

# Epoxydation of Natural Rubber Latices: Methods of Preparation and Properties of Modified Rubbers

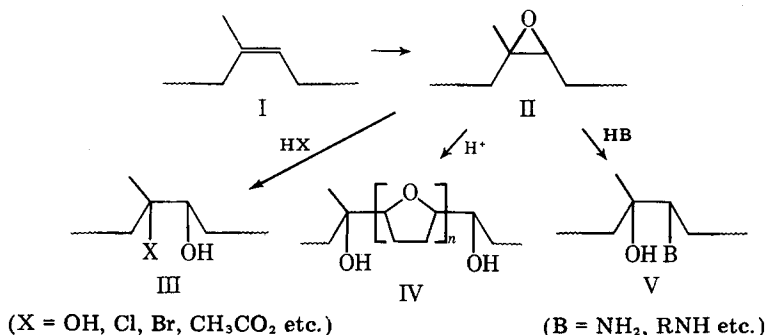
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## Synopsis

Studies in the epoxydation of natural rubber latices are described. Investigated epoxydation routes include the use of bromohydrin intermediates, hydrogen-peroxide-catalyzed systems, and preformed peracetic acid. The latter reagent allows almost quantitative epoxydation of natural rubber up to high modification levels with no detectable side reactions. Kinetic studies show that the peracetic acid epoxydation is second order in peracid and rubber hydrocarbon with an overall activation energy of 56.2 kJ/mol. Epoxydation leads to a progressive increase in  $T_g$  and polymer density with increase in modification level. The effects of modification on solvent swelling and mechanical properties of the DICUP-crosslinked rubbers are reported.

## INTRODUCTION

Diversification of the traditional uses of natural rubber (NR) can be achieved through chemical modification of the base polymer. Epoxydation represents a particularly convenient and versatile method for transformation of the physical properties of NR and in turn provides a potential<sup>†</sup> gateway to a variety of secondary modifications.



The epoxydation of diene polymers has been known for many years and commercial interest in such processes is evidence by a number of patents covering both NR and related synthetic rubbers. To date the majority of rubber epoxydation studies have been restricted to the treatment of rubbers in solution with

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<sup>†</sup> Whereas electrophilic ring opening reactions are well established for epoxydized natural rubber<sup>1-3</sup> and nucleophilic reactions have been studied for model compounds,<sup>4</sup> ENR appears to be relatively unreactive to nucleophilic reagents.<sup>5,6</sup>

organic peracids. NR in particular, has variously been epoxidized in solution by perbenzoic,<sup>7,8</sup> perphthallic,<sup>9</sup> and peracetic<sup>10</sup> acids, or with H<sub>2</sub>O<sub>2</sub>/acetic acid mixtures catalyzed by *p*-toluenesulfonic acids.<sup>5,11</sup> Peracetic acid has also been used for surface epoxidation of NR sheets<sup>10</sup> and for modification of depolymerized rubbers.<sup>12</sup>

However, for NR and those polydienes obtained as latices there is a strong economic incentive to conduct the epoxidation *in situ* so as to minimize processing and solvent costs. Although a number of early attempts at latex epoxidation of NR were reported in the literature,<sup>5,13</sup> it is only recently that the efficient epoxidation of NR latex to high modification levels has been realized.<sup>1,6</sup> This paper reports the details of one such study concerned with the efficient peracetic acid epoxidation of NR latices. Some alternative routes to latex epoxidation are also examined and finally some of the interesting properties of ENR are reported.

## EXPERIMENTAL

### Materials

Fresh field latex (clone RRIM 600) was collected and used within 3 h of tapping. High ammonia (HA) concentrated latex of dry rubber content 62% was kindly supplied by the Rubber Research Institute of Malaysia (RRIM). Vulcastab LW, a nonionic surfactant, was a gift from I.C.I. (Malaysia) Ltd.

Peracetic acid, at a concentration of approximately 3*M*, was prepared by the reaction of acetic anhydride with 30% hydrogen peroxide at 40°C.<sup>14</sup> The peracid solution was analyzed by the method of Greenspan and MacKellar<sup>15</sup> and was found to decompose only slowly (2–3% per month) when stored in the dark at –20°C.

Other chemicals and solvents were purchased as good laboratory grades and were used without further purification.

