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Investigating Crosslinking in Blends by Differential Scanning Calorimetry

S. COOK*#, S. GROVES* AND A.J. TINKER*

Linear correlations between physical crosslink density and T_g, as measured by high DSC, have been demonstrated for NR, BR and SBR gum vulcanisates. The dependence of T_g on crosslink density was similar for both NR and BR vulcanisates but was significantly less than that demonstrated for SBR. In the case of NR, the T_g was also related to the level of sulphur in the compound and hence the efficiency of the cure. To achieve the high level of precision required in the DSC measurements it was found necessary to perform duplicate runs of each sample and to calibrate the instrument before and after each run by measuring the T_g of raw NR (–72°C).

The correlations found between physical crosslink density and T_g for the respective polymers had been used to estimate the physical crosslink density of NR/BR and NR/SBR blends. A suitable calibration for these measurements was found to be a raw rubber (unvulcanised) blend of the same polymer composition rather than the individual raw polymer. Estimates of physical crosslink densities of blends made by DSC compared well with measurements made by swollen state ^1H NMR.

Key words: blends; crosslink density; DSC; NR; BR; SBR; Swollen state NMR; T_g

The dependence of T_g on crosslink density was used in the early presentation of the now established swollen-state NMR as a means of providing independent confirmation that the crosslink distributions revealed in NR/NBR blends were, at least qualitatively, correct[1]. At that time, the complexities of endeavouring to use T_g in this way were not fully appreciated, and the crosslink distributions concerned were so extreme that the experimental errors associated with the DSC measurements were not sufficient to negate the use of the procedure. Here, the potential of DSC to provide useful information on more testing blend systems in which the crosslink distributions are less extreme, NR/BR and NR/SBR, is considered.

EXPERIMENTAL

The formulations of gum NR, BR and SBR vulcanisates used in this work are given in *Tables 1 – 3* respectively, and the formulations of gum blends in *Table 4*.

Masterbatches containing all ingredients other than sulphur and accelerator were prepared in a BR Banbury mixer. Final compounds were prepared by addition of curatives to

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TABLE 1. FORMULATIONS OF NR COMPOUNDS

Masterbatch: NR (SMR CV) 100; Zinc oxide 3.5; Stearic Acid 1.5; TMQ 3

Sulphur (p.h.r.)	0.6	0.9	1.2	1.5	1.8	2.4
CBS (p.h.r.)	0.4	0.6	0.8	1.0	1.2	1.6

TABLE 2. FORMULATIONS OF BR COMPOUNDS

Masterbatch: BR (Europrene Neo-*cis* BR40, Enichem) 100; Zinc oxide 3.5; Stearic acid 1.5; TMQ 3

Sulphur (p.h.r.)	0.45	0.6	0.9	1.2	1.5	1.8	2.4	3.0
CBS (p.h.r.)	0.30	0.4	0.6	0.8	1.0	1.2	1.6	2.0

TABLE 3. FORMULATIONS OF SBR COMPOUNDS

Masterbatch: SBR (Intol 1500®, Enichem) 100; Zinc oxide 3.5; Stearic acid 1.5; TMQ 3

Sulphur (p.h.r.)	0.45	0.6	0.9	1.2	1.5	1.8	2.4	3.0
CBS (p.h.r.)	0.30	0.4	0.6	0.8	1.0	1.2	1.6	2.0

TABLE 4. FORMULATIONS OF BLEND COMPOUNDS

Curatives: Sulphur 2; CBS 1

SMR CV	70	50
BR40	30	–
SBR	–	50
Zinc Oxide	3.5	3.5
Stearic acid	1.5	1.5
TMQ	2.0	2.0

portions of a masterbatch on a cooled two-roll mill. Sheets of 2 mm thickness were compression moulded at 150°C for the time to maximum torque measurement in a Monsanto MDR2000E rheometer, except for the BR compounds containing 0.45 p.h.r. and 0.6 p.h.r. sulphur which were moulded for 1 h.

