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THE APPLICATION OF LOW TEMPERATURE DIFFERENTIAL SCANNING CALORIMETRY TO POLYMER BLEND ANALYSIS

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The temperature regions in which glass transitions (*Tg*'s) occur for a series of blends of polybutadienes with natural rubber and two styrenebutadiene copolymers of different styrene contents have been studied by differential scanning calorimetry. The resulting DSC curves may be used to categorize the polybutadiene, determine the bound styrene content of the styrene-butadiene copolymer and quantify the polybutadiene content of the blends.

Whilst glass transition temperatures (*Tg*'s) of polymers have been studied for a number of years by differential scanning calorimetry (DSC) and differential thermal analysis (DTA), most attention appears to have been given to the relationship between *Tg* and parameters such as molecular weight (molar mass), microstructure, chain branching etc. [1].

In early studies into the rate of crystallization of *cis* 1,4-polybutadiene (BR) when blended with other elastomers Marsh et al. [2] commented that there was some "smearing out of the BR *Tg*" when it was blended with styrene-butadiene random copolymer (SBR) and that this did not occur with blends of polybutadiene and natural rubber (NR). Little attention has been paid to this observation although it was mentioned by Callan, Hess and Scott [3] in a paper mainly concerned with polymer blend compatibility and filler distributions therein.

DSC has been used [4–6] to analyse block copolymers of styrene and butadiene (SBS) and to study the effect which variations in the homopolymers have on the two observed *Tg*'s. It appears to have found little use in the routine analysis of commercial vulcanizates, although it offers analytical data not obtained by the more usually employed techniques of pyrolysis-infrared spectroscopy (PyrIR) and pyrolysis-gas chromatography (PyrGC).

This paper describes how DSC may be used to differentiate between SBR/BR blends and SBR's of low styrene content, how quantitative data on the polymer ratios for SBR/BR and NR/BR blends can be obtained, and how the type of BR (high or low vinyl) may be deduced.

Experimental

Measurements were made using a Perkin–Elmer model DSC 2 (power compensated) instrument equipped with the manufacturer's liquid nitrogen cooled subambient accessory, and the scanning auto-zero accessory. The instrument was allowed to stabilize thermally for at least three hours after its initial filling with liquid nitrogen and the reservoir maintained at least half full during the running of samples. The sample chambers were purged with helium.

The scanning auto-zero reference base line was obtained over the temperature range 140 K to 250 K with both sample and reference holders empty and at a heating rate of 20 deg min^{-1}; in subsequent sample studies this base line would be automatically subtracted in order to eliminate instrumental curvature and present a linear run-in to the region of the *Tg*.

Samples were cut from vulcanized sheets (see below) using a cork borer (5 mm diam), sealed in standard aluminium sample capsules, and DSC curves recorded against a reference of eight aluminium sample capsule lids sealed in one capsule.

The following heating and cooling programme was used for each sample:

1. Cool to 140 K at 360 deg min^{-1}
2. Heat at 20 deg min^{-1} whilst adjusting slope control to give a horizontal run-in to the *Tg*
3. Heat to 400 K at 360 deg min^{-1} and hold for 1 min. to anneal the sample.
4. Cool to 140 K at 360 deg min^{-1}
5. Commence the run proper at 20 deg min^{-1} as soon as thermal equilibrium is reached.

Each DSC curve was subsequently redrawn by hand with any slight slope being corrected, and with the total displacement of the *Tg* being normalized to a constant value. The total displacement was measured from the flat run-in to the *Tg* to the plateau clearly present after completion of the *Tg*. When a weak recovery was observed it was discounted by measuring the displacement to the plateau after the recovery.