### Bromination of NR Latex

Saturated bromine water was prepared by shaking bromine (40 g) with 1 L of distilled water. Thiosulfate analysis indicated a free bromine concentration of 0.21*M*. Latex bromination was accomplished by adding calculated amounts of bromine water dropwise to a well-stirred, ammonia-stabilized, diluted (9% DRC) fresh field latex at room temperature. The brominated latex was subsequently divided into three portions which were treated by one of the following procedures:

**Method I.** The first portion was added to excess methanol. The precipitated rubber was washed extensively, dried under vacuum, and subsequently dissolved in benzene. Methanolic potassium hydroxide was added dropwise to the stirred rubber solution to a pH of 11. After 3 h the modified rubber was again isolated by precipitation and freed from excess hydroxide by two further reprecipitations, followed by vacuum drying at room temperature for 2 days.

**Method II.** Potassium hydroxide was added to the second portion of brominated latex to a pH of 11. After 3 h at room temperature, the rubber was isolated as above.

TABLE I  
Efficiency of Bromohydrin Formation and Subsequent Conversion to Epoxide in Natural Rubber Latex

Bromine added (mol %) <sup>a</sup>	Bromine <sup>b</sup> analyzed (% w/w)	Calculated <sup>c</sup> dibromide (mol %) <sup>a</sup>	Calculated <sup>c</sup> bromohydrin (mol %) <sup>a</sup>	Measured epoxide content <sup>d</sup> (mol %) <sup>a</sup>		
				Method I	Method II	Method III
5.22	7.05	1.37	3.85	0.74	0.58	0.36
7.83	11.4	3.37	4.46	0.48	0.45	0.27
10.5	15.0	4.90	5.60	0.47	0.41	0.16
13.04	16.6	4.46	8.58	0.44	—	0.09
26.10	24.3	3.10	23.0	0.27	0.25	0.13

<sup>a</sup> mol % = (mol of functional group/mol rubber double bonds) × 100.

<sup>b</sup> By oxygen flask combustion.

<sup>c</sup> Calculated assuming quantitative incorporation of bromine as dibromide or bromohydrin.

<sup>d</sup> By direct HBr titration.

**Method III.** The third portion of latex was treated as in Method II but with ammonia as base.

### Hydrogen Peroxide Catalyzed Epoxidation

**H<sub>2</sub>O<sub>2</sub>/CH<sub>3</sub>CN System.** Fresh field latex (25 mL) was buffered to a pH of 11 by the addition of 0.2M KH<sub>2</sub>PO<sub>4</sub>/NaOH solution. Acetonitrile (1.5 mL) was added followed by the dropwise addition of hydrogen peroxide (2.6 mL of 30% diluted with 22.4 mL water). The reaction mixture was maintained with stirring at 50°C for 3 h, after which the modified rubber was isolated by acetic acid coagulation.

**H<sub>2</sub>O<sub>2</sub>/Na<sub>2</sub>WO<sub>4</sub> System.** Latex (10 mL) was stabilized with KHCO<sub>3</sub> (2 g) and treated with 30% hydrogen peroxide (0.46 mL), and sodium tungstate (2 mol % on peroxide), and the mixture was allowed to react overnight at ambient temperatures before isolation of the rubber as above.

### Peracetic Acid Epoxidation

**Procedure 1.** In a typical experiment approximately 50 mL of fresh field latex was weighed into a 250-mL round-bottomed flask equipped with a stirrer. The latex was stabilized by addition of 5 mL of a 10% w/v aqueous solution of vulcastab LW and stirred to ensure thorough mixing before acidification with 5M HCl to a pH of 1. The acidified latex was subsequently diluted to a total volume of 100 mL with distilled water and thermostatted at the requisite temperature in the range 5–35°C. After thermal equilibrium had been achieved, the requisite amount of peracetic acid was added to start the epoxidation reaction. In kinetic runs latex samples (5 mL) were removed at appropriate time intervals. In all cases the ENR was isolated by addition of the latex to 95% ethanol. The precipitated rubbers were sheeted, washed extensively with water, and dried under high vacuum for 2 days before analysis.

**Procedure 2.** This slightly modified procedure was adopted to ensure the complete absence of secondary ring-opened products. Typically, concentrated latex (50 mL) was diluted with water (140 mL) to a DRC of approximately 15% w/v and stabilized with 10 mL of 10% w/v Vulcastab LW solution. The latex

