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Influence of Grade of Natural Rubber on Reversion Behaviour

G.M. BRISTOW*

The reversion behaviour of fifty samples of natural rubber, compounded in a conventional cure system (2.5 p.p.h.r. sulphur, 0.5 p.p.h.r. CBS) has been studied by oscillating disc rheometry at 160°C - 180°C. Over all the samples, the reversion rate varied by a factor of ca. *1.8. Further, while there was considerable scatter, on an average field coagulum grades, such as TSR 20, reverted some 14% faster than grades such as RSS and SMR CV which are prepared by the acid coagulation of latex. The same feature was evident in more limited studies at 100°C - 120°C. The dependence of reversion rate on temperature conforms to the Arrhenius relation with an activation energy of* ca. *104 kJ/mol, independent of grade. This value is* ca. *10% greater than the activation energy for vulcanisation for which published values are* ca. *95 kJ/mol. The rate of reversion decreases with time and the activation energy depends on the extent of reversion. Hence, like vulcanisation, reversion is presumably a complex process. The possibility is mooted that reversion rate assessed in this manner could be used as a further measure of natural rubber quality.*

Reversion, that is the decline in physical properties, such as modulus and resilience, as a consequence of overcure or the exposure of vulcanisates to anaerobic ageing, is a well known feature of natural rubber. The phenomenon is most commonly associated with vulcanisation at high temperatures as, for example, in injection moulding but it is also evident after prolonged exposure of vulcanisates to more modest temperatures as, for example, in heavy duty truck tyres[1]. While the practical significance of reversion lies in the effect on vulcanisate properties, as with cure behaviour, the phenomenon can be most conveniently monitored by rheometer measurements. A typical rheograph for a natural rubber compound prone to reversion is given in *Figure 1*. It is not the purpose of this paper to discuss the chemical changes associated with reversion but it is self evident that the torque-time trace of *Figure 1* results from the interplay of one or more crosslinking processes with reactions resulting in crosslink destruction.

Since reversion is an obviously undesirable feature of natural rubber vulcanisates, it is not surprising that various compounding methods have been developed to offset or minimise its effects. The oldest and best known of these is the use of so-called efficient or semi-efficient vulcanisation systems with relatively high levels of accelerator to sulphur. More recently, balanced cure systems[2] and specific additives[3] have been developed.

The cure behaviour of all grades of natural rubber is influenced to a greater or lesser extent, depending upon the formulation, by the non-rubber species invariably present. The nature of the latter is very dependent on the production procedure employed and hence on the grade or type of rubber. The influence of formulation is especially evident in the ACS 1 mix, which was specifically developed[4] to show maximum response to non-rubbers. Rheographs for typical samples of natural rubber compounded in the ACS 1 system are given in *Figure 2*. While such effects have been

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*Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom

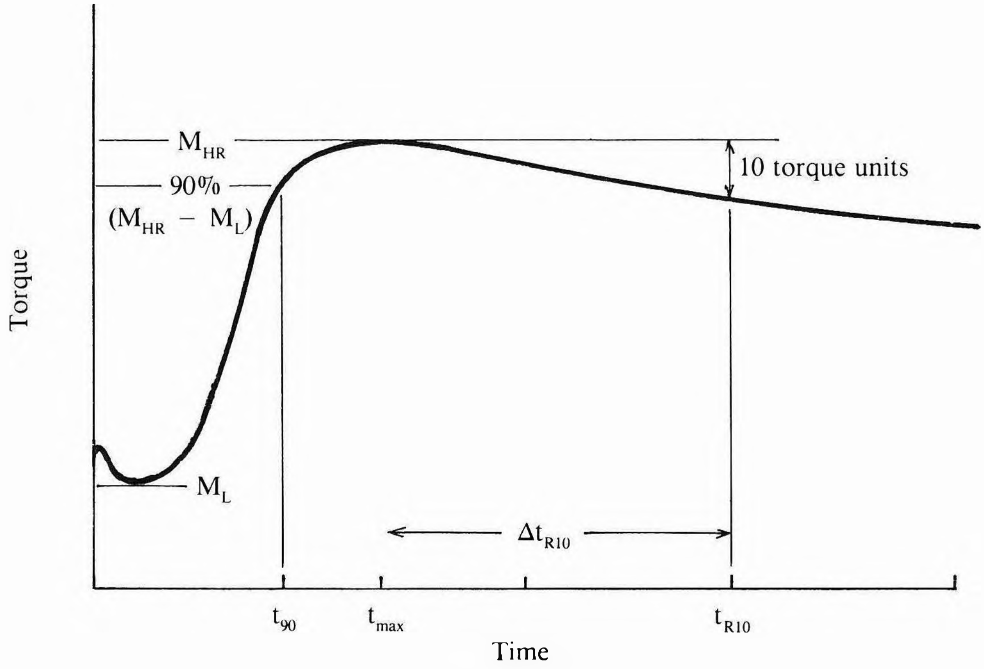


Figure 1. Typical rheograph for a natural rubber compound prone to reversion.

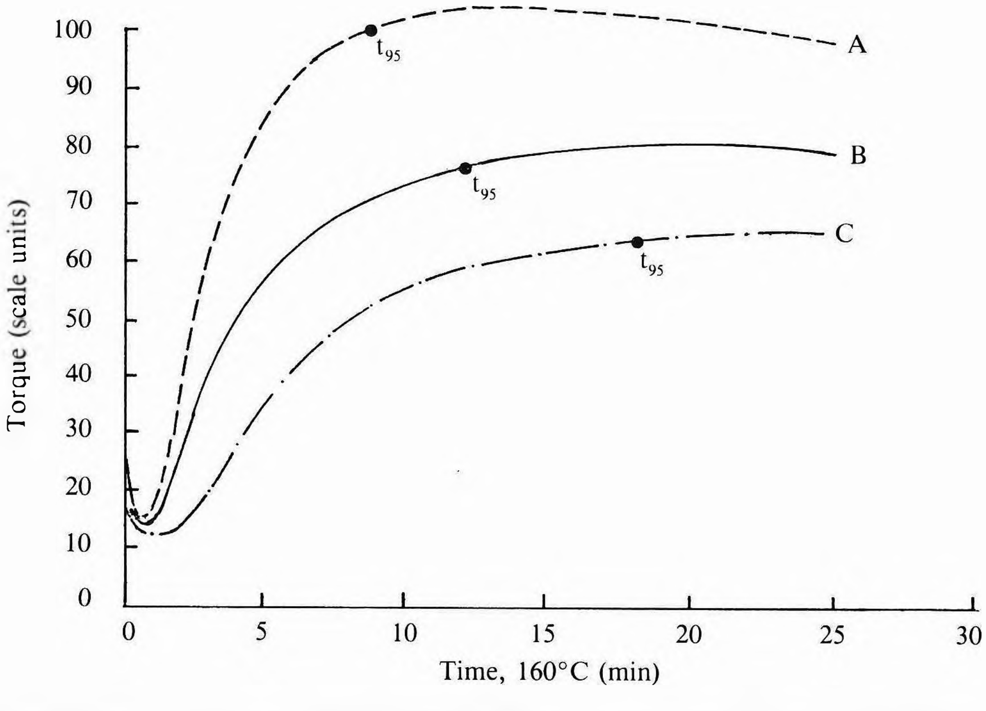
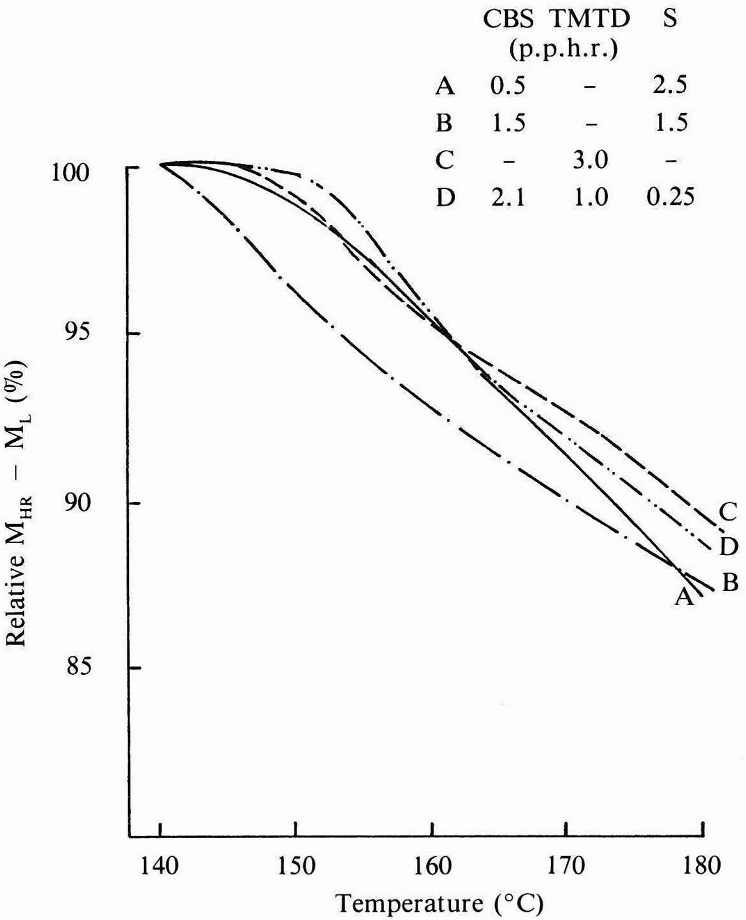


Figure 2. Rheographs for samples of natural rubber when compounded with the ACS 1 recipe.



