

## *Epoxidised Natural Rubber*

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*Epoxidised natural rubber (ENR) is now an established commercial polymer which is produced by the chemical modification of natural rubber. Two grades are available with epoxide contents of 25 and 50 mole%. They have a unique set of properties offering high strength, due to their ability to undergo strain crystallisation, along with increased glass transition temperatures and solubility parameters. These properties are reflected in vulcanisates with increased oil resistance, enhanced adhesive properties, a high degree of damping and reduced gas permeation. Specific interactions, via epoxide groups, result in a high degree of reinforcement with silica fillers without the need for coupling agents. Functional group interactions also result in ENR forming compatible blends with a range of chlorine-containing polymers. Reactions between the epoxide groups in ENR and reactive groups on other polymers result in 'self-vulcanising' blends. Practical formulations and a number of applications, including tyres, are outlined.*

As long ago as 1922, natural rubber (NR) was reacted<sup>1</sup> with a peroxyacid and although the structure of the product was not elucidated epoxidation must have occurred. Since then, a number of conflicting reports have been published on the preparation and properties of epoxidised natural rubber (ENR). A variety of reaction conditions were employed and the products variously described as hard thermoplastic<sup>2,3,4</sup> to soft rubbery polymers<sup>5,6,7</sup>. The epoxidation of NR and other unsaturated polymers was stated to increase solvent resistance and improve wear resistance and mechanical properties<sup>8,9</sup>. However, other publications have reported a reduction in tensile strength properties<sup>10,11</sup>. A number of epoxidised latices have also been studied<sup>9,12,13</sup>.

In the early to mid-1970's, there was renewed interest in the chemical modification of NR to produce other polymeric materials as a result of the oil crises. Epoxidation was an attractive route because of the simple reaction procedure, the reaction can be carried out in the latex phase, and the relatively low cost of reagents involved.

### PREPARATION AND STRUCTURE

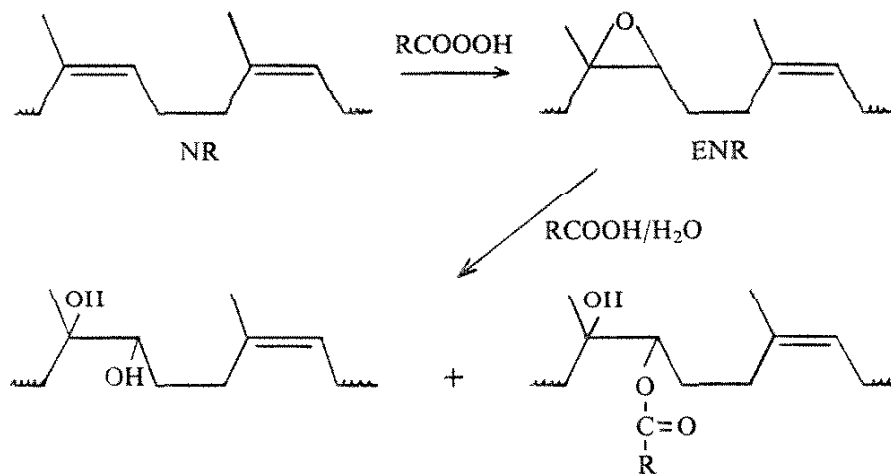
The chemistry of epoxidation of unsaturated low molecular weight compounds is well established<sup>14,15</sup> and it is known that secondary ring-opening reactions of the initially formed epoxide group can occur<sup>16</sup>.

A systematic study<sup>5,17</sup> of the epoxidation of NR latex with peroxyacetic solution revealed that high total acid concentrations and elevated temperatures favoured the formation of secondary ring-opened products. Two distinct types of ring-opened products were obtained depending principally on the level of epoxidation. At low levels of modification, the majority of epoxide groups are isolated and the main ring-opened products are those expected from simple epoxide chemistry<sup>18</sup> (*Scheme 1*). The final product is normally the *trans* diol, but dehydration of the tertiary alcohol can occur. As the level of modification is increased and hence, the number of adjacent epoxide groups, a five-membered cyclic ether becomes the major product<sup>5,19</sup>. This arises from the attack of a ring-opened epoxide on

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Scheme 1

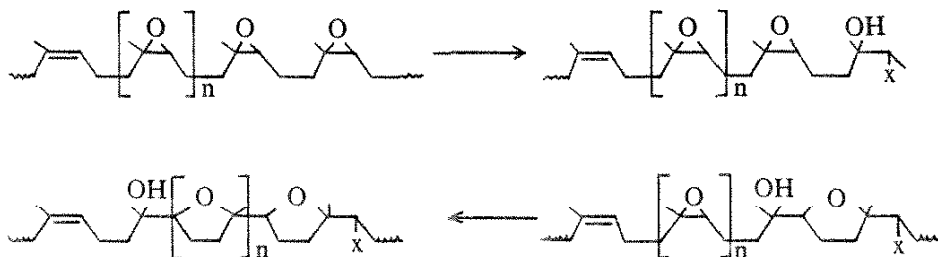
Epoxidation of NR with a peroxyacid and secondary ring-opening of isolated epoxide groups

the adjacent epoxide group with the reaction proceeding along the rubber backbone until stopped by a non-epoxide group or steric considerations (*Scheme 2*). The various ring-opened structures were characterised by a combination of IR and  $^1\text{H}$  NMR spectroscopy and by model chemistry<sup>5,19</sup>. Epoxidation products that contain ring-opened structures are generally insoluble and this can be attributed to the formation of ether crosslinks as illustrated in *Scheme 3*. Such products are observed in the acid catalysed ring-opening of model epoxides.

Ring-opened structures as reported above were also observed by Ng and Gan<sup>4</sup> in the epoxidation of NR latex with hydrogen peroxide and formic acid.

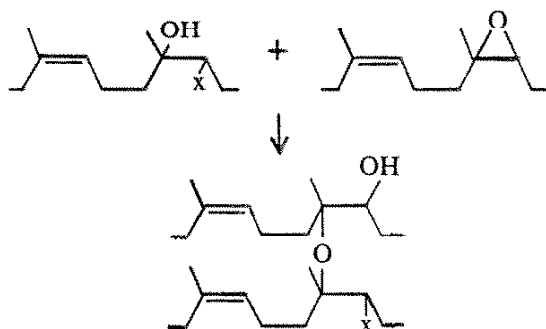
In the light of the established ring-opening chemistry that can occur during the epoxidation of NR, it is easy to understand the variety of products that were reported in the earlier literature on this topic.

Epoxidation of NR to 100 mole% under conditions which favour ring-opening



Scheme 2

Ring-opening of adjacent epoxide groups to yield five-membered cyclic ethers



Scheme 3

Crosslinking of ENR via ring-opened epoxide groups

yields a hard thermoplastic material (I, Scheme 2), termed furanised NR. This material resembles polystyrene in many of its properties<sup>19</sup>.