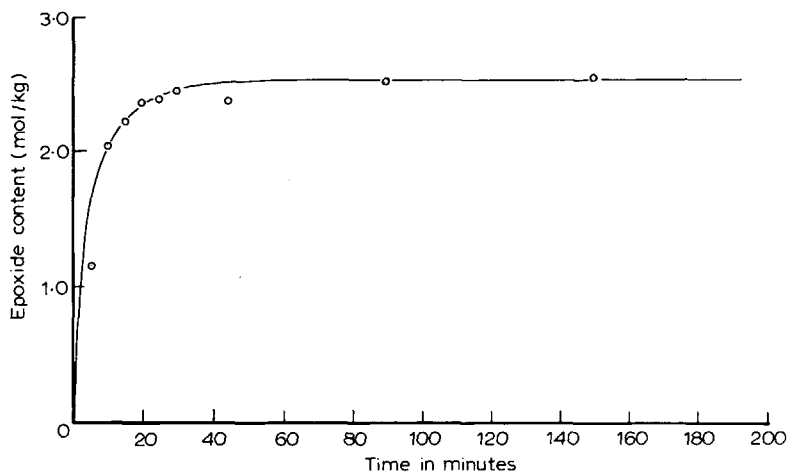


Fig. 1. Rate of peracetic acid epoxidation of natural rubber latex  $T = 30^{\circ}\text{C}$ ; [rubber] =  $187\text{ g dm}^{-3}$ ;  $[\text{CH}_3\text{CO}_3\text{H}] = 0.535\text{ mol dm}^{-3}$ .

was acidified to pH 5–6 with glacial acetic acid (2 mL) before addition of the peracetic acid. Subsequent treatment was identical to Procedure 1.

### Solution Epoxidation

Small samples of ENR were prepared by solution epoxidation to allow comparison of DSC traces. Typically, the requisite amount of *m*-chloroperbenzoic acid in chloroform was added dropwise to a 2% w/v solution of deproteinized natural rubber (DPNR) in chloroform. The rubber solution was maintained at about  $0^{\circ}\text{C}$  with vigorous stirring until the reaction was complete. The ENR was isolated by methanol precipitation and purified by subsequent reprecipitation from chloroform.

### Bromine Analysis

The bromine content of modified rubbers was determined by a Schöniger oxygen flask technique described in detail elsewhere.<sup>16</sup>

### Epoxide Analysis

Low levels of epoxide (up to 15 mol %) were analyzed by a direct HBr titration technique previously described.<sup>17,18</sup> Higher epoxide levels were determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR.<sup>19</sup> Details of these methods are to be published.<sup>20</sup>

### DSC Analysis

DSC measurements were made with a Perkin-Elmer DSC-2C equipped with a liquid nitrogen subambient cooling accessory and employing helium as purge gas. Samples (ca. 10 mg) were pretreated for 5 min at  $127^{\circ}\text{C}$ , rapidly quenched ( $320^{\circ}\text{C}/\text{min}$ ) to  $50^{\circ}\text{C}$  below the anticipated glass transition, and scanned upwards at  $20^{\circ}\text{C}/\text{min}$ . Quoted  $T_g$  values are the onset temperature as computed with

TABLE II  
Efficiency of Epoxidation of NR Latices with Peracetic Acid

Epoxide content of rubber <sup>a</sup> (mol %)	Efficiency of epoxidation <sup>b</sup> (%)	
	Procedure 1 <sup>c</sup>	Procedure 2 <sup>d</sup>
5.5	103	—
10.5	100	106
15.4	98	—
20	90	95
32	—	91
45	—	90
60	—	92
70	—	93
83	—	90

<sup>a</sup> Epoxide content of ENR as determined by HBr titration or NMR.

<sup>b</sup> Efficiency of epoxidation is given by (mol epoxide/mol added peracid) × 100. Values exceeding 100 may represent *in situ* formation of additional peracid.

<sup>c</sup> [RH] = 245 g/L,  $T = 0^{\circ}\text{C}$ ,  $t = 18$  h.

<sup>d</sup> [RH] = 155 g/L,  $T = 5^{\circ}\text{C}$ ,  $t = 6$  h.

the Thermal Analysis Data Station (TADS) standard program supplied by Perkin-Elmer. The instrument was calibrated as described in detail elsewhere.<sup>21</sup>

### ENR Crosslinking

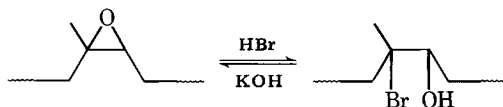
For physical testing the samples of ENR were crosslinked with 2.5 pph di-cumylperoxide preheated at  $100^{\circ}\text{C}$  for 10 min and cured at  $150^{\circ}\text{C}$  for 60 min. The peroxide was incorporated into the rubber samples on a cold two-roll mill.

## RESULTS AND DISCUSSION

### Preparation of Epoxidized Natural Rubber

The currently established routes for latex epoxidation invariably involve reactions in acidic media. Epoxidation under these low pH conditions suffers from the dual drawback of concomitant side reactions and the necessity for additional stabilization of the latex, which in turn compounds the difficulty of subsequent isolation of the product. For these reasons it seemed pertinent to explore the use of epoxidation reactions compatible with alkaline conditions and proven for low molecular weight alkenes but hitherto neglected in latex studies.

