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Epoxidised Natural Rubber

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The reaction of natural rubber with peracids yields a new polymer, the properties of which depend on the degree of epoxidation. The epoxide groups are randomly distributed along the rubber backbone and this together with the stereo-specific nature of the epoxidation reaction and the relatively small size of the oxygen atom, result in a polymer that can strain crystallise and, hence has good strength properties. Hysteresis and resistance to hydrocarbon oils increase with the degree of epoxidation whereas air permeability decreases. At epoxide levels of 50 mole per cent, these properties are comparable to those of some of the speciality synthetic elastomers. Excellent reinforcement of epoxidised natural rubber is obtained with silica fillers, even in the absence of coupling agents. Two levels of epoxidation, 25 mole per cent (ENR-25) and 50 mole per cent (ENR-50), have been studied for their potential as commercial rubbers, and both are available as development materials.

The mechanical properties of natural rubber (NR) are generally superior to those of many synthetic elastomers. However, NR cannot compete with speciality synthetic rubbers such as the butyls and nitriles with regard to gas permeability and oil resistance. The chemical modification of NR has been studied for many years, both as a means of changing the properties of the polymer and as a route to other useful innovative concepts such as bound antioxidants[1], Novor crosslinking systems[2], comb grafts[3] and silica coupling agents[4]. To be commercially viable the technical improvements achieved by modification of NR must also be economically attractive.

The epoxidation of NR and other unsaturated polymers has been reported in the literature[5,6,7]. However, there is little data available on the properties of the products and in some cases the results are conflicting. It has been claimed that epoxidation of unsaturated polymers increases wear and improves solvent resistance, tensile strength and other mechanical properties[7], whereas other workers have reported a reduction in strength properties[8,9].

Epoxidation is an economically attractive method of modifying NR since it is an established industrial method and it utilises cheap reagents. The epoxidation of NR latex has been studied[10] over a range of reaction conditions and the products characterised. Unless the reaction conditions are carefully controlled secondary ring-opening of the epoxide groups can occur and it is the presence of these structures that is responsible for the conflicting property reports in the literature. Under controlled conditions specific levels of epoxidised NR (ENR) are obtained. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy shows that these materials are free from any other chemical modifications. The latter technique was also employed[10] to study the distribution of epoxide groups along the NR backbone. Even though these materials were prepared from NR latex in a two-phase system, the epoxide groups were found to be randomly distributed along the NR molecule.

The glass transition temperatures *(Tg)* of ENR, as measured by differential scanning calorimetry, were single sharp events and the value increased by approximately 1°C per mole per cent epoxidation.

The physical properties of a range of ENR vulcanisates will be discussed with particular emphasis on their strength properties.

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EXPERIMENTAL

All vulcanisates were prepared by standard techniques. The gum formulation was mixed on a two-roll mill and all filled compounds in a Size B Laboratory Banbury at 116 r.p.m. starting at 50°C using the following mix cycle:

0 min : Add rubber (ENR compounded with 0.25 p.h.r. sodium carbonate)
1 min : Add powders (zinc oxide, stearic acid, antioxidant, *etc.*)
1½ min : Add ½ black and process oil
2½ min : Add remainder of black
3½ min : Sweep down feed chute
4 min : Dump

In all cases, the sulphur and accelerators were added later on a two-roll mill and the mixes cured to optimum at 150°C, unless otherwise stated.

The formulations employed are shown in *Tables 1* and *2*.

The following physical testing procedures were employed:

- Tensile strength to *ISO 37*
- Hardness to *ISO 48 (ASTM D1315)*
- Resilience, Dunlop tripsometer, to *BS 903 : Part A8*
- Ring fatigue to *ISO 6943*
- Tear strength, trouser to *ISO 34*
- Air permeability to *ISO 1399*
- Volume swelling to *ISO 1817 (ASTM D471)*
- Abrasion, Akron to *BS 903 : Part A9 Method C.*

TABLE 1. COMPOUND FORMULATIONS

Compound	Formulation 1	2	3	4
Polymer	100	100	100	100
Carbon black (N220)	—	Varies	50	—
Ultra-Sil VN3	—	—	—	50
Aromatic oil	—	5	5	5
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Antioxidant[a]	2	2	2	2
S	1.5	1.5	1.5	1.5
MBS	1.5	1.5	1.5	1.5
DPG	—	—	—	0.5
CTP[b]	—	0.2	—	—