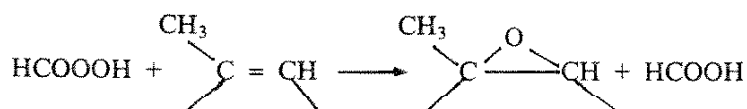
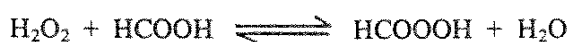
Under carefully controlled conditions, NR latex can be epoxidised to over 75 mole% without the formation of secondary ring-opened structures. Both preformed peroxyacetic acid<sup>5,19</sup> or the *in-situ* generation of peroxyformic acid<sup>20</sup> from hydrogen peroxide and formic acid can be employed (Scheme 4). The latter is the preferred route for commercial production, as only hydrogen peroxide is consumed.

Peroxyacetic acid epoxidation of NR is a second-order reaction with an overall activation energy of 52.6 KJ/mol<sup>7,21</sup>. The major factor in controlling the *in-situ*

epoxidation rate is the formation of the peroxyformic acid from hydrogen peroxide and formic acid<sup>22</sup>. A more detailed study<sup>23</sup> has shown that the double-bond concentration changes in the hydrocarbon phase also affect reaction rates.

Although reaction conditions have been established which yield ENR free from secondary reaction products, <sup>1</sup>H NMR spectra of these materials (Figure 1) do not reveal any information on the structure of products.

Latex epoxidations are two-phase systems and this heterogeneity could control the structure of the products. NR latex particles vary in size from 0.02 μm to over 2.0 μm, if the rate of epoxidation is greater than the rate of diffusion of the preoxycarboxylic acid into the particle then a heterogeneously epoxidised product would be expected. At



Scheme 4

The *in-situ* epoxidation of NR employing hydrogen peroxide and formic acid

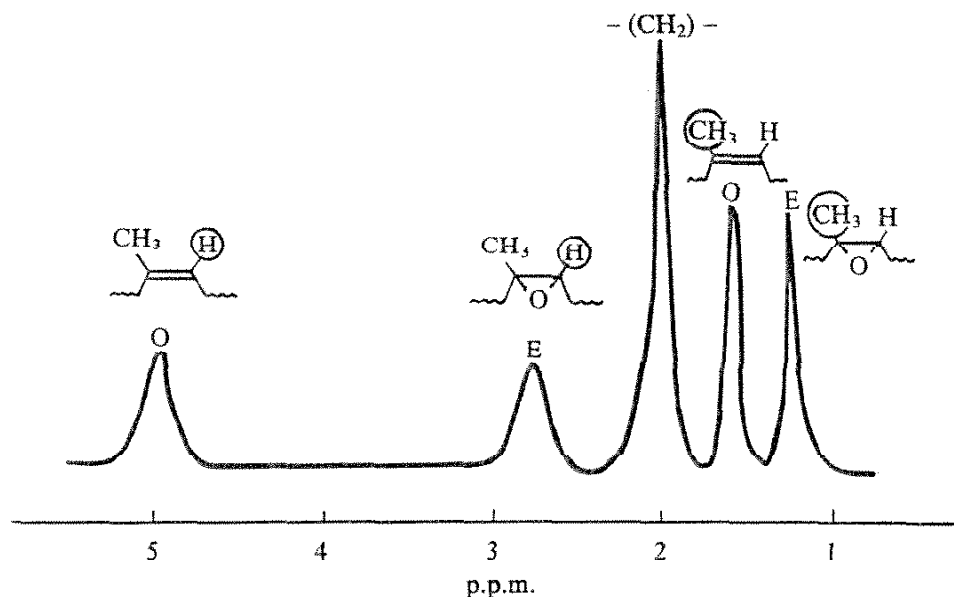


Figure 1.  $^1\text{H}$  NMR spectrum of 50 mole% epoxidised natural rubber.

an epoxidation level of 50 mole% in the extreme case, the outer shell of the latex particle would be epoxidised to 100% while the interior would be unmodified. The mathematics of diffusion of a substance through a medium with which it can simultaneously react are well established<sup>24</sup>. Calculations based on approximate diffusion coefficients and epoxidation rates indicate that diffusion is not the controlling factor. This is supported by size partitioning of NR latex followed by epoxidation; no differences in rate or epoxidation level were observed<sup>25</sup>. Further confirmation is obtained from  $^{13}\text{C}$  NMR. If it is assumed that the epoxidation of unsaturated units is random, then the mole per cent of the variously positioned epoxide groups can be calculated for any level of epoxidation (Figure 2).

The epoxide group sequences of both ENR 20 (20 mole% epoxidised NR) and ENR 50 (50 mole% epoxidised) have been measured by  $^{13}\text{C}$  NMR and the observed sequences match those calculated for a

totally random epoxidation<sup>26</sup>. The  $^{13}\text{C}$  NMR spectrum of ENR 20 is recorded in Figure 3, along with the peak assignments.

An ozonolysis study of ENR also substantiates a random epoxidation process<sup>27</sup>.

Quantitative analysis of epoxide groups utilises tetraethylammonium bromide<sup>28</sup>, hydrochloric or hydrobromic acids, but these reagents when applied to ENR give significantly lower epoxide values than NMR or IR techniques<sup>29</sup>. Where there are two or more adjacent epoxide groups, one reagent molecule initiates ring-opening of the epoxide sequence (Scheme 2). Chemical titrimetric methods of this type thus measure the isolated epoxide groups plus the number of blocks containing two or more epoxide units, and are thus more a measure of the epoxide distribution than the total epoxide content.

Epoxidation reactions are stereo-specific<sup>30</sup> and thus ENR is a *cis* 1,4-polyisoprene with epoxide groups randomly situated along the polymer backbone.

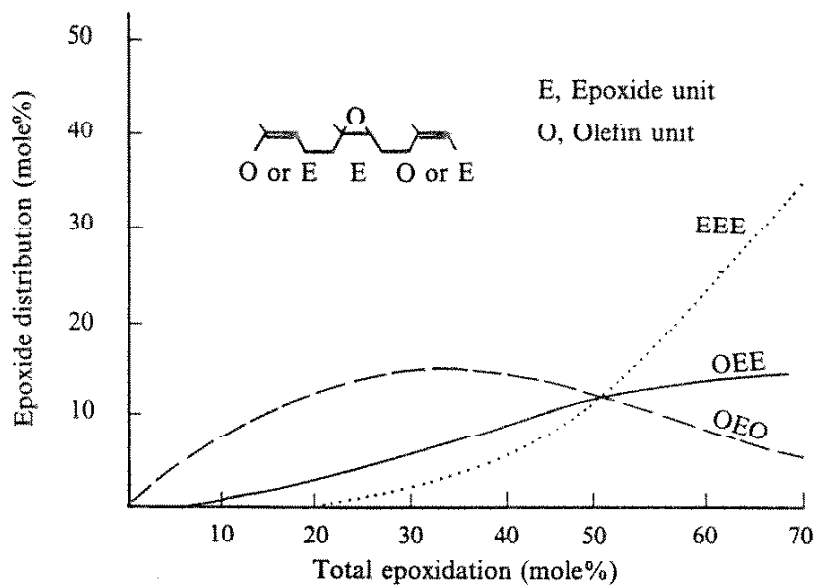


Figure 2. Calculated distribution of epoxide groups for a random epoxidation process.

