

Analysis of epoxidized natural rubber. A comparative study of d.s.c., n.m.r., elemental analysis and direct titration methods

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A comparative analysis of epoxidized natural rubber samples by ^1H and ^{13}C n.m.r., titrimetric, elemental and d.s.c. techniques has been made. Whereas the titrimetric method is only applicable at low epoxy contents (< 15 mol%) both n.m.r. methods give reasonable precision over the compositional range of 20–75 mol%. Elemental analysis appears less reliable. D.s.c. analysis through measurement of T_g provides the highest precision of measurement but requires independent calibration by one or more of the primary methods. The epoxy content may also be related to the polymer density.

(Keywords: epoxidation; natural rubber; analysis; n.m.r.; elemental; d.s.c.; density)

INTRODUCTION

Natural rubber (NR) has been shown to contain low levels of naturally occurring epoxide groups¹⁻⁴, the concentrations of which have been determined by both a direct HBr titration^{2,5} and an indirect degradation method⁶. On the basis of the above work it was suggested that the HBr technique because of its relative speed, simplicity and accuracy should be the method of choice for epoxide analysis. More recently there has been a growing interest in the modification of NR latex by epoxidation with peracids, as the modified material shows certain outstanding properties *vis-à-vis* the unmodified rubber⁷⁻¹⁰. Since an accurate assay of the epoxidized natural rubber (ENR) is a prerequisite for monitoring the process efficiency and establishing the product purity we were motivated to reexamine the methods available for analysis. The results of our findings are disclosed here.

Whereas, certain aspects of the reported work are specific to the analysis of ENR other aspects will find general application particularly in the analysis of other modified rubbers or copolymers.

EXPERIMENTAL

Synthesis of ENR

Concentrated NR latex (HA, dry rubber content, DRC=62% w/w) was diluted with distilled water to a rubber concentration of approximately 15% w/v. The diluted latex was stabilized by the addition of Vulcastab LW (3% w/w on rubber) and acidified to a pH of 5–6 with glacial acetic acid. The latex was thermostatically controlled at 5°C and the requisite amount of freshly prepared¹¹, strong-acid free, peracetic acid was added. After 6 h the ENR was isolated by methanol

precipitation. The coagulated rubber was pressed into thin sheets, washed extensively in running water and dried under high vacuum at 50°C for at least 24 h.

Analysis of ENR

A series of eight ENR samples covering a complete range of composition from 0–100 mol % modification were analysed by the methods summarized below. Samples for spectroscopic and titrimetric analysis were rendered more soluble in the respective solvents by extensive milling on a two roll laboratory mill. Such a procedure does not detectably affect the chemical composition of the polymer but does markedly lower the molecular weight hence aiding dissolution.

D.s.c. analysis

D.s.c. measurements were made with a Perkin-Elmer DSC-2C calorimeter equipped with a liquid nitrogen sub-ambient cooling accessory and employing helium as a purge gas. Rubber samples (*c.a.* 10 mg) were encapsulated in standard, aluminium pans. The samples were pre-treated at 400 K for 5 min, quenched rapidly (320 deg/min) to 50 K below the anticipated glass transition and scanned upwards at 20 deg/min. Quoted T_g values are the onset temperature as computed with the Thermal Analysis Data Station (TADS) programme supplied by Perkin-Elmer. The instrument was calibrated as described in detail elsewhere¹².

Reproducibility of T_g values determined in triplicate was generally within ± 0.2 deg.

HBr titration

Details of this analysis have already been described^{2,5}. Typically the ENR sample (20–100 mg) was dissolved in toluene (10 ml). Crystal violet indicator solution (2 drops of 0.5% w/v in glacial acetic acid) was added and the

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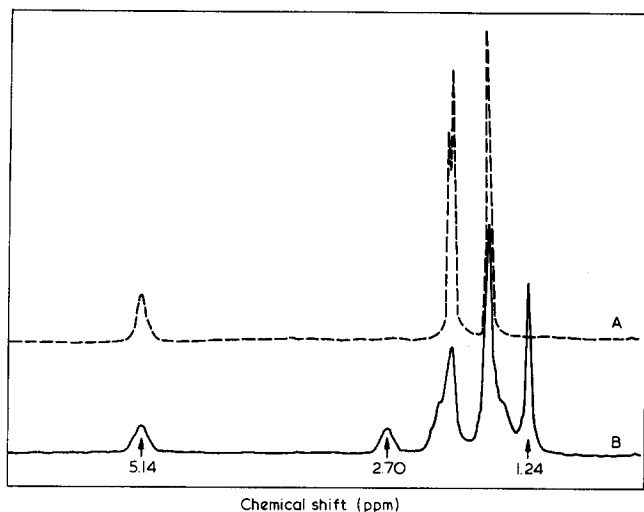


Figure 1 ¹H n.m.r. spectra of (A) partially epoxidized natural rubber and (B) unmodified rubber

sample titrated with 0.02 M HBr in glacial acetic acid to a blue-green end-point which was stable for at least 30 s. Long term stability of the end-point is not to be anticipated as the HBr will slowly add to the polymer unsaturation in the absence of epoxide groups.