Physical crosslink densities of gum NR, BR and SBR vulcanisates were calculated from the Mooney-Rivlin constant C1 estimated from stress-strain measurements performed on an Instron in accordance with procedures developed by Campbell *et al.*[2]; the strain rate was 10% per min. Duplicate estimates were in close accord, generally within 2%.

Physical crosslink densities in the individual elastomers in NR/BR and NR/SBR blends were determined by swollen-state NMR spectroscopy in carbon tetrachloride using a Bruker AC300 300 MHz spectrometer. Details of the experimental procedures adopted have been given previously[3] as have the method for

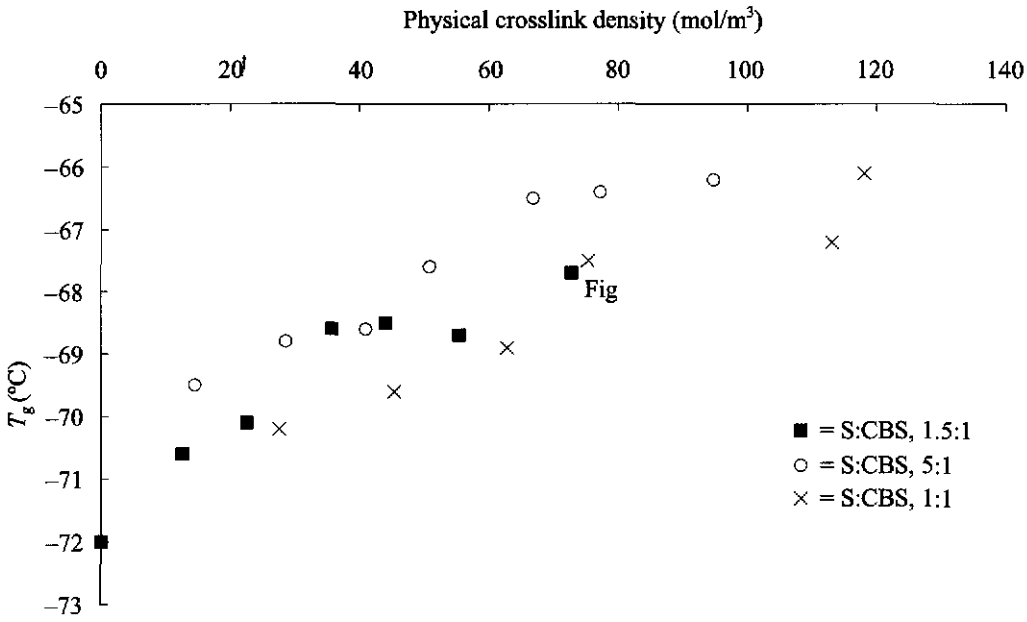

Figure 1. Effect of cure system on relationship between T_g *and physical crosslink density for NR.*

estimating crosslink densities from the spectra of the blends[4]. For the NR and BR, the peak reference offsets used in the estimation of the measure of peak width, H%, were as reported before, −0.1 p.p.m. and +0.1 p.p.m. from the olefin peak positions, respectively[3]. For SBR, the peak reference offset was set at −0.15 p.p.m. from the peak at about 7.4 p.p.m. due to the styrene repeat unit.

Glass transition temperatures were measured using a Perkin-Elmer DSC7 instrument operating between −130°C and −40°C at a heating rate of 20°C/min. The sample size was in the range 10 mg – 14 mg. For single polymer vulcanisates, two measurements were made for duplicate samples of each vulcanisate and the T_g of raw NR was measured before and after each set of four runs. The T_g of the raw NR was used to calibrate the instrument, and T_gs of the vulcanisates are quoted on the basis of −72°C as the T_g of raw NR[5]. When there was undue scatter in the four estimates of T_g for a given vulcanisate (>1°C), a further two measurements were undertaken. For blends, the procedure was modified, by replacing measurements of the T_g of raw NR to calibrate the instrument by measurements of raw blend.

