

# Reaction of Aromatic Amines with Epoxidized Natural Rubber Latex

M. C. S. PERERA, *Rubber Research Institute of Sri Lanka,  
Thelewela Road, Ratmalana, Sri Lanka*

## Synopsis

Since oxidizability of raw rubber is adversely affected by epoxidation, an attempt was made to bind an amine antioxidant to the rubber molecule through the oxirane group. Effective binding was observed only if the latex is neutralized before addition of the amine. Of the three amines used, 4-amino-*para*-phenyl diamine (pAA) reacted faster than *meta*-nitro-aniline (mNA), where as *N*-isopropyl-*N'*-phenyl-*para*-phenyl diamine (IPPD) was the least reactive. Crosslinking was observed with the primary amine, while, with higher epoxy contents, cyclization products were also formed. mNA had little effect on oxidation resistance once it was bound.

## INTRODUCTION

The epoxidation of natural rubber and other unsaturated elastomers is a well-known reaction,<sup>1-3</sup> and it is now established that the epoxidation of natural rubber latex is random.<sup>4-6</sup> In fact, epoxidation is one of the few chemical modifications where the new properties<sup>7,8</sup> given to natural rubber are worth the cost involved. However, the oxidizability of the raw rubber is adversely affected<sup>9</sup> by the epoxidation reaction, and this difficulty is overcome<sup>10</sup> by the addition of a low molecular weight antioxidant just prior to isolation of the rubber from the latex. However, the oxidation resistance of epoxidized natural rubber (ENR) may be improved by binding an amine antioxidant to the polymer through the oxirane group. Polymer-bound aromatic antioxidants containing amino groups are of additional interest due to better efficiency<sup>11,12</sup> and reduced toxicity; therefore, the resulting polymers may also find useful applications as bound antioxidants and polymeric antioxidants.

The reaction between amines and epoxy polymers has been carried out in organic solutions,<sup>13</sup> but for economic reasons the reaction in the latex stage is preferred. A simple reaction has been reported<sup>14</sup> between the natural rubber latex epoxidized to very low levels (1-2%) and amines, but, as discussed in this paper, ENR with higher levels of epoxidation gave rise to many side reactions.

## EXPERIMENTAL

Epoxidized natural rubber latex was prepared by the method described in detail in a previous publication.<sup>5</sup> The latex was neutralized with ammonia after the reaction. The amine suspension was prepared using a high speed grinder by mixing the amine, ammonia, oleic acid, and water. The suspension was added dropwise to epoxidized natural rubber latex, and the mixture was maintained at room temperature (30°C) for 24 h. Samples drawn at intervals

were coagulated by passing steam into it for 10 min. The coagulum was pressed, milled into laces, and dried at 34°C in crepe rubber drying towers for 4 days.

The control ENR sample was prepared by coagulating the epoxidized latex after the addition of a phenolic antioxidant suspension. This coagulum was milled into laces, soaked in sodium carbonate to remove acid impurities, and dried as before.

The nitrogen content of the rubber was measured by the Kjeldhal method (B S test method no. 1673, part 2) and the gel content in benzene using a standard method.<sup>15</sup>

<sup>1</sup>H-NMR spectra were obtained at 200 MHz using a Joel FX 200 spectrometer at 298 K in CDCl<sub>3</sub> (5% wt/VOL) with TMS as the internal standard.

The PRI (plasticity retention index) was measured using a Wallace plastometer (B S test method no. 1673, 1967, part 2), and the activation energy of oxidation was measured using a differential scanning calorimeter (DSC-2B) and the Kissinger method<sup>16</sup> for calculation. Samples of 0.5 mg were scanned in a DSC at 5, 10, 20, 40, and 80 K/min in oxygen atmosphere.

Mixing of chemicals with the dry rubber for the determination of technological properties was done as described in an earlier publication,<sup>17</sup> and the standard physical testing procedures were used.

