Renewable-Resource Materials, edited by
C.E. Carraher and L.H. Sperling.
New York: Plenum, 1986.
Proceedings of the 2nd International Symposium
on Polymeric Renewable Resource Materials,
Miami Beach, Florida, 1985

14

CHEMICAL MODIFICATION OF NATURAL RUBBER AS A ROUTE TO RENEWABLE RESOURCE ELASTOMERS

Ian R. Gelling

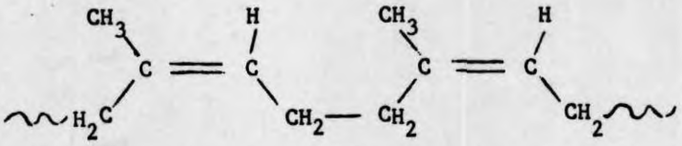
The Malaysian Rubber Producer's Research Association
Tun Abdul Razak Laboratory, Brickendonbury
Hertford SG13 8NL, England

INTRODUCTION

Natural rubber (NR) is commonly obtained from the latex of the Hevea brasiliensis tree, which is indigenous to South America. The latex is contained within a system of anastomosing articulated vessels which occur in the region of the phloem as sheaths concentric with the outer bark. There are limited anastomoses between each ring of vessels forming a continuous network and thus allowing the withdrawal of latex to be made by repetitive tapping without serious damage to the tree. NR can also be obtained from the Guayle plant (Parthenium argentatum) but in this case the latex is present in ordinary parenchyma cells and the whole plant has to be sacrificed to obtain the rubber. A Hevea tree has a useful productive life of between fifteen and twenty years and is by far the most efficient source of natural rubber.

Hevea latex consists of rubber particles ranging in diameter from 0.04 to 2.0 microns dispersed in an aqueous phase. The rubber content of the latex varies between approximately 25 and 35 w/w % depending on climatic conditions and other variables. Also present in the latex are proteins (1.0%), lipids (0.9%), quebtachitol (1.0%), inorganic salts (0.5%) and many other minor components. The vast majority of NR is utilized as a dry product which consists of 95% rubber hydrocarbon and 5% non-rubbers.

The chemical structure of NR hydrocarbon was first elucidated by Harries[2] and Pummerer[3] as a 1,4-polyisoprenoid with the monomer units C_5H_8 joined "head to tail." Modern analytical techniques[4] have confirmed this basic structure and shown that NR is the stereoregular all cis 1,4-polyisoprene (1) with a weight-average molecular weight ($\bar{M}_w$) of one to two million.



(1)

The growth of NR as a large scale commercial polymer commenced with the invention of the pneumatic tyre and increased with the growth of the automotive industry. Production of natural rubber is centred in S.E. Asia, particularly in Malaysia and Indonesia. The growth of NR compared to synthetic rubbers, which are petroleum based products, is illustrated in Fig. 1 with the historic and economic events clearly evident. The severe disruption of supplies during World War II stimulated the development of synthetic rubbers especially in the U.S.A. Cheap and abundant supplies of crude oil in the 1950's and 1960's resulted in a dramatic growth in the production of synthetic rubber, which was briefly checked by the "oil crisis" in the early seventies. Today total rubber consumption is approximately twelve million tonnes per annum of which two thirds is synthetic rubber, mainly styrene butadiene copolymer (SBR) and the remainder NR.

Synthetic rubbers are based on non-renewable crude oil while natural rubber is a renewable resource polymer. The total energy content of synthetic rubbers, from crude oil to finished polymer, can readily be calculated and some values are recorded[5] in Table 1 together

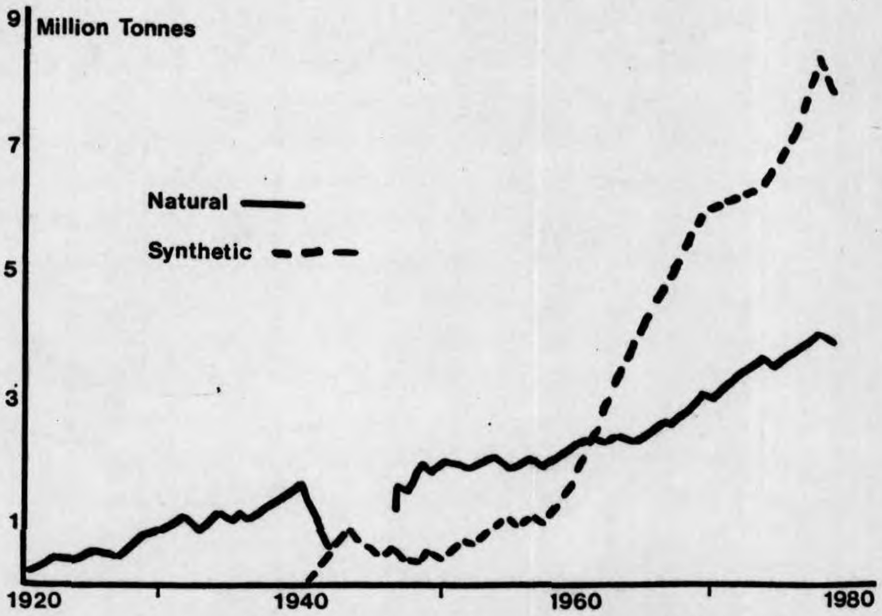


Fig. 1. Annual world production of Natural and Synthetic rubbers.