[a] Poly-2,2,4-trimethyl-1,2-dihydroquinoline
[b] N-Cyclohexylthiophthalimide

TABLE 2. TYRE TREAD FORMULATIONS

Compound	Formulation 6	7	8	9
NR (SMR L)	100			
SBR 1712		100		
ENR-25			100	100
ISAF N220	50	50	25	15
Ultra-Sil VN3	—	—	25	35
Process oil	4	—	4	4
Antioxidant[a]	2	2	2	2
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Sulphur	1.5	1.8	2.4	2.4
TBBS	1.5	0.7	1.0	1.2
CTP[b]	0.1	—	0.2	0.1

All tyres were cured at 150°C for 40 min
[a] N(1,3-dimethylbutyl)-N′-phenyl-*p*-phenylenediamine
[b] N-Cyclohexylthiophthalimide

Rolling Resistance Testing

Rolling resistance was measured from the power consumption of the test tyres under load on a Heenan Froude test rig less the power with the same tyre in skimming contact with the wheel (1.71 m diameter). Initially, all the tyres were conditioned by subjection to a 60 min run-in period at 80 km per hour and 80% of rated load. Inflation pressure was set at 248 KPa (cold) and the tyres (165 × 13) were run to equilibrium temperature conditions for 45 min at 80% of the rated load for the two speeds of test (48 km and 80 km per hour). Three power measurements per tyre were recorded at 15 min intervals for each speed, and the relative ratings calculated from average power readings.

The tearing energy T was calculated from the equation:

$$T = \frac{(\delta w)}{(\delta A)_1} = \frac{2F\lambda}{t} - wE$$

where F is the force applied to each leg of the trouser test piece

t is the sample thickness

w is the sample width

λ is the extension ratio

E is the strain energy per unit volume in the legs of the test piece.

Wide test pieces were employed so $\lambda \approx 1$, $E = 0$ and tearing energy $T = \frac{2F}{t}$.

RESULTS AND DISCUSSION

ENR can be crosslinked using any of the standard sulphur formulations normally employed for NR or by a peroxide system[11]. However, a conventional cure system based on 2.5 p.h.r. sulphur and 0.5 p.h.r. sulphenamide results in vulcanisates with poor ageing characteristics[12]. Sulphur acids produced by the oxidation process attack the epoxide groups ultimately causing crosslink formation, which results in a substantial increase in modulus and consequent reductions in elongation at break and tensile strength. It is, therefore, recommended that all epoxidised NR formulations should contain a base to neutralise these acids and hence improve ageing properties.

Typical cure curves of ENR-25 (25 mole per cent epoxidised NR) and ENR-50 (50 mole per cent epoxidised NR) in a semi-EV formulation *(Table 1, Formulation 1)* are shown in *Figure 1.*

It is well recognised that the dissipative processes which occur in rubbers are important factors in determining their strength. The strength of strain-crystallising rubbers is substantially superior to that of non-strain-crystallising materials, where the dissipative process is predominantly visco-elastic. NR has a stereo-regular structure and hence can undergo strain crystallisation. This is especially reflected in the strength properties of NR gum vulcanisates. The epoxidation process is a stereo-specific reaction[13] and ENR will thus retain the stereo-regular *cis* 1,4-configuration of NR. This, together with the relatively small size of the oxygen atom, suggest that ENR may also undergo strain crystallisation as only minor geometrical rearrangements of the crystalline molecular packing are necessary for the inclusion of the epoxy group. The tensile strength of gum ENR vulcanisates compared to NR and a non-crystallising acrylonitrile-butadiene copolymer (NBR) supports this view which has been confirmed by X-ray data[14] *(Table 3).*

The general physical properties of black-filled ENR vulcanisates are recorded in *Table 4.* As expected, resilience decreased with increasing epoxide content and high tensile strength was observed. However, for strain-crystallising rubbers the tear strength was low and the non-relaxing fatigue decreased with increasing epoxide level, although that of ENR-50 was still nearly an order of magnitude greater than that of the non-crystallising NBR vulcanisate.

In view of these results, the strain-crystallisation dependent properties of ENR have been examined in more detail. As reinforcing fillers have a pronounced effect on the tear strength of rubbers, the initial work was carried out on gum vulcanisates.

