EXPLORATORY TECHNOLOGY GROUP

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(Paper given at NR Day
Poznan, Poland -
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Subject Epoxidized NR

Ref. Project No. 122 T.E. No.

Objective

To evaluate the preparation and properties of epoxidized NR with a view to commercialization.

Summary and Conclusions

Epoxidized NR can be prepared simply and cleanly from NR latex by reaction with organic peracids. Samples have been prepared with epoxide contents from 1 to 90 mole %.

Standard sulphur formulations can be used to vulcanize these materials. With increasing levels of epoxidation the glass transition temperature (Tg) increases with consequent changes in dynamic properties. Epoxidized NRs stress crystallise, have lower rates of stress relaxation than synthetic elastomers with similar resiliencies and have reduced air permeability and improved oil resistance.

Future Work

Further evaluation of properties especially in the presence of fillers. Scaling up of the preparation using a commercially viable method.

Natural Rubber Day Poznan, 25th/26th September, 1979

Epoxidized Natural Rubber

by

I.R. Gelling and J.F. Smith

Introduction

Natural Rubber (NR) is a material that has a very good balance of elastomeric properties and seems destined to remain in use as a general purpose rubber for the foreseeable future. It has, however, experienced continual erosion of some of its traditional uses by special purpose synthetic rubbers which are more particularly suited to certain applications. These special purpose rubbers have also created entirely new applications for rubbery materials.

Chemical modification of NR[1] has for many years been recognised as a potential method for producing new materials. Cyclized, chlorinated and hydrochlorinated NR were produced commercially but have been largely superseded by synthetic products. The increasing costs of petrochemical based materials, including the special purpose polymers is changing the economic status of chemical modification of NR. If modification leads to exceptional properties or if the modification process is a particularly easy one, serious consideration of such modifications now seems warranted.

Epoxidation of NR and other elastomers is well known[2,3,4]. It is one of the simplest chemical modifications of unsaturated elastomers that can be envisaged. This paper will discuss our recent work on the epoxidation process and describe the physical properties of epoxidized NR.

Epoxidation of NR

Epoxidation in solution cannot be considered as a commerically viable process for NR. The cost of preparing a suitable solution of NR and recovering the modified rubber from the solution would be prohibitive. The preferred starting material for all chemical modifications of NR is field latex. Direct epoxidation of latex has been reported for a range of unsaturated polymers[4,5,6,7]. It has also been recognised that secondary ring-opening reactions can give rise to other modifications mainly hydroxy, acetoxy[8] and substituted furans[9].

We have found that NR latex can be epoxidized to very high levels without side reactions provided certain specific precautions are taken. The precautions are:

1. The peracid used must be free from strong mineral acid.

2. The over-all acid concentration must be kept low. As the required level of epoxidation increases the latex must be diluted to compensate for the increased amount of peracid required.

3. The temperature must be maintained below 20°C throughout the reaction.

4. The latex must be washed very thoroughly on a crepe mill to remove all traces of acid before drying.

For laboratory work, low ammonia latex concentrate stabilized with TMTD and zinc oxide was diluted prior to use and stabilised with Ethomeen 18/60, a non-ionic surfactant. The peracid was a solution of peracetic acid (35% w/v) in acetic acid free from strong mineral acids.

Epoxidized NR's with epoxide levels from 10 to 90 mole % have been prepared. The level of epoxidation can be estimated by ^1H nuclear magnetic resonance (nmr) spectroscopy using the characteristic resonances shown in Fig 1 or alternatively from a glass transition temperature calibration curve.

The epoxidized NR materials discussed in the remainder of this paper were prepared with full precautions against side reactions. The absence of groups other than the simple epoxide ring was confirmed by nmr analysis.

Properties of Epoxidized NR

Epoxidation of NR increases the glass transition temperature (Tg) of the polymer in a linear manner from -72° for NR to +5°C for 100 mole %

a.

epoxidized NR (Fig 2) as determined by differential scanning colorimetry (DSC). Mechanical transitions (Tm) involving a peak in the phase angle and associated changes in stiffness are related to the Tg. Epoxidized NR should thus exhibit changes in related properties with increasing levels of epoxidation.

Partially epoxidized NR can be crosslinked with peroxide reagents but the efficiency of the crosslinking reaction decreases rapidly at epoxide levels of over 50 mole % (half the NR double bonds have been replaced by epoxide groups). The crosslinking is presumably completely dependent upon the residual double bonds.

Epoxidized NR vulcanizates, up to 90 mole % epoxidation, have been prepared from a range of standard sulphur formulations, conventional high sulphur to sulphurless TMTD/ZnO. Fig 3 compares Monsanto Rheographs for NR and 50% epoxidized NR using a recipe based on 0.6 phr 2-morpholinothiobenzothiazole (MOR) and 2.5 phr sulphur and Fig 4 shows similar Rheographs for a mix based on tetramethylthiuram disulphide (TMTD) with no free sulphur.