## RESULTS AND DISCUSSION

The extent of reaction (bound amine content) was estimated from the nitrogen content of the acetone-extracted sample after adjusting for the nitrogen content of the starting ENR. It was found that the amines do not react with the oxirane group if the latex is not neutralized before the addition of the amine. This is due to the conversion of the amine to a quarternary

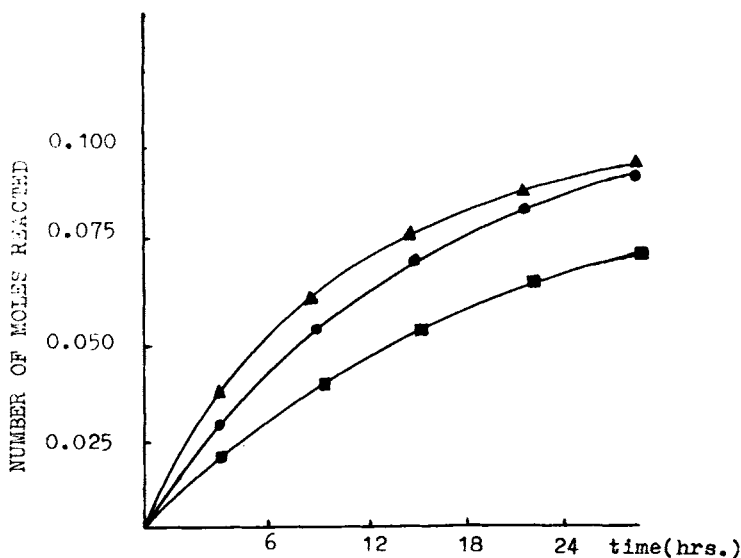


Fig. 1. Rate of reaction of different amines with ENR-10: (▲) pAA, (●) mNA; (■) IPPD.

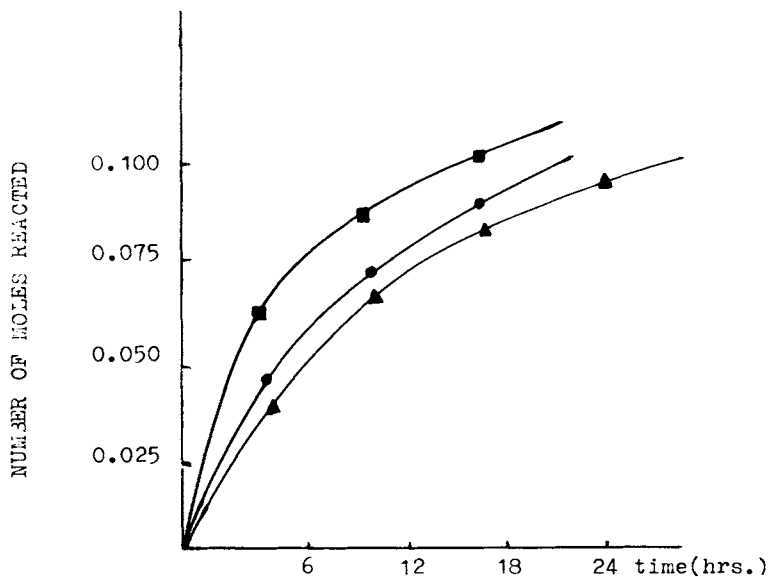


Fig. 2. Dependence of rate of reaction of pAA on the epoxy content of the polymer: (▲) ENR-10; (●) ENR-25; (■) ENR-50.

