

# Effect of Latex Concentration on Epoxidation of Natural Rubber (NR) Latex\*

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## SYNOPSIS

Effect of latex concentration on the extent of epoxidation and physical properties of epoxidized natural rubber (ENR) was evaluated as a function of latex concentration in the range of 20–60% by weight. The epoxidation rate increased with increasing latex concentration. Physical properties and sequence distribution of an epoxy group of ENR with 30 mol % epoxy content was invariant with the latex concentration employed for epoxidation.

## INTRODUCTION

Chemical modifications of natural rubber can be employed to alter the properties of natural rubber.<sup>1</sup> Of these, epoxidation of natural rubber latex using performic acid generated *in situ* has attracted commercial attention as it achieves the optimum cost/performance balance.<sup>2</sup> Pilot plant production of epoxidized natural rubbers (ENRs) with 25 and 50 mol % epoxidation has been reported.<sup>3</sup>

In spite of extensive literature on the properties and applications of ENRs, little work has been reported regarding conditions for synthesis of ENRs by epoxidation using *in situ* performic acid.<sup>4</sup> Gan and Ng<sup>5</sup> and Campbell<sup>6</sup> determined kinetic parameters of epoxidation of NR latex *in situ* by using formic acid and hydrogen peroxide. Campbell showed that reaction products of the epoxidation of NR latex are dependent on the two-phase nature of the reaction system. Similarly, the effect of the epoxidation reaction parameters on formation of side products has been reported.<sup>7</sup> However, no attempt seems to have been made to study the effect of latex concentration, especially > 30%, on the properties and microstructure of epoxidized products. We were somewhat intrigued by the fact that epoxidation of natural rubber generally uses a dilute

latex with 20% solid content. The ability to use latex with higher solids content could have process advantages, such as enhanced reaction rates and greater output per unit volume of the reactor. Furthermore, natural rubber latex is commercially shipped as 60% latex, which according to the present description of the process<sup>4</sup> needs to be diluted prior to epoxidation.

We, therefore, undertook a study of *in situ* epoxidation of natural rubber using formic acid–hydrogen peroxide and with latex concentration varying in the region of 20–60%. We were particularly interested in the effect of this variable on the extent of conversion as well as on the structure and physical property of the ENR so-produced. This paper presents the results of this study.

## EXPERIMENTAL

Natural rubber latex (60% drc) stabilized with ammonia obtained from the Rubber Board, Kottayam, Kerala, India, was used. Formic acid (98.0% purity) obtained from M/s. Ranbaxy Laboratories Ltd., India, was used as received. Hydrogen peroxide (47% by w/w) obtained from M/s National Peroxide was used as such after estimation. A nonionic surfactant, "Linoxyd concentrate," was obtained from M/s. HICO Products, Bombay, India. ENR-25 and ENR-50 samples were obtained from the Rubber Research Institute of Malaysia, Experimental Station, Malaysia.

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### Epoxydation of Natural Rubber (NR) Latex

NR latex (60% drc, 46 g) was taken in a three-neck round-bottom flask equipped with stirrer, thermometer, and dropping funnel. It was neutralized by adding the required quantity of acetic acid. The latex was diluted to 20% by adding distilled water and stabilized with 3 phr Linoxyd concentrate. The required amount of formic acid (4.7 g, 0.25 mol) was added dropwise with stirring and heated to 40°C. Hydrogen peroxide (24 g, 43.6%, 0.75 mol) was added dropwise in 15–20 min and reaction temperature was raised to 50°C and maintained throughout the reaction period. Samples were withdrawn at different time intervals, coagulated with methanol, washed with water and 5% sodium carbonate solution, and water again. The samples were dried in a vacuum oven at 60°C till constant weight.