Gum sulphur vulcanizates of epoxidized NR retain the high tensile strength of NR gum compounds. The tensile properties of a series of epoxidized NR's compounded with MOR (0.6)/S (2.5) and TMTD (3.0)/ZnO (5.0) are recorded in Table 1. This data suggests that epoxidized NR like NR can undergo stress crystallisation even at high levels of modification. The air ageing of epoxidized NR vulcanizates compounded with a high sulphur system is inferior to that of NR (Fig 5), however as the level of sulphur in the formulation is reduced the air ageing improves. The air ageing of a 50% epoxidized NR TMTD/ZnO vulcanizate is comparable to the corresponding NR control.

Some further properties of epoxidized NR's are recorded in Table 2. Increasing the level of epoxidation results in improved fatigue and abrasion resistance, as measured by the Akron test. The improvement in abrasion is probably due at least in part to the increase in hysteresis, Schallamach[10] has shown that hysteresis is an important factor in the abrasion testing of rubbers using slipping wheels.

Fig 6 shows the rebound resilience data in more detail. The curves for the individual epoxidized NR samples show fairly sharp minima and the temperature range over which any individual sample shows high damping is narrow. For practical applications a much broader temperature bandwidth would be required, this can be achieved by blending equal proportions of 25, 50 and 90% epoxidized NR.

Considering the tensile and rebound resilience results together, it can be seen that high damping behaviour at ambient temperatures can be achieved without loss of the high strength and low stress relaxation characteristics of normal NR vulcanizates. This contrasts sharply with the gum vulcanizates of recognised high damping rubbers such as acrylonitrile-butadiene copolymers and butyl rubber which suffer from high stress relaxation and low strength.

Related to the increase in Tg of epoxidized NR and consequent increas in hysteresis at ambient temperature is a marked improvement in wet skid resistance. Comparative wet skid resistance figures for smooth and rough concrete surfaces are recorded in Table 3 for different levels of epoxidation. Optimum skid resistance occurs at 50% epoxidation where the rubber exhibits maximum damping at the temperature of the test (20°C). Under service conditions in the wet, where a tyre surface temperature may be somewhat above ambient, a higher level of epxodiation may be more advantageous. Resistance to skidding on ice at -10°C is adversely affecte by increasing levels of epoxidation. A useful compromise for a tyre application may lie in the region of 25% epoxidation but more work will be necessary to evaluate this possible applicational area.

Epoxidation of NR progressively decreases its air permeability. The permeabilities of NR, epoxidized NRs and some low-permeability synthetic rubbers are summarised in Table 4. The permeabilities are rated relative to an NR control of 100. At 75% epoxidation the epoxidized NR is comparable in performance to butyl rubber and acrylonitrile-butadiene copolymer. Epoxidized NR is to be evaluated as liners for tubeless tyres, as there is an adhesion problem with the material presently in use.

Finally, epoxidation of NR significantly increases its resistance to swelling by hydrocarbons and conversely, decreases its resistance to swelling by polar liquids such as brake fluid. Some representative swelling figures are given in Table 5. At 75% epoxidation, very good resistance to hydrocarbon oils can be obtained and although susceptibility to brake fluid is markedly increased there is no corresponding increase in susceptibility to water.

Although the evaluation of epoxidized NR is only at a relatively early stage, the properties obtained to date and ease of preparation indicate that serious consideration of this modified NR is warranted.

References

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Fig 1

Epoxidation of NR Latex with Peracetic Acid.

Low Acid Concentration; Temperature <20°C.

H^1 n.m.r. Spectra in $CDCl_3$ (p.p.m., HMDS 0·05 p.p.m.).

Fig 2

Variation of Tg with Level of Epoxidation of NR.

