

# D.s.c. studies of the reaction between epoxidized natural rubber and benzoic acid

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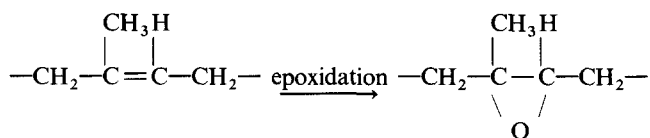
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The reactions between epoxidized natural rubber (ENR) and benzoic acid have been investigated at elevated temperatures, in the range 398–433 K, by differential scanning calorimetry (d.s.c.). The reaction is characterized by a significant increase in the glass transition temperature ( $T_g$ ) of the material, the increase being proportional to the amount of added acid. The kinetics of the reaction have been elucidated by monitoring the rate of change of  $T_g$  with respect to the reaction time as well as by direct measurements of the enthalpy change of reaction. The reaction is found to be first order with respect to benzoic acid and to have an overall activation energy of  $70 \text{ kJ mol}^{-1}$ .  $^{13}\text{C}$  nuclear magnetic resonance studies employing  $^{13}\text{C}$ -enriched benzoic acid showed that the benzoic acid was rapidly incorporated into the polymer main chain with the formation of ester linkages. Secondary, slower reactions were also in evidence but have not been positively identified. The incorporation of benzoic acid leads to a  $T_g$  elevation of about  $3.7 \text{ K mol}^{-1}$  modification and suggests that such reactions might prove useful in changing the physical properties of such rubbers. The significant elevation of  $T_g$  associated with ENR vulcanized by dibasic acids is probably predominantly due to the modified main chain structure rather than the crosslinking network.

(Keywords: epoxidized natural rubber; benzoic acid; d.s.c.;  $T_g$ ; heat flow; kinetics; model reactions; activation energy; crosslinking)

## INTRODUCTION

Diversification of the traditional uses of natural rubber (NR) can be achieved by changing the properties of the base polymer through chemical modification. Epoxidation represents a particularly attractive and convenient method for transforming natural rubber to a new polymer with certain outstanding properties:



Controlled epoxidation of NR results in a progressive increase in the glass transition temperature ( $T_g$ ) and polymer density with the level of modification and in turn imparts higher air impermeability, lower oil swell and wet traction and better bonding to materials like PVC, while retaining the good tensile properties of NR<sup>1-3</sup>.

Epoxidized natural rubber (ENR) contains both epoxide and unsaturated sites. While the double bonds can be crosslinked by sulphur and peroxide, the epoxide groups provide alternative sites for crosslinking with polyfunctional chemicals<sup>4-6</sup>. The effects of dibasic acids on the technological properties of ENR have been reported recently<sup>5</sup>. The reaction of dibasic acids with ENR is generally slow, requiring 6–8 h at an elevated

temperature of 433 K. Changes in physical properties, such as modulus, hardness and resilience, are related to the increased  $T_g$  of the reacted ENR.

In the present work we have chosen to study the reactions of a simple monobasic acid as a model for establishing the mode of action of dibasic crosslinking agents, in particular the cause of the increase in  $T_g$ . The progress of the reaction has been monitored by calorimetric techniques, whereas the product structure has been probed by  $^{13}\text{C}$  nuclear magnetic resonance (n.m.r.).

## EXPERIMENTAL

### Materials

Samples of ENR-50 were supplied by Rubber Research Institute of Malaysia and were nominally of 50 mol% epoxide composition. All other chemicals were used as commercially supplied. The  $^{13}\text{C}$ -enriched benzoic acid  $\text{C}_6\text{H}_5-^{13}\text{COOH}$  (99 at%  $^{13}\text{C}$ ) was purchased from MSD Isotopes, Division of Merck Frosst Canada Inc., Montreal.