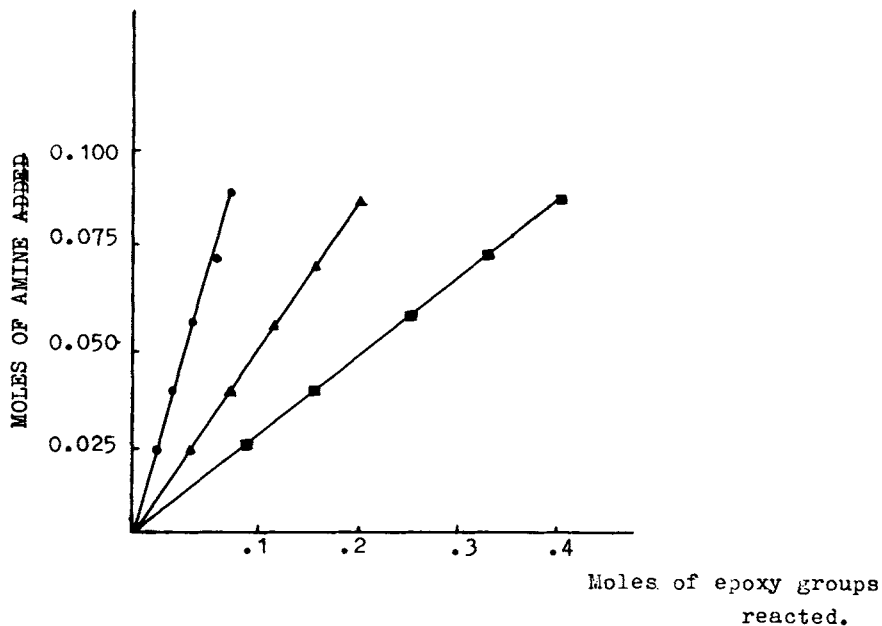
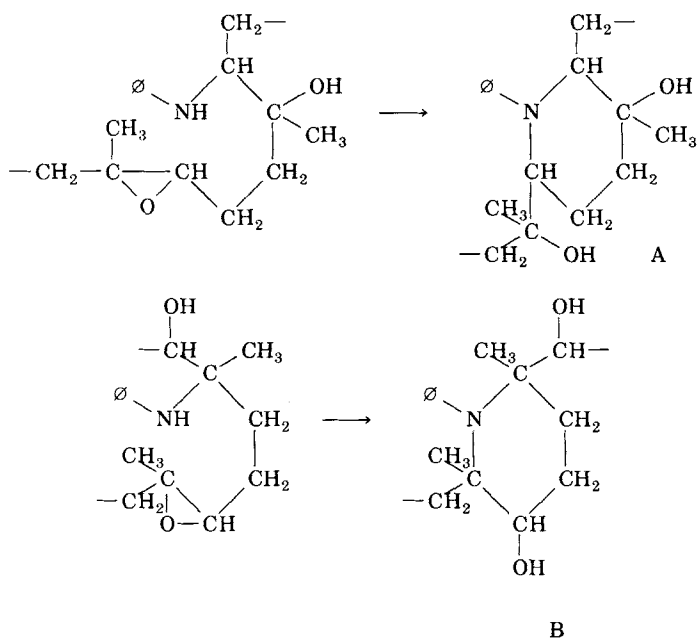


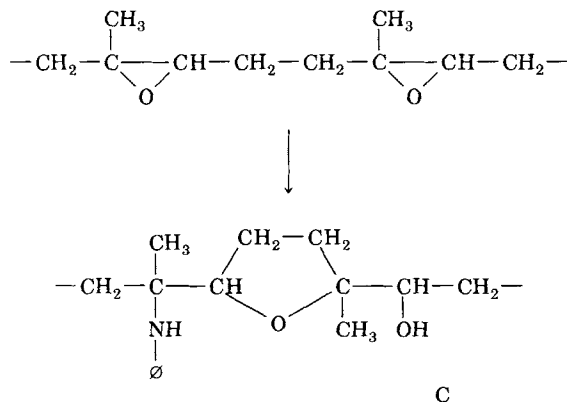
Fig. 3. Relationship between percentage conversion of epoxy groups and amount of amine bonded to the polymer for natural rubber with different epoxy content (pAA was used as the amine and 24 h reaction time): (●) ENR-10; (▲) ENR-25; (■) ENR-50.



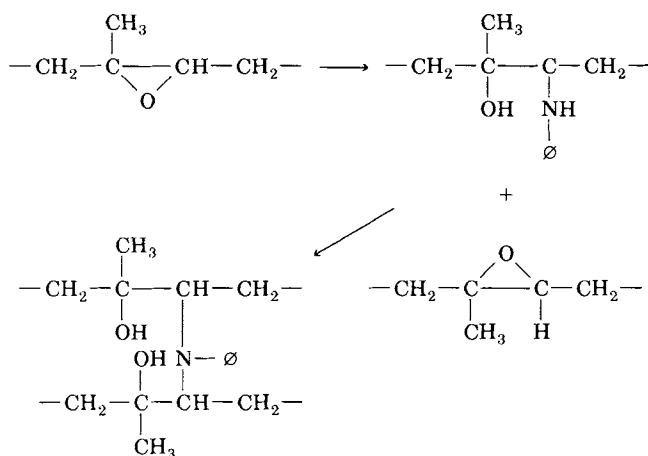
Scheme 1.

ammonium salt in acid medium and the known<sup>18</sup> ring expansion of the oxirane by the ammonium salt to give tetrahydrofuran units.