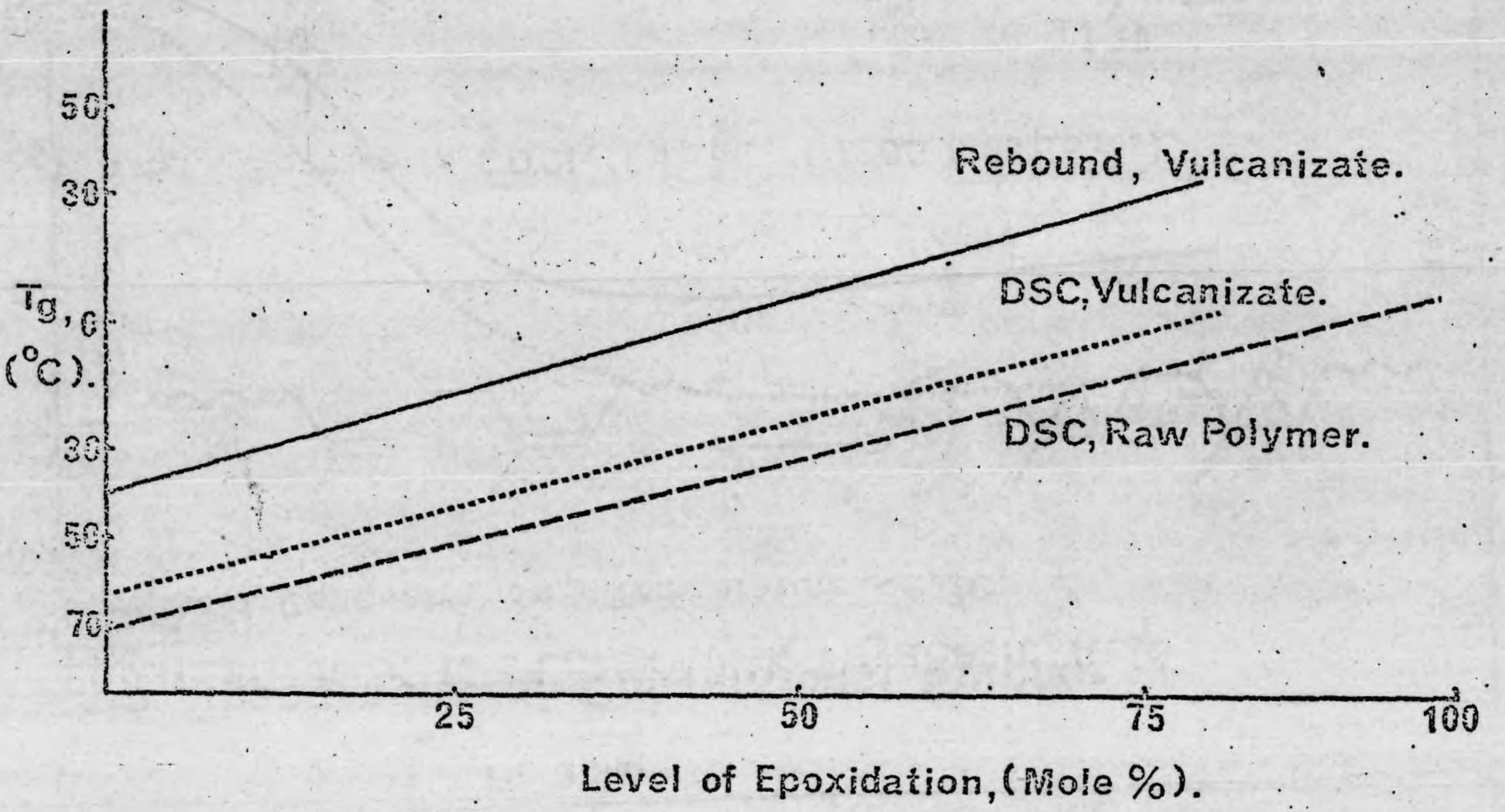

Fig 3

Monsanto Rheographs of Conventional Sulphur Formulations.