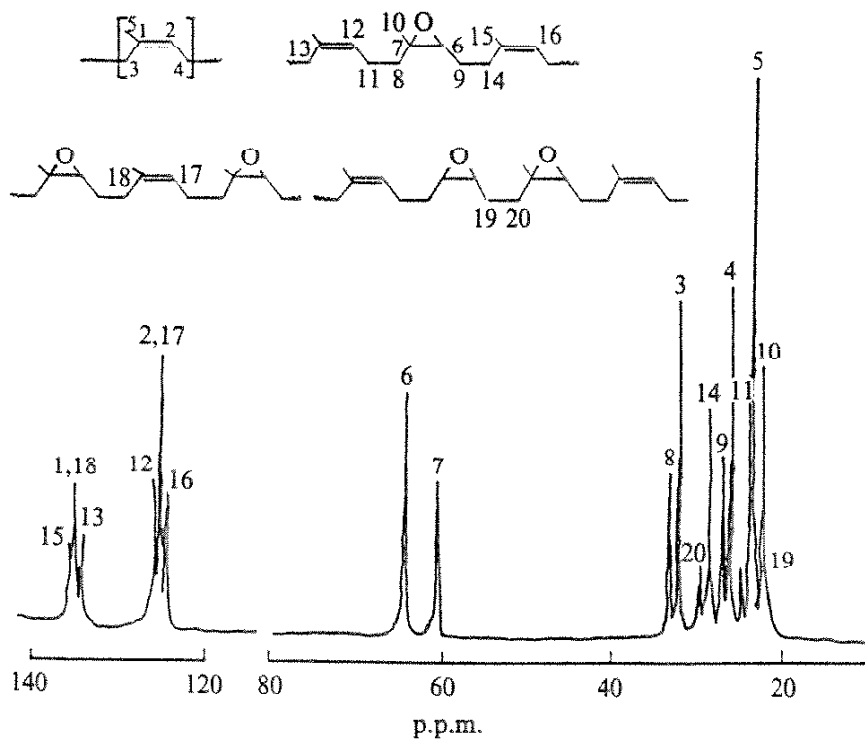


Figure 3.  $^{13}\text{C}$  NMR spectrum of 20 mole% epoxidised natural rubber.

## PROPERTIES

## Raw Rubber

ENR with epoxide levels of 1 – 75 mole% can readily be prepared and a systematic change in properties is observed with the epoxidation level. Currently, two levels, 25 mole% and 50 mole% ENR are produced commercially by Kumpulan Guthrie Berhad in Malaysia and marketed as Epoxyrene 25 and Epoxyrene 50.

Density increases with the extent of epoxidation while refractive indices decrease (Figure 4). For every mole per cent increase in the epoxidation level, the glass transition temperature ( $T_g$ ) increases by 0.93°C.  $T_g$  measurements, related to a calibration curve derived from NMR data, can be used to routinely determine epoxide

levels, as any inhomogeneity due to the presence of ring-opened products is readily observed in a broadening of the transition<sup>26</sup>. The change in  $T_g$  of ENR is clearly reflected in their physical properties which are described in subsequent sections.

The compatibility of a rubber with other polymers or liquids, e.g. its oil resistance, can be related to its solubility parameter. As the level of epoxidation of ENR increases so does the solubility parameter<sup>24</sup> (Table 1), each 1 mole% epoxidation raises the solubility parameter by approximately  $0.031 (\text{Jm}^{-3})^{1/2}$ .

Even at low levels of epoxidation, ENR is significantly more resistant to low temperature crystallisation than NR<sup>31</sup>, e.g.  $\ln \tau_{1/2}$  is increased from 2.5 to 3.65 on epoxidation to 5 mole%. At 50 mole% epoxide (ENR 50) no crystallisation

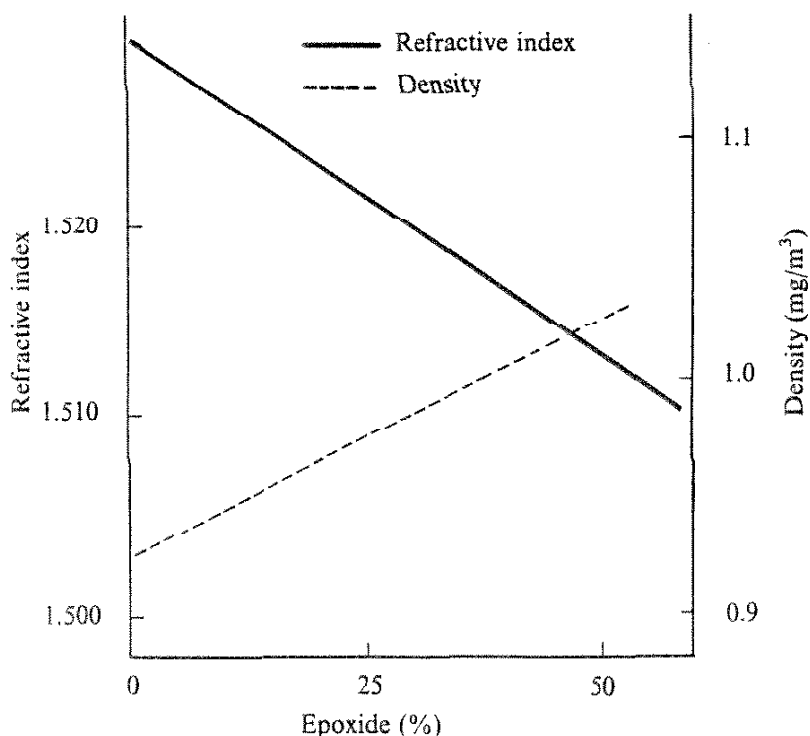


Figure 4. Variation of refractive index and density of ENR with extent of epoxidation.

TABLE 1. SOLUBILITY PARAMETERS OF ENR

ENR (mole% epoxide)	Solubility parameter ( $Jm^{-3}$ ) <sup>1/2</sup>
0	16.7
26	17.4
48	18.2
71	18.6

occurred when the product was stored at 0°C for three months.

Increases in the viscosity of NR occur after production due to storage hardening, which has been reported to be due to aldehyde<sup>32</sup> or epoxide<sup>33</sup> groups on the NR molecule reacting with non-rubber proteins form a small number of crosslinks in the rubber. ENR does not storage harden and Subramaniam<sup>34</sup> has shown that the epoxide group is not responsible for the storage hardening of NR.