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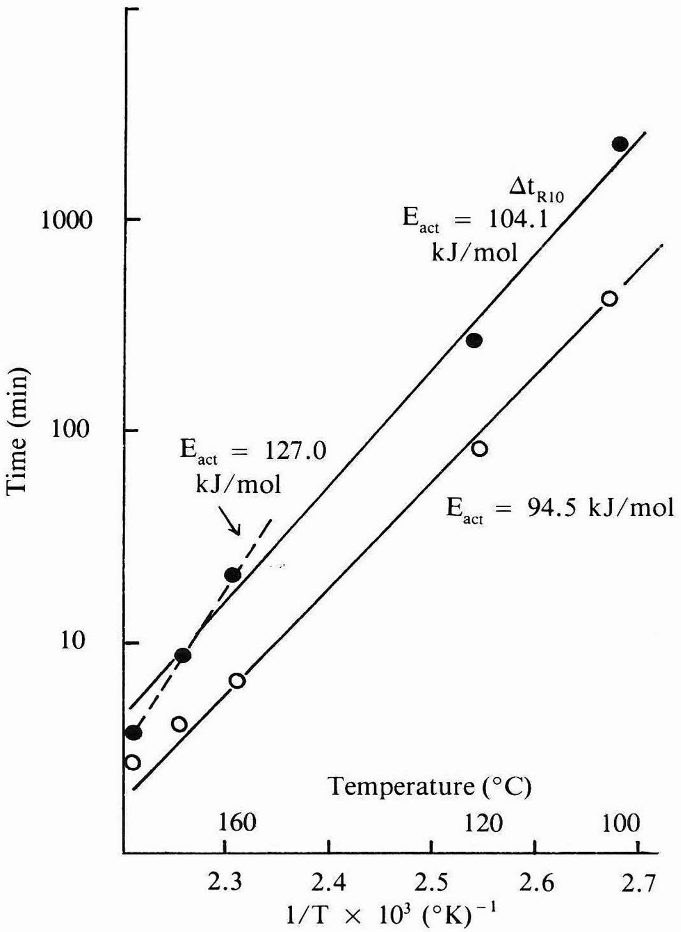

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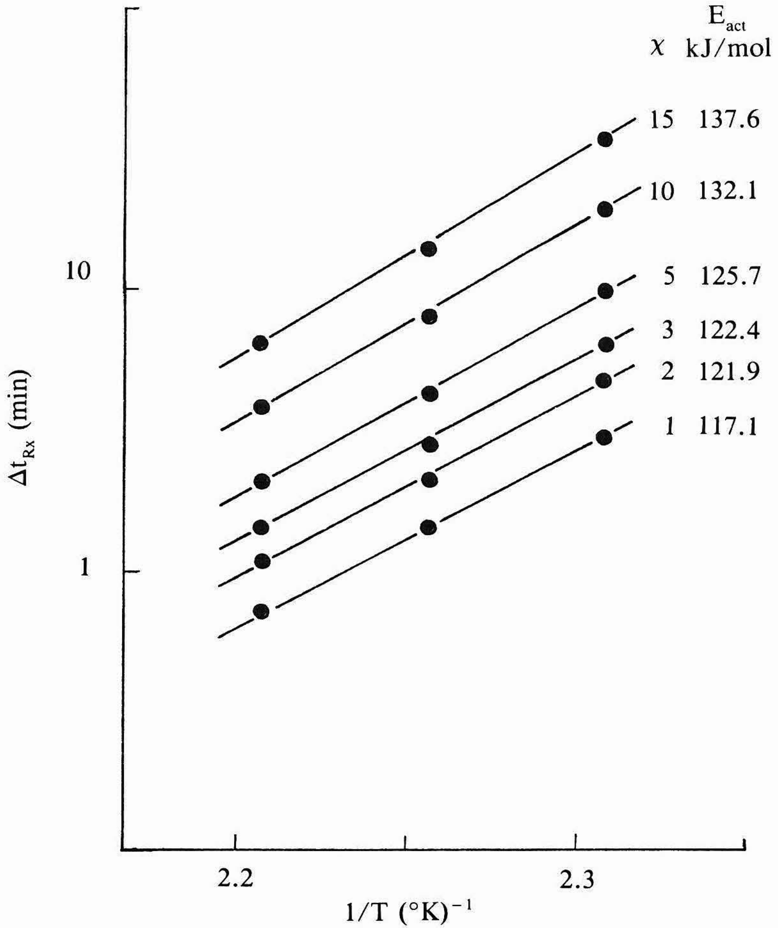

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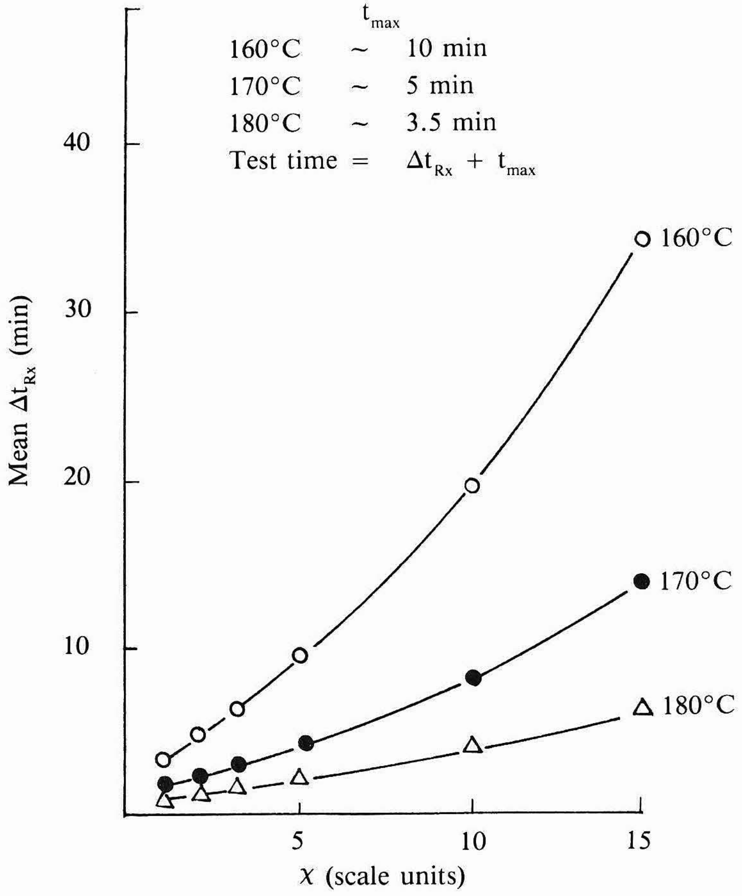


Figure 6. Mean values of Δt_{Rx} as a function of x at 160°C–180°C for nine samples of natural rubber.