To study the effect of latex concentration on the tensile properties of ENR, samples of ENR containing  $30 \pm 2$  mol % epoxy content were prepared on a 200 g scale using 20, 30, 40, 50, and 60% latex, 0.75 mol of formic acid, and 0.75 mol of  $H_2O_2$ . These samples were compounded using the following recipe: ENR 100, sodium carbonate 0.3, stearic acid 2, ZnO-5, Flektol H 2, IASF carbon black 30, MBS 1.5, and S 1.5. Test slabs were cured at 150°C for 20 min.

### CHARACTERIZATION

Tensile properties of vulcanized samples were determined as per ASTM method D412-61T. Hardness was determined by a shore A hardness tester (ASTM D2240-68). Mooney viscosity was determined on a Mooney viscometer model NBS series 300 USA as per ASTM method D1646-61.

#### Epoxy Content

Epoxy content of ENR samples was determined by  $^1H$ - and  $^{13}C$ -NMR methods as the titrimetric method gave erratic results at higher epoxy levels.<sup>8,9</sup>

$^1H$ -NMR spectra were recorded on Bruker WH-90 spectrometer operating at 90 MHz and were collected in 8 K data points, 1800 Hz spectral width, 3 s pulse width, and acquisition time 2.2 s in 5% w/v  $CDCl_3$  with TMS as internal standard. Well-resolved spectra could be obtained even though the solution was in the form of a gel. For quantitative studies, the extent of the reaction was calculated by measuring the areas under the peaks of oxirane and olefinic regions with the help of an electronic integrator.

$^{13}C$ -NMR spectra were recorded on Bruker MSL-300 spectrometer operating at 75.47 MHz with

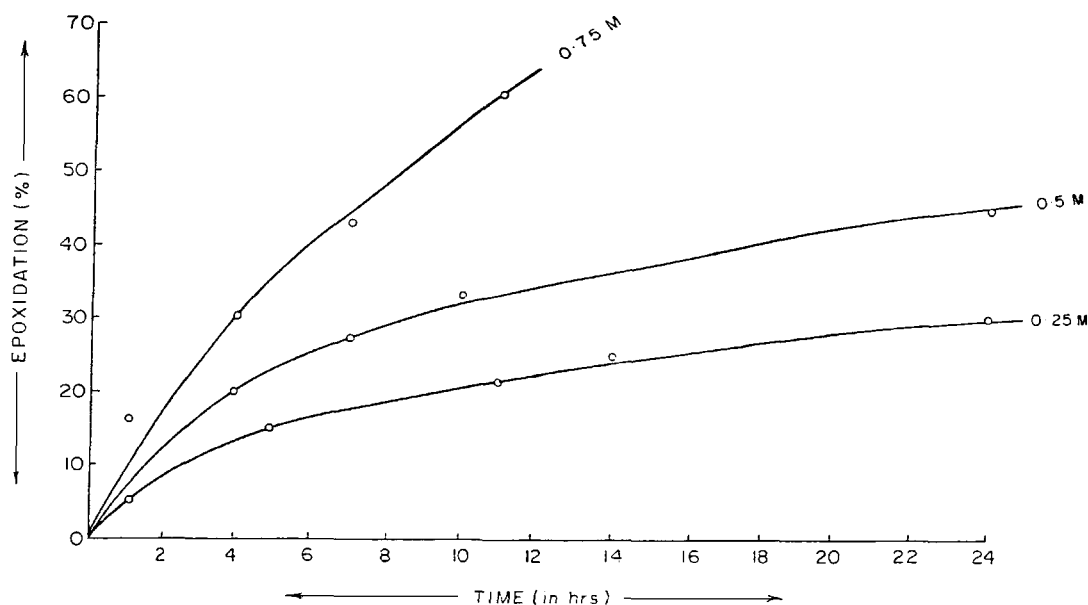


Figure 1 Effect of concentration of formic acid on epoxydation of 20% latex.