#### Compounding and Vulcanisation

Epoxyrene 25 and Epoxyrene 50 have Mooney viscosities in the range 70 to 100 units but break down more readily than NR of comparable viscosity<sup>35</sup> and thus require little if any premastication. Generally, their processing characteristics are similar to those of NR, although problems can be encountered with low viscosity ENR, in that compounds can stick to processing equipment. One suggested solution is to add low levels of sulphur at the start of the mix cycle<sup>36</sup> but it is more appropriate to include a process aid in the formulation, e.g. Struktol A60 or an equivalent material at 3 – 5 p.p.h.r., which effectively overcomes this problem.

ENR can be vulcanised by any of the standard sulphur, peroxide or Novor formulations normally employed to cross-link unsaturated polymers<sup>37</sup>. Dibasic carboxylic acids can also be used<sup>38</sup>.

Although acceptable cure characteristics are obtained from a conventional high

sulphur formulation (Tables 2 and 3), this system is not recommended for ENR because the vulcanisates have poor ageing characteristics. To optimise the ageing resistance of ENR, it is essential that the vulcanisates are basic. Stronger bases are more effective but can result in a loss of processing safety<sup>39</sup>. Calcium stearate is an effective antidegradant which does not reduce processing safety. Recommended semi-EV and EV formulations for ENR and their cure characteristics are recorded in Tables 2 and 3 respectively.

#### Vulcanisates

Practically all chemical modifications of NR result in a reduction in basic strength properties. This is due to the disruption of the stereo-regularity of the NR backbone and hence, inhibition of strain crystallisation. Because of the stereo-specificity of the epoxidation reaction and spacial position of the epoxide oxygen atom, ENR undergoes strain crystallisation<sup>40</sup>. It is only at epoxide levels in excess of 50 mole% that a marked reduction in the level of crystallinity is observed (Table 4), suggesting that the NR unit cell, four isoprene units, can accept two epoxide groups without undue disruption. The high tensile (Table 4) and tear strengths (Figure 5) of unfilled ENR vulcanisates<sup>3,41</sup> reflect their ability to strain crystallise.

The properties of ENR vulcanisates are dominated by their ability to strain crystallise and the changes in  $T_g$  and solubility parameter that occur on epoxidation.

The increase in  $T_g$  and hence, increase in ambient temperature hysteresis can be related to a number of changes in property that occur on epoxidation of NR. Damping increases and thus, rebound resilience decreases (Table 5). The temperature/hysteresis profiles of a number of epoxidised NR are recorded in Figure 6. Air permeability decreases (Table 5)<sup>19</sup>, peel adhesion increases<sup>34</sup> as does wet traction<sup>39,42</sup>. The latter is dealt with in more detail in the section under applications. The

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TABLE 2. FORMULATIONS FOR ENR

Compound	1 Conventional	Formulation 2 Semi-EV	3 EV
Polymer	100	100	100
Filler	Varies	Varies	Varies
Process oil	Varies	Varies	Varies
Calcium stearate	5	5	5
Zinc oxide	5	5	5
Stearic acid	2	2	2
Antioxidant <sup>a</sup>	?	?	?
Antioxidant <sup>b</sup>	1.5	1.5	1.5
Paraffinic wax	3	3	3
Sulphur	2.5	1.5	0.5
CBS <sup>c</sup>	0.6	-	2.5
MBS <sup>d</sup>	-	1.5	-
TMTM <sup>e</sup>	-	1.5	-

<sup>a</sup>N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

<sup>b</sup>Poly-2,2,4-trimethyl-1,2-dihydroquinoline

<sup>c</sup>N-cyclohexylbenzothiazole-2-sulphenamide

<sup>d</sup>2-morpholinothiobenzothiazole-2-sulphenamide

<sup>e</sup>Tetramethylthiuram monosulphide

resistance of ENR to non-polar fluids increases with the increase in solubility parameter<sup>30</sup>. Swelling values of ENR 50 in ASTM oils fall between those of poly-chloroprene (CR) and a medium acrylonitrile butadiene rubber (NBR). In polar solvents, the reverse is observed, resistance decreases with increasing epoxide content<sup>43</sup> (Table 5).

Solubility parameters are also a factor in both the uncured and cured adhesion of ENR to other polymers<sup>43</sup>.

The properties of black filled ENR vulcanisates are compared with those of NR and NBR in Table 5. Slightly lower tear strengths are observed with ENR compared to NR at similar black loadings, but this can be corrected by a slight increase in the loading or use of a more reinforcing black. Although the

non-relaxing fatigue values of the ENR are lower than that of NR, the ENR 50 values are still nearly an order of magnitude greater than those of a non-crystallising rubber such as NBR.

To optimise the reinforcement properties of silica in NR and other rubbers, a silane coupling agent is employed. High reinforcement with silica fillers is obtained with ENR without the use of coupling agents. This is reflected in vulcanisate properties (Table 6) which are comparable to a similarly loaded black compound and are superior to a silica filled NR vulcanisate formulated without the use of a coupling agent. These differences are particularly marked with regard to modulus, compression set, heat build-up and abrasion properties.

TABLE 3. VULCANISATION CHARACTERISTICS OF ENR

Vulcanisation characteristics	Formulation <sup>a</sup>								
	1		2			3			
	NR	ENR 50	NR	ENR 25	ENR 50	NR	ENR 25	ENR 50	NR
Mooney scorch, 120°C, t <sub>5</sub> (min)	20	14	20	21	38	13	12	28	
Monsanto rheograph, 150°C, Arc±1 t <sub>95</sub> (min)	16	25	10	8	13.5	24	19	15	
t <sub>max</sub> (min)	-	-	13	12	18	60	40	23	
ΔT (d N.m.)	19.2	25.9	23.7	31.6	30.5	27.1	28.2	25.9	

<sup>a</sup>Contain 50 p.p.h.r. of N330 carbon black. The ENR 50 mixes also contain 0.2 p.p.h.r. of a pre-vulcanisation inhibitor, N-cyclohexylthiophthalimide.

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TABLE 4. PHYSICAL PROPERTIES OF ENR VULCANISATES<sup>a</sup> AND DEGREE OF CRYSTALLINITY

Property	Vulcanisate			
	NR	ENR 25	ENR 50	ENR 75
Stress at 100% extension (MPa)	0.74	0.69	0.78	0.96
Tensile strength (MPa)	25.8	24.1	30.9	28.4
Elongation at break (%)	760	789	762	622
Degree of crystallinity <sup>b</sup>	11	11	10	4
Unit cell volume (mm <sup>3</sup> )	0.955	0.985	0.999	1.036

<sup>a</sup>Polymer 100; ZnO, 5 p.p.h.r.; stearic acid, 2 p.p.h.r.; antioxidant, 2 p.p.h.r.; S, 2.5 p.p.h.r.; MBS, 0.6 p.p.h.r.

<sup>b</sup>400% extension, 20°C for 1.5 h.