ENR-10 (10% epoxidized natural rubber) latex (100 g of dry rubber) after being ammoniated was reacted with 0.1 mol of the amine. The results are illustrated in Figure 1, according to which 4-amino-*para*-phenyldiamine (pAA) reacts faster than *meta*-nitroaniline (mNA). This was due to the activated amine group in the pAA. But the secondary amine group of *N*-isopropyl-*N'*-phenyl-*para*-phenylene diamine (IPPD) is sterically hindered, and therefore,



Scheme 2.



Scheme 3.

is the least active. Increase in epoxy content leads to an increase in the reaction rate, as illustrated in Figure 2.

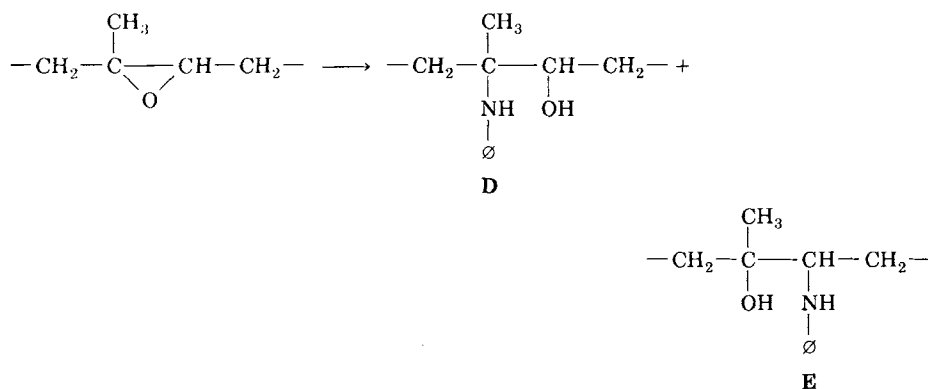
The percentage conversion was also estimated from the intensity of the oxirane hydrogen peak<sup>5</sup> at 2.68 ppm in the <sup>1</sup>H-NMR spectra. This is shown in Figure 3 for the reaction with pAA. With ENR-10, there is a good agreement between the conversion values calculated by both methods (nitrogen content and <sup>1</sup>H-NMR), but, as the epoxy content increases, the values diverge. The NMR method gives a higher conversion value. This is due to the reactions shown in Schemes 1, 2 (Ref. 18), and 3 where more than one epoxy group takes part in the reaction for each amine group bonded to the polymer. The difference between the two values is less for reactions involving IPPD, since the reactions in schemes 1 and 3 are not possible with the secondary amine group in the IPPD molecule. The higher gel content values (Table I) in the products with pAA and mNA confirm the presence of the reaction in Scheme 3 which leads to a crosslink.

TABLE I  
Gel Content and Resistance to Oxidation of the Raw Rubbers

Rubber	Amine	Gel content (%)	Activation energy (kJ/mol)	PRI
NR	—	1.2	108.5	66
ENR-10 <sup>a</sup>	—	3.1	84.3	41
ENR-10	mNA	26.3	86.0	44
ENR-10	pAA	28.1	110.1	68
ENR-10	IPPD	3.3	112.7	71
ENR-50 <sup>b</sup>	—	10.1	65.0	22
ENR-50	mNA	35.8	70.0	26
ENR-50	pAA	36.1	95.5	52
ENR-50	IPPD	9.8	98.3	58

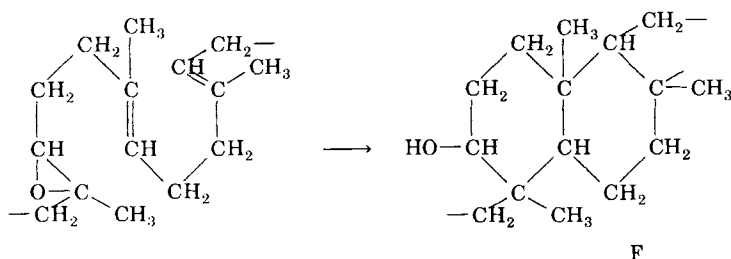
<sup>a</sup>10% epoxidized natural rubber.

<sup>b</sup>50% epoxidized natural rubber.



Scheme 4.