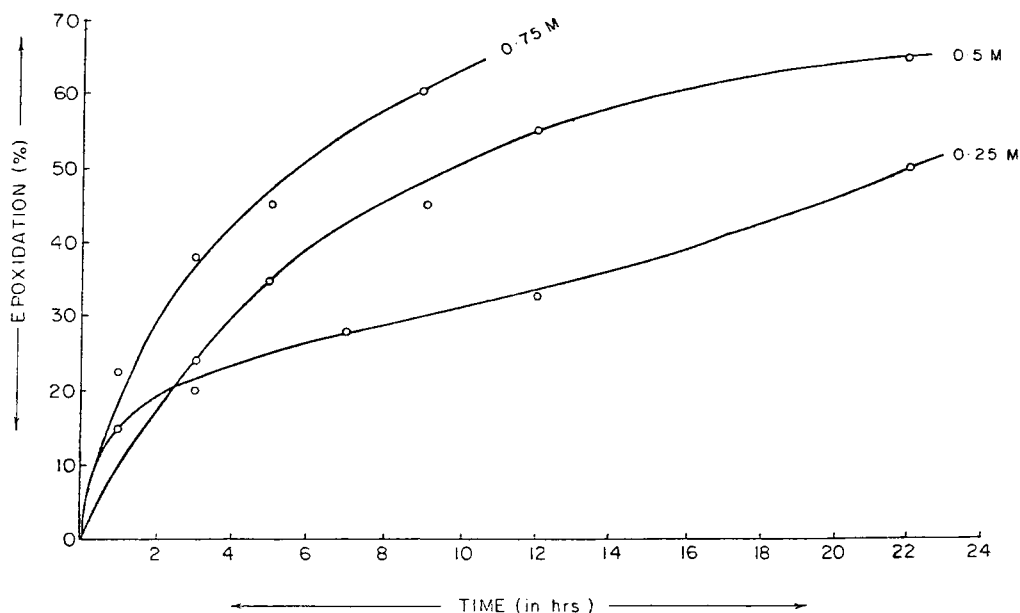


Figure 2 Effect of concentration of formic acid on epoxidation of 30% latex.

a spectral width of 20,000 Hz and pulse width of 6 s ( $90^\circ$  pulse).

## RESULTS AND DISCUSSION

NR latex with different dilutions (from 60 to 20% by weight) was epoxidized with 0.75 mol of 47% by

weight hydrogen peroxide and 0.25, 0.50, and 0.75 mol of formic acid at  $50^\circ\text{C}$ . The extent of epoxidation was estimated by  $^1\text{H-NMR}$  by periodic withdrawal of the sample. Mol % epoxidation was plotted against reaction time for differing formic acid concentrations and is shown in Figures 1-4. The extent of epoxidation increases with concentration of