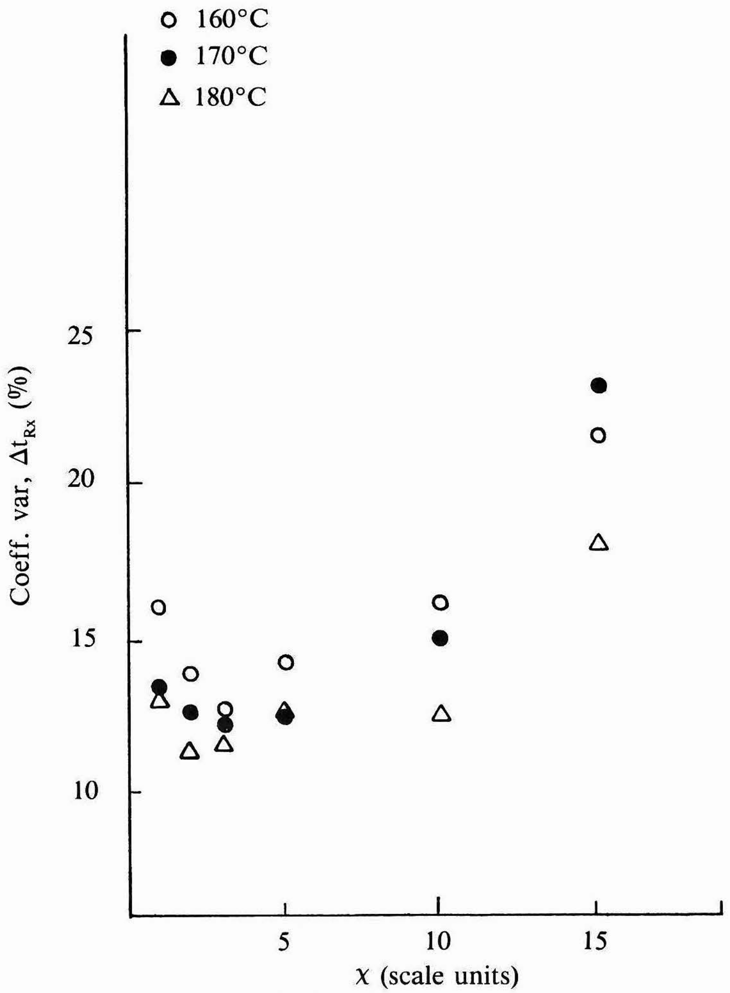


Figure 7. Coefficient of variation of Δt_{Rx} over nine samples of natural rubber.

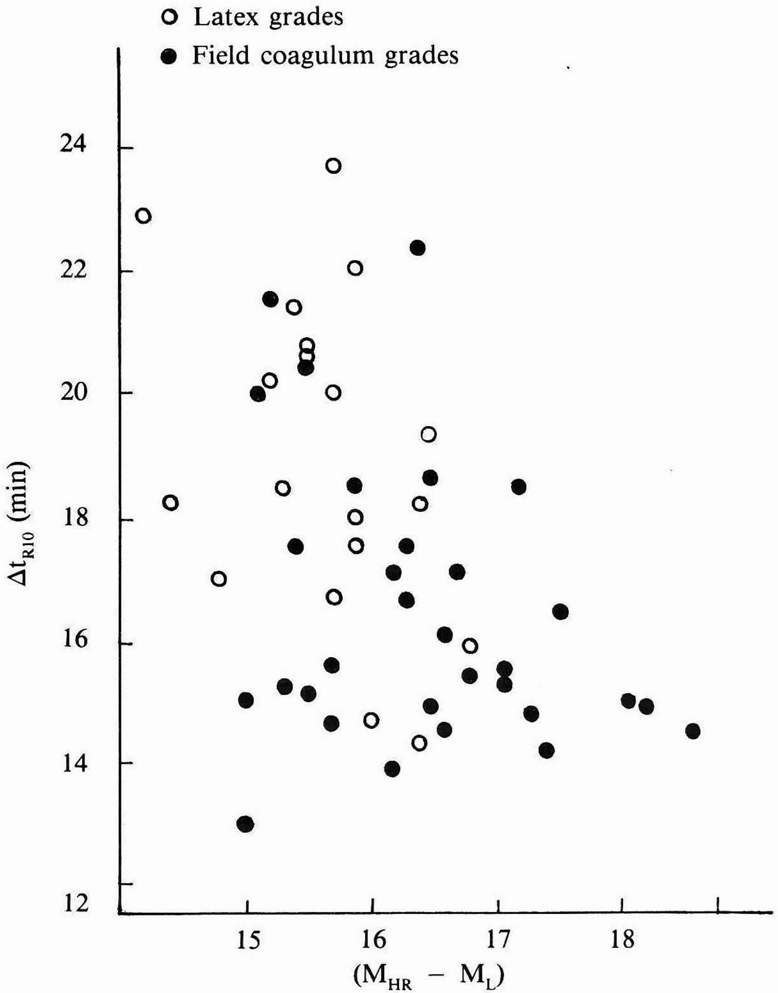
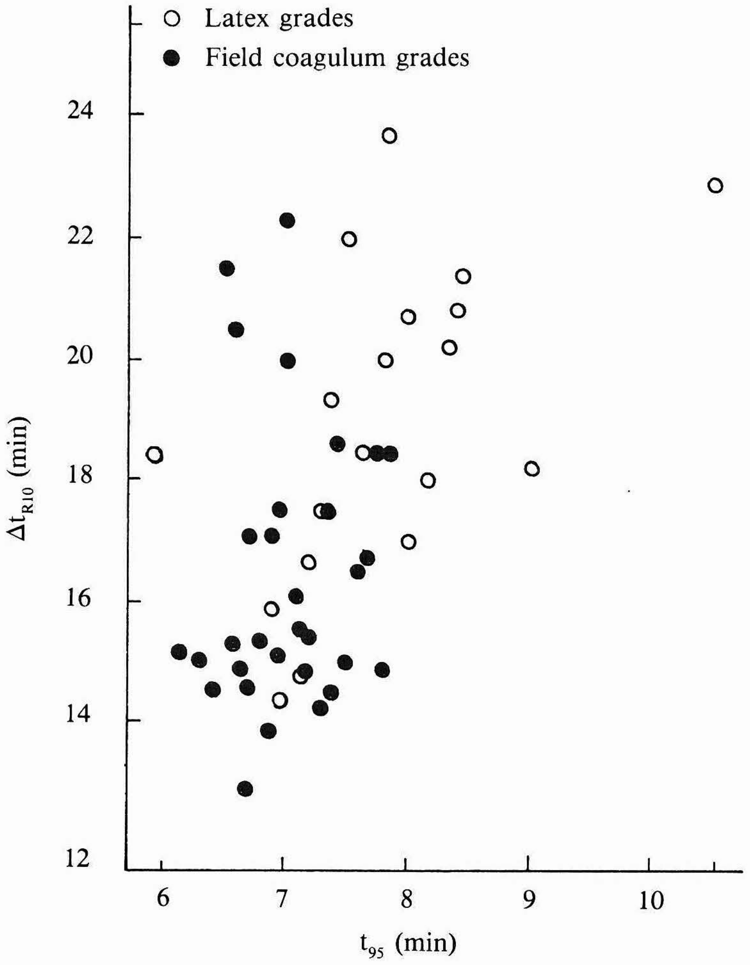


Figure 8. Reversion at 160°C and expressed as Δt_{R10} for fifty samples of natural rubber as a function of $M_{HR} - M_L$.



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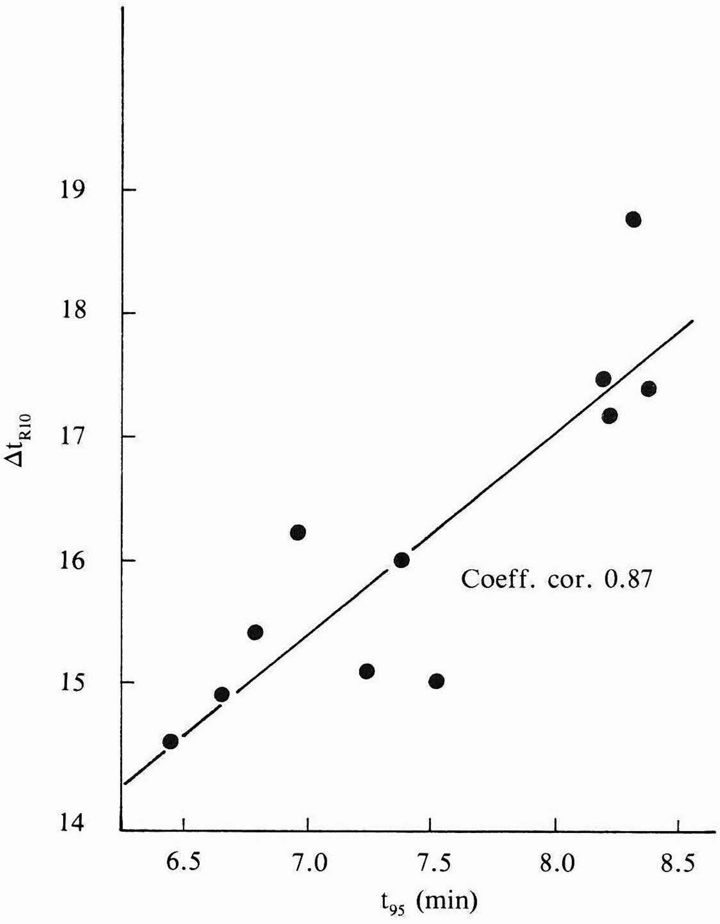

Figure 10. Correlation between Δt_{R10} and t_{95} for eleven samples of TSR 10 from a single production lot.