RESULTS AND DISCUSSION

The dependence of T_g on physical crosslink density (n_{phys}) for the gum NR vulcanisates is presented in *Figure 1* in the context of the earlier data[1] for more (1:1 S:CBS) and less (5:1 S:CBS) efficient sulphur cure systems.

TABLE 5. LINEAR REGRESSION ANALYSIS OF DEPENDENCE OF T_g ON PHYSICAL CROSSLINK DENSITY FOR GUM VULCANISATES

Elastomer	Intercept (°C)	Slope (°C/molm^3)	r^2
NR (5:1 S:CBS)	–70.1	0.0459	0.935
NR (1:1 S:CBS)	–71.3	0.0416	0.921
NR (1:5:1 S:CBS)	–70.9	0.0462	0.858
BR (1:5:1 S:CBS)	–114.4	0.0485	0.923
SBR (1:5:1 S:CBS)	–57.9	0.109	0.926

TABLE 6. DEPENDENCE OF CRYSTALLIZATION OF BR ON CROSSLINK DENSITY

Physical crosslink density (mol/m^3)	Crystallization Exotherm (J/g)	Crystallization Temperature (°C)
0	29.5	–73.8
2.0	32.2	–65.4
4.1	28.3	–62.9
21.6	25.8	–60.3
38.5	21.4	–59.0
59.1	11.6	–52.6
61.3	None seen	
78.0	None seen	
95.2	None seen	

As expected, the new data lie between the other two data sets; this is apparent in the comparison of the intercepts and slopes of the linear regressions given in *Table 5*.

A difficulty arises in performing the measurements of T_g on BR; this elastomer crystallizes during the first heating cycle, precluding a second measurement of T_g on the sample. It was necessary to modify the general procedure used for the measurements in order to obviate this problem. The sample was cooled to –130°C, heated to –90°C, cooled back to –130°C, and then heated to –50°. This enabled two measurements of T_g and a single measurement of the crystallization event on each sample. The magnitude of the crystallization exotherm decreased with increasing crosslink density whilst the temperature at the maximum increased (*Table 6*). No crystallization was observed under these conditions when the crosslink density exceeded 60 mol/m^3. This is consistent with the effects of decreasing mobility as crosslink density increases and increasing main chain modifications due to increasing curative levels.

When comparing the behaviour of different elastomers, it is more useful to consider the shift in T_g arising from vulcanisation. The dependence of T_g on crosslink density is presented in this way for all three gum vulcanisates in *Figure 2*. It is evident that, whilst NR and BR have similar dependences, the increase in T_g of SBR with crosslink density is much greater (*Table 5*).

Initial attempts to investigate crosslinking in vulcanised blends by using the same procedures for measuring T_g by DSC gave obviously invalid results; in some instances the T_g values estimated were below the T_g of the raw elastomer. Measurements performed on raw blends of NR and BR and NR and SBR demonstrated that, for the former combination in particular, the presence of one elastomer affects the T_g measured for the other. The effects are small, but in the context of the low dependence of T_g on crosslink density, they are significant. As an example, in two separate observations for 50:50 NR:BR blends, the NR T_g was observed to be depressed (–1.7°C and –1.9°C) whilst the BR T_g was observed to be increased by 0.5°C on both occasions. The standard procedure was modified by replacing measurements on raw NR before and after runs on a vulcanisate with measurements on a comparable raw blend. The T_g values for the components of the blend were then quoted only as the shift relative to the T_g of the relevant elastomer in the comparable raw blend.

A swollen-state NMR spectroscopy technique for estimating crosslink densities in blends has become established[1,3,4,6–10]. There