Materials

Vulcanized sheets were prepared to the following recipe:

Polymer(s)	100	Sheets 1 mm thick cured
SRF Black	50	150°/30 min (NR/BR)
ZnO	5	150°/45 min (SBR/BR)
Stearic acid	2	
IPPD	1	
S	2.5	
CBS	0.6	

Polymers used were:

NR:	SMR 10		
BR:	Europrene Cis-4		93% cis
BR:	Diene	50 NF	36% cis
BR:	Diene	55 NF	36% cis
SBR:	Intol	1500	23.5% styrene
SBR:	Copo	1505	9.5% styrene

Results and discussion

Figure 1 illustrates the original DSC curves, through the glass transition region, of raw NR and BR (50 NF). It will be noted that both elastomers show a degree of recovery on completion of their devitrification process, but this is absent when the polymers are vulcanized so there is little difficulty in carrying out the normalization and slope-adjusting procedures. The weights of the two samples were virtually identical at 21.8 mg (NR) and 21.9 mg (BR) and measurement of the total endothermic displacements show that the increase in specific heat capacity is essentially identical for the two elastomers.

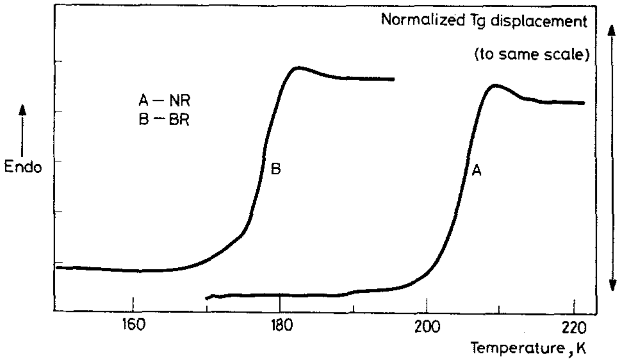

Fig. 1 Typical DSC curves of NR and BR (50 NF) as obtained

Figure 2 illustrates the glass transition temperature regions of six vulcanizates prepared using the six reference polymers individually, together with that of raw NR, which was used as a calibration reference standard for each series of runs. Because observed *Tg*'s vary with heating rate, and this variation itself appears to have some degree of instrument dependence, the calibration value taken for the *Tg* of raw NR (200.5 K) was that obtained by the extrapolation to zero heating rate of a series of values determined over a range of heating rates [7]. It will be observed

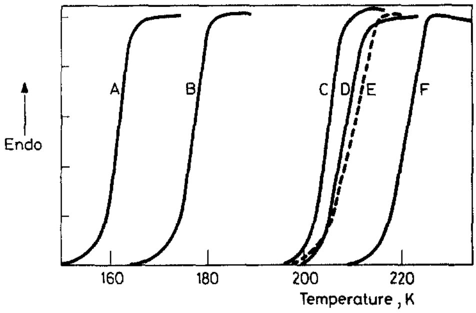

Fig. 2 Normalized glass transitions of reference vulcanizates calibrated against raw NR

that the *Tg*'s of 50 NF and 55 NF are indistinguishable. It should be further noted that vulcanization of NR results in the *Tg* being increased by some 3 K [7] and that, whilst the *Tg* of the 1505 is some 15 K below that of 1500, the widths from onset to completion of all the transitions are very similar.

Natural rubber-polybutadiene blends

Figures 3 and 4 illustrate the curves obtained from a series of blends of NR with the three different BR's. As would be expected those of NR/50 NF are extremely similar to that of NR/55 NF. Two separate *Tg*'s, indicative of two incompatible phases, are clearly visible with a well defined plateau between them. The data obtained from Fig. 1 would suggest that the displacement for the base line to the plateau, expressed as a fraction of the total endothermic displacement through the *TG*, could be used to quantify the BR content of the blend and, if the measurement is taken at an arbitrary 195 K, this is indeed found to be the case. The data are

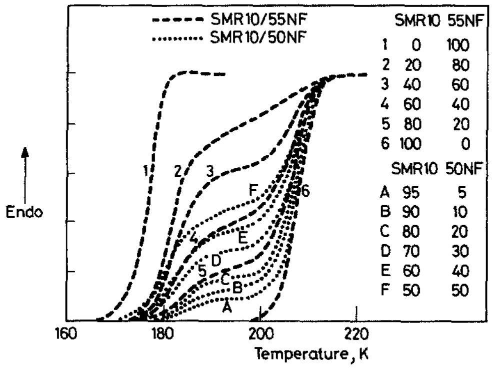

Fig. 3 *Tg* of NR/BR vulcanizates SMR10/50 NF; SMR10/55 NF. Normalized to the same total displacement as the reference samples (Fig. 2)