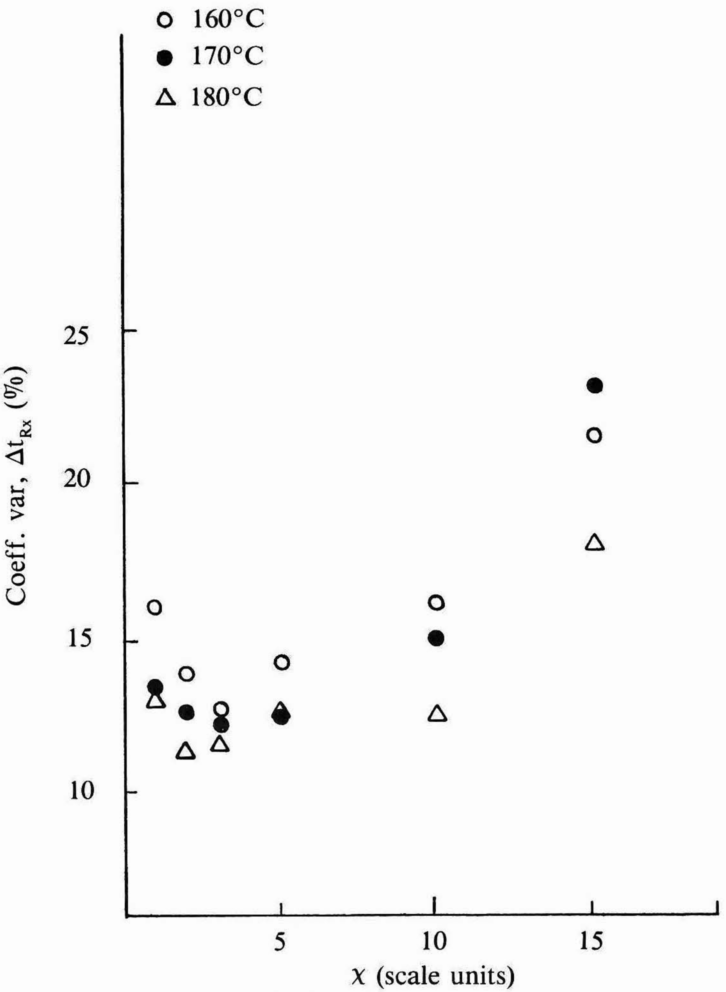

Figure 7. Coefficient of variation of Δt_{Rx} over nine samples of natural rubber.

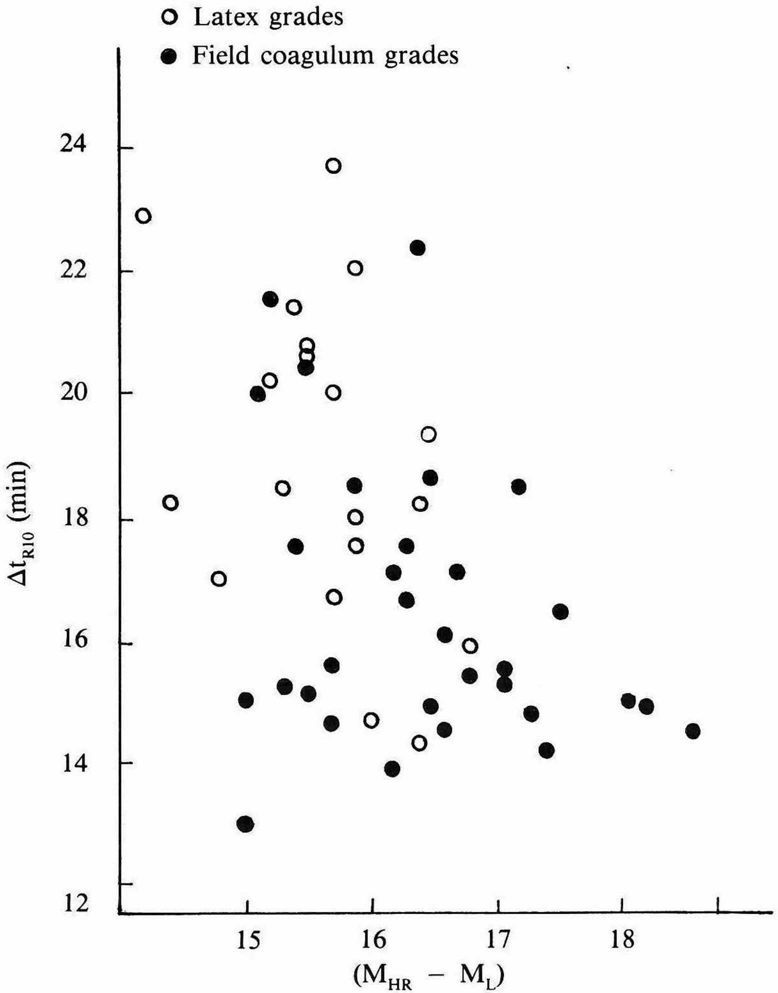

Figure 8. Reversion at 160°C and expressed as Δt_{R10} for fifty samples of natural rubber as a function of $M_{HR} - M_L$.

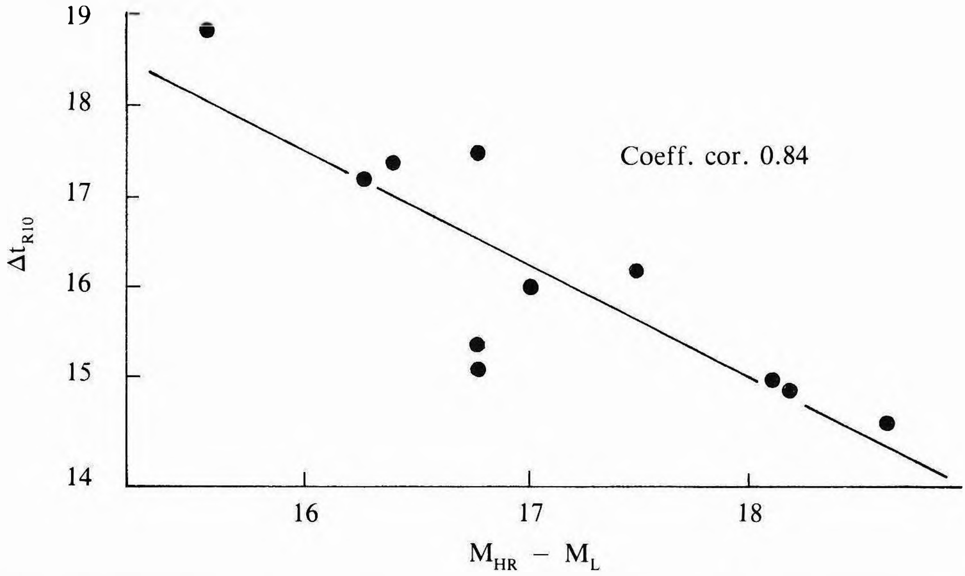

Figure 11. Correlation between Δt_{R10} and $M_{HR} - M_L$ for eleven samples of TSR 10 from a single production lot.