N.m.r. analysis

Samples were run as approximately 5% w/v solutions in deuterated chloroform in 5 mm tubes using tetramethylsilane (TMS) as the internal standard. The ¹³C n.m.r. and ¹H spectra were measured at ambient temperatures (approximately 301 K) using a Joel JNM-FX 100 Fourier transform n.m.r. spectrometer operated at sweep widths of 250 ppm and 10 ppm respectively. Peak intensities were measured by electronic integration.

Elemental analysis

Three independent series of analyses for C, H and N were performed on the whole range of ENR samples by the Rubber Research Institute of Malaysia, AMDEL Microanalytical Service, Australia, and Perkin Elmer Instruments (Australia). Analyses were performed on ENR samples which had been further dried at 333 K under high vacuum to minimize interference by trace moisture or other volatiles. Epoxy content was calculated from the %C analysis after making allowance for low levels of protein, as deduced from %N present.

Polymer density measurement

Density of the modified rubber was measured by a density gradient method utilizing several small pieces of sample at approximately 298 K.

RESULTS AND DISCUSSION

Epoxidized diene polymers including ENR have previously been analysed by a variety of techniques including: chemical methods such as HCl¹³ or HBr^{2,24} titration; near i.r.¹⁵; ¹H n.m.r.^{8,15,16}; ¹³C n.m.r.¹⁷ and elemental analysis^{8,9}. Whereas, the above are all essentially primary methods it is also possible to make use of indirect measurements of parameters such as T_g or density which may be related to the epoxy content by an independent calibration. The relative merits of the above methods for ENR analysis are discussed below.

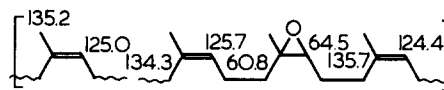
N.m.r. analysis

The proton spectra run at 100 MHz were characterized by rather broad but readily assignable resonances (Figure 1). Epoxidation leads to a very significant shift of the methyl protons, the disappearance of olefinic proton (5.14 ppm) and the appearance of a methine resonance (2.70 ppm) due to the proton attached to the oxirane ring. Due to partial overlap of the methyl resonance at this resolution, epoxy content was determined by the ratio of the integrated areas of the olefinic and epoxy methine protons as in earlier work¹⁶. Thus the epoxidation level is given by the relationship:

$$\text{mol \% epoxide} = 100 \left(\frac{A_{2.70}}{A_{5.14} + A_{2.70}} \right)$$

The precision of the analysis is dependent on the degree of modification since at very low or very high epoxidation levels errors in the epoxy methine or olefinic proton integrals become large. However, for ENR compositions in the range 20–75 mol % the reproducibility of duplicate measurements was found to be within ±1.5 mol %. The proton analysis could be improved by measurements at higher resolution which would permit the use of the methyl resonance ratios.

The ¹³C spectrum of partially modified ENR (Figure 2) is essentially identical to that reported¹⁷ earlier for epoxidized *cis*-1,4-polyisoprene. Chemical shifts of the olefinic and epoxy ring carbons are summarized below.



Since earlier workers¹⁷ have shown that the olefinic resonances at approximately 125 ppm and the oxirane carbon at 64.5 ppm are characterized by full NOE and short similar T₁ values, the ratio of these peak areas were used for quantitative measurements. Thus the epoxidation level was determined from the relationship:

$$\text{mol \% epoxide} = 100 \left(\frac{A_{64.5}}{A_{64.5} + A_{124.4, 125.0, 125.7}} \right)$$

In common with the proton measurements, errors are accentuated at high and low epoxidation levels. However,