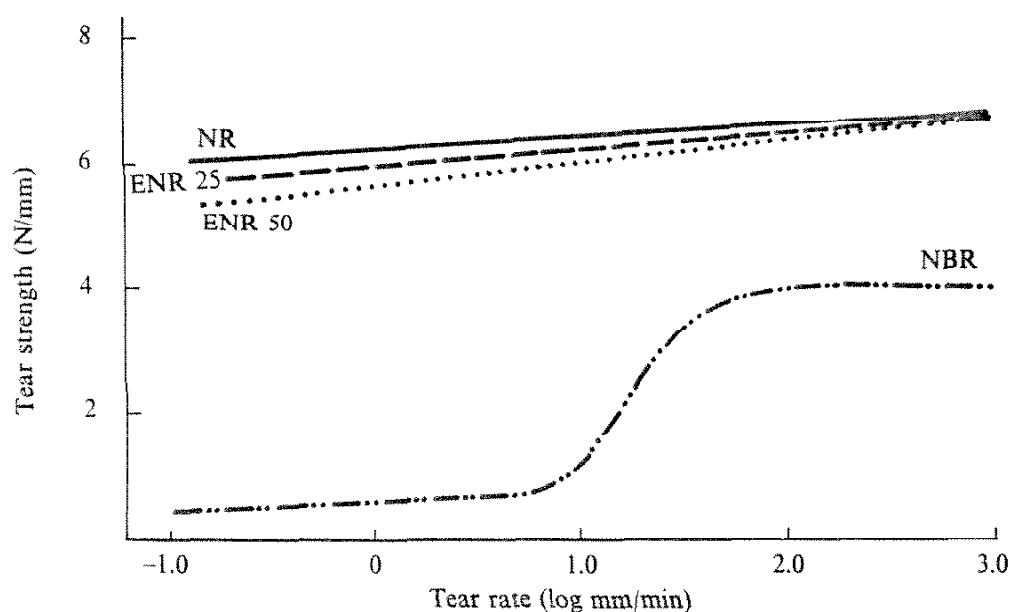


Figure 5. Tearing energies of NR, ENR 25 and ENR 50 compared to a non-strain crystallising NBR.

#### Ageing

Epoxidation reduces the unsaturation in NR and would thus be expected to improve resistance to oxidation. This is observed in simple oxygen absorption experiments, but conventional high sulphur (S, 2.5 p.p.h.r.;

sulphenamide accelerator, 0.5 p.p.h.r.) ENR vulcanisates are more prone to oxidative ageing, observed as a rapid increase in stiffness, than a comparable NR vulcanisate. This is not a characteristic of ENR itself as both ENR and NR peroxide vulcanisates have similar ageing

TABLE 5. COMPARATIVE PROPERTIES OF NR, ENR AND NBR VULCANISATES<sup>a</sup>

Property	Vulcanisate			
	NR	ENR 25	ENR 50	NBR <sup>b</sup>
Hardness (IRHD)	59	56	59	61
Modulus, 100% (MPa)	1.45	1.41	1.85	2.3
Modulus, 300% (MPa)	7.8	6.9	8.8	9.2
Tensile strength (MPa)	27.1	25.9	27.8	15.8
Elongation at break (%)	550	590	560	365
Tension fatigue, rings				
0% – 100%, extn (kcs)	70	65	89	39
50% – 150%, extn (kcs)	> 1 200	695	360	35
Tear strength (KN/m)	15	6	12	9
Compression set, 24 h/70°C (%)	17	15	17	18
Resilience, Dunlop, 23°C (%)	78	60	25	31
Goodrich HBU, $\Delta T^{\circ}\text{C}$ from 23°C, 30 min	44	46	52	87
Akron abrasion ( $\text{mm}^3/500 \text{ rev.}$ )	45	18	12	13
DIN abrasion ( $\text{mm}^3$ )	221	216	410	378
Air ageing, 3 days/100°C				
Modulus at 100% (% change)	+17	+37	+15	+23
Modulus at 300% (% change)	+28	+42	+27	+37
Tensile strength (% change)	-27	-25	-11	-3
Elongation at break (% change)	-21	-29	-19	-8
Oil resistance				
Volume swelling, 70 h/70°C (%)				
ASTM No. 1 oil	66	73	-5	-4
ASTM No. 2 oil	114	28	6	2
ASTM No. 3 oil	191	108	21	12
Ethanol, 70 h/23°C	-0.15	15	28	16
Air permeability, 23°C				
( $\text{M}^6 \cdot \text{s}^{-1} \cdot \text{N}^{-1} \times 10^{18}$ )	27.0	8.0	1.98	2.2

<sup>a</sup>Formulation; polymer, 100; 30 p.p.h.r. N220 black, 5 p.p.h.r. process oil, 5 p.p.h.r. calcium stearate, 5 p.p.h.r. ZnO, 2 p.p.h.r. stearic acid, 2 p.p.h.r. N-(1,3 dimethylbutyl)-N'-phenyl-p-phenylenediamine, 0.3 p.p.h.r. sulphur, 2.4 p.p.h.r. MBS, 1.6 p.p.h.r. TMTD. Cured to  $t_{\text{MAX}}$  at 150°C

<sup>b</sup>34% acrylonitrile butadiene rubber

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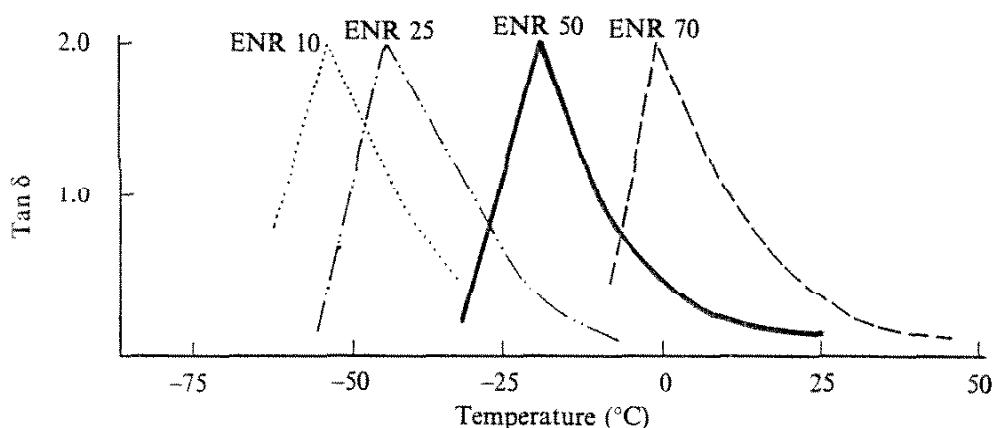


Figure 6. Effect of epoxidation level on temperature/hysteresis profile of ENR.