with the non-renewable energy content of NR eg. fertilizers, processing and transport. Thus the synthetic rubber industry consumes 24 million tonnes of oil per annum (the energy content of a tonne of crude oil is approximately 50GJ) or 450,000 barrels of oil per day.

In certain applications the choice between NR and a general purpose synthetic rubber is based on financial considerations, but in other areas technical considerations will be the determining factor. For example, NR cannot compete with some of the speciality synthetics with regard to oil resistance and gas permeability properties. It has been recognised for many years that chemical modification can change the physical properties of NR, and thus extend its applicational area. Provided the modification is energy efficient, this approach could result in considerable savings of non-renewable energy.

The chemical modification of NR is reviewed with the emphasis on recent work, which has both the technical and economic potential to replace some oil-based synthetic rubbers.

Table 1

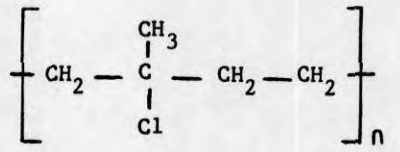
Non-renewable Energy Content of Rubbers

	GJ/tonne
SBR	156
Butyl rubber	209
Polychloroprene	144
EPDM	170
Natural Rubber	15

CHEMICAL MODIFICATION OF NATURAL RUBBER

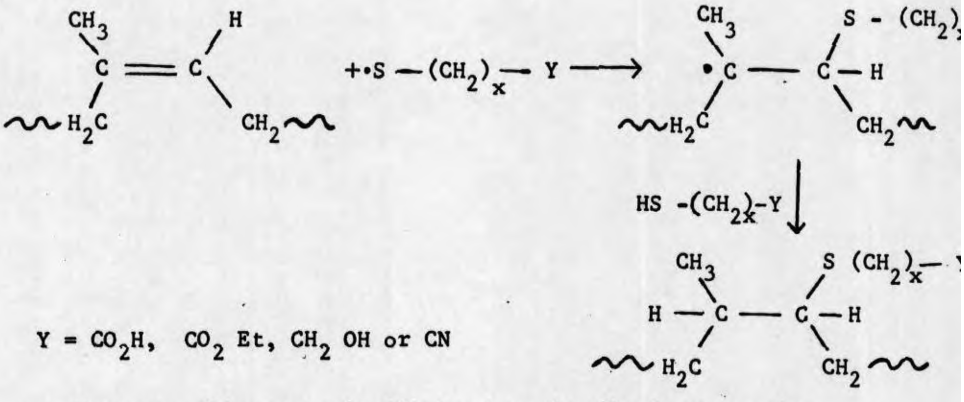
In theory natural rubber can be treated as a simple olefin and should therefore undergo the many chemical reactions of this species. However, in practice the non-rubbers can compete or interfere with many reactions and the polymeric nature can cause special problems. A large number of chemical modifications have been investigated in the past with some success. Chlorinated[6,7], hydrochlorinated (2), and cyclized natural rubber[9] were all produced as commercial materials. Chlorinated rubber, a white thermoplastic powder, was principally employed in protective paints and coatings where resistance to chemical or corrosive atmospheres was required. The hydrochlorinated derivative was utilized as a packaging film (Pliofilm, Goodyear Tire and Rubber Co.) and cyclized rubber as a thermoplastic resin. Today these materials have been largely superseded by oil based products.

Thiols and related compounds add to the double bond of NR (1) by a free radical mechanism.[10]



$$\left[-CH_2-C(CH_3)(Cl)-CH_2-CH_2- \right]_n$$

(2)



Y = CO_2H, CO_2Et, CH_2OH or CN

However, this type of addition has the disadvantage that cis-trans isomerisation can be induced by the intermediate thiyl radical. Nitrenes and carbenes[11], maleic anhydride and maleimides[12], nitrones[13], and aldehydes[14], are among the other classes of chemicals that have been employed to modify NR, but all have technical or economic disadvantages.

It is now recognized that any chemical modification of NR must obey the following criteria if it is to be technologically and commercially viable.

1. Reagents should be specific and not induce changes in the natural rubber molecule (ie degradation, cyclization, crosslinking etc) other than that intended.