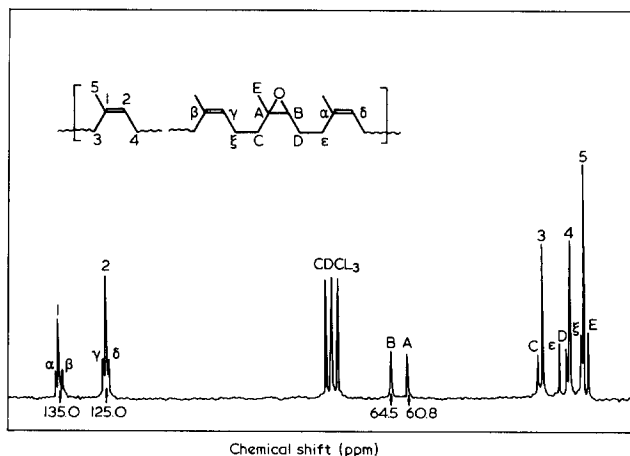


Figure 2 ¹³C n.m.r. spectrum of partially epoxidized natural rubber

Table 1 Analysis of epoxidized natural rubber

Anticipated ^a	Epoxidation level (mol %)			Elemental analysis			<i>T_g</i> (K)	Density (g cm ⁻³)
	HBr	¹ H n.m.r.	¹³ C n.m.r.	I ^b	II ^c	III ^d		
0	—	—	—	—	—	—	206.8	0.898
10	7.5	10.8	10.5	5.0	6.8	9.1	212.9	0.906
20	14.2	18.9	19.1	15.9	15.4	17.4	220.2	0.917
35	22.1	31.8	31.8	29.5	32.5	27.0	231.0	0.937
50	28.0	45.2	45.1	40.9	44.9	45.9	243.1	0.965
65	31.3	59.7	60.4	52.3	65.2	61.1	256.6	0.986
75	32.6	67.2	73.7	69.2	73.6	77.2	267.3	—
90	32.6	82.4	83.6	84.5	94.5	90.4	276.3	—

^a based on amount of per-acetic acid added

^b based on %C measured by RRIM

^c based on %C measured by AMDEL

^d based on %C measured by Perkin-Elmer, Australia.

The values are the mean of duplicate analyses which in no case differed by more than 0.4%w. Average difference of duplicates over whole series was 0.17%w.

over the range 20–75 mol % the reproducibility of duplicate measurements was found to be somewhat superior to the proton analysis at ± 0.8 mol %.

Elemental analysis

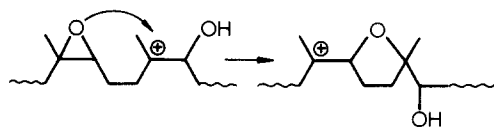
The epoxy content of the modified rubbers was calculated from the %C analysis after allowing for the protein content of the modified rubbers (%N=0.26). Reproducibility of the carbon content as determined by duplicate analysis of the same sample by the same laboratory was generally within $\pm 0.23\%$ (absolute). This corresponds to a reproducibility of about ± 1 mol % for an ENR composition of 50 mol %. However, the second and third set of data (Table 1) lead to consistently higher results which diverge more widely from the first set than would be predicted from the above reproducibility, and is apparently due to a systematic error in one or both of the analyses. At the same time random errors are also apparent as evidenced by the widely divergent result for the 65 mol % sample where the analyses differ by 12.9 mol %. There would seem no satisfactory explanation for this effect although one cannot exclude the possibility of sample inhomogeneity which would be accentuated by the small samples required for micro-analysis.

Little advantage is likely to be gained by analysis based on %H or %O and consequently it must be concluded that elemental analysis as available on a routine service basis does not lead to highly precise compositional data for ENR.

HBr titration

Direct titration of the oxirane ring with HBr has earlier² been shown to be essentially quantitative and with few interferences for epoxidized polyisoprene at low modification levels (< 5 mol %). In this present work the titrimetric technique is characterized by low analysis figures, at modification levels above 15 mol % (Table 1). This may in part be due to limited solubility at higher modification levels as well as cyclization side reactions between adjacent epoxy groups. The cyclization will be unimportant at low modification levels due to the low frequency of adjacent oxiran rings.

In the absence of the above complications the HBr



method is a rapid technique being appropriate for analysis of ENR in the region < 15 mol % where the spectroscopic techniques are less accurate.

D.s.c. analysis

As has already been disclosed⁸⁻¹⁰ the T_g of ENR varies linearly with molar epoxy content. Since the T_g can be readily and precisely measured by d.s.c. such an analysis permits determination of the ENR composition if an independent calibration is made. A typical calibration is shown in Figure 3 employing HBr analysis at low epoxy levels and the mean of the n.m.r. and EA figures at higher levels. Since the T_g value increases by 0.85 K/mol % and since the reproducibility of triplicate analyses is generally within ± 0.2 K it follows that the precision of the d.s.c. analysis is approximately ± 0.25 mol % over the whole compositional range. The overall accuracy of the method is clearly determined by that of the independent calibration.