### Preparation of ENR mixes with additives

About  $10 \pm 0.5 \text{ g}$  of ENR was milled into a flat sheet on a laboratory two-roll mill at room temperature. The required amount of additive chemical was spread on the sheet, which was then carefully rolled up. The sample was homogenized by milling. It was weighed to ensure

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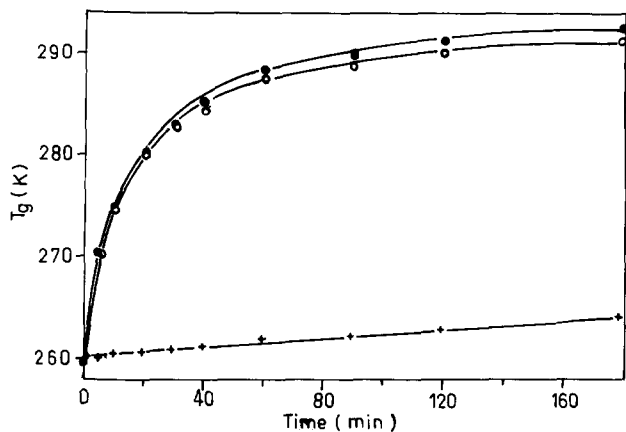


Figure 1 Change in  $T_g$  with reaction time. ●, sample heated at 433 K, benzoic acid loading 12.5 pph; +, control, ENR without any benzoic acid; ○, 12.5 pph loading minus the control

that there was no excessive loss of ingredients during the milling.

#### D.s.c. analysis

Differential scanning calorimetry (d.s.c.) measurements were made with a Perkin-Elmer DSC-2C calorimeter equipped with a sub-ambient cooling accessory and using nitrogen as flow gas. Details of calibration have been given elsewhere<sup>7</sup>.

Samples of ENR ( $\approx 13$  mg) containing a known amount of additive were encapsulated in volatile sample pans. Reactions were conducted in the instrument. Samples were introduced into the d.s.c. at 300 K, heated rapidly ( $320 \text{ K min}^{-1}$ ) to the test temperature and at prescribed time intervals quenched to 210 K for  $T_g$  measurement. All  $T_g$  values were measured at a scan rate of  $20 \text{ K min}^{-1}$  and evaluated with the Thermal Analysis Data Station (TADS) program supplied by Perkin-Elmer. Reproducibility of  $T_g$  values determined in triplicate was within  $\pm 0.2 \text{ K}$ . Quoted  $T_g$  values are the mid-point temperatures as computed with the TADS program.

The isothermal experiments were conducted with the Perkin-Elmer ISOTHERMAL programme. Samples ( $\approx 10$  mg) were inserted into the d.s.c. at 300 K and after 2 min equilibration were ramped to the reaction temperature at  $80 \text{ K min}^{-1}$  and held at the isothermal temperature for the required period. After reaction, samples were cooled to 300 K and rerun under identical conditions, but with shortened reaction time ( $\approx 10$  min), to obtain the baseline curves. Under these conditions thermal equilibrium was reached within about 2 min. The final corrected experimental curve was obtained by subtraction of the control baseline from the initial curve.

#### N.m.r. studies

For the  $^{13}\text{C}$  n.m.r. investigations, samples of ENR milled with the required amount of enriched\* benzoic acid were sealed in glass tubes under vacuum. They were then immersed in an oil bath set at 433 K for various times. The glass tubes were cut open after they had been cooled down.  $^{13}\text{C}$  n.m.r. spectra were measured at

\*The use of enriched benzoic acid permitted the monitoring of the n.m.r. signals at low levels of incorporation when the product was still soluble in the n.m.r. solvent. Normal levels of un-enriched reagent lead to an intractable product and very poor spectral resolution.

ambient temperatures using a Joel JNM-FX 100 Fourier transform n.m.r. spectrometer operated at sweep widths of 250 and 10 ppm. Peak intensities were measured by electronic integration. Samples were run as approximately 4% w/v solutions in deuterated chloroform in 10 mm tubes using tetramethylsilane (TMS) as the internal standard. To produce reasonably well resolved spectra, 5000 scans were made.

## RESULTS AND DISCUSSION

### Overall course of reaction

The ENR-50 samples used in this study had an initial  $T_g$  of  $\approx 260 \text{ K}$ . Blending of varying amounts of benzoic acid into the rubber had only a marginal effect on the  $T_g$  value, which, however, tends to decrease slightly at higher loadings, possibly due to a plasticization effect. Storing of the compounded rubbers at ambient temperatures (298 K) for several days showed only very modest increases in  $T_g$  of about 1–2 K. However, when such samples were heated at elevated temperatures (433 K) a rapid increase in  $T_g$  occurred over a period of about 60 min. After this rapid increase, a further slow elevation of the  $T_g$  continued over the next 24 h and this parallels changes which occur with the control ENR under similar heat treatment (Figure 1).