**The Bromohydrin Route.** During the course of investigations relating to the presence of naturally occurring amino and epoxy groups in NR it was shown that the formation of rubber bromohydrin could be quantitatively reversed<sup>17</sup>:



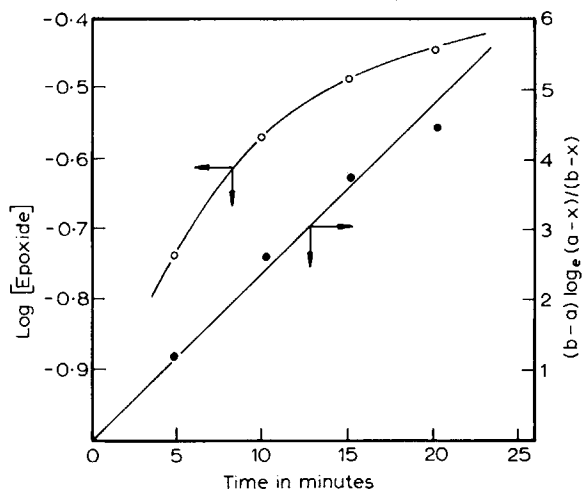
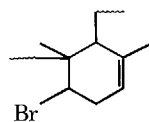


Fig. 2. First- and second-order plots for the peracetic acid epoxidation of natural rubber latex. Experimental conditions as in Fig. 1. (O) First order plot; (●) second order plot.

Consequently, it appeared reasonable to synthesize ENR via the intermediacy of the bromohydrin, which in turn can be readily generated by the reaction of bromine water with trisubstituted olefins.<sup>4</sup> Preliminary experiments showed that neither anionic (sodium lauryl sulfate) nor nonionic (Vulcastab LW) surfactants were suitable for stabilization of rubber latices in the presence of bromine. However, high pH conditions (ammonia or potassium hydroxide) prevented coagulation. The results of the addition of bromine water to NR latices are summarized in Table I. Bromine reacts readily with the rubber hydrocarbon as judged by the rapid decolorization of the bromine water and the significant incorporation of bromine into the modified rubbers. It seems likely that the reaction of bromine water leads to the formation of both dibromide and bromohydrin moieties, and the relative proportion of these has been inferred from the bromine content of the rubber, assuming exclusive formation of these groups and efficient consumption of the bromine. The possibility of cyclized groups such as VI,



(VI)

cannot be excluded as such groups would lead to low bromine analysis and inefficient conversion to epoxide. The conversion of bromohydrin to epoxide is disappointingly poor as the highest efficiency is only 19% by any of the methods used. (It was subsequently found that the efficiency could be improved to about 25 mol % by increasing the latex pH during bromination to pH 13.) The efficiency of epoxidation drops dramatically with increased bromine content decreasing to a mere 1% for added bromine concentration of 26 mol %. Since elsewhere<sup>17</sup> it has been shown that NR-bromohydrin can be efficiently converted to epoxide under the conditions employed, it must be concluded that brom-

TABLE III  
Comparison of Second-Order Rate Constants for Peracetic Acid Epoxidation of Polyisoprene Latices at Various Temperatures

Temp (°C)	Rate Constant ( $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \times 10^4$ )	
	NR latex	Synthetic latex <sup>a</sup>
0	0.362	—
15	—	1.42
16.5	1.05	—
20	—	2.19
25	—	3.78
30	3.70	6.07
35	4.90	8.73

<sup>a</sup> Data taken from Ref. 25 for epoxidation of synthetic polyisoprene latex.

ohydrin is inefficiently formed in NR latices. Particularly at high modification levels dibromide and cyclized structures such as VI must predominate.

**Hydrogen Peroxide Catalyzed Latex Epoxidation.** Hydrogen peroxide alone or catalyzed by tungsten salts<sup>22</sup> or nitrile compounds<sup>23,24</sup> have found use as efficient epoxidation agents for low molecular weight alkenes. Application of these reagents to HA concentrated latex at room temperature gave no significant epoxidation (<1%). However, the  $\text{H}_2\text{O}_2/\text{CH}_3\text{CN}$  system when added to fresh field latex, in the absence of ammonia, gave rise to a 7% conversion to epoxide. This increased efficiency in unpreserved latex suggests that ammonia probably interferes with this reaction.