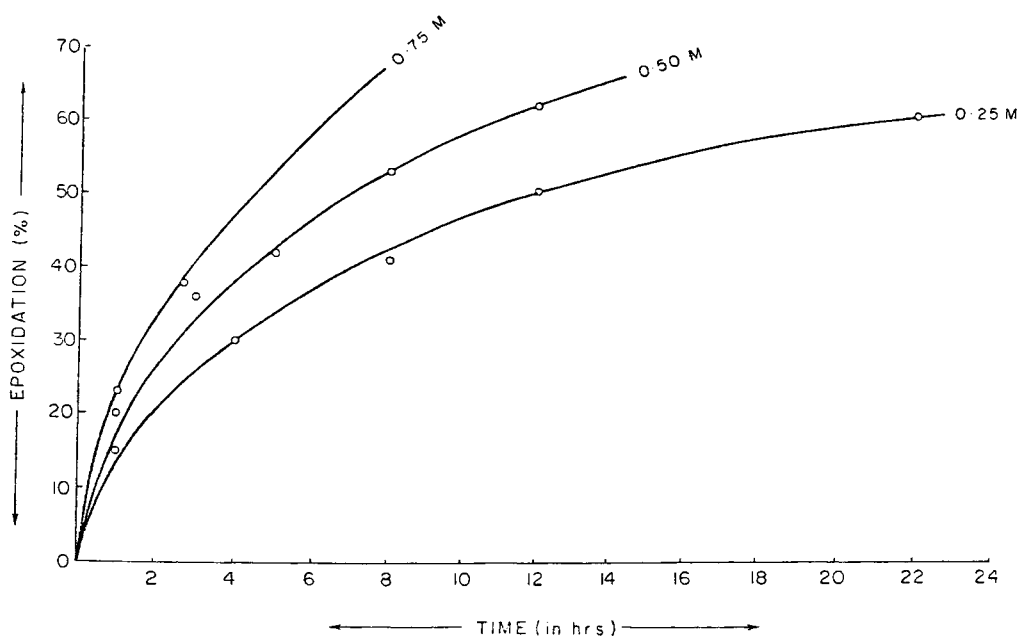
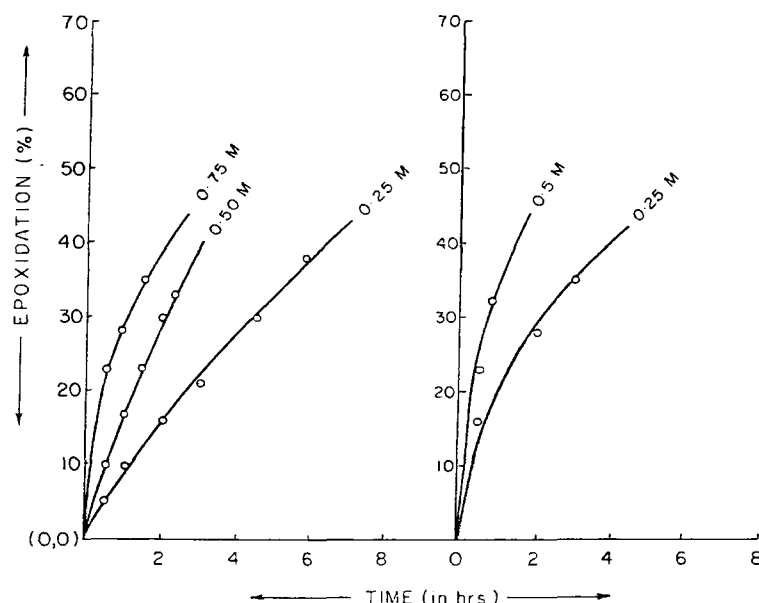


Figure 3 Effect of concentration of formic acid on epoxidation of 40% latex.



**Figure 4** Effect of concentration of formic acid on epoxidation of 50% (left) and 60% (right) latex.

formic acid at a given peroxide concentration. With increasing solid content, the latex showed a pronounced tendency to coagulate at progressively lower mol % epoxidation, especially at higher formic acid concentration. For example, using 50% latex concentration and 0.75 mol of formic acid, coagulation occurred within 2 h (35 mol % epoxy content) (Fig. 4), whereas under similar conditions but with a latex concentration of 60%, coagulation occurred in 30 min (30 mol % epoxy content). Higher epoxidation rates at higher latex concentration is in agreement with the observations of Campbell.<sup>6</sup> Epoxidation of natural rubber, 50 and 25 mol %, could be achieved

in 3 and 10 h, respectively, at 50°C using 0.75 mol  $\text{H}_2\text{O}_2$ /0.25 mol  $\text{HCO}_2\text{H}$  and a latex concentration of 40%. Processes described in the patent literature using a 20% latex require substantially longer reaction times.<sup>4</sup>

The mechanical properties of compounded ENR with  $30 \pm 2$  mol % epoxidation generated from lattices of 20, 30, 40, 50, and 60% concentration were determined and compared with a commercial sample of ENR (30 mol % epoxidation) obtained from the Rubber Research Institute of Malaysia. The results indicate that mechanical properties are essentially invariant with the latex concentration used in epox-