Non-strain-crystallising rubbers such as SBR and NBR tear in a time-dependent manner when subjected to a constant load; whereas, with strain-crystallising rubbers, tear is independent of time below their critical tearing energy. Above this value, catastrophic tearing occurs. NR, ENR-25 and ENR-50 gum vulcanisates all exhibited a critical tearing energy as expected for strain-crystallising rubbers. No time-dependent crack growth was observed but above the critical tearing energy, tear was catastrophic. The effects of tearing rate and

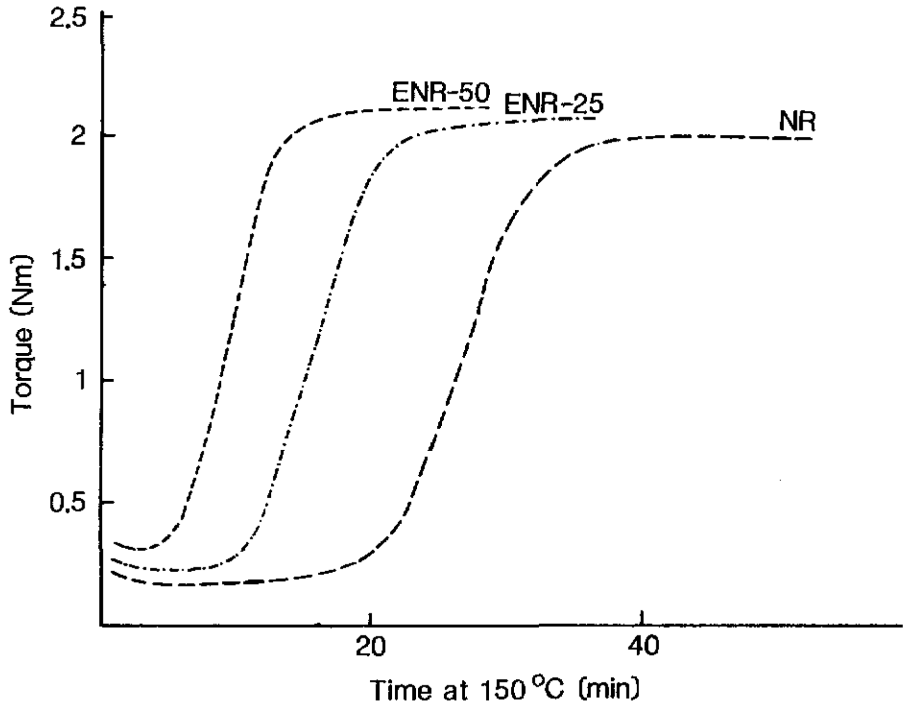

Figure 1. Monsanto rheographs of NR, ENR-25 and ENR-50 in a semi-EV formulation (Formulation 1, Table 1).

temperature on the strength of vulcanisates of similar moduli are shown in *Figures 2* and *3*. This data strongly supports the view that ENR like NR strain crystallise in contrast to such polymers as SBR. However, it was noted that the ENR-50 values were significantly lower than those of NR and ENR-25, which may indicate a reduced degree of crystallinity in this case.

None of the above results explain the observed low tear strength of ENR in black-filled (30 p.h.r. N220) vulcanisates *(Table 3)*. High tear strength is normally associated with 'knotty' tearing which depends on the rate, temperature, the type and level of black filler and the degree of anisotropy[15]. To date, only a limited study of these variables has been carried out, but high ENR tear strength in black-filled systems can be achieved. The effect of black (N220) level on the tearing energy of NR, ENR-25, ENR-50, SBR and NBR vulcanisates is recorded in *Figure 4* at a test piece extension rate of 10 mm

TABLE 3. TENSILE STRENGTH OF GUM VULCANISATES (FORMULATION 1)

Property	Gum vulcanisate			
	NR	ENR-25	ENR-50	NBR[a]
Tensile strength (MPa)	29.0	31.0	25.0	12.4
Modulus at 100% extension (MPa)	0.93	0.92	0.89	1.12
Modulus at 300% extension (MPa)	2.29	2.23	2.13	1.83
Elongation at break (%)	665	680	660	630

[a] 34% acrylonitrile content

TABLE 4. PHYSICAL PROPERTIES OF ENR VULCANISATES COMPARED TO NR AND NBR VULCANISATES (FORMULATION 2, TABLE 1, 30 P.H.R. N220 BLACK)