Monitoring the enthalpy of reaction under parallel conditions is informative since it confirms the presence of an initial exothermic reaction which is effectively complete within the first 60 min (Figure 2). The approximate enthalpy of reaction is  $242 \text{ kJ mol}^{-1}$  benzoic acid, assuming that all the acid is reacted in this initial period. However, the much slower secondary reaction cannot be detected under these conditions since the corresponding heat flow is below the critical detection limit.

### The influence of benzoic acid loading

Having established procedures for monitoring the changes that occur when ENR is heated with benzoic acid at elevated temperatures, it seemed appropriate to investigate the effect of varying levels of acid on the above reaction. Accordingly, the reaction was monitored for ENR compounded with 2.5–21 pph of benzoic acid (these levels correspond to an equivalence of between

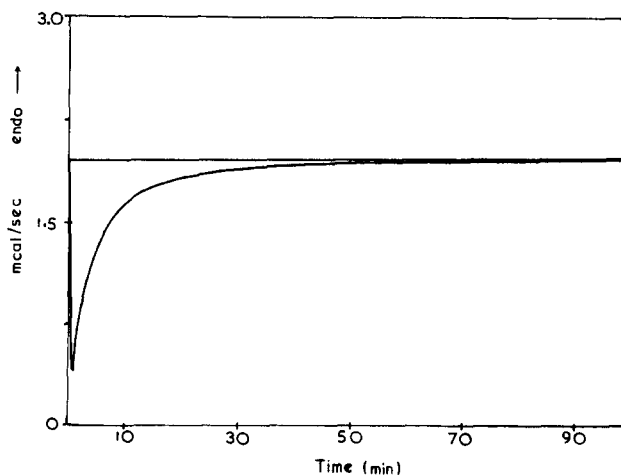


Figure 2 Isothermal scan for sample of ENR with 12.5 pph benzoic acid sealed in a volatile sample pan. Scan temperature 433 K (1 cal = 4.184 J)

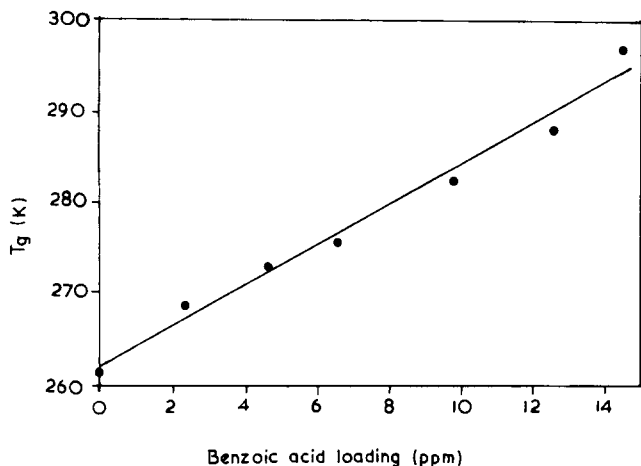
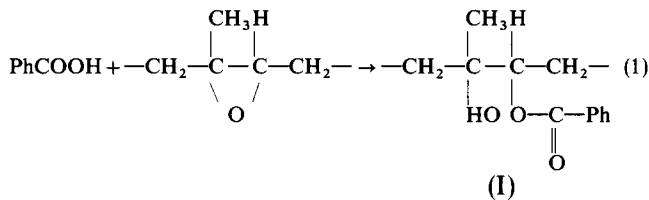


Figure 3  $T_g$  enhancement at various benzoic acid loadings for reaction at 433 K for 60 min

3 and 25% of the total level of epoxide present in the ENR, assuming that the reaction has a one-to-one stoichiometry).

All the samples studied showed a similar reaction profile to that recorded in *Figures 1* and *2*. However, both the  $T_g$  and the enthalpy of reaction increased in step with the loading of acid. Thus, at a given reaction time, the increase in  $T_g$  is directly proportional to the acid loading (*Figure 3*). This suggests that, where there is at least a fivefold excess of epoxide over benzoic acid, the reaction is effectively quantitative.