**Table I** Mechanical Properties of Epoxidized Natural Rubber

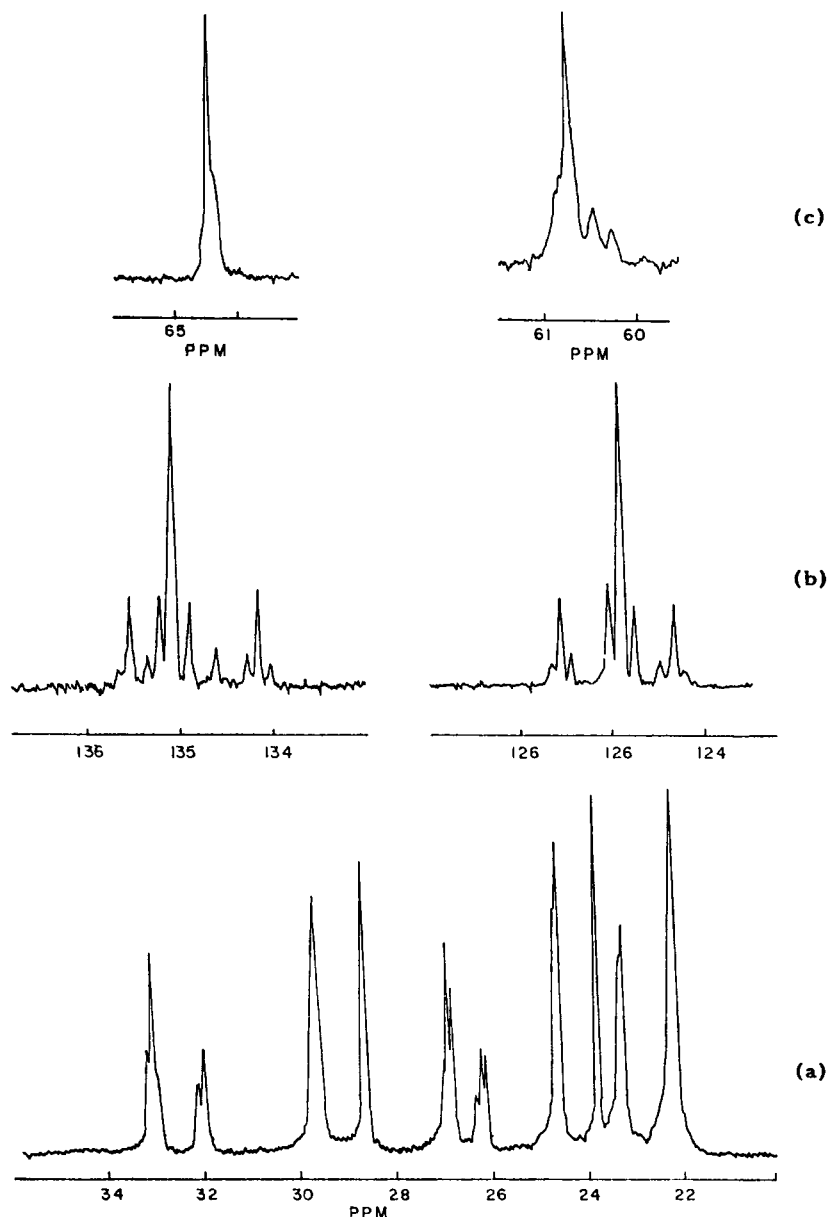
Sample No.	Latex Concentration (wt %)	Epoxidation (mol %)	Tensile Strength ( $\text{kg}/\text{cm}^2$ ) <sup>a</sup>	% Elongation at Break <sup>b</sup>	Mooney Viscosity <sup>c</sup> ( $\text{ML}_{1+4}$ )	Hardness (Shore A <sup>d</sup> )
1	20	29	158	630	91	47
2	30	29	160	650	90	47
3	40	28	155	610	88	46
4	50	31	170	625	92	47
5	60	30	170	650	92	48
6	ENR 25	30	162	600	95	47

<sup>a</sup> ASTM D412-61T.

<sup>b</sup> ASTM D412-61T.

<sup>c</sup> ASTM D1646-61.