Recently¹⁸ it has been shown that the d.s.c. method may be used to measure the T_g value of NR in latex the value of which is identical to that in dry rubber. Application of this approach to epoxidized latices would allow direct determination of the rubber composition in the latex. This could be a useful approach for quality control purposes.

D.s.c. analysis also permits the detection and estimation of blends of ENR and NR since such mixtures are characterized by two distinct T_g values¹⁰. Such an estimation could not readily be achieved by the titrimetric or n.m.r. methods discussed above.

The only drawback to this approach is that it is restricted to the analysis of compositionally pure ENR. The presence of significant side-products derived by cyclization, hydrolysis or esterification would nullify the validity of the calibration.

Density measurement

The density of ENR (Table 1) increases in a parallel manner to that observed for the glass transition. Figure 4

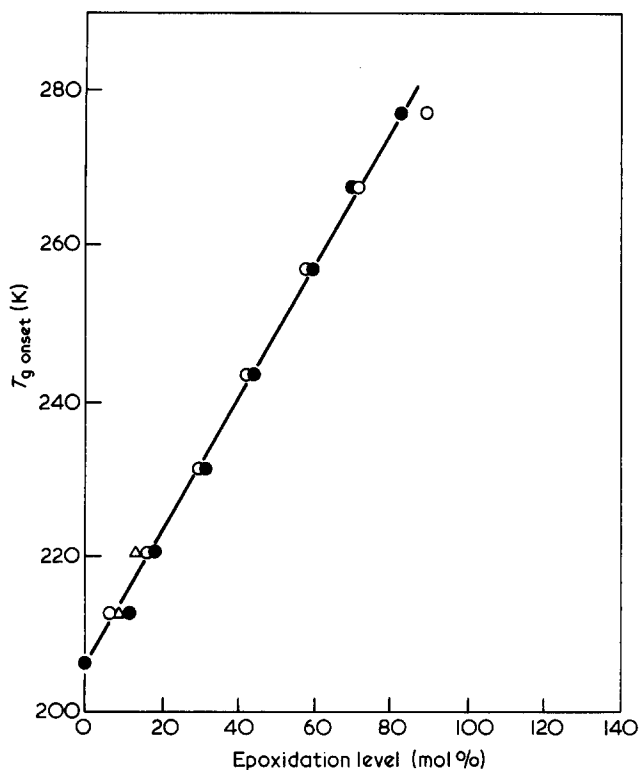


Figure 3 Dependent of T_g on molar composition of ENR (●) mean of n.m.r. data; (○) mean of carbon analysis; (Δ) HBr titration

indeed shows that the T_g value is directly related to the polymer density.

Consequently the polymer density may be used as a convenient low cost measure of the epoxy content subject to the same constraints as the d.s.c. analysis.

CONCLUSIONS

Whereas direct HBr analysis of ENR gives fairly accurate information at low (< 15 mol %) modification, levels both ^1H and ^{13}C -n.m.r. provide the best primary methods of analysis over the range 20–75 mol %. Elemental analysis appears less satisfactory. D.s.c. analysis appears to provide the highest precision of the methods examined but is subject to independent calibration by a primary method. Density measurement is a low cost alternative to the d.s.c. approach.

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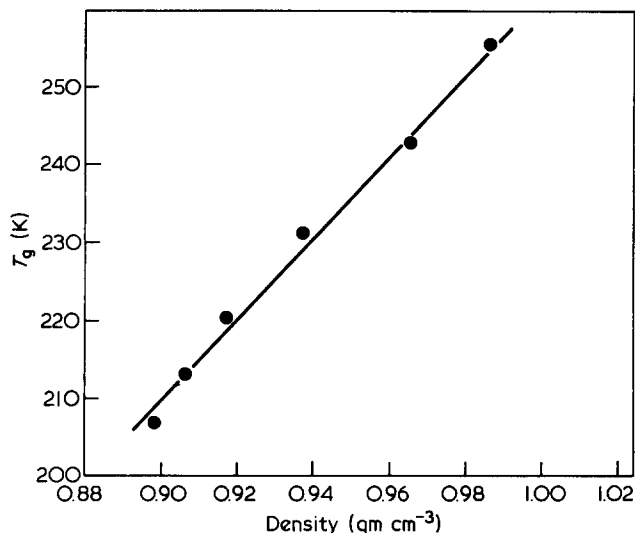


Figure 4 Relationship of T_g and density of various ENR compositions

under Vote F and the assistance of the Rubber Research Institute of Malaysia and John Fursdon of Perkin Elmer (Australia) in determining the elemental composition of the ENR samples.

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