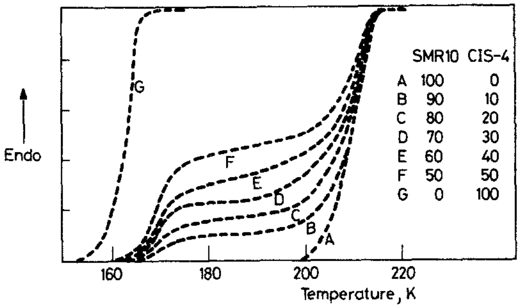

Fig. 4 T_g of NR/BR vulcanizates SMR10/cis-4. Normalized to the same total displacement as the reference samples (Fig. 2)

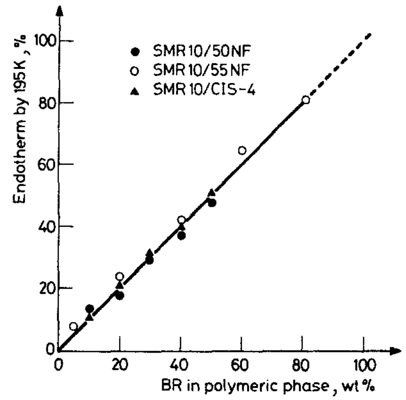

Fig. 5 Correlation between wt% BR in the polymeric phase (with NR) and % of devitrification endotherm occurring by 195 K

illustrated in Fig. 5, against a line representing a 1 : 1 correlation plot. Linear regression analysis of all the points obtained for the three blends illustrated shows a slope of 0.96 ± 0.06 and a residual standard deviation of 2.2 (intercept 1.1).

Styrene-butadiene copolymer/polybutadiene blends

The "smearing out" of the BR T_g, as described by Marsh [2] is clearly evident in the series of Figs 6–10 which illustrate the different transitions resulting from the merging of the individual T_g's of the two polymers which are fully compatible in all proportions. The lack of any plateaux makes quantification of the BR content more difficult than in the case of NR/BR blends but it can be seen from Fig. 11 that, if the extent of displacement of the transition is again measured at 195 K relative to the extent of displacement of the total transition (of NR/BR) one obtains valid results for the BR content of the high vinyl types (50 NF or 55 NF) but low values for the

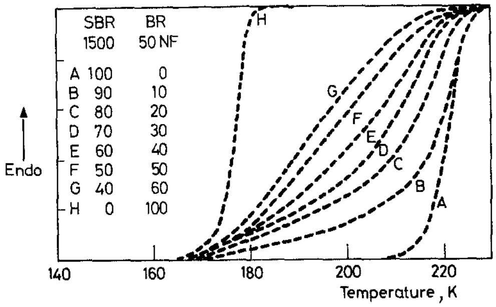

Fig. 6 *Tg* of SBR/BR vulcanizates 1500/50 NF. Normalized to the same total displacement as the reference samples (Fig. 2)

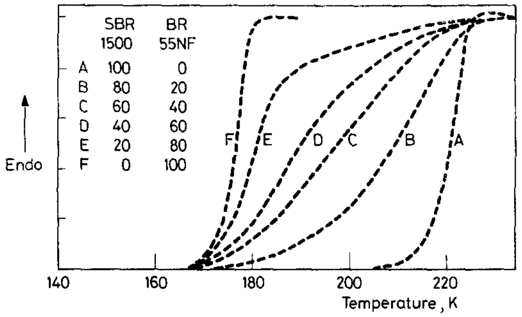

Fig. 7 *Tg* of SBR/BR vulcanizates 1500/55 NF. Normalized to the same total displacement as the reference samples (Fig. 2)