The low efficiencies in all these methods is probably related to the difficulty in obtaining efficient transfer of the active water-soluble intermediates to the rubber particles in the latex.

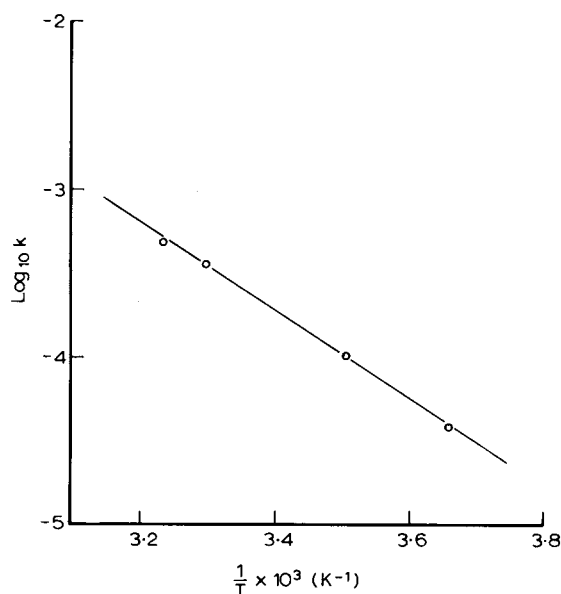
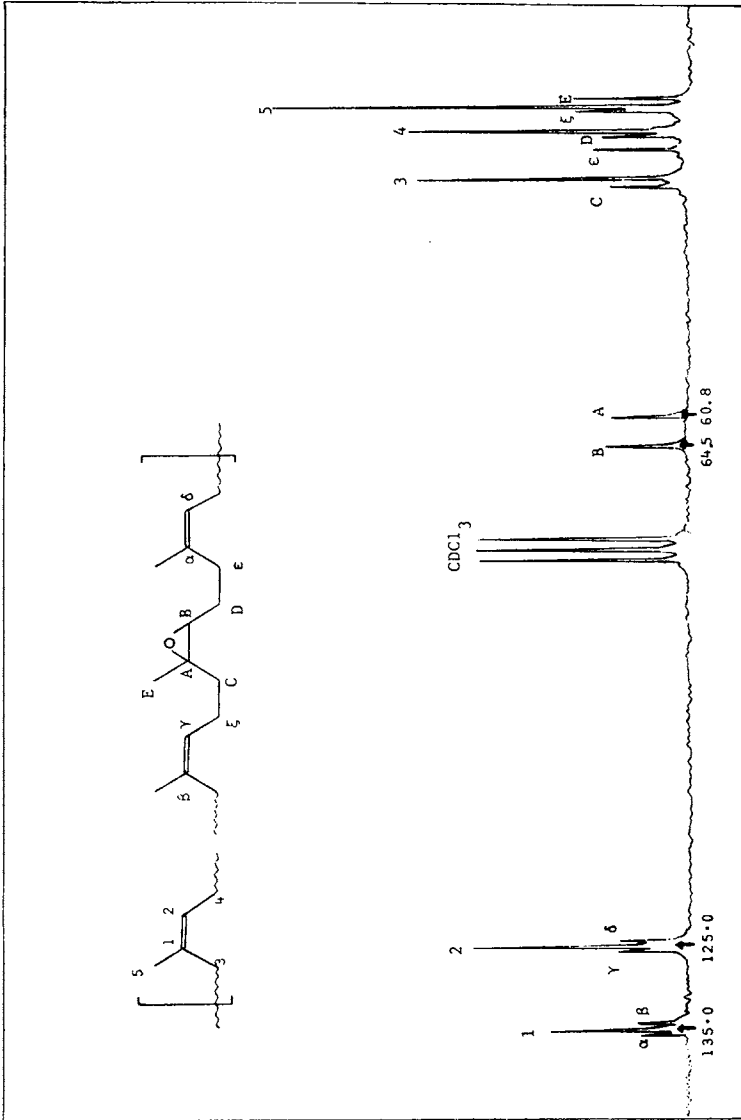


Fig. 3. Arrhenius plot for peracetic acid epoxidation of natural rubber.



Chemical Shift (ppm).

Fig. 4.  $^{13}\text{C}$ -NMR of partially epoxidized natural rubber.