This correspondence between the increase in  $T_g$  and the extent of modification has been noted previously in studies of  $T_g$  as an additive property of the component groups making up linear polymers<sup>8</sup>. Furthermore, the direct relationship between the level of modification and the  $T_g$  increase is a notable feature of these systems and has been demonstrated earlier for the epoxide modification of NR, which is characterized by an increase of  $0.85 \text{ K mol}^{-1}$  epoxidation<sup>9</sup>. In this case the increase in  $T_g$  is much larger, being equivalent to about  $3.7 \text{ K mol}^{-1}$  modification. This difference is consistent with the bulky and polar structure of the likely ring-opened product (I):



In particular, the presence of the polar hydroxyl group, which introduces the possibility of inter- and intra-molecular hydrogen bonding, is probably a significant factor.

It is noteworthy that the thermal curves of both the starting material and the modified product show only a single  $T_g$ , indicating that both materials are effectively random copolymers<sup>2,10</sup>.

#### Reaction kinetics

An analysis of the data provided by the change in  $T_g$  as a function of time allows the possibility of further quantifying the rate of reaction. Thus, if it is assumed that the change in  $T_g$  of ENR is directly proportional to

the extent of ring-opening reaction with benzoic acid, and this does appear to be the case at low loadings, then the rate of reaction should be given by the expression:

$$\frac{dT_g}{dt} = C \left\{ -\frac{d[\text{BA}]}{dt} \right\} = Ck[\text{E}]^m[\text{BA}]^n \quad (2)$$

where  $k$  is the rate constant,  $C$  a proportionality constant,  $[\text{E}]$  epoxide concentration in ENR,  $[\text{BA}]$  benzoic acid concentration, and  $m$  and  $n$  the respective orders of reaction. Equation (2) may be transformed to the form:

$$\begin{aligned} \log\left(\frac{dT_g}{dt}\right) &= \log Ck[\text{E}]^m[\text{BA}]^n \\ &= \log\{Ck[\text{E}]^m\} + n\log[\text{BA}] \end{aligned} \quad (3)$$

For a particular composition of ENR and using initial rate conditions the term  $[\text{E}]$  may be regarded as constant and equation (3) may be simplified to:

$$\log\left(\frac{dT_g}{dt}\right) = D + n\log[\text{BA}] \quad (4)$$

where  $D$  is a constant.

The initial rate of change of  $T_g$  may be obtained from plots of  $dT_g/dt$  versus reaction time as shown in *Figure 4* for samples of varying acid concentrations. (The values of  $dT_g/dt$  are interpolated from the gradient of plots of  $T_g$  versus reaction time, e.g. *Figure 1*). The extrapolated intersection of the curve with the y-axis represents the maximum initial rate, where  $[\text{BA}]$  is equivalent to the initial acid concentration.

The dependence of the initial rate on acid concentration may now be demonstrated as shown in *Figure 5*. The slope of this logarithmic plot of initial rate versus acid concentration is  $1.03 \pm 0.02$ , showing that the reaction is approximately first order with respect to benzoic acid.

#### Temperature dependence of the reaction

Further studies were carried out at one acid loading (12.5 ppH) at temperatures in the range 398–433 K. In each case the initial rate of reaction was determined. As anticipated, the rate of reaction was enhanced by elevated temperature.

An Arrhenius equation may be used to evaluate the overall activation energy of the process. Thus, substituting