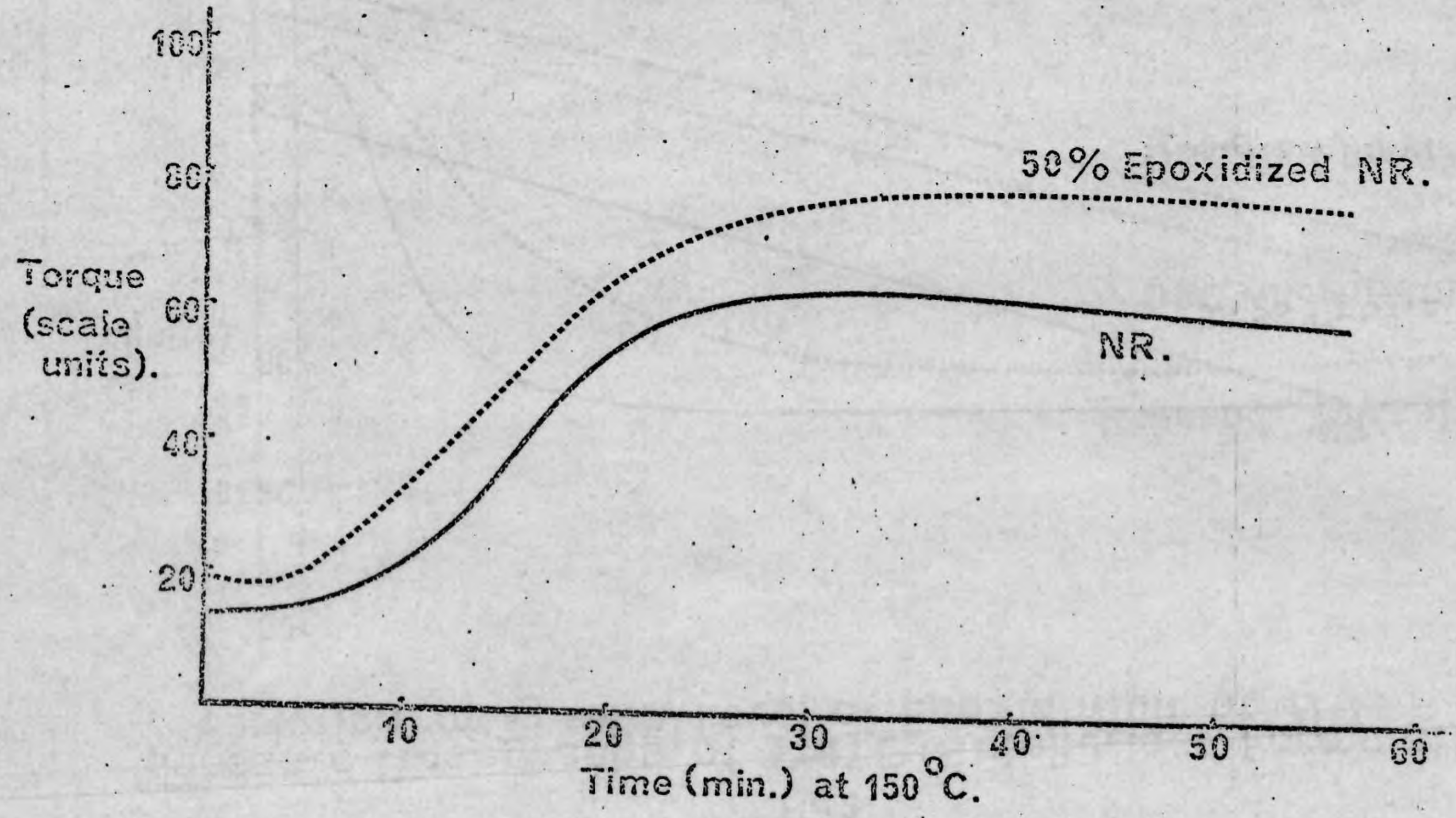

Fig 4

Monsanto Rheographs of TMTD Sulphurless Formulations.