2. No catalysts that are poisoned by non-rubbers should be employed.

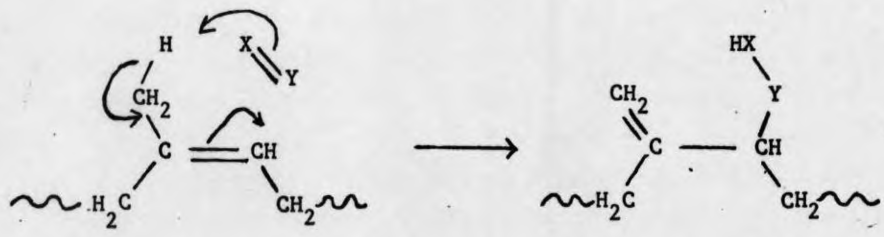
3. Reactions should be capable of being carried out with high efficiency in latex or during conventional dry rubber mixing or curing.

4. Reagents and processes should be cheap.

During the last few years a number of reactions have been studied which fit the above criteria and have the potential to yield commercially viable materials.

'Ene' Reactions

The general 'ene' reaction is illustrated below and early work with nitroso 'ene' reagents lead to rubber-bound antioxidants[15] and a novel di-urethane (Novor) crosslinking system[16]. Subsequently, azodicarboxylates have been examined in some detail as 'ene' reagents



X = Y can be $-N=O$, $-N=N$, $>C=S$, $>C=O$, $>C=C<$
as it is known that their reaction with most olefins is insensitive to radical initiators or scavengers and to solvent type[17].

Ethyl N-phenylcarbamoylazoformate (ENPCAF) (3) readily reacts with dry NR (1) and modification can be carried out in an internal mixer as part a of standard rubber compounding exercise. Substantial changes in physical properties can be achieved and a variety of functional groups introduced onto the rubber backbone[18] by substitution of the phenyl group.

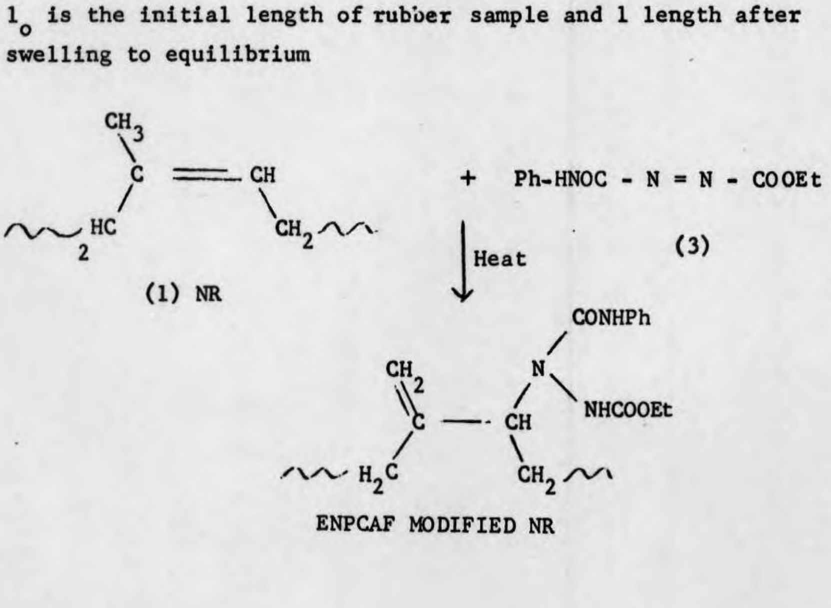
The effect of ENPCAF modification on the gas permeability and solvent resistance properties is illustrated in Table 2.

Table 2

Effect of ENPCAF modification on the gas permeability and solvent resistance of Natural Rubber

Modification level (mole %)	Permeability const, p/N_2 gas $(cm^2s^{-1}\ atm^{-1}) \times 10^8$	Linear Swelling in Petroleum ether (60-80) l/l_o
0	3.5	1.51
5	2.04	1.3
10	0.98	1.2

l_o is the initial length of rubber sample and l length after swelling to equilibrium



(1) NR

(3)

ENPCAF MODIFIED NR

The introduction of a trialkoxysilyl group $[-CH_2CH_2CH_2Si(OR)_3]$ into the ENPCAF molecule results in a modification that also functions as a silane coupling agent[19], which enhances the degree of reinforcement by silica fillers.

The hydrazo-ester pendent groups, introduced by ENPCAF modification, are very polar and readily undergo hydrogen bonding with one another. This interaction retards the rate of crystallization of NR. A modification level of one mole % has been estimated to be sufficient to delay the crystallization hardening that occurs when NR is stored or transported at low temperatures.