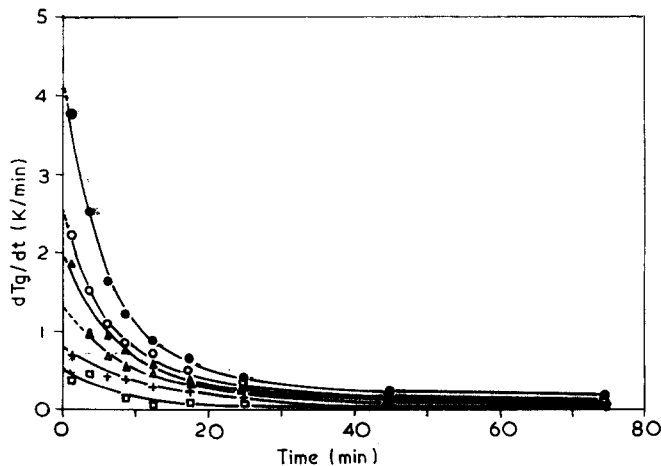
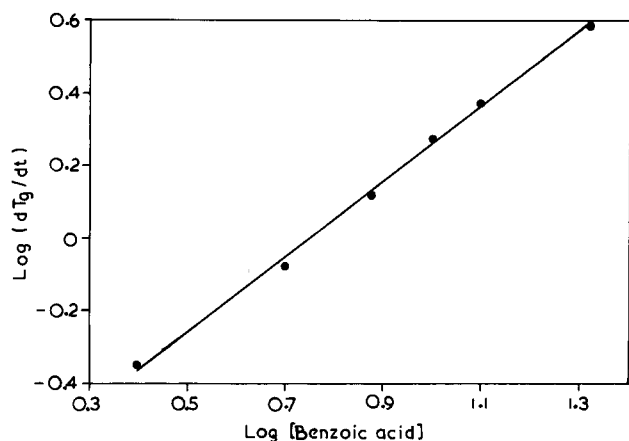
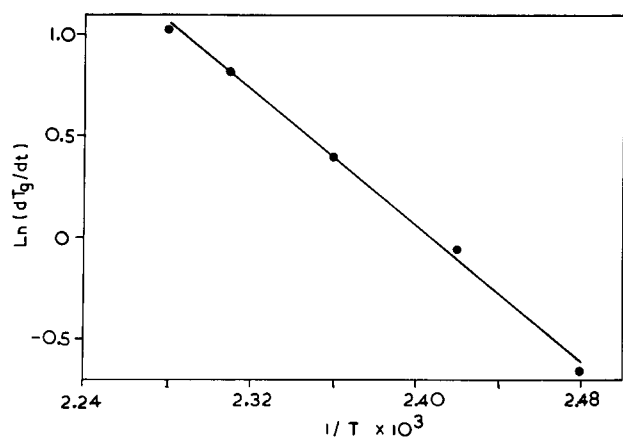


Figure 4  $dT_g/dt$  versus reaction time for reaction at 433 K with benzoic acid loadings (ppH): □, 2.5; +, 5; △, 7.5; ▲, 10; ○, 12.5; ●, 21


 Figure 5 Log (dT<sub>g</sub>/dt) versus log [benzoic acid]

 Figure 6 Ln(dT<sub>g</sub>/dt) versus 1/T

for  $k = A \exp(-Ea/RT)$  in equation (2) leads to the expression:

$$\frac{dT_g}{dt} = Ck[E]^m[BA]^n = \{C[E]^m[BA]^n\}A \exp(-Ea/RT) \quad (5)$$

which may be transformed to:

$$\ln \frac{dT_g}{dt} = \ln\{C[E]^m[BA]^n A\} - \frac{Ea}{RT} \quad (6)$$

When using initial rate data, a plot of  $\ln (dT_g/dt)$  versus  $1/T$  should be linear. Figure 6 demonstrates that this is in fact the case. This overall activation energy derived from the slope of the plot is  $70.5 \pm 0.4 \text{ kJ mol}^{-1}$ . This very high activation energy explains why the room temperature reaction is negligible over a period of days since the rate of reaction is over 7000 times faster at a temperature of 433 K than at 298 K.

#### Isothermal measurements

Similar kinetic analyses may be based on the data from isothermal experiments. Figure 2 demonstrated that the maximum heat flow occurs at the onset of the reaction when the rate is maximized and reduces effectively to zero as the reaction is completed. It thus seems appropriate to use the expression  $dH/dt$  as a measure of the rate of reaction. Thus, by analogy with equation (2), we can

write:

$$\frac{dH}{dt} = C'k[E]^m[BA]^n \quad (7)$$

where  $C'$  is a proportionality constant, and  $k$ ,  $m$  and  $n$  are defined in equation (2). Equation (7) can be simplified to

$$\log\left(\frac{dH}{dt}\right) = \log D' + \log[BA]^n \quad (8)$$

where  $D' = C'k[E]^m$  should be a constant, considering the initial conditions. The initial value of  $dH/dt$  may be readily derived from plots of  $dH/dt$  versus  $t$ , the heat flow value being obtained directly from the thermal curve (Figure 2).