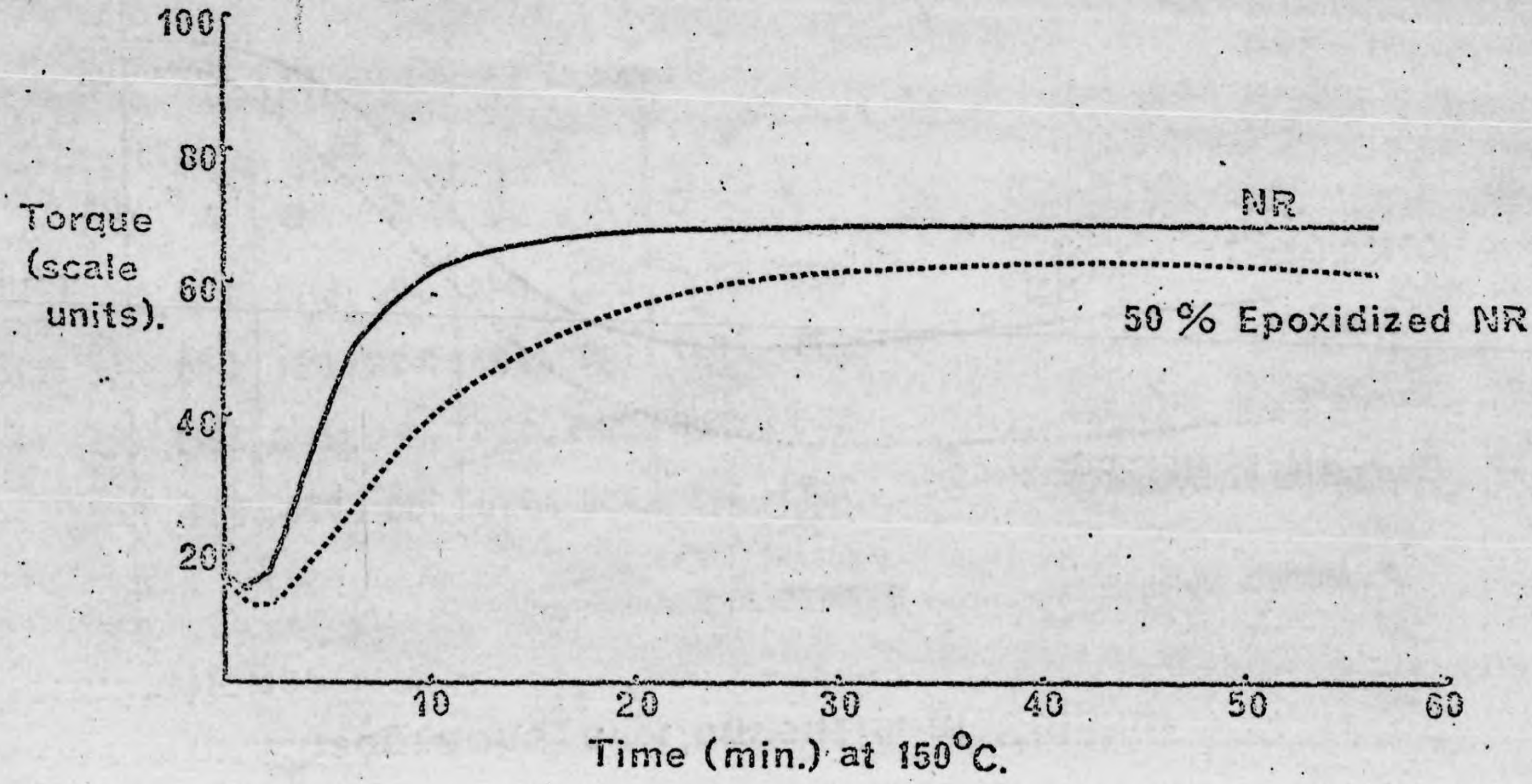

Fig 2

Variation of Tg with Level of Epoxidation of NR.