TABLE 6. COMPARATIVE PHYSICAL PROPERTIES OF BLACK AND SILICA FILLED ENR VULCANISATES

Property	50 p.p.h.r. N330 black <sup>a</sup>			50 p.p.h.r. silica <sup>b</sup>		
	NR	ENR 25	ENR 50	NR	ENR 25	ENR 50
Hardness (IRHD)	65	69	73	69	67	68
Modulus at 300% (MPa)	11.9	12.4	13.5	5.8	12.8	12.6
Tensile strength (MPa)	29.4	25.5	24.5	23.7	21.0	27.4
Elongation at break (%)	495	435	500	720	405	435
Compression set (25%)						
24 h/70°C (%)	18	17	21	32	18	22
Akron abrasion						
(mm <sup>3</sup> /500 rev)	21	14	11	63	15	14
Goodrich HBU, ΔT°C						
(30 min from 100°C)	7	7	23	47	7	19

<sup>a</sup>1 p.p.h.r. MBS polymer, filler, 5 p.p.h.r. process oil, 5 p.p.h.r. zinc oxide, 2 p.p.h.r. stearic acid, 2 p.p.h.r. antioxidant, 2 p.p.h.r. sulphur

<sup>b</sup>1 p.p.h.r. MBS polymer, filler, 5 p.p.h.r. process oil, 5 p.p.h.r. zinc oxide, 2 p.p.h.r. stearic acid, 2 p.p.h.r. antioxidant, 2 p.p.h.r. sulphur of diphenyl guanidine (DPG)

characteristics. Semi-EV and EV ENR vulcanisates (Formulations 2 and 3, Tables 2 and 3) have comparable tensile strength retentions to the corresponding NR vulcanisates. However, even at high temperatures, these ENR vulcanisates stiffen

whereas those based on NR soften. Analysis of aged conventional ENR 50 vulcanisates recorded a reduction in the number of epoxide groups, and increases in glass transition temperature and crosslink density. The oxidation of sulphides, model crosslinks,

yields sulphenic acid and such acids ring-open epoxide groups. This type of mechanism has been shown<sup>37</sup> to be responsible for the oxidative hardening of ENR vulcanisates and fortunately can be controlled by the addition of a base to ENR formulations. The effect of calcium stearate, the preferred base, on the ageing properties of ENR vulcanisates is recorded in *Figure 7*.

As the level of epoxidation increases and the unsaturation is reduced, the ozone resistance of unprotected ENR increases. However, the response of ENR, like that of NBR, to chemical antiozonants is poor due to their diffusion characteristics<sup>44</sup>. Adequate ozone protection can be obtained to meet most service conditions by employing a combination of wax and chemical antiozonant.

#### Adhesion

The strength of adhesion of rubbers to substrates depends on a number of factors. The energy required to peel a rubber off a substrate is related to the thermodynamic work and hysteretic energy loss of the rubber compound. Particularly high adhesion is observed between ENR and chlorinated polymers (*Table 7*)<sup>42</sup>, this is due to specific interactions e.g. hydrogen bonding or dipole interactions, between the epoxide groups and the chlorinated polymer. The adhesive strength of ENR to NBR increases with the extent of epoxidation, while the reverse is observed with NR (*Table 7*) where the difference in solubility parameter increases with the extent of the epoxidation.

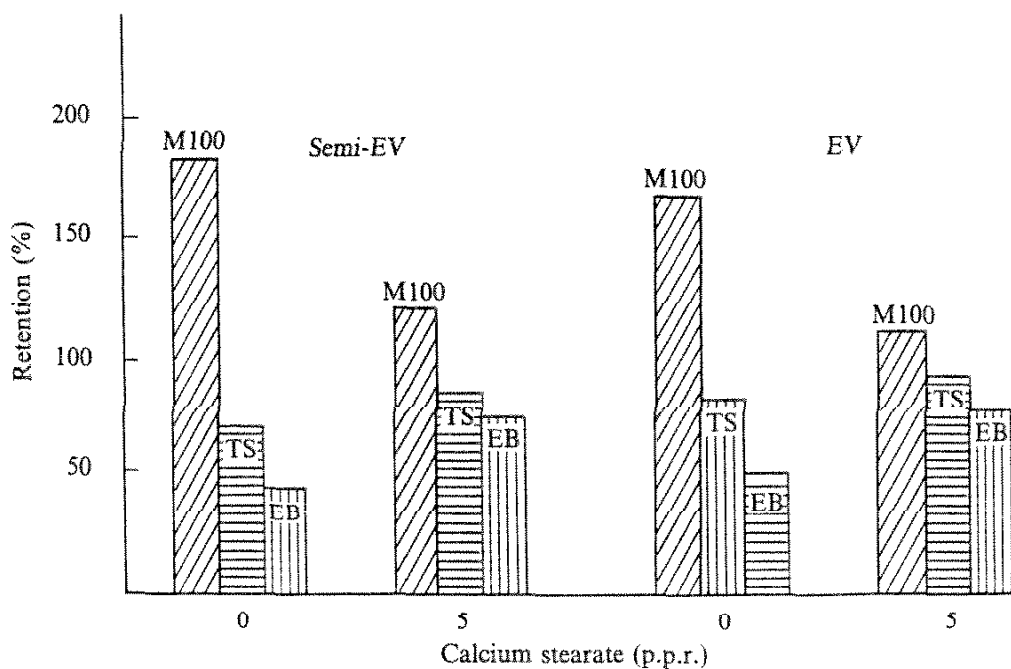


Figure 7. Air aged properties, three days at 100°C, of ENR 50 vulcanisates (50 p.p.h.r. N-330 black and 5 p.p.h.r. process oil; semi-EV Formulation 2 and EV Formulation 3 in Table 2).

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TABLE 7. CURED ADHESION OF ENR TO OTHER POLYMERS

Ply composition	Adhesive strength (N/mm)
NR/NR	11.1 <sup>a</sup>
ER/ENR 25	6.6 <sup>b</sup>
NR/ENR 50	0.8 <sup>b</sup>
NR/PVC	0.4 <sup>b</sup>
NR/PVC <sup>c</sup>	10.8 <sup>a</sup>
ENR 25/PVC	2.6 <sup>b</sup>
ENR 50/PVC	9.8 <sup>a</sup>
NR/NBR	0.4 <sup>b</sup>
ENR 25/NBR	10.0 <sup>a</sup>
ENR 50/NBR	10.0 <sup>a</sup>
ENR 25/CR	12.0 <sup>a</sup>
ENR 50/CR	12.0 <sup>a</sup>

<sup>a</sup>Rubber failure

<sup>b</sup>Bond failure

<sup>c</sup>A blend of NR/ENR 50 (50:50) applied as a solvent-based adhesive

The adhesive strength to other substrates, nylon<sup>32</sup>, brass coated steel<sup>30</sup> and glass<sup>37</sup> is increased by epoxidation. Compared to NR a three-fold increase was observed in the adhesive peel strength of ENR 25 to brass-coated steel<sup>46</sup> and a factor of ten in that of ENR 50 to nylon<sup>45</sup>. In both results, the increase in visco-elasticity will be a contributory factor.

A number of adhesive systems have been developed, which are based on ENR, these will be dealt with in the section on applications.