<sup>d</sup> ASTM 2240-68.



**Figure 5**  $^{13}\text{C}$ -NMR spectra of 30% ENR-expanded region of (a) methyl and methylene carbons, (b) olefinic carbons, and (c) oxirane carbons.

idation and match reasonably well with commercial samples (Table I).

The properties of epoxidized natural rubber are known to depend both on the secondary ring-opened structures present as an impurity as well as on the sequence distribution of the epoxide unit along the chain.  $^{13}\text{C}$ -NMR studies have established<sup>5</sup> that in spite of the physical heterogeneity of latex systems epoxidation is quite random. It was, therefore, of interest to verify whether random epoxidation occurred even at higher solid contents and under re-

action conditions close to the coagulation point of the latex.

Careful examination of  $^1\text{H}$ -NMR as well as  $^{13}\text{C}$ -NMR spectra showed that in none of the ENR samples synthesized during this study were secondary ring-opened products (formyl ester, hydroxyl, furan, or pyran) present. After establishing the purity of the samples, it was of interest to see if latex concentration had any effect on the sequence distribution of epoxy units in the polymer chain. ENR samples containing  $30 \pm 2\%$  epoxy content synthe-

**Table II**  $^{13}\text{C}$ -NMR: Resonance Assignments for Methyl and Methylene Carbons

Resonance	Chemical Shift (ppm)	Assignments	Signal Intensity (%)						
			ENR-30, <sup>a</sup> Samples Obtained from Latex (%)					ENR-25 <sup>b</sup>	ENR-50 <sup>c</sup>
			20	30	40	50	60		
C <sub>1</sub> -1	33.09	C <sup>1</sup> EC	12.05	11.51	11.37	12.59	8.54	13.15	9.64
C <sub>1</sub> -2	32.98	C <sup>1</sup> EE	5.15	3.85	4.40	7.60	3.08	8.03	18.63
C <sub>1</sub> -3	32.09	C <sup>1</sup> CC	44.51	50.09	50.64	35.43	63.79	35.20	6.40
C <sub>1</sub> -4	31.94	C <sup>1</sup> CE	15.89	14.58	13.19	16.78	10.01	16.45	10.53
C <sub>1</sub> -5	29.59	E <sup>1</sup> EC, E <sup>1</sup> EE	3.66	2.81	3.22	5.09	2.48	6.60	25.45
C <sub>1</sub> -6	28.60	E <sup>1</sup> CC, E <sup>1</sup> CE	18.73	17.17	17.11	22.52	12.09	20.60	29.34
C <sub>4</sub> -1	26.98	CE <sup>4</sup> C	12.02	11.09	11.48	12.50	8.44	12.49	8.11
C <sub>4</sub> -2	26.87	EE <sup>4</sup> C	7.13	5.80	5.69	10.05	4.34	9.88	16.80
C <sub>4</sub> -3	26.28	C <sup>4</sup> CC	41.69	49.15	47.16	33.38	61.14	30.65	13.19
C <sub>4</sub> -4	26.19	EC <sup>4</sup> C	17.96	15.27	16.98	18.51	11.80	21.09	8.79
C <sub>4</sub> -5	24.60	EE <sup>4</sup> E, CE <sup>4</sup> E	3.32	2.37	2.60	4.98	2.24	5.17	24.34
C <sub>4</sub> -6	23.78	EC <sup>4</sup> E, CC <sup>4</sup> E	17.86	15.94	16.08	20.58	12.04	20.71	29.76
C <sub>5</sub> -1	23.32	<sup>5</sup> C	72.09	73.94	75.66	65.18	82.65	67.66	38.08
C <sub>5</sub> -2	22.20	<sup>5</sup> E	27.91	26.06	26.34	34.82	17.35	32.34	61.92

<sup>a</sup> 30 mol % epoxy content.<sup>b</sup> Analyzed for 30 mol % epoxy content (commercial sample).<sup>c</sup> Analyzed for 60 mol % epoxy content (commercial sample).