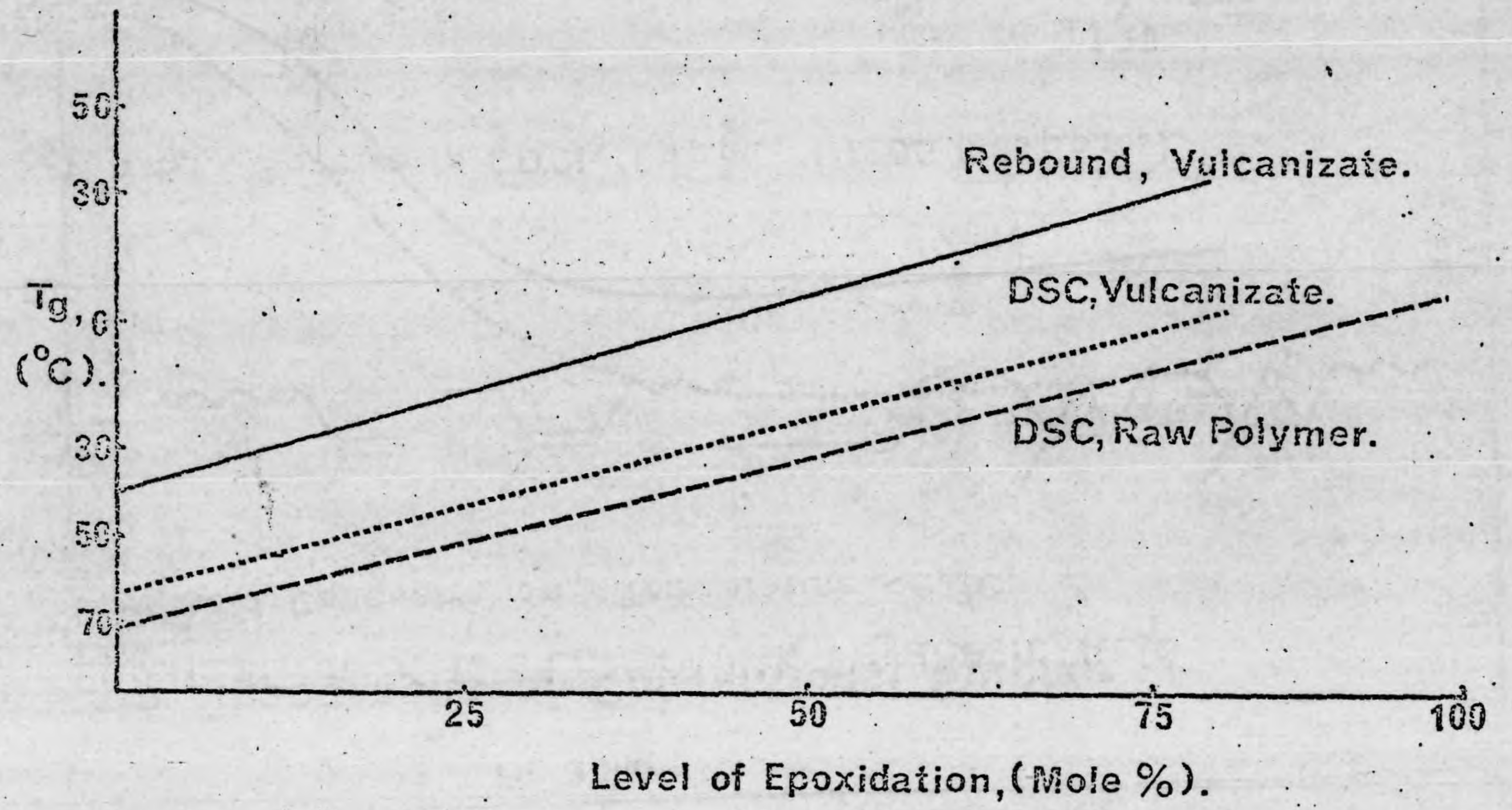

Fig 3

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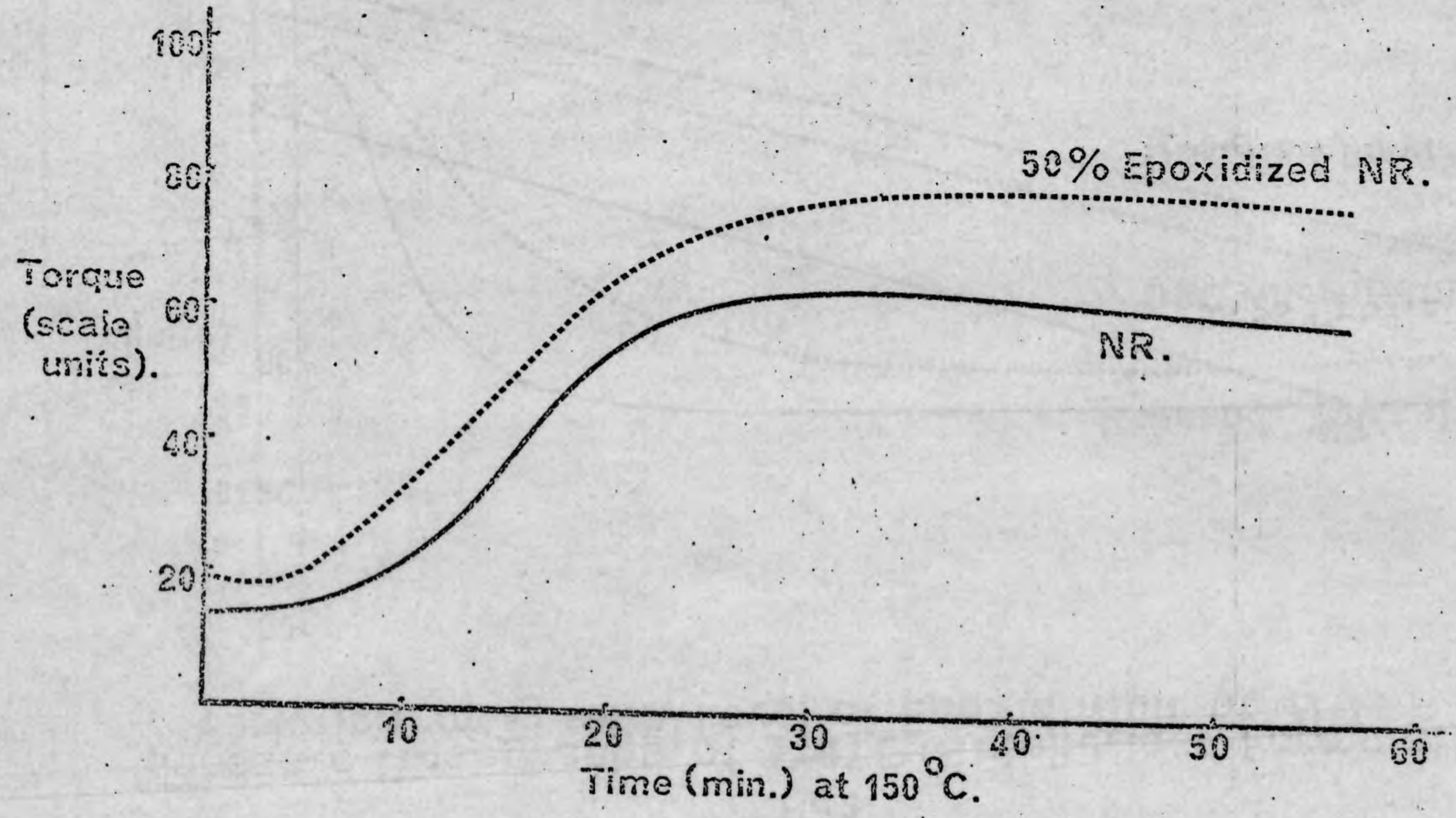

Table 1

Tensile Properties of Epoxidized NR Gum Vulcanizates

	Level of Epoxidation (%)							
	0		25		50		75	
	A	B	A	B	A	B	A	B
M 100 (M Pa)	0·73	0·67	0·63	0·58	0·78	0·69	1·06	0·79
M 300 (M Pa)	1·70	1·47	1·41	1·21	2·23	1·51	3·00	1·64
Tensile Strength (M Pa)	25·3	22·3	23·6	19·5	31·4	21·6	28·9	18·3
Elongation at Break (%)	769	743	799	770	758	728	622	721