Property	Vulcanisate			
	NR	ENR-25[a]	ENR-50[a]	NBR[b]
Mooney scorch, t_5 at 120°C (min)	48	30	25	20
Time to optimum cure at 150°C (min)	24	17	23	50
Tensile strength (MPa)	30.6	28.4	28.3	15.3
Modulus at 100% extension (MPa)	1.53	1.83	1.95	2.2
Modulus at 300% extension (MPa)	7.7	8.9	8.8	9.5
Elongation at break (%)	660	590	580	365
Hardness (IRHD)	56	57	64	61
Resilience, Dunlop at 23°C (%)	76	66	19	32
Compression set, 24 h/70°C (%)	21	22	30	17
Ring fatigue				
0%-100% extension (kcs)	103	165	250	38
50%-150% extension (kcs)	1 300	1 200	330	35
Tear strength, trouser (KN/m)	16	8	7	9
Abrasion, Akron (mm^3/500 rev.)	22	14	12	11
Goodrich HBU, 5.7 mm stroke, 10.9 kg load from 23°C for 30 min, ΔT(°C)	40	40	42	88

[a] Formulation includes 0.25 p.h.r. sodium carbonate

[b] 34% acrylonitrile content

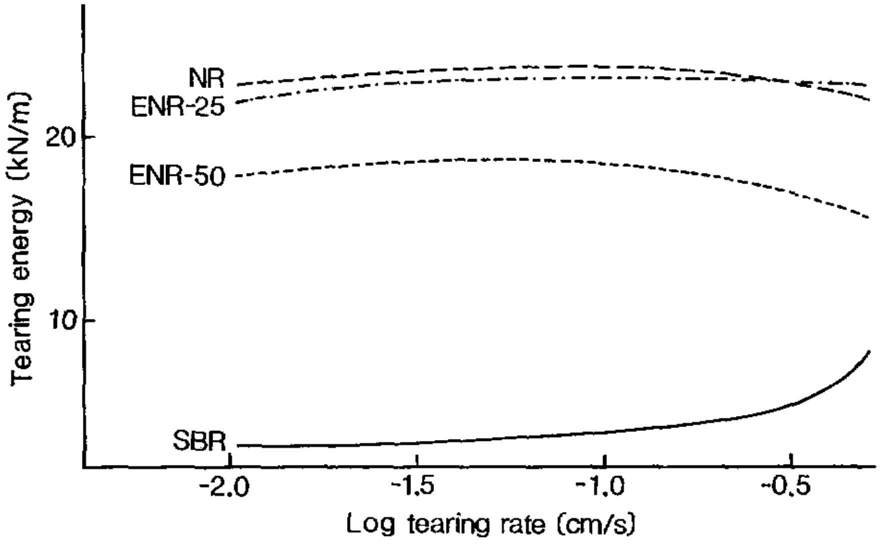

Figure 2. Plot of tearing energy against rate at 23°C for gum vulcanisates (Formulation 1).