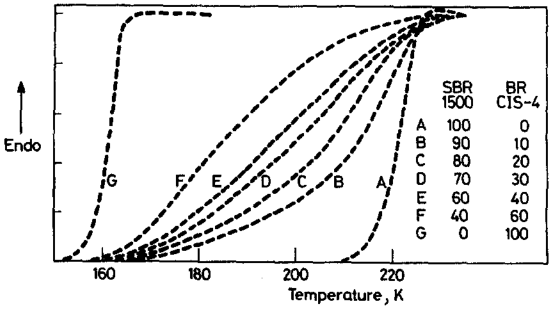

Fig. 8 *Tg* SBR/BR vulcanizates 1500/cis-4. Normalized to the same total displacement as the reference samples (Fig. 2)

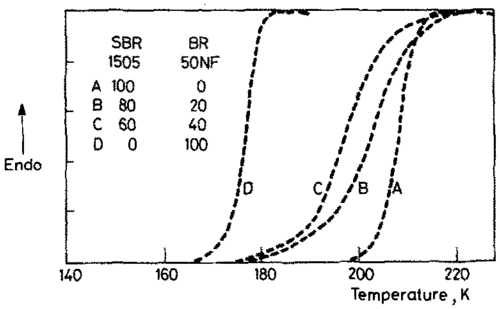

Fig. 9 *Tg* of SBR/BR vulcanizates 1505/50 NF. Normalized to the same total displacement as the reference samples (Fig. 2)

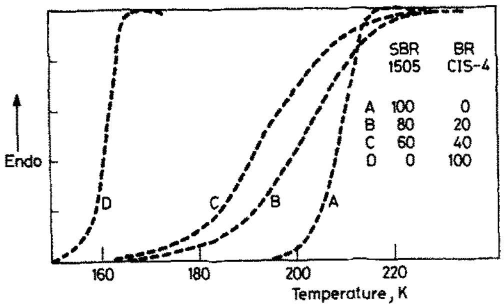

Fig. 10 *Tg* of SBR/BR vulcanizates 1505/cis-4. Normalized to the same total displacement as the reference samples (Fig. 2)

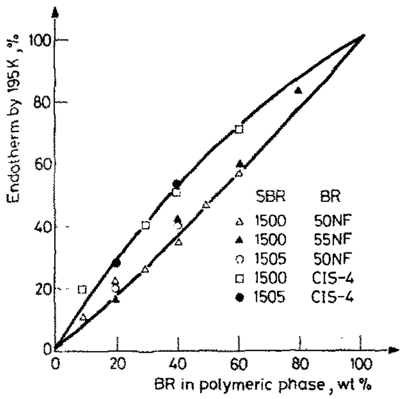

Fig. 11 Correlation between wt% BR in polymeric phase (with SBR) and % of devitrification endotherm occurring by 195 K

low vinyl (cis-4) BR. This is to be expected due to the lower *Tg* of the latter, compared with the *Tg*'s of the other BR's, and although a better calibration plot can be constructed if the displacement is measured at 190 K, it is probably more convenient to work at one calibration temperature (195 K), use the onset temperature of the *Tg* to define the type of BR and then select the appropriate calibration plot to quantify the BR analysis.

Pyrolysis-infrared spectroscopy and pyrolysis-gas chromatography are used extensively in polymer blend analysis but both suffer from the limitation that they are unable to differentiate between SBR/BR blends and low styrene SBR's. This may not only give a completely wrong interpretation of the data should a low styrene (ca. 10%) SBR be used, but it can also cause confusion in the marginal situation of an analysis indicating an apparent blend composition of 90% SBR/10% BR. This could represent the correct formulation but there is also the possibility of a 20–21% SBR having been used, or indeed of the result being close to experimental variability for a 100% SBR of 23.5% styrene content. The difference between a 10% styrene SBR and SBR/BR blends of a similar overall styrene content can be seen in Fig. 12, whilst the difference in onset temperatures enables the type of SR used to be deduced.