A, MOR/S Vulcanizate. B, TMTD/ZnO Vulcanizate

Fig 5

Ageing of 50 mole% Epoxidized NR Vulcanizates

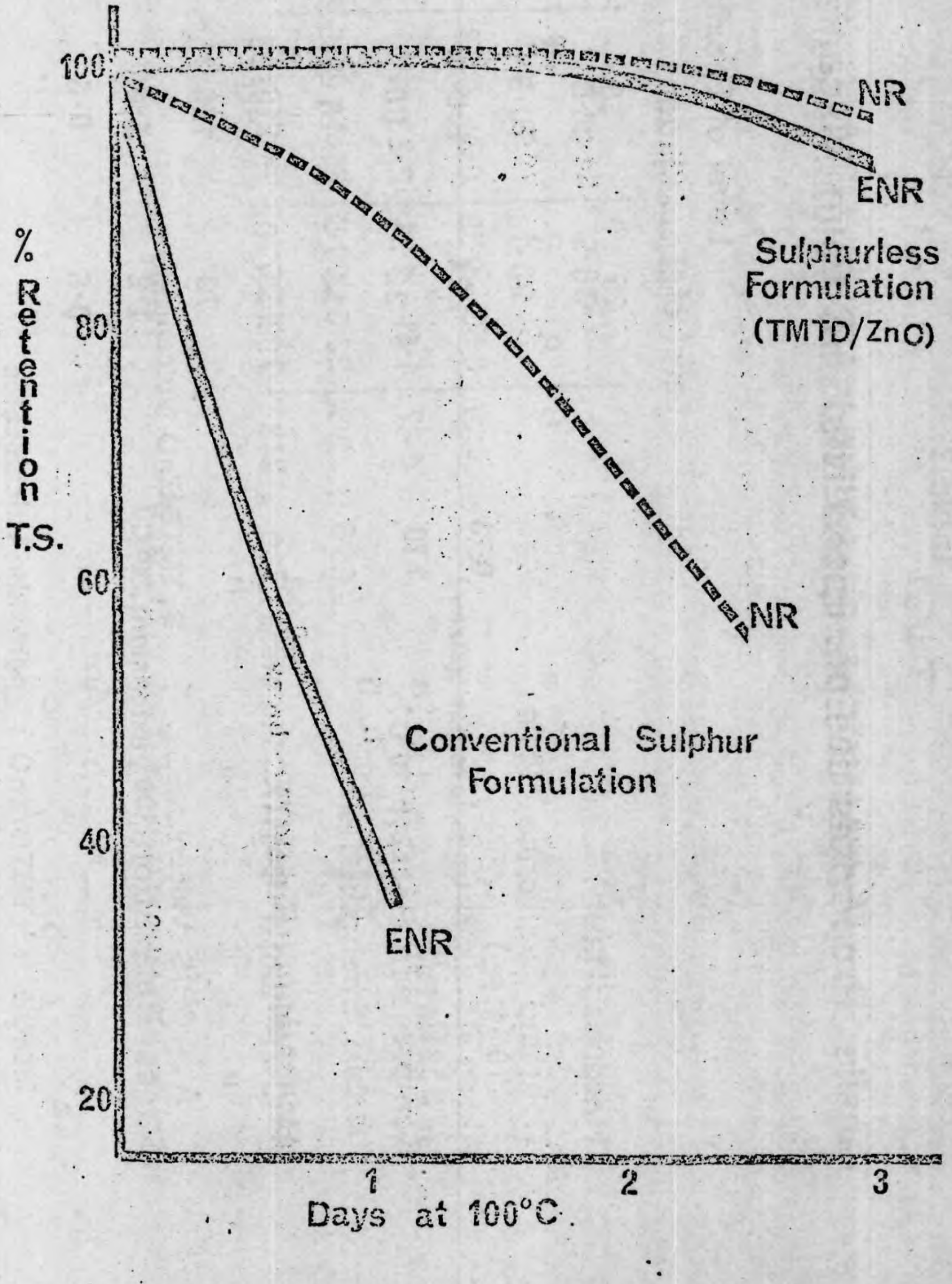

Table 2

Properties of Epoxidized NR Gum Vulcanizates

	Level of Epoxidation(%)			
	0	25	50	75
Hardness(IRHD)[a]	35·5	34·5	37	37
Rebound Resilience %(23°C)[a]	90·1	70·8	45·2	5·0
Akron Abrasion(mgs.loss per 500rev)[a]	224	169	24	8
Compression Set(24h/70°C)[a]	22	30	36	44
" " "[b]	14	8	7	6
Ring Fatigue(0–100%)(KCS to break)[a]	155	216	238	191
" " "[b]	70	124	142	293
Stress Relaxation(100% extension; 30°C)[a]	1·2	1·4	1·4	1·2
" " "[c]	0·6	0·6	0·7	0·9

[a] MOR/S ; [b] TMTD/ZnO ; [c] peroxide; vulcanizates.

Fig 6

Rebound Resilience of Epoxidized NR Vulcanizates.