### Blends

For polymer blends to be truly compatible, the Gibbs free energy of mixing must be negative. The entropies of mixing of polymers are small because of their high molecular weights and thus the majority of miscible blends occur because of specific interactions e.g. hydrogen bonding, between

the two materials. Ng<sup>48</sup> and Haidzir<sup>49</sup> have studied blends of NR with ENR, and ENR blends with a range of epoxide contents. Even when the difference in epoxide level between the blend components was only 10 mole% two-phase systems were still obtained. The properties of blends are largely determined by the phase morphology<sup>49</sup> and this is particularly marked with regard to air permeability. Blends of ENR 50 with *cis* 1,4-polybutadiene<sup>50</sup> (BR) and styrene butadiene copolymer<sup>51</sup> (SBR) are also two-phase systems and in the former case, optimum properties are reported<sup>51</sup> to occur at a blend ratio of 60/40 ENR 50/BR. Although blends of ENR 50 and a medium acrylonitrile NBR only exhibit one glass transition temperature, due to the proximity of the component values, phase contrast optical microscopy clearly shows the presence of two phases<sup>52</sup>.

The epoxide group in ENR can act as a proton acceptor and the possibility of specific interactions between ENR and chlorine containing polymers initiated a number of blend studies.

Of the ENR blend systems studied, those with PVC have received by far the greatest attention. Subsequent to a report<sup>53</sup> on the high adhesion between ENR 50 and PVC, Margaritis *et al.*<sup>54</sup> showed that these materials are miscible across the complete composition range as determined by phase contrast micrographs and glass transition measurements. The S shape of the blend glass transition/composition curve supports the existence of hydrogen bonding between the two polymers as a similar dependence<sup>55</sup> was observed in other miscible blends where hydrogen bonding was independently established.

Only partial miscibility was observed between 25 mole% epoxidised NR and PVC.

Workers from the Indian Institute of Technology have published data on both rigid<sup>56</sup> and plasticised<sup>57</sup> PVC/ENR blends confirming the single-phase nature

of the PVC/ENR 50 materials. Mechanical properties, over a range of compositions, were reported and the failure mechanism studied by scanning electron microscopy<sup>58,59</sup>. Values of tensile and tear strengths (*Table 8*) were lower and the elongation at break higher than the additive values of the components. Nasir *et al.*<sup>60</sup> have also published studies in this area. The effect of mixing conditions and blend compositions on tensile and tear strengths were reported for both unvulcanised and sulphur cross-linked blends. The dynamic vulcanisation of PVC/ENR blends has also been reported<sup>61</sup>.

The melt viscosity of plasticised PVC increases with the increase of ENR 50 content of the blend<sup>62</sup>, but with rigid PVC/ENR blends, an improvement in processability was observed<sup>63</sup>.

The addition of PVC to ENR significantly improves ozone resistance<sup>64</sup>. Flame resistance is also increased<sup>65</sup>. Rigid and plasticised PVC/ENR 50 blends with a minimum of 33% and 55% ENR respectively have limiting oxygen index (LOI) values in excess of 21, the criteria for self-extinguishing or flame-resistant materials. ENR also acts as antidegradant for PVC limiting the evolution of hydrogen chloride, the first step in its degradation<sup>66</sup>.

Chlorinated polyethylene<sup>66</sup>, chlorosulphonated polyethylene<sup>67,68</sup>, chlorinated polypropylene<sup>69</sup>, poly (vinylidene chloride - alkyl acrylate) copolymer<sup>69</sup> and

chloroprene<sup>70</sup> blends with ENR have also been studied.

Blends of two chlorinated polyethylenes (CPE), 25% and 48% chlorine content, with ENR 25 and ENR 50 were evaluated. Of the four blend systems, only the ENR 50/CPE 25 system was incompatible. The rest were miscible (ENR 50/CPE 48) or miscible at certain compositions. The addition of low levels of ENR 50 to CPE 48 increases the modulus and elongation at break but this trend is reversed on increasing the ENR content. Chloroprene/ENR 50 blends are miscible across the complete composition range. To-date, no information has been published on the mechanical or rheological properties of these blends.

At high temperatures, carboxylic acids react with the oxirane group in ENR. Blends of ENR 50 with carboxylated NBR undergo crosslinking without the addition of curatives. Such materials have been termed 'self-vulcanising blends'<sup>71,72,73</sup>. Physical properties of gum vulcanisates are poor, but the addition of a reinforcing filler increases mechanical properties to acceptable values (*Table 9*). No crosslinking was observed with ENR 25 and carboxylated NBR. Based on calorimetric and dynamic glass transition data, these blends are reported to be one-phase systems<sup>72</sup>.

Blends of carboxylated NBR and poly-chloroprene are also 'self vulcanisable' but are a two-phase immiscible system<sup>74</sup>. It

TABLE 8. PHYSICAL PROPERTIES OF ENR/PVC BLENDS

Blend composition (wt% ENR 50)	Property			
	Hardness (Shore D)	Tensile strength (MPa)	Tear (MPa)	Elongation at break (%)
20	75	40 (18)	210	40 (400)
40	42	23 (12)	140	245 (510)
60	22	10 (9)	50	320 (720)
80	8	3 (5)	10	325 (720)

Figures within brackets are values for plasticised PVC containing 40 p.p.h.r. dioctyl phthalate (DOP)

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TABLE 9. PHYSICAL PROPERTIES OF 'SELF-VULCANISING' ENR BLENDS

Blend system	Hardness (Shore A)	M100% (MPa)	Property		Resilience (%) 23°C	Tear (N/mm)
			TS (MPa)	EB (%)		
ENR 50/carboxylated NBR						
100/100	40	1.28	3.6	273	62	12.6
100/50	32	1.18	3.0	327	55	11.1
100/50 <sup>a</sup>	54	1.25	22.3	634	41	38.5
50/100 <sup>a</sup>	55	1.57	20.6	538	47	38.0
ENR 50/Hypalon						
100/100	75	6.18	10.0	205	21	12.8

<sup>a</sup>Contains 45 p.p.h.r. of N220 carbon black

has been reported that the addition of ENR 50 to this system results in a tertiary miscible blend<sup>75</sup>.

The chlorosulphonyl groups in chlorosulphonated polyethylene react with ENR and blending also yields a self-vulcanising system<sup>67,76,77</sup>. The broad glass transition observed with this blend is probably indicative of the occurrence of extensive epoxide ring opening.

### Thermoplastic Elastomers

Thermoplastic elastomers (TPE) are a rapidly expanding class of materials. One group of materials is based on a dynamically vulcanised elastomer and a thermoplastic, commonly polypropylene<sup>78</sup>. TPE based on ENR, covering a range of hardnesses have been produced<sup>79</sup>. Tensile and tear properties are typical of dynamically vulcanised blends of elastomers and polypropylene, while exhibiting excellent oil resistant and air ageing properties (*Tables 10 and 11*).