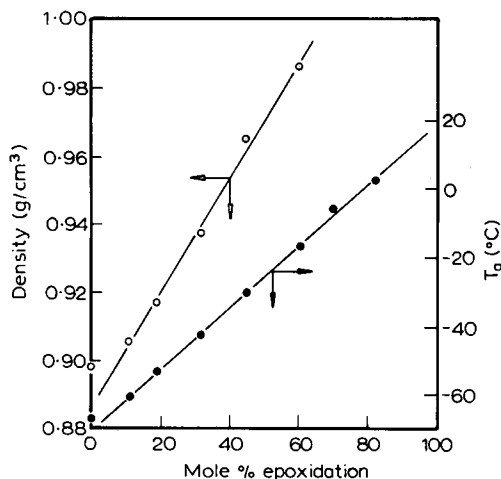


Fig. 5. Variation of  $T_g$  and density with epoxide content of modified gum rubber.

**Peroxyacetic Acid Epoxidation of NR Latex.** Since the alternative methods of epoxidation appear inefficient for NR latex, it was decided to investigate the proven peracid method. Peroxyacetic acid was chosen for its ease of preparation, stability, and compatibility with both the aqueous and hydrocarbon phases of the latex.

Initial experiments (Procedure 1) involved the addition of preformed peroxyacetic acid to stabilized fresh field latex acidified with hydrochloric acid. Epoxidation proved to be rapid at 30°C (Fig. 1) being effectively complete within 30 min at this temperature. At lower temperatures the reaction proceeds more slowly requiring some 18–24 h for completion at 0°C. The efficiency of the epoxidation reaction is excellent, especially at moderately low modification levels where conversion of the peroxyacetic acid is effectively quantitative (Table II). At these low modification levels and temperatures there is no evidence of ring opened epoxide groups as judged by the absence of carbonyl and hydroxyl absorptions in the IR spectra of the modified rubbers. This contrasts with the reaction of *in situ* generated performic acid,<sup>2</sup> in which epoxide formation is accompanied by extensive amounts of secondary products type III and IV. Ring opening is clearly accelerated by the higher acidity of formic versus acetic acid and the lower pH conditions used in the earlier study.

Analysis of the rate of epoxidation shows reasonable correlation (Fig. 2) with the anticipated second-order kinetics:

$$R_{\text{epox}} = k[\text{RH}][\text{CH}_3\text{CO}_3\text{H}]$$

at least for modification levels of 15 mol %. The epoxidation rates are also of similar order of magnitude to those obtained earlier<sup>25</sup> for the peroxyacetic acid epoxidation of synthetic polyisoprene latices (Table III). Differences are to be anticipated due to variation in particle size distribution and polyisoprene structures. The overall activation energy of epoxidation 56.2 kJ/mol as derived from the Arrhenius plot (Fig. 3) is, however, lower than the figure of 65.9 kJ/mol reported<sup>25</sup> for the synthetic latex. The observed difference may be associated with the presence of repeating units derived from 1,2- and 3,4-addition modes.

TABLE IV  
The Glass Transition Characteristics of NR and ENR Homopolymers and Blends

Sample	$T_g$ (°C) <sup>a</sup>		$\Delta C_p$ <sup>b</sup> (cal·g <sup>-1</sup> ·deg <sup>-1</sup> )
	Onset	Midpoint	
NR	-66.8	-64.9	0.104
ENR <sup>c</sup>	-27.9	-25.7	0.111
NR/ENR <sup>d</sup>	-66.9/-27.2	-64.9/-23.9	0.053/0.056
NR/ENR <sup>e</sup>	-66.8/-24.4	-63.9/-21.8	0.055/0.044

<sup>a</sup> The significance of onset and midpoint values has been discussed in detail elsewhere.<sup>21</sup>

<sup>b</sup>  $\Delta C_p$  is the change in heat capacity associated with the respective glass transition.

<sup>c</sup> Epoxy content 47 mol %.

<sup>d</sup> 50/50 % w/w mix of NR and ENR blended on two-roll mill.

<sup>e</sup> 50/50 % w/w mix of NR and ENR obtained by coprecipitation.

These isomers are known to have higher activation energies in epoxidation than the NR *cis*-1,4- structure.

Subsequent epoxidation studies were carried out with HA concentrated latices. These were stabilized (Vulcastab LW) and neutralized with acetic acid before the addition of peracetic acid (Procedure 2). Epoxidation rates were very similar to the experiments conducted above with fresh latex acidified with hydrochloric acid, and, moreover, high epoxidation efficiencies were maintained even at high modification levels (Table II). This latter procedure is preferable since the absence of strong mineral acid reduces the possibility of acid catalyzed ring opening reactions.

The cleanness of the peracetic acid reaction under these conditions is confirmed by the <sup>13</sup>C-NMR spectrum of highly modified ENR (Fig. 4), which shows only resonances characteristic of the epoxide and unmodified chain.