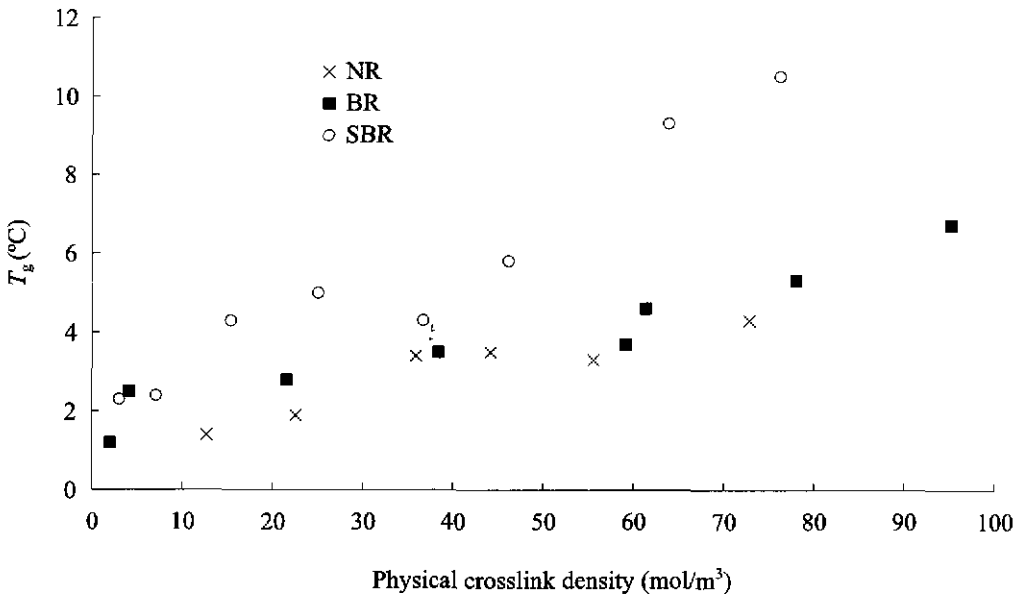

Figure 2. Dependence of ΔT_g on physical crosslink density for NR, BR and SBR gum vulcanisates.

has been considerable characterisation of NR/BR blends, in particular covering aspects such as the effect of efficiency of the cure system[7,8], the type of sulphenamide accelerator used[8,9], the change in distribution of crosslinks between the two elastomers in the blend during vulcanisation[9], and dependence of the distribution of crosslinks on cure temperature[3,8,10]. Investigation of blends of NR with SBR has not been reported previously, hence it is necessary to present here the calibration cure relating the measure of peak width used, H%, to n_{phys} (*Figure 3*). Although experience suggests that the relationship should be somewhat sigmoidal, in practice there is little justification to use other than the linear fit indicated on the plot:

$$H\% = 16.13 + 0.73n_{phys}$$
$$r^2 = 0.985$$

The procedure for obtaining peak widths of the components of a blend requires correction terms to allow for the overlapping of signals from the two elastomers4 for NR contributions at the SBR aromatic peak:

$$P\%H = 0.2912H\% - 0.00977H\%^2 + 0.000103H\%^3$$
$$R\%H = 0.3299H\% - 0.01078H\%^2 + 0.000133H\%^3,$$

and for SBR contributions at the NR olefinic peak:

$$P\%H = -6.658 + 1.543H\%$$
$$R\%H = 2.453H\% - 0.0265H\%^2 + 0.000136H\%^3$$

When considering endeavouring to deduce the crosslink densities in the individual