ENR have also been added to NR/polyethylene and NR/polypropylene-based TPE as compatibilising agents<sup>80,81</sup>.

Thermoplastic elastomers have also been produced by blending ENR and a styrene-acrylonitrile (SAN) copolymer<sup>82</sup>.

Tensile, and tear strength and abrasion resistance increased with content of SAN while the reverse was observed with regard to impact resistance and elongation at break.

The compatibility of ENR with hydroxyl containing polymeric resins has also been investigated. Compatibility was greatest when the resin contained acidic hydrogens, due to hydrogen-bonding interactions<sup>83</sup>.

### APPLICATIONS

The increases in glass transition temperature and solubility parameter that occur on epoxidation, plus the ability of ENR to undergo strain crystallisation, suggest a wide range of potential applications, some of which are discussed below. In addition the epoxide groups in ENR have been studied as sites for a novel crosslinking reaction<sup>84</sup>, as a means of introducing rubber bound antioxidants<sup>84,85</sup> and as intermediates for further chemical modification<sup>86,87</sup>.

### Adhesives

Adhesive compositions based on epoxidised natural rubber have been developed for the bonding of vulcanised rubbers of differing polarity<sup>88</sup> and rubber compounds

TABLE 10. PHYSICAL PROPERTIES OF ENR-BASED TPE

Property	TPENR Hardness (Shore A)		
	65	75	85
M100% (MPa)	3.7	5.0	6.2
Tensile strength (MPa)	6.5	8.8	9.6
Elongation at break (%)	240	260	255
Tear strength (N/mm)	23	31	36
Compression set, 24 h/70°C (%)	36	39	45
Volume swelling, ASTM No. 3 oil 72 h/125°C (%)	14	17	17

TABLE 11. PERCENTAGE RETENTION OF PROPERTIES ON AGEING A 65 HARD TPENR

Property	ASTM NO 3 oil 72 h/125°C	Air 168 h/125°C	Air 168 h/135°C
M100	94	109	130
TS	76	104	132
EB	79	102	117

to steel<sup>89</sup>. The adhesive and sealant properties of ENR have also been utilised in the area of epoxy resin technology<sup>90</sup> and to develop glazing sealing systems<sup>91</sup>.

Low molecular weight epoxidised natural rubbers have been produced as part of UNIDO-sponsored research programme, the main use of these materials is considered to be adhesives<sup>92</sup>.

#### Tyres

The tyre is by far the largest single market for rubber and is also the largest potential market for ENR.

The high wet traction properties of ENR<sup>39</sup> make them attractive for tyre treads but other properties such as rolling

resistance and wear need to be considered. The hysteresis temperature profile of ENR 25 is such that both safety from high wet traction and good fuel economy from low rolling resistance can be obtained<sup>39</sup>. Generally, high wet traction values are achieved at the expense of fuel economy. The relative rolling resistance and wet traction properties of ENR 25 compared to those of NR and of SBR are recorded in *Figure 8*. The partial replacement of the carbon black filler by silica further enhances fuel economy. This substitution is easy with ENR because of the high reinforcement obtained without the need to resort to coupling agents. Tyre wear properties of ENR 25 black and black/silica (35/15) filled compounds are comparable with an NR tread stock. Improvement in wear are obtained by blending with BR rubber.

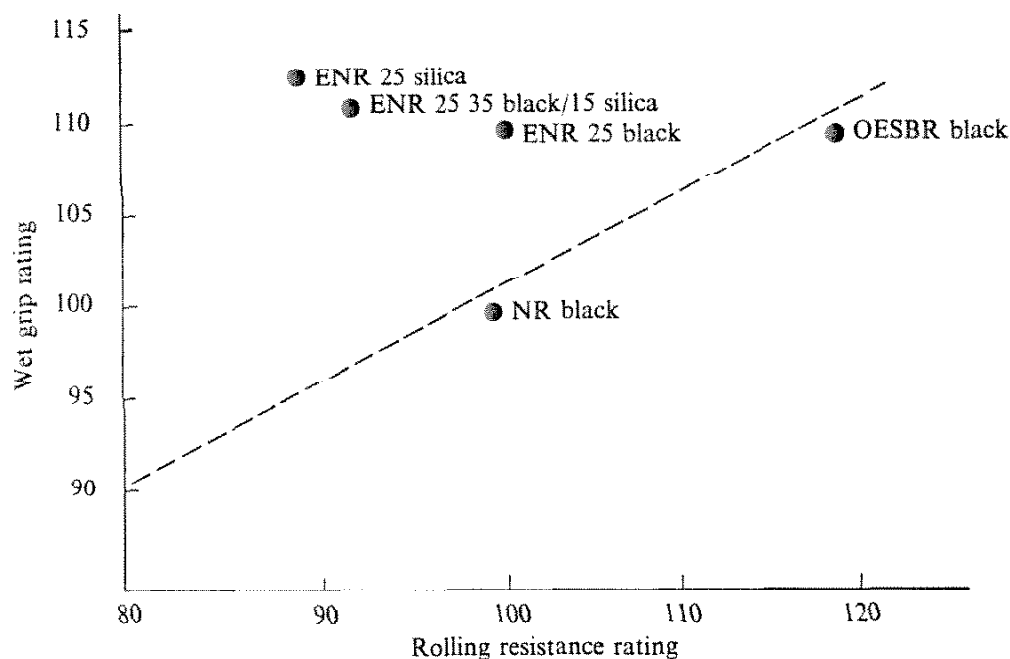


Figure 8. Plot of rolling resistance and wet traction properties of ENR 25 compared to similar NR and OESBR tyre compounds.

Although this result in a slight reduction in wet traction, tyre treads based on ENR 25 blended with 30 p.p.h.r. BR have rolling resistances similar to that of NR and wet grip and wear properties comparable to those of OESBR<sup>93</sup>. Blends of ENR 50 and NR have also been evaluated with particular emphasis placed on the safety aspects of motorcycle tyres<sup>94</sup>.

ENR 50 has been investigated as a replacement for butyl rubbers in tyre inner liners and tubes. Tyres with ENR 50/NR (60/40) inner liners have been manufactured in Malaysia and during an extensive test programme compared favourably with a standard chlorobutyl/NR liner compound<sup>95</sup>. Other publications<sup>96,97</sup> confirm the air retention properties of ENR-based inner liners but consider the higher rate of water vapour permeation, compared to a chlorobutyl, to be a disadvantage.

#### General Rubber Goods

ENR have found commercial applications in a wide range of areas, e.g. their hysteresis properties are utilised in both mechanical and acoustic damping devices and in speciality shoe soles to give high wet grip. ENR are used in the construction of composite conveyor belts because of their adhesive properties and the combination of high strength and low resilience of ENR-based conveyor belts are advantageous under severe service conditions.

Now that ENR are established commercial rubbers, marketed as Epoxyrene 25 and Epoxyrene 50, their use in applications and market volume are expected to increase rapidly.

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