Thermoplastic rubbers, ie materials which behave as if vulcanized at ambient temperatures but which can be processed like plastics at elevated temperatures, are becoming increasingly important, as significant savings in both production and energy costs can be achieved. Thermoplastic NR's have been developed by employing the azo 'ene' reaction to attach polystyrene chains to the NR backbone in the form of a comb effect. Anionically

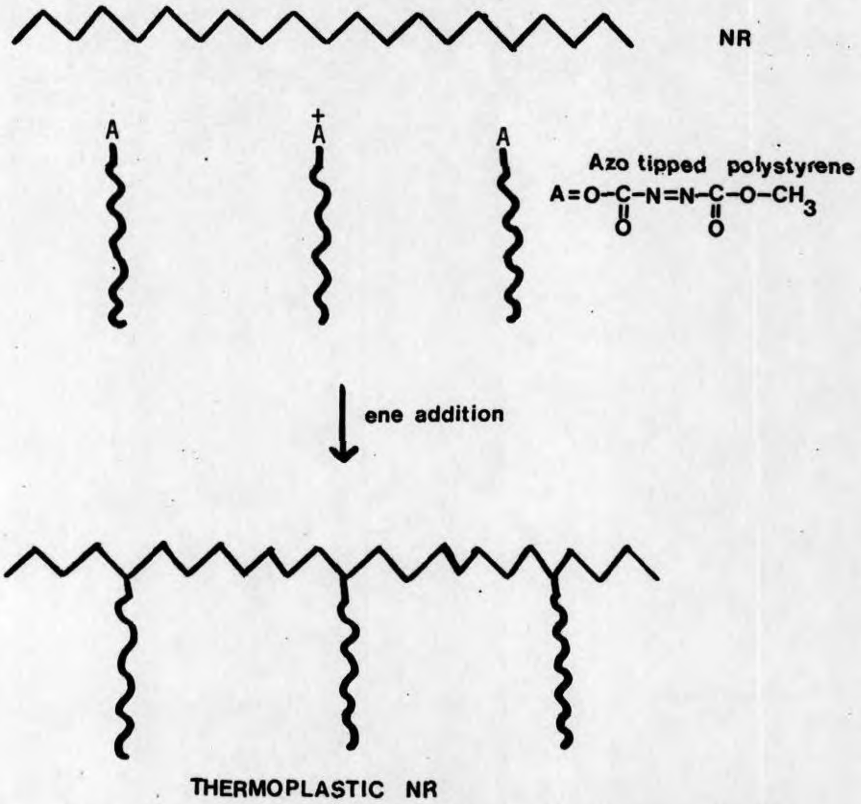


Fig. 2. The grafting of azo tipped polystyrene onto NR.

polymerised polystyrene with a terminal hydroxyl group is modified to yield a terminal azo group. At high shear and at temperatures above the softening point of polystyrene the mixing of NR and azo tipped material yield a graft copolymer (Fig.2)[20,26]. Grafting efficiencies of over 70% can be obtained. Within well defined limits these graft materials show thermoplastic rubber properties - very similar to the styrene butadiene styrene (SBS) block copolymers. Optimum strength properties are obtained with polystyrene molecular weights of around 8000 (Fig. 3) and at a polystyrene content of 40% w/w (Fig. 4).

At present these NR graft materials are not cost competitive with the all synthetic SBS block copolymers in general applications, as the azo tipping chemistry is relatively expensive and the natural rubber based materials cannot be oil extended to the same extent as the SBS copolymers. However, they have potential as adhesives and blending aids. A variety of polymers, including blends of different materials can be grafted onto NR by this technique.

Although not a chemical modification in the true sense, thermoplastic NR can also be obtained by blending NR with polyolefins at high shear rates and temperatures in excess of the melting point of the polyolefin phase[22]. A range of materials based on