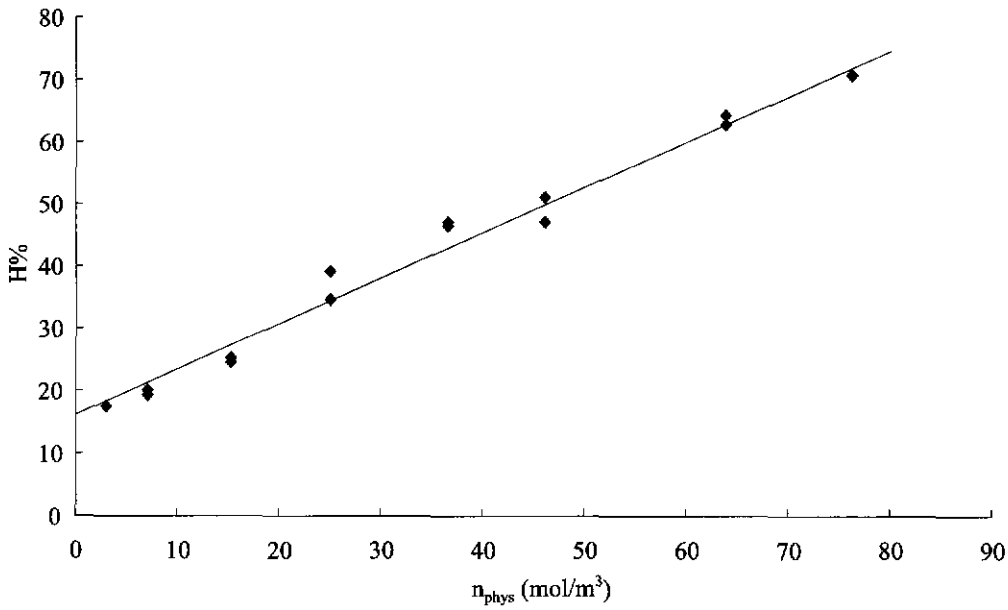

Figure 3. Dependence of H% on physical crosslink density for SBR 1500.

TABLE 7. COMPARISON OF CROSSLINK DENSITIES IN NR/BR AND SBR/BR BLENDS ESTIMATED BY DSC AND SWOLLEN-STATE NMR

Estimated	Crosslink density (mol/m^3)			
	70:30 NR:BR		50:50 NR:SBR	
	NR	BR	NR	SBR
From T_g by DSC	50	73	43	38
From NMR	53	69	52	45

elastomer components of a vulcanised blend from the observed shifts in T_g, it is important to recognise that there is a source of uncertainty other than experimental error. For a single elastomer, it is shown that the shift in T_g is dependent on the efficiency of the cure system used. It is also known that the sulphur and accelerator may not partition similarly between two elastomers. The sulphur added to a blend of elastomers A and B might partition preferentially in elastomer A whilst the accelerator might partition in favour of elastomer B, for instance. Whilst matters might change during the vulcanisation process, it is evident that elastomer A is likely to experience the action of a cure system which is less efficient (higher sulphur: accelerator ratio) than was added to the blend as a whole whilst elastomer B is likely to experience the action of a more efficient cure system. Against this concern, there is the evidence of *Figure 1*, which suggest that, at least for NR, modest uncertainty regarding the effective efficiency of the cure system operating in a particular component of a blend will not introduce undue error in the estimate of crosslink density.

With this in mind, data are presented in *Table 7* for 70:30 NR:BR and 50:50 NR:SBR blends vulcanised with 2 p.h.r. sulphur and 1 p.h.r. CBS, not the 1.5:1 ratio used in generating the relationship given in *Table 5*. Estimations of crosslink densities for the two blend components were however made using the relationships developed for NR and BR compounds cured with a S:CBS ratio of 1.5:1. For the 70:30 NR:BR blend, the crosslink densities estimated for the NR and BR phases from the DSC measurements are in remarkably good accord with values obtained from swollen-state NMR. The agreement is less good for the 50:50 NR:SBR blend, but may be deemed reasonable in the light of the experimental difficulties.

CONCLUSIONS

Provided appropriate calibration procedures are used and the measurements made with care, it is possible to use T_g as measured by DSC as a means of estimating crosslink densities in vulcanised blends. It will not be possible to apply the procedure to all blends, SBR/BR blends cannot be investigated by this technique because extensive phase mixing at the interface during vulcanisation has a profound effect on T_g. The low dependence of T_g on crosslink density, the dependence also on cure system coupled with the uncertainty regarding the efficiency of the cure system actually operating in the individual phases of a blend mean that the technique has limited accuracy. However, it should be

possible to obtain useful information on black-filled vulcanisates Relative to swollen-state NMR spectroscopy, the procedure is at least as time-consuming and experimentally more demanding On the other hand, for saturated or low-unsaturation elastomers such as EPDM it should be less demanding than the alternative of swollen-state ^{13}C NMR spectroscopy

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