### Properties of Epoxidized Natural Rubber

**Glass Transition Temperature and Density.** Main-chain modification of polydienes invariably lead to enhanced  $T_g$  values due to lowered rotational freedom of the modified repeating unit. Epoxide modification of the NR mainchain results in a progressive increase in  $T_g$  with level of modification (Fig.

TABLE V  
Comparative Swelling of Crosslinked NR and ENR in Various Solvents

Modification level (mol %)	Solvent swelling <sup>a</sup> (g solvent/g rubber)			
	Petroleum ether ( $\epsilon = 1.9$ ) <sup>b</sup>	Benzene ( $\epsilon = 2.3$ ) <sup>b</sup>	<i>n</i> -Butanol ( $\epsilon = 17.5$ ) <sup>b</sup>	<i>N,N</i> -dimethyl formamide ( $\epsilon = 36.7$ ) <sup>b</sup>
Control	1.86	2.78	0.06	0.07
5.5	1.68	2.87	0.13	0.09
10.5	1.48	2.97	0.24	0.15
15.4	1.24	2.99	0.40	0.23
20.4	1.00	2.73	0.54	0.34

<sup>a</sup> Equilibrium values at ambient temperatures ( $\sim 27^\circ\text{C}$ ).

<sup>b</sup> Dielectric constant a measure of solvent polarity.

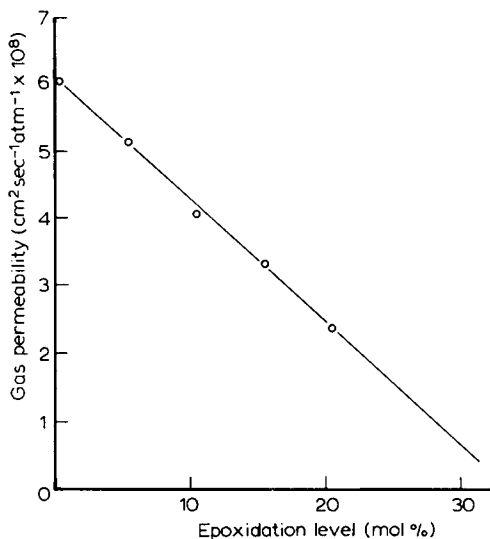


Fig. 6. Dependence of air permeability on the epoxide content of DICUP crosslinked rubbers (values obtained at 27°C using air at 100 psi).

5). Similar trends have been observed elsewhere for epoxidized polybutadiene<sup>26</sup> and for ENR.<sup>1,27</sup> In this work the  $T_g$  of the unmodified NR (-67°C) is raised to +18°C for the fully epoxidized rubber compared to ranges of -72-+5°C<sup>1</sup> and -69-+15°C<sup>27</sup> reported by other workers. It is noteworthy that the progressive increase in the glass transition temperature parallels a concomitant increase in polymer density (Fig. 5). This is indicative that the increased  $T_g$  results from a reduction in free volume of the chain segments.

Whereas ENR at every modification level examined shows only one  $T_g$ , blends of ENR with NR show two distinct  $T_g$  values characteristic of the unmodified and modified polymers, respectively (Table IV). This infers that the latex-prepared ENR must be regarded as a random copolymer since the presence of extensive blocks of epoxy modification should lead to distinct  $T_g$  phenomenon in the modified rubber. This in turn suggests that the peracid rapidly penetrates the latex rubber particles giving uniform epoxidation of the rubber hydrocarbon. Confirmation of this premise is supplied by solution epoxidation with *m*-chloroperbenzoic acid, which gives ENR with  $T_g$  characteristics identical to the latex-produced material.

**Solvent Swelling of ENR.** Epoxide modification of NR significantly increases the polarity of the molecule and hence its susceptibility to swelling by a variety of solvents. Table V summarizes swelling data for modified rubbers crosslinked with DICUP. It is evident that epoxidation decreases the degree of swelling in nonpolar solvents such as saturated hydrocarbons. However, ENR is more susceptible than NR to more polar solvents such as butanol and dimethylformamide, the solvent swell being directly proportional to the epoxide level.