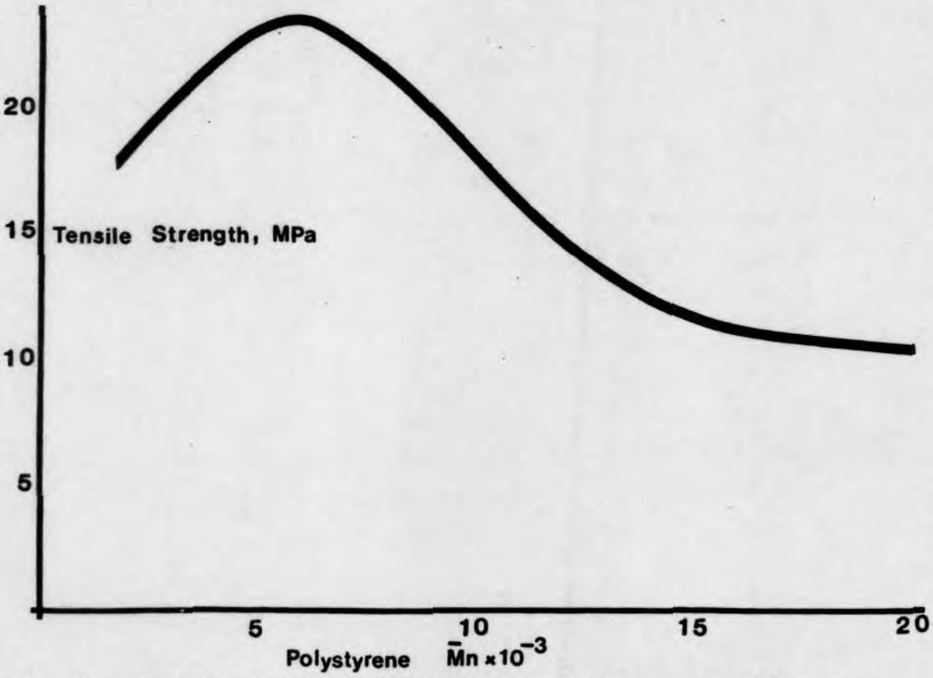


Fig. 3. Tensile strength as a function of polystyrene Molecular weight for azo graft polystyrene 40/NR 60 thermoplastic rubbers.

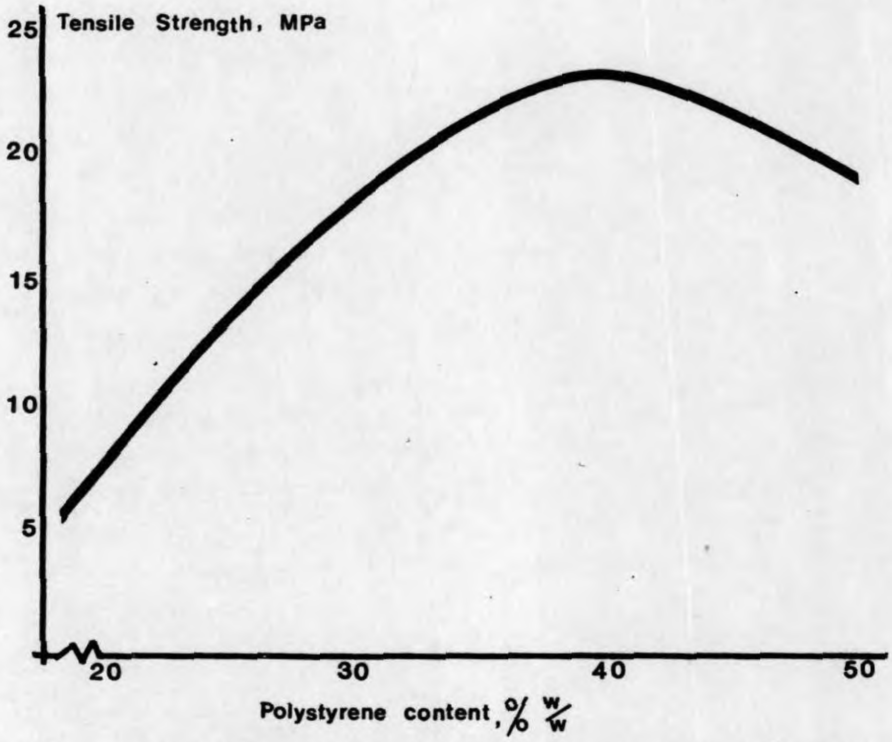


Fig. 4. Tensile strength as a function of polystyrene ($\bar{M}n$ 8200) content for NR thermoplastic rubbers.

polypropylene and polyethylene have been produced and the properties vary with the polyolefin composition. At high polyolefin concentrations the NR basically acts as a modifier to improve impact strength, but at lower levels of polyolefin the products are thermoplastic rubbers. The physical properties of these blends are very similar to the EPDM/polyolefin materials. These NR based materials are currently undergoing commercial development and are expected to be economically attractive, especially in NR producing countries.

Epoxidized Natural Rubber

Of the recent chemical modifications of NR, epoxidized natural rubber (ENR) is the most attractive from both a technical and economic viewpoint. Under controlled conditions the reaction of NR latex with either a 35% w/w solution of peroxyacetic acid[23] or peroxyformic acid, formed 'in-situ' from hydrogen peroxide and formic acid[24], yields epoxidized natural rubbers (Fig. 5). The latter method is more attractive from an economic standpoint.

A range of ENR's, 25-75 mole % epoxidized, have been prepared and within the limits of detection of the analytical techniques employed no other modifications were observed.

Infrared spectra showed absorptions at 870 and 1240 cm^{-1} (epoxide), but absorptions due to hydroxyl or carbonyl groups which are characteristic of secondary epoxide ring-opened structures were absent. The ^{1}H nuclear magnetic reasonance (n.m.r.) spectra[25] were consistent with published data on epoxidized synthetic cis, 1,4-polyisoprene[26]. The signals at 2.7 or 5.05 ppm were used to determine the degree of epoxidation and good agreement was observed between these results and elemental oxygen data. The properties of these materials will depend to a significant extent on the epoxide unit sequence distribution. Although these materials were prepared from latex and the physical constraints of this heterogeneous system could well control the epoxide unit distribution, ^{13}C n.m.r. showed the epoxide groups to be randomly dispersed along the polymer backbone[27,28].