The structures of the products were studied by means of  $^1\text{H-NMR}$  spectra. When the reaction was carried out in polar solvents, with phenol catalyst, both normal and abnormal additions have been observed<sup>13</sup> to give products A and B in Scheme 1 and products D and E in Scheme 4. The possibility of Schemes 2 and 3 also cannot be eliminated as discussed above. Further, a cyclization reaction similar to that observed in squalene-3,2-oxide<sup>19</sup> and polyisoprene<sup>20</sup> as given in Scheme 5 should also be considered. The  $^1\text{H-NMR}$  chemical shifts of the compounds formed in the reaction shown in Schemes 1–5 are given in Table II. It is difficult to separate out all the products from the  $^1\text{H-NMR}$  peaks between 3 and 4 ppm. For example, the peak at 3.4 ppm indicates the presence of both C and D structures, and the peak at 3.9 ppm indicates the presence of both C and E structures as well as A. Since there was no amine binding when the reaction was carried out in acidic media, the existence of the peaks at 3.4 and 3.9 ppm in the  $^1\text{H-NMR}$  spectra of the products confirms the presence of the ring expansion<sup>21</sup> to give structure C (Scheme 2). However, a small amount of structure F (Scheme 5) is also evident from the small peak at 0.85 ppm. The absence of the peak at 3.4 ppm in the  $^1\text{H-NMR}$  spectrum of amine-bound ENR-10 (reaction done in basic media) confirmed the absence of the reaction in Scheme 2 and also rules out the abnormal addition yielding the product D. Thus the possibility of the abnormal addition yielding the structures B and D in the product from ENR-25 and ENR-50 also could be eliminated. However, the peaks at 1.15 and 3.9 ppm in the  $^1\text{H-NMR}$  spectra of the amine-bound ENR-25 and ENR-50 confirm the



Scheme 5.

TABLE II  
<sup>1</sup>H-NMR Chemical Shifts

Product	Proton	<sup>1</sup> H-NMR chemical shifts (ppm)	Reference
—	Olefinic hydrogen	5.1	23
—	Oxirane hydrogen	2.68	5
A	$\begin{array}{c}   \\ -\text{CH}-\text{NH} \\   \end{array}$	3.9	24
C	$\begin{array}{c}   \\ -\text{CH}-\text{O}-\text{(ring)} \\   \end{array}$	3.9	—
	$\begin{array}{c}   \\ \text{CH}_3-\text{C}-\text{O}- \\   \end{array}$	1.15	21
	$\begin{array}{c}   \\ -\text{CH}-\text{OH (outside ring)} \\   \end{array}$	3.4	—
D	$\begin{array}{c}   \\ -\text{CH}-\text{OH} \\   \end{array}$	3.4	21, 24
	$\begin{array}{c}   \\ \text{CH}_3-\text{C}-\text{NH}- \\   \end{array}$	1.0	—
E	$\begin{array}{c}   \\ -\text{CH}-\text{NH} \\   \end{array}$	3.9	24
F	$\begin{array}{c}   \\ \text{CH}_3-\text{C}- \\   \end{array}$	0.85	20