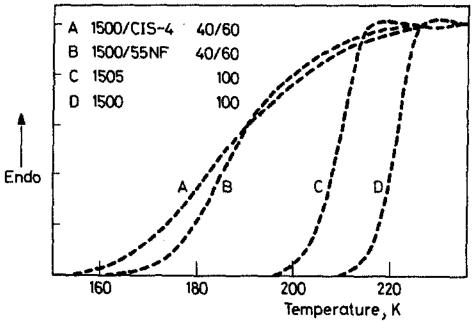

Fig. 12 *Tg*'s of three samples containing 10% styrene together with reference SBR 1500 (23.5% styrene). Normalized to the same to total displacement as the reference samples (Fig. 2)

The detection of 10% BR in SBR/BR blends has already been illustrated in Figs 6–10 and is again straightforward. A 20% styrene SBR would have a *Tg* some 3 K below that of a 1500 type SBR containing 23.5% styrene and the DSC curves would be parallel. Although there is some evidence [8] that different vulcanization systems have marginal effects on the precise temperature and shape of the curves through the *Tg* of a particular polymer, these differences approach experimental reproducibility for technologically viable systems in common usage and would not introduce a significant error in the interpretation of those data.

One further application of this technique to the analysis of NR blends concerns the possible misinterpretation of the PyrIR spectrum of a natural rubber/ethylene propylene terpolymer blend (NR/EPDM). It is difficult to observe low levels of EPDM in such a blend and, as its concentration increases, the presence of an absorbance at 910 cm^{-1} (11.0 μ) is often mistakenly assigned to BR. Differentiation between these two possibilities can quickly be effected by DSC examination as the *Tg* of EPDM, although varying with the ethylene: propylene ratio, occurs above that of NR and does not affect the horizontal run-in to the *Tg* of the latter.

Conclusion

The shape of the DSC curve through the glass transition of blends of natural rubber or styrene-butadiene rubbers with polybutadienes can be used to obtain good quantitative analysis of the blends, to differentiate between high and low vinyl polybutadienes, and to determine the copolymerized styrene content of the styrene butadiene rubber. In the case of NR/BR blends the accuracy of the BR determination is comparable with values obtained by PyrIR and PyrGC although it requires much less sample than the former and is a non-destructive technique. Visual inspection of the SBR/BR data (Fig. 11) would suggest that the accuracy of the BR determination in this instance is similar to that when NR/BR blends are considered but for SBR/BR blends the information is not obtainable by the more common pyrolytic techniques.

It seems probable that the limiting factor in the precision of these analyses is the manual manipulation of the data. The use of a modern micro-processor controlled instrument, with facilities for both slewing and normalizing the data after acquisition could result in easier and more precise interpretation of the data.

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References

1 C. Kow, M. Morton and L. J. Fetters, Rubber Chem. Technoi., 55 (1982) 245.

2 P. A. Marsh, A. Voet, L. D. Price and T. J. Mullons, Rubber Chem. Technol., 40 (1967) 344.

3 J. E. Callan, W. M. Hess and C. E. Scott, Rubber Chem. Technol., 44 (1971) 814.

4 K. K. Chakraborty, Rubber India, 26 (3) (1974) 14.

5 G. S. Fielding Russel, Rubber Chem. Technol., 45 (1972) 259.

6 R. M. Ikeda, M. L. Wallach and R. J. Angelo, in Block Copolymers, S. L. Aggarwal (Ed.), Pergamon Press, New York, 1969.

7 M. J. R. Loadman, J. Thermal Anal., 30 (1985) 929.

8 M. J. R. Loadman, unpublished work.

Zusammenfassung — Die Temperaturbereiche, in denen bei einer Reihe von Gemischen von Butadien mit natürlichem Kautschuk und bei zwei Styrol-Butadien-Kopolymeren mit verschiedenem Styrolgehalt Glastransformationen erfolgen, wurden mittels DSC untersucht. Die erhaltenen DSC-Kurven können zur Kategorisierung des Polybutadiens und zur Bestimmung des Gehalts an gebundenem Styrol in Styrol-Polybutadien-Kopolymeren und des Polybutadiengehalts der Gemische verwendet werden.

Резюме — С помощью дифференциальной сканирующей калориметрии изучены температуры стеклообразования (T_g) ряда смесей полибутадиенов с природным каучуком и двух стиролбутадиеновых сополимеров с различным содержанием стирола. Кривые ДСК могут быть использованы для распределения полибутадиена по классам, определения содержания связанного стирола в стирол-бутадиеновом сополимере и количественного определения полибутадиена в смесях.