The dependence of the initial rate, as measured by heat flow, on the benzoic acid concentration is shown in Figure 7. Again the logarithmic plot is linear and the order of reaction with respect to benzoic acid, as derived from the gradient of the plot, is  $1.07 \pm 0.06$ . This is in good agreement with the data based on the rate of change of  $T_g$  discussed above.

An Arrhenius analysis may also be evaluated based on the isothermal data. By analogy with equations (5) and (6):

$$\frac{dH}{dt} = kC'[E]^m[BA]^n = C'[E]^m[BA]^n A \exp(-Ea/RT) \quad (9)$$

$$\ln(dH/dt) = \ln\{AC'[E]^m[BA]^n\} - Ea/RT \quad (10)$$

where  $C'$  is the corresponding constant for the heat flow data. The Arrhenius plot is shown in Figure 8. The gradient corresponds to an overall activation energy of the process of  $67.6 \pm 0.4 \text{ kJ mol}^{-1}$ , which is in close agreement with the value obtained from the analysis of the  $T_g$  data.

#### The nature of the reaction

The calorimetric studies described above clearly indicate that a specific interaction occurs between benzoic acid and epoxidized natural rubber when heated at elevated temperatures. The reaction appears to occur in two stages: an initial rapid interaction, which is largely complete within 60 min and gives rise to a substantial rise in the  $T_g$  of the material; and a much slower modification which occurs over a further period of 24 h.

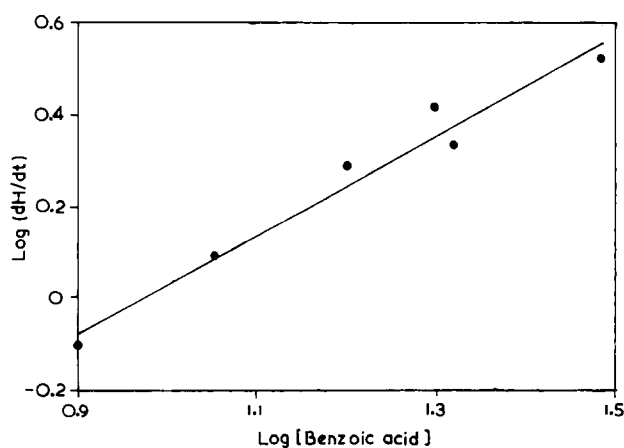


Figure 7 Log(dH/dt) versus log [benzoic acid]

In an earlier study<sup>5</sup> investigating the interaction of dibasic acids with ENR, infrared (i.r.) evidence was provided to show the presence of ester groups such as those present in structure (I). In this work an attempt was made to characterize the product by <sup>13</sup>C n.m.r. Unfortunately, at levels of incorporation required to give a detectable signal, the n.m.r. spectrum of the modified rubber is very poorly resolved. (This may in part be due to the very significant increase in  $T_g$ , which indicates a large decrease in the rotational freedom of polymer segments.) To circumvent this problem it was decided to work with <sup>13</sup>C-enriched benzoic acid at loadings of 2 pph.

Figure 9 summarizes the <sup>13</sup>C n.m.r. spectra of the initial ENR/benzoic acid mix as well as the product after heating for 1 h and 24 h at 433 K. The initial spectrum shows carbon peaks consistent with earlier reported data<sup>9,11</sup> as