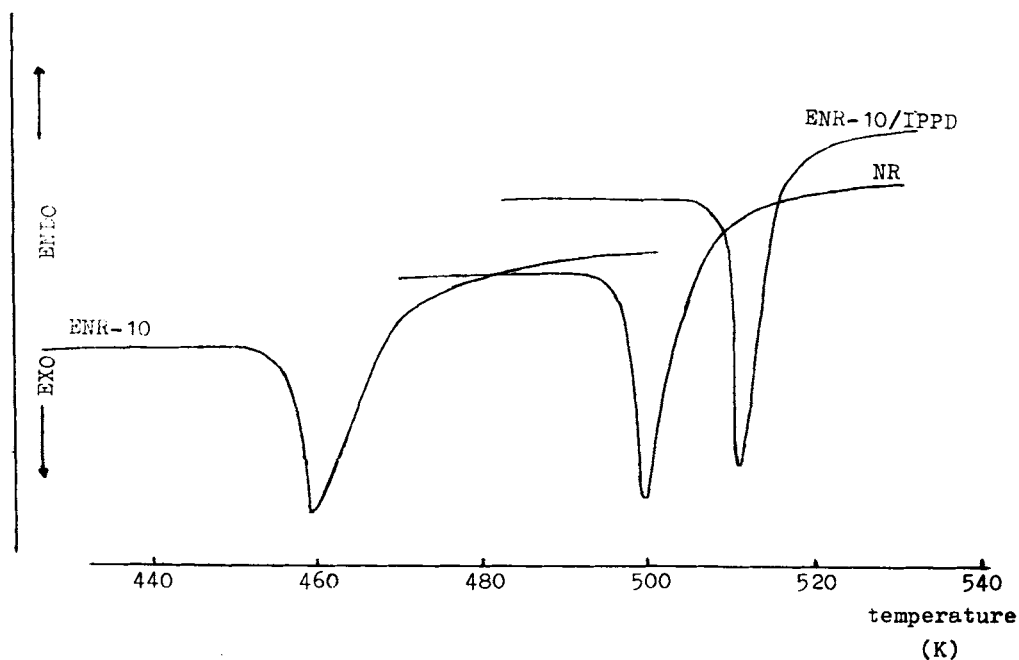


Fig. 4. Thermographs of NR, ENR-10, and IPPD-bound ENR-10.

TABLE III  
Physical Properties of ENR Vulcanizates

	Amine-bound ENR-25	ENR-25
Tensile strength (MPa)	25.6	25.0
Elongation at break (%)	580	560
Hardness	52	53
Dunlop resilience at 23°C (%)	59	59
Compression set (24 h/70°C)	15	14
Abrasion (mm <sup>3</sup> /500 rev)	15	15
Air aging (3 days/100°C)		
Tensile strength (% drop)	-20	-26
Elongation at break (% drop)	-25	-33
Percentage volume increase (4 days, 23°C in ASTM oil no. 2)	3	3

presence of structures A and E, while the absence of a shoulder at 0.85 ppm rules out structure F in these products.

Samples for oxidizability testing were prepared by adding only 0.025 mol of the amine. Values of the plasticity retention index (PRI, a measure of oxidizability of raw natural rubber) and the activation energy calculated by DSC are presented in Table I, and the thermograph is shown in Figure 4. The

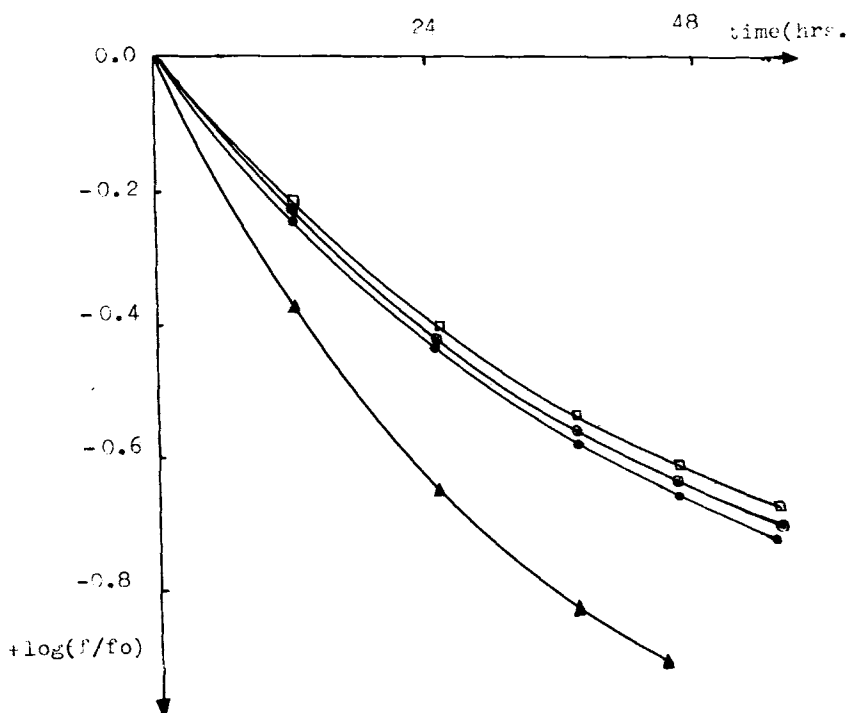


Fig. 5. Stress relaxation of the vulcanizates: amine-bound (□)ENR-25; (○)ENR-25; (●)acetone-extracted, amine-bound ENR-25; (▲)acetone-extracted ENR-25.



results show that the resistance to oxidation of ENR could be improved by binding pAA or IPPD through some of the epoxy groups. But the product with mNA had very little effect on oxidation resistance. This is due to the formation of tertiary amine groups with mNA (explained earlier), and, since the tertiary amine group has no labile hydrogen, the contribution to oxidative stability is minimal. Even pAA undergoes similar reactions through the primary amine group, but the more hindered amine in the pAA is free and contributes to the oxidation stability.