sized by using different latex concentrations (20, 30, 40, 50, and 60% by weight) were studied by  $^{13}\text{C}$ -NMR spectra. The methylene carbon lines were assigned on the basis of triad sequences, olefinic in

terms of pentad and oxirane as triads as suggested by Bradbury and Parera.<sup>10</sup> In the present study, we observed 22, 13, and 11 lines for the methylene, olefinic, and oxirane carbons, respectively [Fig. 5 (a),

**Table III**  $^{13}\text{C}$ -NMR: Resonance Assignments for Olefinic C<sub>3</sub>-Carbon Atoms

Resonance	Chemical Shift (ppm)	Assignments	Signal Intensity (%)						
			ENR-30, <sup>a</sup> Samples Obtained from Latex (%)					ENR-25 <sup>b</sup>	ENR-50 <sup>c</sup>
			20	30	40	50	60		
C <sub>3</sub> -1	125.56	CEC <sup>3</sup> CC	11.70	11.97	11.44	12.29	8.70	12.70	15.12
C <sub>3</sub> -2	125.44	CEC <sup>3</sup> CE, EEC <sup>3</sup> CC, EEC <sup>3</sup> CE	4.71	5.37	3.73	6.35	2.74	6.65	10.74
C <sub>3</sub> -3	125.03	EEC <sup>3</sup> EE	16.49	15.71	14.89	16.78	12.26	17.78	27.78
C <sub>3</sub> -4	124.90	CCC <sup>3</sup> CC	36.19	35.96	41.49	30.46	59.20	28.19	18.60
C <sub>3</sub> -5	124.76	CCC <sup>3</sup> CE	11.98	11.27	11.91	12.52	7.60	12.74	6.13
C <sub>3</sub> -6	124.48	ECC <sup>3</sup> EC	4.82	5.02	3.47	5.61	2.26	6.47	2.84
C <sub>3</sub> -7	124.33	CCC <sup>3</sup> EC	10.94	10.96	10.55	11.73	6.90	10.84	8.69
C <sub>3</sub> -8	124.23	ECC <sup>3</sup> EE, CCC <sup>3</sup> EE	3.18	3.57	2.52	4.27	1.22	5.64	11.09

<sup>a</sup> 30 mol % epoxy content.<sup>b</sup> Analyzed for 30 mol % epoxy content (commercial sample).<sup>c</sup> Analyzed for 60 mol % epoxy content (commercial sample).

**Table IV**  $^{13}\text{C}$ -NMR: Resonance Assignments for Olefinic  $\text{C}_2$ -Carbon Atoms

Resonance	Chemical Shift (ppm)	Assignments	Signal Intensity (%)						
			ENR-30, <sup>a</sup> Samples Obtained from Latex (%)					ENR-25 <sup>b</sup>	ENR-50 <sup>c</sup>
			20	30	40	50	60		
C <sub>2</sub> -1	135.50	CC <sup>2</sup> CEC, CC <sup>2</sup> CEE, EC <sup>2</sup> CEE	11.43	11.38	10.60	11.04	8.41	11.60	7.72
C <sub>2</sub> -2	135.30	EC <sup>2</sup> CEC	5.71	3.73	4.66	5.87	3.39	8.99	10.82
C <sub>2</sub> -3	135.20	CC <sup>2</sup> CCE	13.54	12.16	12.96	12.10	9.36	14.57	6.52
C <sub>2</sub> -4	135.08	CC <sup>2</sup> CCC, EC <sup>2</sup> CCE	32.64	39.0	37.87	26.29	58.76	24.88	9.14
C <sub>2</sub> -5	134.88	EC <sup>2</sup> CCC	11.23	11.43	11.68	12.04	7.29	11.63	6.98
C <sub>2</sub> -6	134.60	EE <sup>2</sup> CEE, EE <sup>2</sup> CEC, CE <sup>2</sup> CEE, CE <sup>2</sup> CEC	6.22	5.09	4.26	8.98	3.22	7.94	28.98
C <sub>2</sub> -7	134.26	CE <sup>2</sup> CCE	6.15	3.92	4.96	7.88	2.7	6.95	11.97
C <sub>2</sub> -8	134.14	CE <sup>2</sup> CCC, EE <sup>2</sup> CCC, EE <sup>2</sup> CCE	13.09	13.29	13.05	15.78	7.87	13.42	17.13