The epoxidation of NR results in a systematic change in many properties. Every mole % epoxidation raises the glass transition temperature (Tg), as measured by differential scanning calorimetry, by 1°C, and this and other changes are reflected in the physical properties of the materials.

ENR can be crosslinked using any of the standard sulphur formations normally employed for NR[29] or by a peroxide system, although in the latter case the efficiency decreases with increasing degree of epoxidation. The comparative vulcanization characteristics of ENR's and NR are illustrated in Fig. 6.

The tensile strengths of ENR gum vulcanizates (Table 3) are high and characteristic of polymers that undergo strain crystallization, and this can be attributed to the stereospecificity of the epoxidation reaction[31] together with the relatively small size of the oxygen atom.

The ability of ENR's to strain crystallise is also reflected in the non-relaxing fatigue properties (Table 3). Although the number of cycles to failure decreases with increasing epoxide content, the fatigue resistance of ENR-50 is still an order of magnitude greater than a comparable non-crystallizing rubber such as acrylonitrile (31%)butadiene (NBR) copolymer (Table 3).

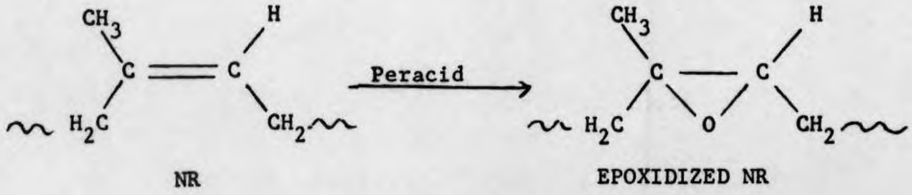


Fig. 5. Epoxidation of NR

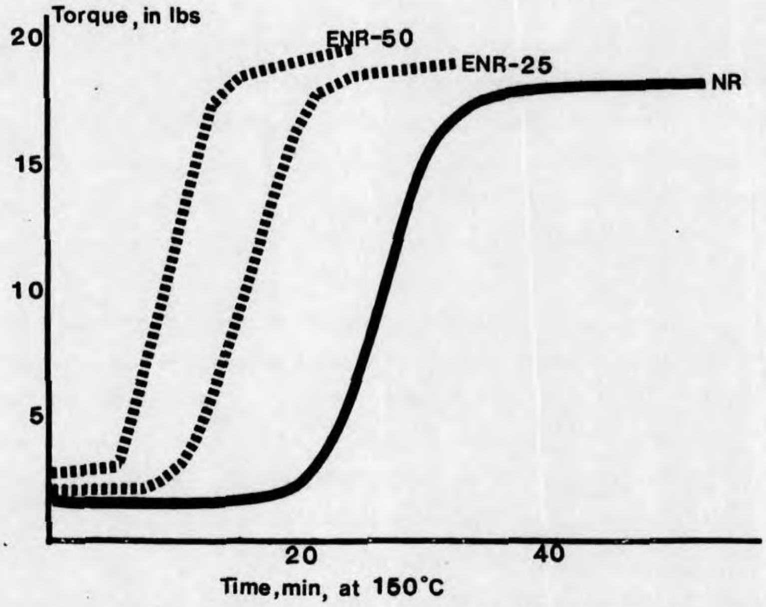


Fig. 6. Vulcanization characteristics of ENR-25 and ENR-50 compared to NR in a semi EV formulation, S 1.5, MOR 1.5.