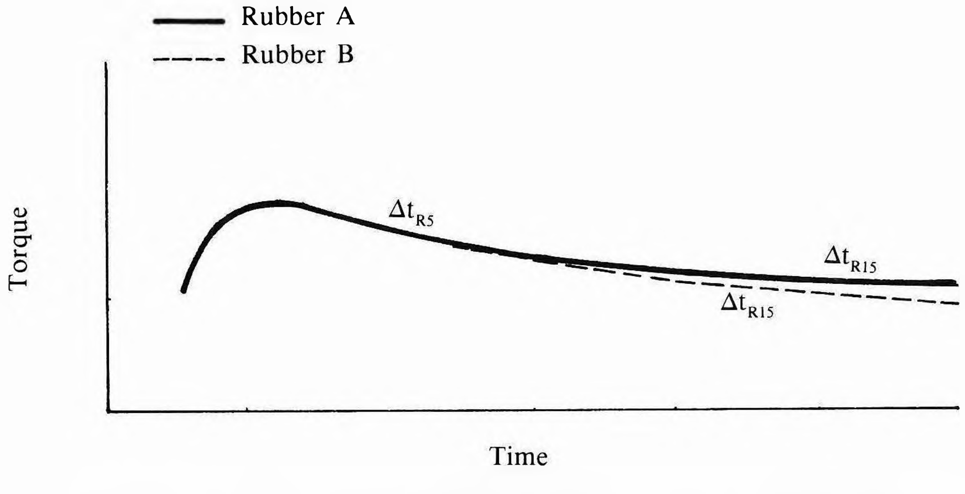

Figure 12. Rheographs for two samples of natural rubber, A and B, having identical values of Δt_{R5} but differing in Δt_{R15}.

well recognised for many years, no similar consideration seems to have been given to the possible dependence of reversion behaviour on type and grade of natural rubber. Some preliminary results indicative of the existence of effects of the type of natural rubber have been published recently[5] and the prime purpose of this paper is to present the results of a more extensive study.

It should perhaps be stressed that, as defined here, reversion is the loss of properties on overcure at any temperature and not the complementary decline in vulcanisate properties at optimum cure as the cure temperature is raised. As shown in *Figure 3,* such effects are apparent with *all* accelerated sulphur systems and, though doubtless related in origin to reversion, are not discussed in this paper.

EXPERIMENTAL

The samples of natural rubber tested were for the most part obtained from consumers' stocks. Materials of various grades and from various producing territories were examined to ensure coverage of as wide a range of commercially available types as possible. Samples were mill-blended according to the procedure used for SMR before further compounding by conventional two-roll mill mixing[6].

A Monsanto R100 rheometer was used with MPC dies and a rotor oscillation of ±1°. A recorder range of full scale deflection of 25 in-lb (28.25 dNm) was used throughout and since, as far as possible, torque values were estimated to ±0.1 scale units, torque has been conveniently expressed in scale units. The characterisation of cure behaviour by rheometry is the subject of international specification in *ISO 3417,* which defines the various cure parameters indicated in *Figure 1.* No such standard procedure exists for the quantification of reversion. The simplest approach, and that which has been adopted here, is to estimate the time after t_{max} for the torque to decrease x units from the maximum value, to give the parameters Δt_{Rx} of *Figure 1* where $x = 1, 2,$ *etc.* scale units. It is recognised, however, that this simple approach does not adequately describe reversion at longer times, where the rate of torque decrease often declines.

A further potential complicating factor in the simple approach is the possible dependence of reversion rate (Δt_{Rx}) cure rate. As shown in *Table 1,* highly boosted conventional cure systems do in fact undergo more rapid reversion but mild boosting has little influence. The effects are not however entirely self-consistent and it seems likely that the more modest variations in cure rate arising from changes in non-rubber content will have little influence on reversion.

RESULTS

Some justification for the procedure used to assess reversion is seen in *Figure 4,* where Δt_{R10} as a function of temperature for *Compound A* clearly follows an Arrhenius-type relation with an activation energy of *ca.* 104 kJ/mol over the temperature range 100°C to 180°C. This is some 10% greater than the activation energy of *ca.* 95 kJ/mol for vulcanisation derived from a similar analysis of the t_{95} values over the temperature range 100°C to 160°C. Progressive deviations in t_{95} are evident at higher temperatures, doubtless due to a significant contribution of the heating up time of the test piece in the die cavity to the apparent t_{95} value. The value of *ca.* 95 kJ/mol for the activation energy for vulcanisation is in close accord with those reported by Barker[7]. Just as vulcanisation is known to be a complex process involving more than one step, so too, reversion would appear to be complex. This is evident in the non-linear nature of most rheometer torque–time traces during reversion and further supported by dependence of the activation energy over the temperature range 160°C to 180°C on the extent of reversion, x, shown in *Figure 5.* It will be noted that the relatively high activation energies shown here are consistent with the higher values over this temperature range in *Figure 4.*

A subsidiary aim of the studies reported here was to consider the possibility of developing a routine test procedure to characterise the intrinsic reversion rate of a sample of natural rubber. Maximum discrimination is obviously desirable and to achieve this three variables can be considered, *viz.*:

a) *Type of compound.* An obvious requirement is that a compound showing a fair measure of reversion must be used.

b) *Test temperature.* This must be high enough for reversion to be fairly rapid but the use of test temperatures much over 160°C with natural rubber gum compounds is associated with the production of a very sticky 'spew' and consequent prolonged cleaning between tests. This is not only inconvenient but detracts from instrument temperature stability.

c) *Extent of reversion (i.e. x in* Δt_{Rx}*).* A limitation here for manual rheometers and probably also for computerised instruments, will be that experimental error is likely to preclude the use of x values less than 5.

An overall constraint is the need to limit the total test time (cure plus reversion) for a test to be used for routine control purposes.

As regards type of compound, the ACS 1 mix, which does undergo reversion, though not normally tested so as to show this, would be an obvious choice. There are, however, several objections. First, as shown in *Table 1,* for a rubber of average cure rate (*B* in *Figure 2*) a test temperature of 170°C - 180°C would be required to obtain a modest degree of reversion ($x = 10$) in an acceptable test time. Even these temperatures would not be adequate for materials which are less responsive to this cure system (*C* in *Figure 2*). Second, despite the observations above on the relation of cure and reversion rates, the wide range of cure behaviour which is the special feature of the ACS 1 system, could well influence or even invalidate the assessment of reversion rate as Δt_{Rx}. Date for two other formulations, with conventional and semi-EV levels of CBS and sulphur are also given in *Table 2.* Clearly, the reversion rate of the semi-EV system is too low for a control test at 160°C and the simple conventional CBS/S system was therefore selected as most appropriate for a routine test.

The effects of test temperature and extent of reversion, b) and c) above, are inevitably interrelated. The effect of test temperature over the range 160°C to 180°C is shown in *Figure 6.* To achieve clarity, the *mean values* of Δt_{Rx} for nine samples of natural rubber differing appreciably in reversion rate are plotted for x values ranging from 1 to 15 scale units. At 160°C for $x = 10$ scale units, Δt_{R10} *ca.* 20 min giving a total test time of *ca.* 30 min. This decreases to 7 - 8 min at 180°C. However, maximum discrimination is equally, if not more, important and this has been characterised in the present instance as the coefficient of variation of Δt_{Rx} over the nine samples. *Figure 7* shows that discrimination decreases at the higher test temperatures. The experimental convenience of using a fairly modest test temperature of 160°C is therefore reinforced by considerations of discrimination. Data illustrative of test repeatability for the selected compound at 160°C are given in *Table 3* and analysed in *Table 4.* The data refer to four rheometer tests on each of four mixes prepared from two rubbers differing appreciably in reversion rate. The results of *Table 3* show that despite the well known difficulty in obtaining a precise value for t_{max} for a curve showing a flat maximum and the need to estimate torque values to ±0.1 scale units, the values of Δt_{Rx} show good repeatability and are quite comparable in this respect to the conventional rheometer parameters such as M_{HR} and t_{95}. As would be expected, repeatability of Δt_{R2} is less than that for higher values of x but rather surprisingly, little different as between Δt_{R5} and Δt_{R10}.