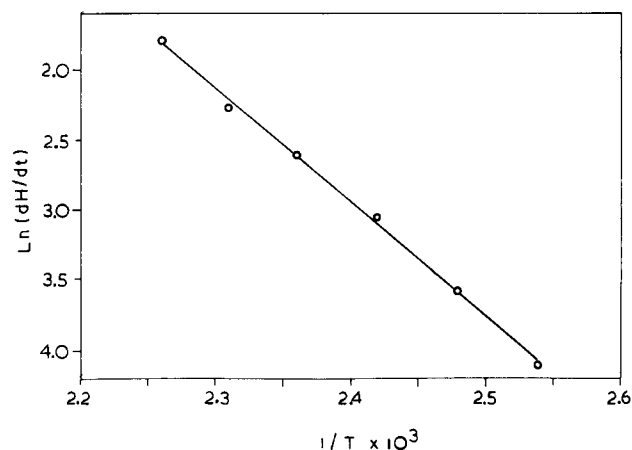


Figure 8  $\text{Ln}(dH/dt)$  versus  $1/T$

well as the presence of the carboxylic carbon of the enriched benzoic acid, which appears at 171 ppm. The aromatic carbon atoms which are not enriched are not detectable. After 1 h the most significant change is that the carbonyl carbon has shifted upfield to 166 ppm, which is consistent with the formation of an ester grouping  $-\text{COOR}$ . The total absence of a residual peak at 171 ppm confirms that all of the benzoic acid is consumed within 60 min at 433 K, and the appearance of an ester carbon suggests that the proposed reaction scheme represented by equation (1) is plausible.

Further information may be deduced from a quantitative analysis of the epoxide content derived from the ratio of the oxirane peaks (at 60.8 and 64.5 ppm) to the olefinic peaks (centred at 125 and 135 ppm). The variation in this ratio is summarized in Table 1. It is immediately apparent that, whereas the number of oxirane groups decreases significantly over the first hour, during which time all the benzoic acid is consumed, the decrease continues past this point and hence cannot be solely attributed to reactions such as that depicted in equation (1). Note also that, at a level of 2 pph, the initial molar ratio of oxirane groups to benzoic acid is approximately 44:1. Thus a simple one-to-one inter-

Table 1 Reaction of ENR with 2 pph benzoic acid at 433 K: ratio of oxirane carbons to vinylic carbons

Reaction time (h)	Ratio of oxirane carbons to vinylic carbons	Epoxide groups in ENR (mol%)
0 (initial)	1.14	53.5
1	1.08	51.9
24	0.81	44.9

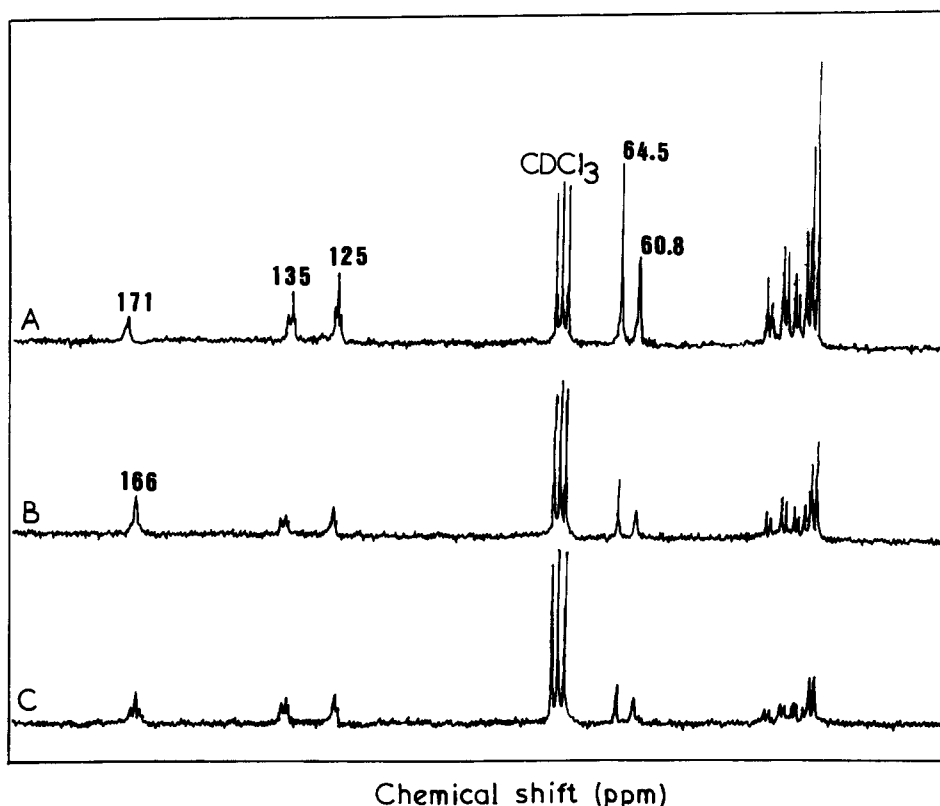


Figure 9 <sup>13</sup>C n.m.r. of ENR compounded with 2 pph benzoic acid. Spectra at the initial conditions (A), after 1 h at 433 K (B), and after 24 h at 433 K (C)

