] with the assignments made as illustrated in *Figure 1*.

Davey and Loadman[13] demonstrate that the % epoxide can be determined from the ratio of the epoxide CH-O (64.4 p.p.m.) *vs* the sum of the CH-O + total CH = signals (125.1 p.p.m.).



A = 134.7 p.p.m.

B = 125.1 p.p.m.

C = 32.0 p.p.m.

D = 26.2 p.p.m.

E = 23.4 p.p.m.

F = 64.4 p.p.m.

G = 60.3–60.8 p.p.m.

H = 33.1 p.p.m.

I = 27.0 p.p.m.

J = 22.3 p.p.m.

K = 23.9 p.p.m.

L = 125.6 p.p.m.

M = 134.3 p.p.m.

N = 28.7 p.p.m.

O = 135.1–135.7 p.p.m.

P = 124.5 p.p.m.

Q = 125.1 p.p.m.

R = 135.2 p.p.m.

S = 24.7 p.p.m.

T = 29.7 p.p.m.

Figure 1. Assignment of ^{13}C NMR spectrum of ENR.

However, due to overlap of the NR bands with the ENR isoprene bands this cannot be carried out when additional NR is present. Thus an alternative method, using the glass transition temperatures of the materials must be used to determine the epoxide content when NR is also present[13].

The ENR 50 samples used for these experiments was found to have an epoxide content of 54.1% by ^{1}H NMR and 54.9% by ^{13}C NMR.

Estimation of NR/ENR Ratio

Once the epoxide level of the ENR present has been determined the NR/ENR ratio can be obtained using swollen state ^{13}C NMR. In this case NR olefin *vs* the ENR epoxide CH-O bands are used *i.e.* the ratio of the 125.1 p.p.m. and the 64.4 p.p.m. bands.

The calculation is as follows:

Corrected ENR integral:

(C) Epoxide **CO** integral (64.4 p.p.m.) × (100/% epoxide)

Corrected NR integral:

(D) C=H (125.1 p.p.m.) integral – [(100–%epoxide)/100] × **(C)**

Wt portion of ENR

(E) Corrected ENR integral (C) × {68 + [16 × (%epoxide/100)]*}

Wt portion of NR

(F) Corrected NR integral (D) × 68**

The results of the application of this technique to the samples listed in *Table 6* are listed in *Table 12*

TABLE 12 RATIO OF NR/ENR 50 IN VULCANISED BLENDS

NR/ENR 50 ratio	Ratio determined using standard ^{13}C conditions	Ratio determined using gated decoupling
20/80	24/76	26/74
40/60	46/54	48/52
50/50	53/47	53/47
60/40	67/33	67/33
80/20	87/13	85/15

In each case there is a lower proportion of the ENR 50 phase determined than there is known to be present whether standard, or gated, decoupling is used. This is not true of a raw mixture of the two elastomers where the proportions of each phase can be accurately determined. There is an obvious similarity to the study of NR/NBR blends, with additional crosslinking in the ENR phase resulting in the detection of less of this elastomer. Although only one set of NR/ENR 50 blends has been examined the similarity to the case of the NR/NBR blends does once again show that the method cannot be used for accurately quantifying the NR/ENR ratio in vulcanised blends

CONCLUSIONS

The examination of solvent-swollen vulcanisates blends by FT-NMR spectroscopy with a view to polymer identification has been discussed Whilst the quantitative analysis of copolymer constituent monomers has been shown to be viable for a wide variety of crosslink densities in both single polymer systems and blends, the quantitative data obtained from blend analyses show a deviation from the 'true' result, with the extent of that deviation being related to the degree of maldistribution of crosslinks between the two components of the blend.

The procedure, therefore, offers a convenient way of qualitatively identifying the individual polymers in a blend and of quantifying the components of a homopolymer It may also have potential in research studies of crosslink systems where a comparison of 'known' and 'determined' blend compositions may simply provide data on the uneven distribution of crosslinks without recourse to the time-consuming preparation of standards and the construction of standard calibration graphs

Small variations in the relative crosslink densities of individual polymers of a vulcanised blend can have substantial effects on the physical properties of the overall vulcanisate In a quality control environment, this procedure offers a convenient method for monitoring the consistency of the crosslink distribution ratio

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*Average molecular weight of ENR unit

**68 is molecular weight of the isoprene unit

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