Data for rheometer cure and reversion behaviour at 160°C for fifty samples of natural rubber are given in *Table 5.* While these materials covered a wide range of grades and types, no attempt has been made to classify the samples fully, only latex or field coagulum origin is indicated. As shown in *Figures 8* and *9* and by the analysis in *Table 6,* a wide range of reversion behaviour is evident. There is some evidence for differentiation between latex grades (mean Δt_{R10} = 18.95) and field coagulum materials (mean Δt_{R10} = 16.44) and application of the *t*-test to the data shows that this

TABLE 1. INFLUENCE OF FURTHER ACCELERATION ON THE CURE AND REVERSION PARAMETERS OF A CONVENTIONAL CURE SYSTEM

Natural rubber	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5
CBS	0.5	0.7	0.5	0.5	0.5
DPG	—	—	0.1	—	—
TMTM	—	—	—	0.1	—
TMTD	—	—	—	—	0.1
Rheometer 160°C					
$M_{HR} - M_L$	15.9	16.6	16.5	16.8	17.1
t_{s1}	2.92	3.50	2.80	2.92	2.28
t_{90}	6.90	6.88	6.48	5.10	4.27
t_{95}	7.80	7.58	7.28	5.40	4.67
t_{max}	10.6	10.1	10.4	7.0	5.9
Δt_{R2}	4.6	4.2	4.5	2.1	3.1
Δt_{R5}	9.5	9.0	9.4	6.3	7.1
Δt_{R10}	20.4	19.7	19.5	15.5	16.4
Mooney Scorch 160°C					
min	18	30	25	31	26
+5	12.1	16.3	12.9	13.5	9.5

TABLE 2. REVERSION OF ACS 1, CONVENTIONAL AND SEMI-EV CURE SYSTEMS AT 160°C - 180°C

Item	Cure system			Item	Cure system		
	ACS 1	Conventional	Semi-EV		ACS 1	Conventional	Semi-EV
Natural rubber[a]	100	100	100	170°C			
Zinc oxide	6	5	5	t_{95}	6.1	4.7	4.2
Stearic acid	0.5	1	1	t_{max}	9.8	6.3	5.0
CBS	—	0.5	1.5	Δt_{R2}	5.5	2	3.5
MBT	0.5	—	—	Δt_{R5}	11	4.5	8.5
S	3.5	2.5	1.5	Δt_{R10}	—	9	15.5
160°C				180°C			
t_{95}	10.6	7.6	6.7	t_{95}	3.8	3.2	3.0
t_{max}	18	11	9	t_{max}	5.6	4.0	3.3
Δt_{R2}	20	4.5	10.5	Δt_{R2}	2.4	1.2	1.4
Δt_{R5}	> 40	9.5	23	Δt_{R5}	4.8	2.2	3.2
Δt_{10}	—	20	> 40	Δt_{R10}	—	4.2	7.6

[a] Rubber B of Figure

TABLE 3. INTER AND INTRA BATCH REPEATABILITY IN RHEOMETER CURE AND REVERSION PARAMETERS AT 160°C (BATCHES A1–A4 SLOWER CURING RUBBER AND B1–B4 FASTER CURING RUBBER)

Parameter	Batch															
	A1				A2				A3				A4			
$M_{HR} - M_L$	15.7	15.5	15.5	15.5	15.0	15.0	15.0	15.0	15.6	15.4	15.4	15.2	15.6	15.5	15.5	15.5
t_{S1}	2.90	2.75	2.72	2.75	2.80	2.72	2.72	2.68	2.82	2.72	2.67	2.82	2.92	2.83	2.67	2.70
t_{90}	6.78	6.53	6.30	6.43	6.78	6.50	6.50	6.37	6.70	6.40	6.35	6.50	6.80	6.52	6.35	6.28
t_{95}	7.58	7.43	7.20	7.23	7.68	7.30	7.30	7.17	7.61	7.20	7.15	7.30	7.60	7.42	7.15	7.18
t_{max}	10.4	10.2	10.0	10.0	10.7	10.1	10.3	10.1	10.8	10.1	10.0	10.2	10.4	10.4	10.1	10.1
Δt_{R2}	4.3	4.6	4.3	4.2	4.3	4.7	4.4	4.4	4.3	4.5	4.5	4.8	4.7	4.6	4.7	4.7
Δt_{R5}	9.2	9.6	9.3	9.2	9.3	9.8	9.5	9.1	9.3	9.6	9.5	9.9	9.7	9.6	9.8	9.7
Δt_{R10}	19.4	20.4	19.8	19.7	20.4	20.7	20.2	19.9	20.2	20.9	20.2	21.0	20.8	20.7	20.8	20.7
	B1				B2				B3				B4			
$M_{HR} - M_L$	15.8	16.0	15.7	15.7	15.8	15.8	15.9	15.9	15.8	15.8	15.8	15.9	15.7	15.8	15.8	15.7
t_{S1}	2.73	2.72	2.75	2.73	2.72	2.85	2.68	2.70	2.73	2.77	2.67	2.72	2.72	2.73	2.65	2.72
t_{90}	6.02	6.02	6.03	6.02	6.00	6.03	5.87	5.88	6.02	5.95	5.85	5.90	5.93	5.82	5.83	5.80
t_{95}	6.72	6.82	6.73	6.72	6.70	6.72	6.67	6.58	6.72	6.65	6.55	6.70	6.63	6.52	6.53	6.50
t_{max}	9.0	9.2	9.1	9.2	9.1	9.1	9.0	9.1	9.1	9.1	9.1	9.1	9.0	9.0	9.1	9.2
Δt_{R2}	3.7	3.9	4.2	3.9	3.8	3.8	3.9	3.9	3.8	4.1	3.9	3.9	3.9	3.9	3.8	3.8
Δt_{R5}	7.5	7.7	7.9	7.8	7.6	7.6	7.8	7.7	7.6	7.9	7.6	7.9	7.8	7.8	7.7	7.8
Δt_{R10}	15.0	15.2	15.7	15.7	15.3	15.3	15.5	15.6	15.4	15.8	15.6	15.8	15.6	15.8	15.4	15.8

TABLE 4. ANALYSIS OF DATA OF *TABLE 3*

Parameter	Rubber A — slower curing				Rubber B — faster curing			
	Mean[a]	s.d.[a]	c.v. (%)[a]	F[b]	Mean[a]	s.d.[a]	c.v. (%)[a]	F[b]
$M_{HR} - M_L$	15.37	0.24	1.59	26.4	15.81	0.09	0.54	1.00
t_{S1}	2.76	0.08	2.83	0.32	2.73	0.05	1.65	0.20
t_{90}	6.51	0.17	2.67	0.061	5.94	0.09	1.44	5.51
t_{95}	7.34	0.18	2.50	0.052	6.65	0.09	1.39	7.24
t_{max}	10.24	0.24	2.36	0.25	9.09	0.07	0.75	0.44
Δt_{R2}	4.50	0.19	4.22	2.86	3.89	0.12	3.10	0.46
Δt_{R5}	9.51	0.25	2.59	2.24	7.73	0.13	1.62	0.41
Δt_{R10}	20.36	0.48	2.34	5.40	15.53	0.24	1.57	1.36

[a] for sixteen tests

[b] four tests on each of four mixes

$$F = \frac{\textit{Variance between mixes (df=3)}}{\text{Variance within mixes (df=12)}}$$

TABLE 5. CURE AND REVERSION PARAMETERS AT 160°C FOR FIFTY SAMPLES OF NATURAL RUBBER

Sample	$M_{HR} - M_L$	t_{95}	Δt_{R2}	Δt_{R5}	Δt_{R10}	Δt_{R15}	Grade[a]
1	16.5	7.37	4.8	9.7	19.3	34.6	L
2	15.5	8.43	4.7	9.6	20.8	40.0	L
3	15.9	7.52	4.7	10.4	22.0	40.0	L
4	15.5	8.02	5.1	10.1	20.7	38.5	L
5	15.7	7.85	5.0	10.7	23.7	45.1	L
6	16.4	7.03	4.7	10.2	22.3	41.8	FC
7	15.9	7.78	4.9	9.7	18.5	31.2	FC
8	15.2	8.35	4.9	9.7	20.2	39.3	L
9	15.6	7.82	4.7	9.5	20.0	37.8	L
10	16.6	7.13	4.0	8.0	16.1	27.3	FC
11	16.9	7.85	4.5	9.0	18.6	32.5	FC
12	15.1	7.03	5.4	10.4	20.0	34.0	FC
13	17.5	7.62	4.3	8.6	16.5	27.0	FC
14	17.3	7.15	3.7	6.6	14.8	24.8	FC
15	17.4	7.32	3.6	7.2	14.2	23.5	FC
16	16.6	7.40	4.0	7.7	14.5	23.8	FC
17	16.5	7.82	4.3	7.8	14.9	25.0	FC
18	16.3	7.67	4.3	8.5	16.7	28.4	FC
19	17.1	7.23	4.0	7.8	15.5	26.2	FC
20	15.9	8.20	4.0	8.7	18.0	32.5	L
21	14.8	8.03	4.5	8.6	17.0	30.1	L
22	14.4	9.03	4.1	8.9	18.2	35.3	L
23	16.0	7.16	3.8	7.5	14.7	25.0	L
24	16.4	5.95	4.7	9.2	18.2	30.4	L
25	17.1	6.62	4.0	7.9	15.3	25.4	FC
26	15.4	7.35	4.5	8.8	17.5	29.8	FC
27	16.2	6.90	3.5	7.0	13.9	23.2	FC
28	16.7	6.90	4.4	8.6	17.1	29.3	FC
29	15.5	6.63	5.2	10.5	20.5	36.0	FC
30	16.3	6.97	4.3	8.7	17.5	30.3	FC
31	15.7	6.73	3.7	7.7	14.6	24.0	FC
32	15.0	6.73	3.4	6.8	12.9	21.5	FC

TABLE 5. CURE AND REVERSION PARAMETERS AT 160°C FOR FIFTY SAMPLES OF NATURAL RUBBER (CONTD.)