**Gas Permeability of Crosslinked ENR.** The air permeabilities reported here were measured with BS equipment attached to an automatic oxidation apparatus working in reverse mode. There is a marked reduction in the air permeability of the material with increase in level of modification (Fig. 6). The

TABLE VI  
Effect of Epoxidation on the Physical Properties of Crosslinked Natural Rubber

Modification level (mol %)	Modulus ( $\text{MN}\cdot\text{m}^{-2}$ )			Relaxed modulus MR 100 ( $\text{MN}\cdot\text{m}^{-2}$ )	Tensile strength ( $\text{MN}\cdot\text{m}^{-2}$ )	Elongation at break (%)	Hardness (IRHD)	Dunlop resilience (%)			
	At 200%								At 300%		
	At 100%	At 200%	At 300%						At 100%	At 200%	At 300%
Control	1.0	1.8	3.1	0.95	5.7	390	43	81.8			
5.5	1.1	1.9	3.4	0.99	7.0	380	43	81.1			
10.5	1.1	2.0	3.4	—	7.6	400	43	79.6			
15.4	1.1	2.0	3.7	—	7.6	380	44	79.5			
20.4	1.3	—	—	—	2.0	180	45	74.3			
30.0	1.0	2.0	—	—	1.0	200	—	—			

decrease in the rate of gaseous diffusion through the rubber may be correlated with the reduced segmental rotation rates and increased sample density (Fig. 5).

**Mechanical Properties of Crosslinked ENR.** Some of the mechanical properties of DICUP crosslinked ENR are summarized in Table VI. At moderate modification levels ENR is characterized by slightly improved modulus and tensile strength compared to the control. At epoxide levels of 20 mol % and above the tensile strength is significantly lower, but this may be a reflection of the decreased crosslinking efficiency of DICUP reported at high modification levels.<sup>1</sup> Not unexpectedly, epoxide modification leads to an increased hardness and reduced resilience, both related to the increased  $T_g$  of the modified rubber.

The good strength properties under stress are consistent with the reported ability of ENR to strain crystallize in a similar fashion to unmodified NR.<sup>27</sup>

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## References

1. I. R. Gelling and J. F. Smith, Preprints International Rubber Conference, Venice, Oct. 1979, pp. 140-149.
2. S. C. Ng and L. H. Gan, *Eur. Polym. J.*, **17**, 1073 (1981).
3. D. R. Burfield and S. N. Gan, *Polymer*, **18**, 607 (1977).
4. D. R. Burfield, S. N. Gan, and R. H. Smithers, *J. Chem. Soc., Perkin I*, 666 (1977).
5. T. Colclough, *Trans. Inst. Rubber Ind.*, **38**, T11 (1962).
6. K. S. Law, Ph.D. Thesis, University of Malaya, Kuala Lumpur, Malaysia, 1978.
7. I. M. Kolthoff, T. S. Lee, and M. A. Mairs, *J. Polym. Sci., Polym. Chem. Ed.*, **2**, 206, 220 (1973).
8. A. Saffer and B. L. Johnson, *Ind. Eng. Chem.*, **40**, 538 (1948).
9. C. Roux, R. Pautrat, R. Cheritat, and C. Pinazzi, *Compt. Rend.*, **258**, 5442 (1964).
10. J. A. Mairs and J. Todd, *J. Chem. Soc.*, **1932**, 386.
11. B. M. Badran and E. M. Abdel-Bary, *Chem. Ind.*, 314 (1977).
12. O. Henberger and L. N. Owen, *J. Chem. Soc.*, **1952**, 910.
13. G. F. Bloomfield, *J. Soc. Chem. Ind.*, **52**, 121T (1934).
14. H. Batzer, *Chem. Ind.*, 179 (1964).
15. F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).
16. E. L. McCaffery, *Laboratory Preparation for Macromolecular Chemistry*, McGraw-Hill, New York, 1970.
17. D. R. Burfield and S. N. Gan, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2725 (1975).
18. D. R. Burfield, *Br. Polym. J.*, **3**, 78 (1977).
19. R. V. Gemmer and M. A. Golub, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2985 (1978).
20. D. R. Burfield, K. S. Law, K. L. Lim, and S. Ng, *Polymer* (in press).
21. D. R. Burfield and K. L. Lim, *Macromolecules*, **16**, 1170 (1983).
22. D. Swern, Ed., *Organic Peroxides*, Wiley-Interscience, New York, 1971, Vol. 2.
23. G. B. Payne, P. H. Deming, and P. H. Williams, *J. Org. Chem.*, **26**, 659 (1961).
24. L. A. Arias, S. Adkins, C. J. Nagel, and R. D. Bach, *J. Org. Chem.*, **48**, 888 (1983).
25. E. F. Bukanova, I. A. Tutorskii, and E. G. Boikacheva, *Vysokomol. Soedin Ser. A*, **18**, 2223 (1976).
26. D. Zuchowska, *Polymer*, **22**, 1073 (1981).
27. C. K. L. Davies, S. V. Wolfe, I. R. Gelling, and A. G. Thomas, *Polymer*, **24**, 107 (1983).

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