<sup>a</sup> 30 mol % epoxy content.<sup>b</sup> Analyzed for 30 mol % epoxy content (commercial sample).<sup>c</sup> Analyzed for 60 mol % epoxy content (commercial sample).

(b), and (c)]. The extra lines over and above those observed by Bradbury and Parera<sup>10</sup> may be due to higher orders of sequences detectable under the higher resolution of the spectrophotometer. However, no attempt was made to make fresh assignment of sequences for these extra lines. Each set of lines

was normalized to 100% signal intensity. The normalized intensities of ENR samples along with commercial samples (ENR-25 and ENR-50 samples of the Rubber Research Institute of Malaysia) are shown in Tables II–V. The tables show that signal intensities of any particular sequence are reasonably

**Table V**  $^{13}\text{C}$ -NMR: Resonance Assignments for Oxirane Region

Resonance	Chemical Shift (ppm)	Assignments	Signal Intensity (%)						
			ENR-30, <sup>a</sup> Samples Obtained from Latex (%)					ENR-25 <sup>b</sup>	ENR-50 <sup>c</sup>
			20	30	40	50	60		
C <sub>2</sub> -10	60.80	E <sup>2</sup> EC	16.98	7.96	10.01	16.16	14.77	—	24.59
C <sub>2</sub> -11	60.71	C <sup>2</sup> EC	63.61	75.45	75.33	58.70	73.83	71.30	29.46
C <sub>2</sub> -12	60.44	E <sup>2</sup> EE	12.33	9.70	9.78	14.87	7.33	16.71	30.39
C <sub>2</sub> -13	60.24	C <sup>2</sup> EE	7.01	6.89	4.86	10.44	4.07	11.99	15.55
C <sub>3</sub> -9	64.40	CE <sup>3</sup> C, EE <sup>3</sup> C	70.88	74.94	73.50	66.00	64.9	62.48	53.01
C <sub>3</sub> -10	64.32	EE <sup>3</sup> E, CE <sup>3</sup> E	29.20	25.06	26.50	34.00	35.1	38.52	46.99

<sup>a</sup> 30 mol % epoxy content.<sup>b</sup> Analyzed for 30 mol % epoxy content (commercial sample).<sup>c</sup> Analyzed for 60 mol % epoxy content (commercial sample).

similar for all the samples under study, indicating that latex concentration does not alter the sequence distribution even up to 50% of latex concentration. They also favorably compare with a commercial ENR-25 sample (analyzed in our laboratory as having 30% epoxy content). However, major deviations are observed when epoxidation was conducted using 60% latex concentration. These results are in good agreement with the results of physical property measurements described earlier. Based on these results and on the observation that intensities of methylenic carbons are invariant, it can be concluded that ENRs produced with latex concentrations between 20 and 50% by weight result in a reasonably random placement of the epoxy groups along the chain and that its sequence is independent of latex concentration.

## CONCLUSIONS

Latex epoxidation of natural rubber using *in situ*-generated performic acid can be conveniently carried out in up to 40% latex concentration. Increasing latex concentration leads to quicker coagulation of rubber for a given mol % epoxidation. The physical properties of compounded ENR (30 mol % epoxidation) are invariant with the latex concentration originally used and compare well with commercially available products. Both  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR studies show that latex concentration has no effect on the

sequence distribution of the polymer. Even at higher latex concentrations, epoxidation leads to reasonably random placement of epoxy group along the chain. The ability to use higher latex concentration may translate into significant process advantages in terms of reduced reaction time and increased output per unit volume of the reactor.

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