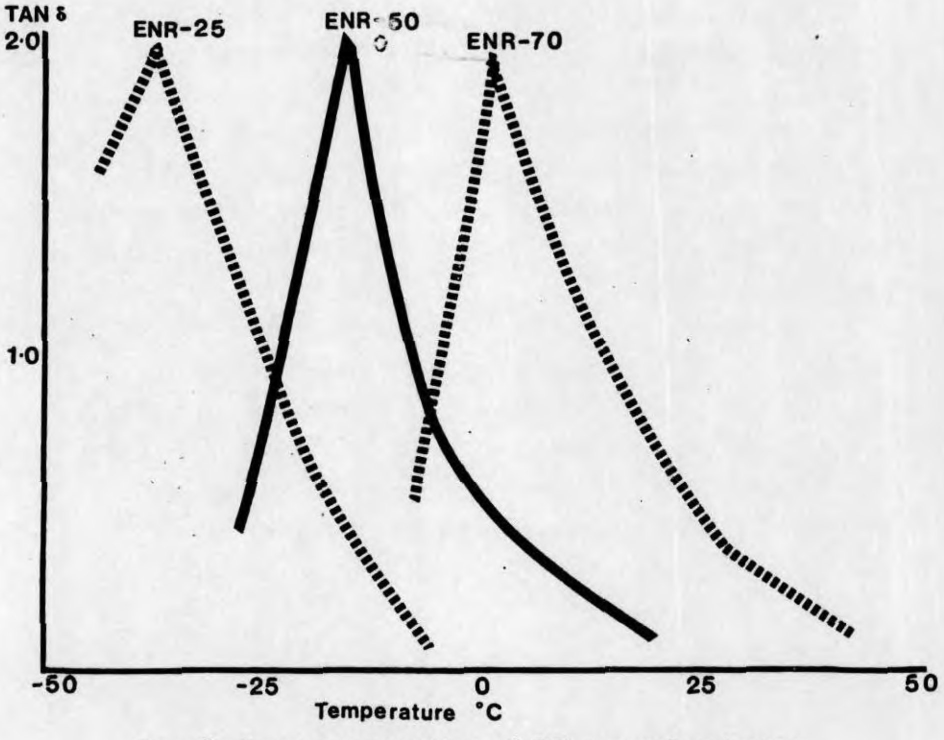


Fig. 7. Damping properties of ENR gum vulcanizates.

Table 3

Physical properties of ENR vulcanizates

Gum vulcanizates[a]	NR	ENR-25	ENR-50	ENR-75
Modulus at 100% extension (MPa)	0.68	0.69	0.74	0.95
Tensile strength (MPa)	25.7	24.3	28.3	27.9
Elongation at break (%)	760	770	770	650
Degree of crystallinity %[b]	11	11	10	4
Wet skid Resistance[c] (Concrete)	100	130	132	-
Black filled vulcanizates[a] (30 phr N220)	NR	ENR-25	ENR-50	NBR
Modulus at 100% extension (MPa)	1.5	1.8	1.9	1.6
Tensile strength (MPa)	32.6	28.4	28.3	17.4
Elongation at break (%)	660	590	580	704
Hardness (IRHD)	57	59	61	58
Dunlop Resilience (23°)	78	67	21	31
Ring Fatigue (KCS)				
0-100% extension	103	165	230	41
50-150% extension	1560	1206	550	39
Oil resistance				
% Volume change 70h/100°C				
ASTM No 1 oil	87	14	-0.5	-0.2
ASTM No 2 oil	141	69	12	14
ASTM No 3 oil	225	137	38	29

[a] Semi EV formulation, S 1.5/MBS 1.5 phr cured to opt. at 150°C.

[b] Determined from the variation of peak intensity of the amorphous halo in the X-ray diffraction patterns of samples strained to 400%.

[c] The NR control was taken as 100 and the other results noted accordingly.

The increase in the Tg of ENR with the degree of epoxidation is reflected in the damping properties (Fig. 7) and reduction in gas permeability (Table 4).

Table 4

Comparative air permeabilities at 23°C

	Permeation Constant $\times 10^8$ (cm^2/sec/atmos)
NR	6.1
ENR-25	1.5
ENR-50	0.51
ENR-70	0.15
IIR	0.41
NBR	0.30

The change in hysteresis also results in an increase in the wet coefficient of friction. Data obtained with the portable wet skid tester (Stanley, London) are recorded in Table 3.

Increasing levels of epoxidation significantly improve the resistance to hydrocarbon oils (Table 3) and solvents, although the reverse in time for more polar liquids such as hydraulic brake fluids.

Most fillers require the use of a coupling agent to maximise the reinforcement with silica fillers, however, with ENR a high degree of reinforcement is obtained in the absence of coupling agent. This effect is illustrated in Table 5, similar properties are obtained from black and silica filled ENR's.

Table 5

Comparison of Black and Silica filled vulcanizates[a]

	NR		ENR-25		ENR-50	
	Black	Silica	Black	Silica	Black	Silica
Hardness (IRHD)	65	69	69	67	73	68
Modulus at 300% (MPa)	11.9	5.8	12.4	12.8	13.5	12.6
Tensile strength (MPa)	29.4	23.2	25.4	21.0	24.5	22.4
Elongation at break (%)	495	720	435	405	500	435
Akron Abrasion (mm^3/500 rev)	21	63	14	15	11	14
Compression Set (%)	18	32	17	18	21	22
Ring Fatigue (0-100%) Kcs.	70	51	65	52	93	58

[a] 50 phr silica or N330 black in Semi EV formulation (S 1.5 phr/MBS 1.5 phr) cured to optimum at 150°C.

The epoxidation of NR results in significant property changes, which open up new market areas. Potential applications include oil resistant products, adhesives, high wet grip and low rolling resistant tyre tread compounds, inner tubes and tyre liners and belting. Current estimates from a one tonne pilot plant indicate that on a commercial basis ENR should be price competitive with the synthetic materials.