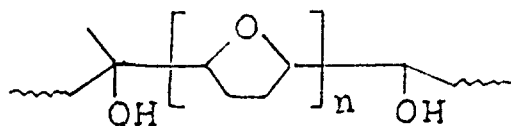
**Table 2** Comparison of  $T_g$  enhancement by benzoic<sup>a</sup> and adipic<sup>b</sup> acids

Reaction time and conditions	Glass transition temperature (K)	
	Benzoic acid	Adipic acid
Initial	260.4	260.2
24 h @ 300 K	261.2	261.0
1 h @ 433 K	273.3	274.4

<sup>a</sup> 4.7 pph loading<sup>b</sup> 5 pph loading

action should lead to a reduction of the epoxide content from 53.5 to  $\approx 52.3$  mol%. The observed reduction of the epoxide content to 51.9 mol% within the first hour suggests that reactions in this period may not be restricted to simple ring opening with benzoic acid. (This evidence is not conclusive since the reproducibility of the  $^{13}\text{C}$  n.m.r. measurement is only about 1 mol%<sup>9</sup>.)

Perhaps the simplest explanation of the disappearance of epoxide groups is the furanization of adjacent groups catalysed by the presence of the benzoic acid. This would result in structures such as:



However, such blocks must inevitably be short since ENR has been shown to be an essentially random copolymer<sup>2,10</sup> and the modified material only shows a single  $T_g$  in these calorimetric studies. Notwithstanding the above, the ring-opening reaction by benzoic acid leading to ester formation is still believed to be the dominant reaction in the early stages, since the n.m.r. studies show that the acid is rapidly consumed and the increase in  $T_g$  at low reaction times is directly proportional to the level of added acid.

#### Comparison with dibasic acids

Earlier studies have shown that vulcanization of ENR with dibasic carboxylic acids is associated with a significant increase in the  $T_g$  of the material. It seemed of interest to compare the elevation of  $T_g$  brought about by equivalent amounts of benzoic acid and a crosslinking agent such as adipic acid. The results are summarized in Table 2. It can be seen that both benzoic and adipic acids give rise to similar increases in  $T_g$ . Neglecting concomitant changes in the control, this is equivalent to 4.6 K mol%<sup>-1</sup> benzoic acid and 5.7 K mol%<sup>-1</sup> adipic acid. However, adipic acid is bifunctional and if both groups react this would be equivalent to 2.85 K mol%<sup>-1</sup>. Since the product of the monofunctional reaction of

adipic acid with ENR would still retain one carboxylic group, capable of interchain hydrogen bonding, it is likely that this structure would have a greater contribution to an increase in  $T_g$  than the analogous benzoic acid residue. Consequently, these results suggest that, under the reaction conditions (1 h at 433 K), adipic acid reacts mainly monofunctionally. This would be consistent with the earlier vulcanization studies, which estimated that a cure time of 6–8 h was necessary at a temperature of 433 K for complete reaction<sup>5</sup>.

However, these inferences should be tempered by the observation that for DICUP crosslinked natural rubber the increase in  $T_g$  per crosslink is approximately 2.7 K mol%<sup>-1</sup> (Reference 12). This could mean that introduction of a crosslink by reaction of a second acid group might not lead to further elevation of the  $T_g$ . It appears clear that the dominant reason for an increase in  $T_g$  is main chain modification rather than crosslink formation *per se*.

#### CONCLUSION

This study has shown that d.s.c. techniques may be successfully applied to the elucidation of the kinetics of the interaction between benzoic acid and epoxidized natural rubber at elevated temperatures. Benzoic acid is incorporated into the polymer main chain through a ring-opening reaction which is first order with respect to benzoic acid. The activation energy of this reaction is approximately 70 kJ mol<sup>-1</sup>. The primary reaction is accompanied by a substantial increase in  $T_g$ , which would be expected to have a significant influence on the bulk properties of the material. Other concomitant secondary reactions are believed to occur but these have yet to be conclusively identified.

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