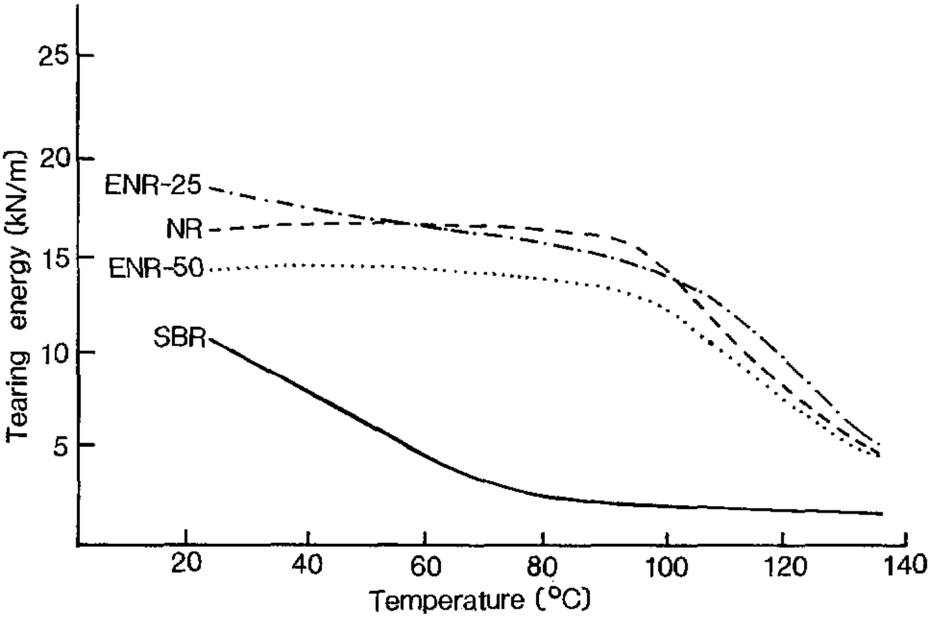

Figure 3. The effect of temperature on tearing energy of gum vulcanisates (Formulation 1). Tear rate log -0.78 cm per second.

per minute and 23°C. Below 40 p.h.r. of black the tearing energy of ENR-25 and ENR-50 is low, but beyond this point, a substantial increase occurs. A similar increase was observed with NR, whereas the tearing energy of the non-crystallising rubbers decreased. At a faster test rate, 500 mm per minute, the tear energy of ENR-25 at high black loading was 50% higher than that of NR.

The different behaviour of ENR in black-filled systems cannot be due to a lack of general reinforcement as other properties e.g. tensile modulus and modulus contradict this view. It is unlikely that the black filler interferes with the strain crystallisation process as this does not occur with NR[15] and non-relaxing fatigue data *(Figure 5)* indicate that strain crystallisation still occurs in ENR black-filled vulcanisates. It was noted that the carbon black dispersion of many of the ENR vulcanisates was poor in comparison to the other rubbers, and this may well result in inadequate anisotropy to enhance knotty tear. Alternative processing techniques are currently being investigated to check this idea.

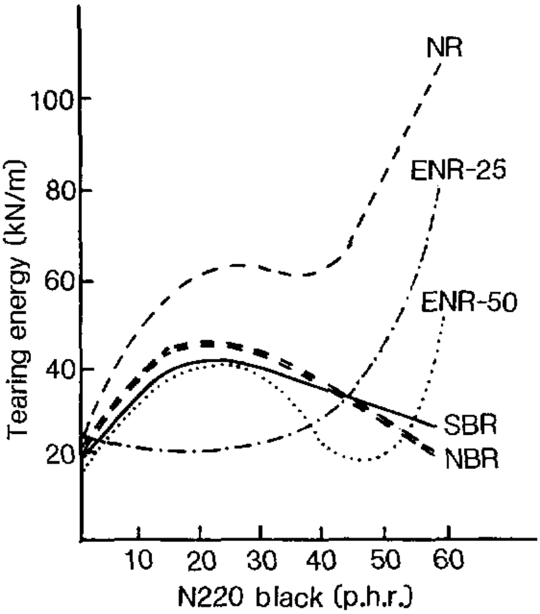

Figure 4. The effect of black (N220) loading on the tear energy of vulcanisates (Formulation 2).

TABLE 5. OIL RESISTANCE OF ENR VULCANISATES COMPARED TO NR, CR AND NBR

Property	Polymer				
	NR	ENR-25	ENR-50	CR	NBR
Percentage volume swelling (70 h/100°C)					
ASTM No. 1 oil	97	16	−2	3	−4
ASTM No. 2 oil	141	86	13	33	6
ASTM No. 3 oil	235	167	39	59	26
Percentage retention of tensile strength (70 h/100°C) in ASTM No. 3 oil	9	22	72	51	78

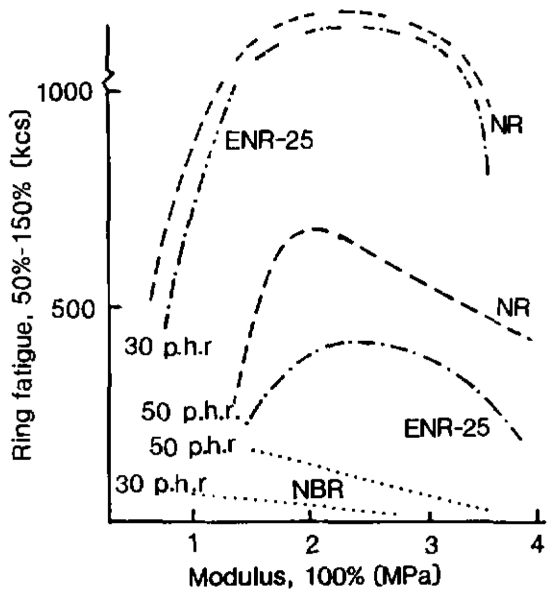

Figure 5. Non-relaxing fatigue properties of NR, ENR-25 and NBR vulcanisates (Formulation 2).