CONCLUSIONS

Chemical modification of NR can be used to produce new materials, which can compete both technically and economically with certain oil based synthetic elastomers. In the longer term other forms of modified NR should become cost competitive as oil based products become more expensive.

Every tonne of synthetic rubber that can be replaced by a naturally derived product will save in the region of three tonnes of crude oil. This assumes that the modification chemistry is not based on crude oil or energy intensive, which is true in the case of ENR and the other modifications described.

Any increased demand for NR can readily be met. Currently the NR yield in Western Malaysia is 1300 Kg/hectare/year, but new clones have been developed which can produce up to 5000 Kg/hectare/year and yield stimulants can further increase the immediate supply of NR.

REFERENCES

1. B. L. Archer, D. Barnard, E. G. Cockbain, P. B. Dickenson and A. I. McMullen, Composition of Hevea Latex, in: "The Chemistry and Physics of Rubber-Like Substances", L. Bateman, ed., Maclaren & Sons Ltd., London (1963).
2. C. D. Harries, "Untersuchungen uber die Naturlichen und kunstlechen Kaukschukarten", Springer, Berlin (1919).
3. R. Pummerer, G. Ebermeyer and K. Gerlach, Ber, 64, 809(1931). R. Pummerer, G. Matthews and L. Socias-Vinals, Ber, 69, 170 (1936).
4. M. A. Golub, M.S. Hsu and L. A. Wilson, Rubber Chem. Tech., 48, 953 (1975).
5. F. Burton, Product energy in the rubber industry, Elastomerics, 22 (1978).
6. J. Le Bras and A. Delande, "Les Derives Chemiques du Cautchouc Natural", Dunod, Paris (1950).
7. G. F. Bloomfield and E. H. Farmer, J. Soc. Chem. Ind. 53, 43T, 47T (1934).
8. G. J. Van Veersen, Proceedings Second Rubber Technical Conference, London (1948).
9. H. L. Fisher, Ind. Eng. Chem., 19, 1325 (1927).
10. J. I. Cunneen, C. G. Moore and B. R. Shephard, J. Appl. Polymer Sci., 3 (7), 11 (1960).
11. M. L. Kaplan, P.G. Bebbington and R. L. Hartless, J. Polym. Sci. Polym. Lett. Ed., 11, 357 (1973)
12. C. Pinnazzi, J. C. Danjard and R. Pautrat, Proc. Nat. Rubber Conference, Kuala Lumpur, 555, (1960).
13. A. C. Udding, British Patent 1,343,554 (1972).
14. C. Pinazzi, R. Pautrat and R. Cheritat. Makromolek. Chem., 70, 260 (1964).
15. M. E. Cain, K. F. Gazeley, I. R. Gelling and P. M. Lewis, Rubber Chem. Technol, 45 204 (1972).

16. C.S.L. Baker, Kautschuk und Gummi, 36, 677 (1983).
17. H.M.R. Hoffmann, 'The ene reaction', Angew. Chem. Int. Ed. 8 (8) 556 (1969).
18. D. Barnard, K. Dawes and P. G. Mente, 'Chemical Modification of Natural Rubber', Proc. Int. Rubber Conf., Kuala Lumpur, 4,215 (1975).
19. K. Dawes and R. J. Rowley, Chemical Modification of NR - a new silane coupling agent. Rubbercon 77, Paper 18, Brighton, England (1971).
20. D. S. Campbell and A. J. Tinker, Polymer, 25, 1146 (1984).
21. D. S. Campbell, P. G. Mente, A. J. Tinker, Kautschuk und Gummi Kunststoffe, 34, 636 (1981).
22. D. S. Campbell, D. J. Elliott and M. A. Wheelans, NR Technology, 9, 21 (1978).
23. I. R. Gelling and J. F. Smith, Proceedings of Int. Rubber Conf., Venice, 1, 140 (1979).
24. British Patent Appl. 2, 113, 692 (1983).
25. C.S.L. Baker, I. R. Gelling and R. Newell, Rubber Chem. Technol., 58 (1) 67, (1985)
26. H. V. Gemmer and M. A. Golub, J. Polymer Sci. (Chem. Ed) 16, 2985 (1978).
27. I. R. Gelling, Rubber Chem. Tech , 58 (1), 86 (1985).
28. J. E. Davey and M. J. R. Loadman, British Polym. J., 16, 134 (1984).
29. I. R. Gelling and N. J. Morrison, Rubber Chem. Tech. 58(2), 243 (1985).
30. C. Davies, S. Wolfe, I. R. Gelling and A. G. Thomas, Polymer, 24, 107 (1983).
31. L. P. Witnauer and D. Swern, J. Amer. Chem. Soc., 72 3364 (1950).