Sample	$M_{HR} - M_L$	t_{95}	Δt_{R2}	Δt_{R5}	Δt_{R10}	Δt_{R15}	Grade[a]
33	15.0	6.33	4.1	8.0	15.0	24.3	FC
34	15.3	6.18	4.2	8.0	15.2	24.7	FC
35	15.3	7.68	4.8	9.4	18.5	31.7	L
36	16.8	6.90	4.3	8.3	15.9	27.0	L
37	16.4	7.03	3.8	7.4	14.3	23.3	L
38	15.7	7.23	4.2	8.4	16.7	29.0	L
39	14.2	10.47	5.0	10.6	22.9	47.0	L
40	15.4	8.48	4.9	10.1	21.4	42.4	L
41	15.9	7.32	4.4	8.7	17.5	31.0	L
42	15.5	7.00	3.8	7.7	15.1	23.9	FC
43	15.7	7.18	4.3	8.1	15.6	26.0	FC
44	16.2	6.72	4.2	8.5	17.1	28.9	FC
45	15.2	6.52	5.4	11.1	21.5	37.8	FC
46	16.5	7.45	4.7	9.5	18.6	32.2	FC
47	18.2	6.67	3.4	7.8	14.9	24.5	FC
48	16.8	6.80	3.9	8.0	15.4	25.4	FC
49	18.6	6.45	3.7	7.3	14.5	23.7	FC
50	18.1	7.53	3.9	7.5	15.0	24.8	FC

[a] L—latex grade, FC—field coagulum grade

TABLE 6. ANALYSIS OF DATA OF *TABLE 5*

Item	$M_{HR} - M_L$	t_{95}	Δt_{R2}	Δt_{R5}	Δt_{R10}	Δt_{R15}
Max	18.6	10.47	5.4	11.1	23.7	47.0
Min.	14.2	5.95	3.4	6.6	12.9	21.5
Mean	16.11	7.35	4.33	8.51	17.39	30.42
s.d.	0.94	0.774	0.51	1.50	2.70	6.49
c.v. (%)	5.82	10.53	11.85	17.59	15.54	21.32

TABLE 7. CURE AND REVERSION PARAMETERS AT 160°C FOR ELEVEN SAMPLES TAKEN FROM A SINGLE LOT OF TSR 10

Sample	$M_{HR} - M_L$	t_{95}	Δt_{R2}	Δt_{R5}	Δt_{R10}	Δt_{R15}
1	18.2	6.67	3.4	7.8	14.9	24.5
2	16.8	6.80	3.9	8.0	15.4	25.4
3	18.6	6.45	3.7	7.3	14.5	23.7
4	18.1	7.53	3.9	7.5	15.0	24.8
5	17.0	7.40	4.1	8.2	16.0	26.7
6	16.5	8.40	4.6	8.8	17.4	30.4
7	16.8	7.25	3.6	7.4	15.1	26.4
8	16.3	8.25	4.1	8.4	17.2	30.7
9	16.8	8.20	4.3	8.5	17.5	30.7
10	15.6	8.33	5.2	10.0	18.8	31.7
11	17.5	6.97	4.4	8.4	16.2	26.5
Mean	17.1	7.48	4.1	8.2	16.2	27.4
s.d.	0.9	0.72	0.5	0.8	1.4	2.9
c.v. (%)	5.3	9.6	11.8	9.4	8.5	10.6

difference is highly significant. Latex rubber therefore reverts less readily. While the CBS/S cure system is far less responsive to non-rubbers than is the ACS 1 system there is, as shown in *Table 6,* some variation in state of cure, $M_{HR} - M_L$, and appreciably more in rate of cure, t_{95}. *Figures 8* and *9* show, however, no correlation between these cure parameters and Δt_{R10} (and also, in plots not presented here, with Δt_{R2} and Δt_{R15}). The reversion rate is therefore a truly *independent* measure of rubber quality. Over a very restricted range of rubber samples, some correlation between cure behaviour and reversion rate is evident. An example for eleven samples of TSR 10 taken from a single production lot is given in *Table 7* and *Figures 10* and *11*. Some correlation with both rate and state of cure is evident.

In the above considerations it has been tacitly assumed that reversion can be characterised by single value of Δt_{Rx} and by implication therefore that during reversion torque decreases linearly with time.

However, as noted earlier, this not generally the case, the torque *versus* time trace is more or less curved. The situation depicted in *Figure 12* can therefore arise, in which materials having comparable values of Δt_{R5} show quite different extents of reversion at longer times. Such differences are clearly apparent in the correlation between Δt_{R5} and Δt_{R15} given in *Figure 13*. Thus, not only are latex rubbers less prone to reversion than field coagulum grades, but the differential is increased with increasing extent of reversion. Finally, as shown in *Figure 14*, differences in reversion behaviour between latex and field coagulum rubber observed at temperatures of 160°C - 180°C appropriate for high temperatures vulcanisation are found to a comparable extent at much lower temperatures where reversion will impact upon service performance.

CONCLUSIONS

The data presented here confirm previous very limited evidence that field coagulum grades of natural rubber revert rather more rapidly than latex grades both at temperatures of 160°C - 180°C appropriate for laboratory testing and also at 100°C - 120°C, temperatures more relevant to stringent service conditions. The difference presumably stems mainly from the characteristic differences in non-rubber content between natural rubber prepared by these routes. The participation of non-rubbers would be expected to be only a second-order effect and, consistent with this, the activation energy for reversion is not obviously dependent on the grade of rubber. Since reversion is well recognised as a deficiency of natural rubber, a quantitative characterisation could usefully feature in the overall assessment of natural rubber quality. In this context, the data presented here suggest that rheometer measurements at 160°C using a conventional CBS/S cure system have the requisite level of repeatability and discrimination for such a routine test. Reproducibility remains to be assessed.

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Development of Molecular Markers for Hevea

F.C. LOW* AND M.D. GALE**

The development of restriction fragment length polymorphisms (RFLP) techniques as molecular markers for Hevea *is described. Two* Hevea *libraries containing genomic DNA sequences (genomic library) and complementary DNA (cDNA) sequences (cDNA library) were generated. Using an anonymous DNA probe from the* Hevea *genomic library, polymorphisms between* Hevea *species and between* Hevea *clones were detected. The potential usefulness of RFLP techniques in* Hevea *breeding programmes is discussed.*

Restriction fragment length polymorphisms (RFLP) have been proposed as potentially useful molecular markers for genetic analysis in higher plants[1-5]. RFLP are differences in fragment lengths when genomic deoxyribonucleic acids (DNA) of genetically distinct individuals are digested with a particular restriction endonuclease (RE). These differences are the result of heritable changes in the DNA. Point mutations create or destroy restriction endonuclease sites, while DNA rearrangements, insertions or deletions alter their relative positions.

As genetic markers, RFLP promise to be numerous[6]. RFLP have several characteristics which are of particular ultility in genetic improvement programmes. These include co-dorminant expression, multiple allelic forms, developmental stability and the absence of pleiotropic effect on other characters. RFLP analysis is a potentially powerful tool for assaying genetic variability. It is also useful in the study of inheritance of quantitative characters. If RFLP analysis can be applied as successfully to *Hevea* as to tomato[4,7,8], barley[9], pea[10] and lettuce[11], it will then provide the *Hevea* plant breeder with an efficient and powerful early selection tool. The present screening of *Hevea* by conventional methods can only be performed at least two years after planting. Since RFLP analysis can be performed much earlier, the technique is of value in culling and in shortening the selection time for *Hevea*. Ultimately, RFLP will be developed as genetic markers for the construction of a total genetic map of the *Hevea* genome.