The epoxidation of NR also results in a considerable increase in oil resistance and reduction in gas permeability. Swelling tests in a series of standard oils have demonstrated that at the 25 mole per cent epoxidation level there is a substantial improvement over NR and at 50 mole per cent epoxidation the oil resistance is comparable to those of some of the speciality synthetic elastomers. *Table 5* compares the oil resistance properties of ENR with those of NR, polychloroprene (CR) and a medium NBR (34% acrylonitrile content). The oil resistance of ENR-50 falls between those of polychloroprene and NBR.

Similar improvements are observed with regard to gas permeability. The air permeability of ENR-25 and ENR-50 are compared to those of other polymers in *Table 6*.

Another distinctive feature of ENR is the high reinforcement obtained with silica fillers. Silica reinforces ENR-25 and ENR-50 to an equal extent to that obtained with carbon black without the addition of a silane coupling agent. The comparative properties of silica-filled and black-filled NR and ENR are demonstrated in *Table 7*. The relative low reinforcement of the

TABLE 6. COMPARATIVE AIR PERMEABILITIES OF RUBBERS AT 30°C

Rubber	Air permeability[a]
NR[a]	100
ENR-25	32
ENR-50	8
SBR-1500	48
Butyl	6
NBR (39% ACN content)	4

[a] NR value taken as 100 and other results rated accordingly

TABLE 7. COMPARISON OF BLACK-FILLED AND SILICA-FILLED VULCANISATES (FORMULATIONS 3 AND 4)

Property	NR		ENR-25		ENR-50	
	Black	Silica	Black	Silica	Black	Silica
Time to optimum cure at 150°C (min)	22	35	17	30	19	32
Hardness (IRHD)	65	69	69	67	73	68
Tensile strength (MPa)	29.4	23.2	25.4	21.0	24.5	22.4
Modulus at 300% (MPa)	11.9	5.8	12.4	12.8	13.5	12.6
Elongation at break (%)	495	720	435	405	500	435
Abrasion, Din (mm^3)	199	364	212	250	278	289
Abrasion, Akron (mm^3/500 rev.)	21	63	14	15	11	14
Compression set, 24 h/70°C (%)	18	32	17	18	21	22
Ring fatigue, 0%–100% (kcs)	70	51	65	52	93	58
Goodrich HBU, 5.7 mm stroke, 10.9 kg load from 23°C for 30 min, ΔT (°C)	7	47	7	7	23	19

silica-filled NR vulcanisate is reflected in the lower modulus, increased abrasion and higher Goodrich heat build-up. In contrast neither ENR-25 nor ENR-50 show any significant variation in these properties on changing from 50 parts N330 to 50 parts silica.

With increasing levels of epoxidation hysteresis also increases and this is reflected in increased wet grip and lower resilience at ambient temperatures. Both these properties are important tyre tread parameters and it has been shown[16] that, with general-purpose rubbers, improved wet grip usually results in increased rolling resistance. However, at elevated temperatures the hysteresis of ENR-25 compounds decreases *(Figure 6)* and hence the rolling resistance decreases. Thus, the relatively cool tyre surface in contact with a wet road should exhibit good wet grip, while the bulk of the tread at higher temperature will have low rolling resistance.

Tyres retreaded with a series of ENR compounds have been examined for wet grip by recording skid path lengths using a two-wheel Schallamach trailer[17]. Rolling resistance has also been measured on a Heenan Froude test rig. The results are recorded in the form of a Morton and Krol plot in *Figure 7*. Clearly, the ENR compounds have both high wet grip and low rolling resistance, and therefore have potential as tyre tread compounds[11].

CONCLUSIONS

Natural rubber can be epoxidised at the latex stage to yield a new polymer — ENR. With increasing epoxide content, oil resistance and hysteresis increase, and gas permeability decreases. But unlike many synthetic polymers with similar properties, ENR can strain crystallise. A high degree of reinforcement is obtained with silica fillers in the absence of coupling agents.

These properties suggest a wide range of potential applications for ENR many of which are being evaluated e.g. tyres, belting, oil hose, seals, various engineering applications including mountings and shoe soling.