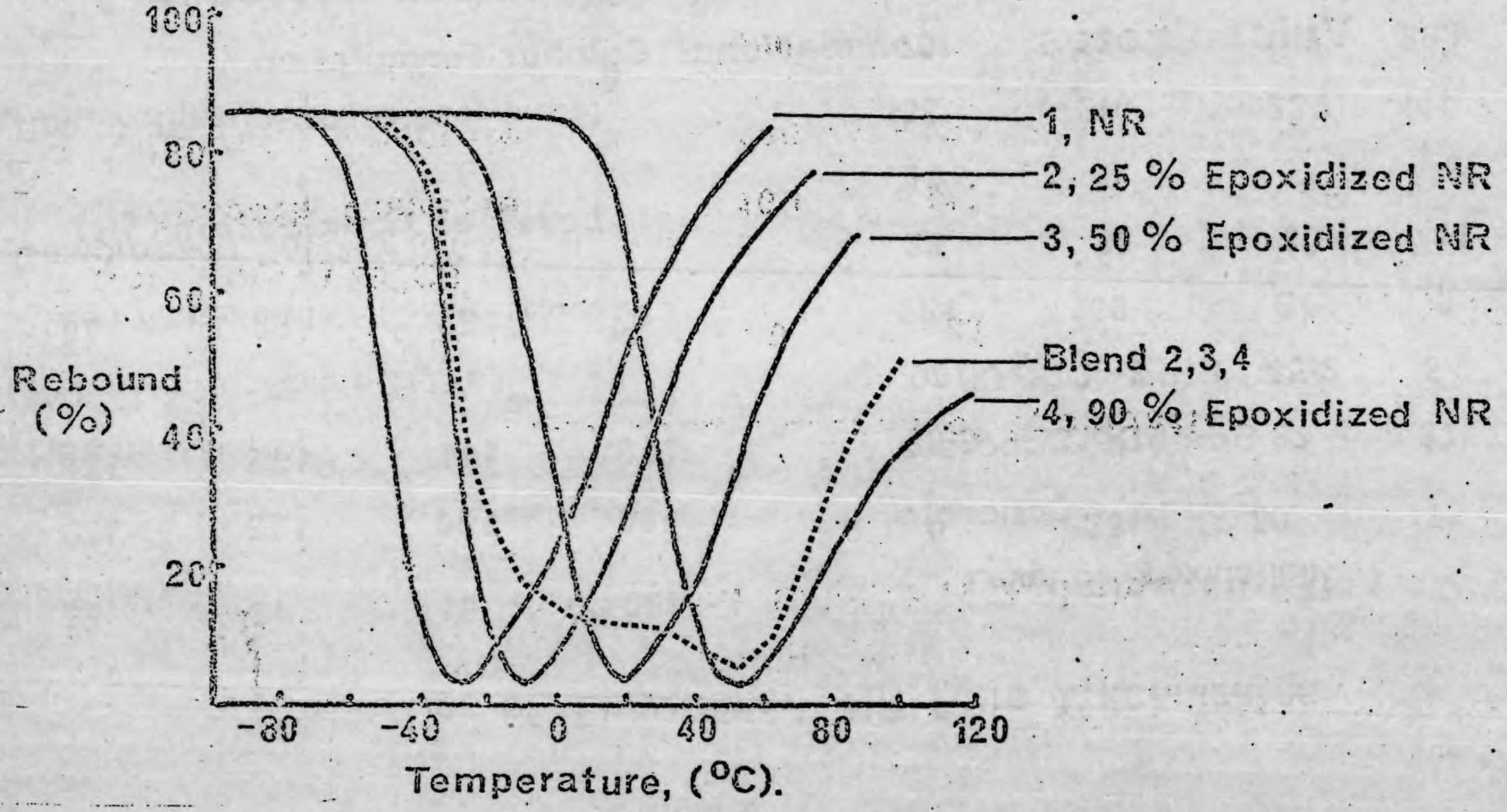

Table 3

Relative Skid Resistance of Epoxidized NR Gum Vulcanizates. Conventional Sulphur Formulation.

	Level of Epoxidation (%)			
	0	25	50	70
Wet Skid (20°C.)				
Smooth Concrete	100	141	156	124
Rough Concrete	100	130	132	118
Ice Skid (−10°C.)	100	91	48	27

Table 4

Relative Air Permeabilities of Elastomers.

NR	100
25% Epoxidized NR	30
50 % Epoxidized NR	12
75 % Epoxidized NR	5
SBR-1500	50
Butyl Rubber	5
Acrylonitrile/butadiene copolymer (40:60)	3

Table 5

Swelling of Epoxidized NR Gum Vulcanizates.

Conventional Sulphur Formulation; % Wt. Increase at Stated Time.

Swelling Agent	Level of Epoxidation (%)			
	0	25	50	75
n-Decane (equilibrium)	178·0	–	18·0	1·8
ASTM No.1 Oil (15 days)	63·5	10·1	0·8	0·3
ASTM No.3 Oil (15 days)	235·4	131·4	16·1	1·3
Water (28 days)	2·9	1·9	3·1	2·9
Engine Oil (70 days)	165·0	52·5	42·0	0·01
Brake Fluid (20 days)	3·0	12·0	32·0	57·5