The physical properties of the vulcanizates of an amine-bound product are compared with the corresponding ENR in Table III. (The semi-EV formulation used was the same as in the previous publication.<sup>17</sup>) In fact the oxidative stability is better in the amine-bound product, in keeping with the previous observation<sup>22</sup> that the antioxidant when bound to the polymer is better dispersed molecularly and hence is more effective. Stress-relaxation studies shown in Figure 5 confirm this. When extracted with acetone, the amine-treated samples maintained their resistance to oxidation, confirming that the amine is bound to the network.

## CONCLUSIONS

When the amine antioxidant was added without neutralizing the latex, there was no addition of the amine to the rubber molecule, but ring expansion of the oxirane occurred. Once the medium was neutralized, addition took place; and with secondary amines, crosslinking and cyclization also occurred. Therefore, the addition product from mNA showed very little resistance to oxidation while the products from pAA and IPPD improved the oxidation stability of ENR.

## References

1. R. Pummer and P. A. Burkard, *Ber.*, **55**, 3458 (1922).
2. Hercules Powder Co., Br. Pat. 892361; *Chem. Abstr.*, **57**, 48774 (1961).
3. C. Raux, P. Pautrat, R. Cheritat, F. Ledran, and J. C. Danjard, *J. Polym. Sci. C*, **16**, 4687 (1969).
4. D. R. Burfield, K. K. Lim, and K. S. Law, *J. Appl. Polym. Sci.*, **29**, 1661 (1984).
5. J. H. Bradbury and M. C. S. Perera, *J. Appl. Polym. Sci.*, **30**, 3347 (1986).
6. M. C. S. Perera, J. E. Elix, and J. H. Bradbury, *J. Appl. Polym. Sci.*, **36**, 105 (1988).
7. Societe Nationales des Petroles Aquitaine, Br. Pat. 108331; *Chem. Abstr.*, **64**, 5277 (1966).
8. I. R. Gelling and J. F. Smith, *Proc. Int. Rubber Conf. Venice*, 1979, p. 140.
9. Malaysian Natural Rubber Producers Research Association, Annual Report, 1983.
10. I. R. Gelling, Br. U.K. Pat. Appl. G B 2: 692,113 (1983).
11. G. Scott, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **35**, 123 (1979).
12. V. P. Kirpicher and N. S. Demnina, *Vestn. Leningrad Univ. Fiz. Khim.*, **3**, 126 (1978); *Chem. Abstr.*, **90**, 73063 (1979).
13. S. Jayawardene, D. Reyx, D. Durand, and C. P. Pinazzi, *Makromol. Chem.*, **185**, 2089 (1984).
14. P. H. Lye and H. K. Toh, *J. Polym. Sci. Polym. Lett. Ed.*, **22**, 327 (1984).
15. P. W. Allen and G. M. Bristow, *J. Appl. Polym. Sci.*, **7**, 603 (1963).
16. H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).
17. M. C. S. Perera, *J. Appl. Polym. Sci.*, **34**, 2591 (1987).
18. W. J. Schultz and A. R. Katritzky, U.S. Pat. 4309516 (1982).

19. E. E. Van Tamelen, *Acc. Chem. Z.*, **96**, 1 (1972).
20. R. K. Agnihotri, D. Falcon, and E. C. Fredricks, *J. Polym. Sci. A-1*, **10**, 1839 (1972).
21. M. C. S. Perera, J. E. Elix, and J. H. Bradbury, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 637 (1988).
22. K. W. S. Kularatne and G. Scott, *Eur. Polym. J.*, **14**, 835 (1972).
23. M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).
24. S. Jayawardene, D. Reyx, D. Durand, and C. P. Pinazzi, *Makromol. Chem., Rapid Commun.*, **4**, 449 (1983).

Received January 18, 1989

Accepted January 23, 1989