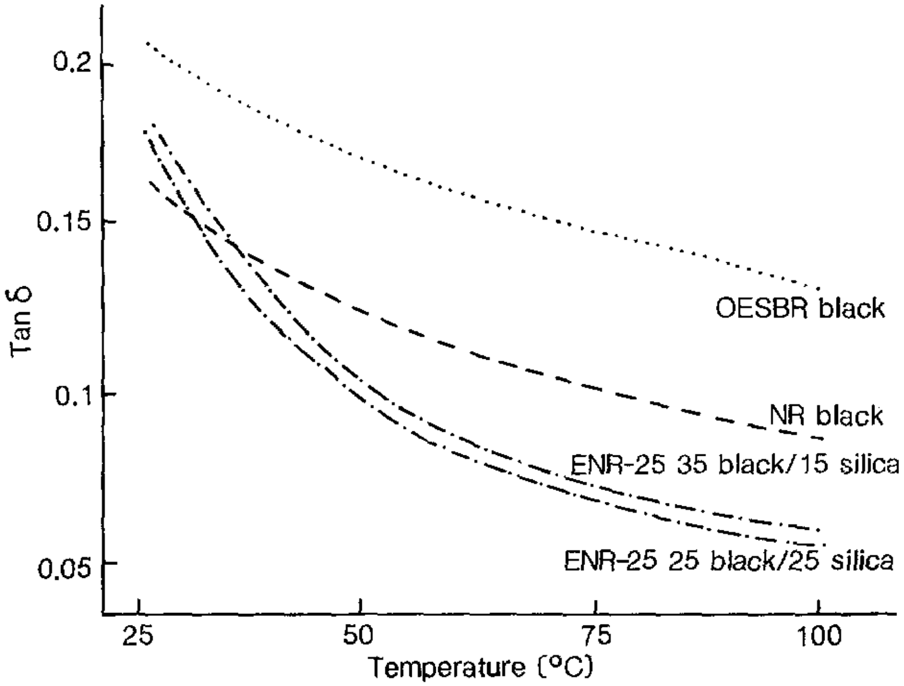

Figure 6. The effect of temperature on the hysteresis properties of tyre tread compounds (Formulations 6-9). Obtained from the Dunlop rotary power loss test.

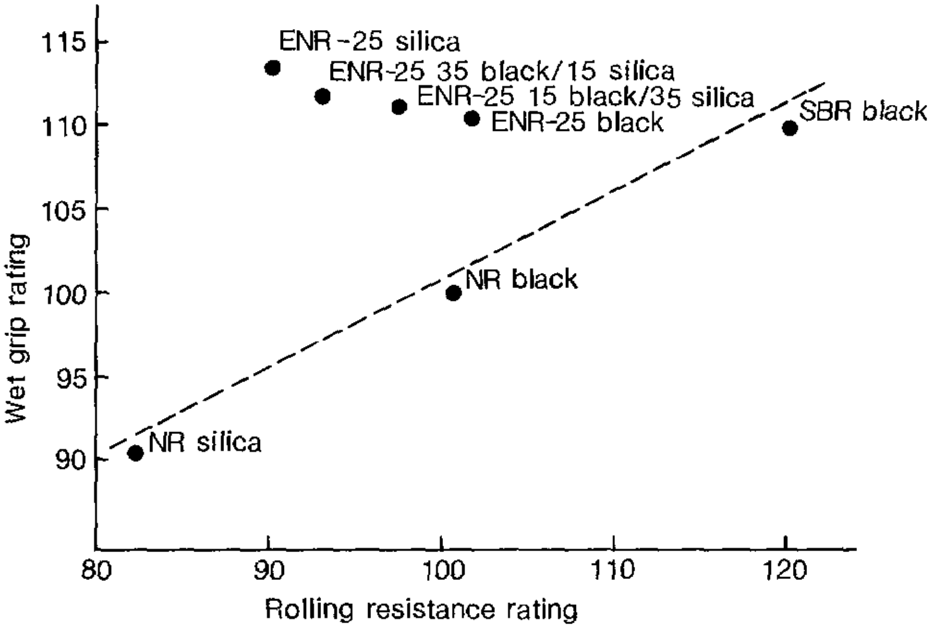

Figure 7. Wet grip/rolling resistance ratings of steel radial tyres retreaded with various rubbers.

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