MATERIALS AND METHODS

Plant Material

Four *Hevea* genotypes which were cultivated in the RRIM Experiment Station at Sungei Buloh were used. These consisted of two *Hevea brasiliensis* clones, RRIM 600 *(Field 19C)* and RRIM 628 *(Field 14)* and two *Hevea* species, *H. pauciflora* (HHB 12/3, *Field 67C*) and *H. camargoana* (1/4, 1/5, *Field 45N*).

DNA Analysis

Genomic DNA from the above genotypes were isolated by the method described by Sharp *et al.*[12] Young *Hevea* leaves were pulverised after lyophilisation and DNA was extracted from them by digestion at 37°C for 1–2 h in extraction buffer [100 mM Tris.Cl pH 8.5, 100 mM NaCl, 50 mM EDTA, 2% sodium dodecylsulphate (SDS), 0.05 mg/ml proteinase K]. This was followed by extraction with phenol/chloroform and precipitation with isopropanol. The precipitate was dissolved in TE (10 mM Tris.Cl pH 8.0, 1 mM EDTA). After the removal of ribonucleic acid (RNA) contamination by digestion at 37°C for 30 min with boiled ribonuclease A (RNase A) at 1 μg/ml, the DNA was again precipitated with isopropanol and dissolved in TE.

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*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia
**AFRC-IPSR Cambridge Laboratory, U.K.

Nineteen restriction endonucleases (RE) were studied *(Table 1)*. Aliquots (5 μg) of DNA were digested for 16–20 h with the selected RE under the conditions recommended by the supplier (Bethesda Research Laboratories). Genomic digests with these enzymes were electrophoresed through large agarose (0.8% for six-base cutters and 1.2% for four-base cutters) slabs with TAE (0.04 *M* Tris-acetate, 0.001 *M* EDTA) as the electrophoresis buffer. These were then transferred to nylon membranes (Genescreen Plus, Dupont) by the alkaline Southern blotting technique of Reed and Mann[13].

TABLE 1. RESTRICTION ENDONUCLEASES USED FOR RFLP DETECTION

6-base cutters	4-base cutters
*Apa*I	*Alu*I
*Bam*HI	*Dde*I
*Bgl*II	*Hae*III
*Dra*I	*Hha*I
*Eco*RI	*Hinf*I
*Eco*RV	*Mbo*I
*Hind*III	*Msp*I
*Sal*I	*Rsa*I
*Sst*I	*Taq*I
*Pvu*II	

Hybridisation and Washing Conditions

The conditions for hybridisation and washing were similar to those described[12]. Following Southern blotting, nylon membranes were prehybridised at 65°C in hybridisation solution (0.6 *M* NaCl, 20 mM Pipes pH 6.8, 4 mM EDTA, 0.2% Ficoll 400, 0.2% polyvinylpyrollidone (PVP), 1% SDS, 0.5% sodium pyrophosphate containing 500 μg/ml autoclaved salmon sperm DNA). After 4–5 h of prehybridisation, the prehybridisation solution was replaced by a similar solution containing the ^{32}P-labelled probe. Hybridisation was then allowed to proceed for 16 h at 65°C. After hybridisation, the membranes were washed sequentially with 2XSSC (0.3 *M* NaCl/0.03 *M* sodium citrate, pH 6.8), 0.1% SDS, and 0.5XSSC, 0.1% SDS for 30 min each at 65°C. Autoradiography was carried out at −70°C by exposure of the membrane to KODAK XAR-5 film between two intensifying screens for four days.

Construction of Libraries

DNA fragments of 500–2000 basepairs (bp) obtained from PstI digestion of *H. brasiliensis* clone RRIM 600 genomic DNA were isolated. These were successfully cloned into pUC18 plasmids and transformed into *E. coli* strain MC1022 to generate a genomic library. Clones were screened by ampicillin resistance. Clones carrying recombinant plasmids were purified and the recombinant plasmids were isolated by the proteinase K mini-preparation plasmid isolation method of Pruitt[14].

Total messenger RNA (mRNA) was isolated from young *Hevea* leaves by the method of Baulcombe and Buffard[15]. Double-stranded complementary DNA (cDNA) was synthesised by the cDNA synthesis system from Amersham. The cDNA was subsequently cloned into the *Pst*I site of plasmid vector *p*UC18 with the help of dephosphorylated 8-mer linkers (New England Biolabs). Following transformation into *E. coli* strain MC1022, a small cDNA library was created. 'Recombinant plasmids from the cDNA library were isolated from each clone by the proteinase K mini-preparation plasmid isolation procedure of Pruitt[14]. After digestion with *Pst*I, the sizes of these cDNA were determined by electrophoresis on agarose with lambda DNA digested with *Hind*III, as molecular weight markers.

Hybridisation Probes

Several named heterologous probes like wheat chlorophyll a/b binding (cab) protein (from N. H. Chua, Rockefeller University, New York), wheat ribulose carboxylase small sub-unit (from Plant Breeding Institute, Cambridge) and rice nitrate reductase (from A. Kleinhofs, Washington State University, Pullman) were used as probes.

Besides the above-named heterologous probes, a genomic DNA (gDNA) and complementary DNA (cDNA) clone, isolated from the newly generated *Hevea* genomic and cDNA libraries respectively were also used. These were labelled with P^{32} by the method of Feinberg and Vogelstein[16] and used as an anonymous probe against genomic digests of *Hevea* with the same conditions of hybridisation and washings as that used for the named heterologous probes.

RESULTS AND DISCUSSION

Size of DNA Inserts

After electrophoresis on agarose and with the assistance of molecular size markers generated from a *Hind*III digest of lambda DNA, the size of cDNA inserts was estimated to be 300–2000 basepairs (bp) in length *(Figure 1)*. The size of the gDNA probe used in the above hybridisation was deduced similarly to be approximately 800 bp in length.

Named Probes

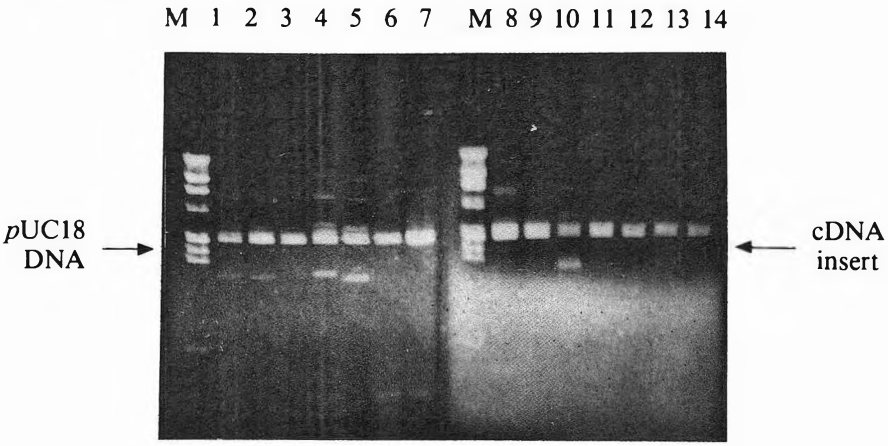
Hybridisations with the above-named cDNA probes *viz.* wheat cab protein, small sub-unit of wheat ribulose carboxylase and rice nitrate reductase, with genomic digests of *Hevea* DNA did not show any homology (results not shown). The lack of homology with these heterologous probes might be because all these probes were from monocotyledonous plants. A higher homology to *Hevea* genomic sequences might be obtained with cDNA probes from dicotyledonous plants.

Demonstration of Polymorphisms

When genomic digests of *Hevea* DNA were hybridised with an anonymous gDNA probe, polymorphisms within *H. brasiliensis* clones (RRIM 600 and RRIM 628) as well as between *Hevea* species were seen (*Figures 2* and *3*). DNA from barley (a monocotyledonous plant) which was included into one of the blots *(Figure 2)* as a control, was shown to have no homology with the gDNA clone of *Hevea* (this is not unexpected as the probes were derived from monocotyledonous plants).

Similar hybridisations with one of the cDNA clones (*p*CP 7) showed less distinct results *(Figure 4)*.

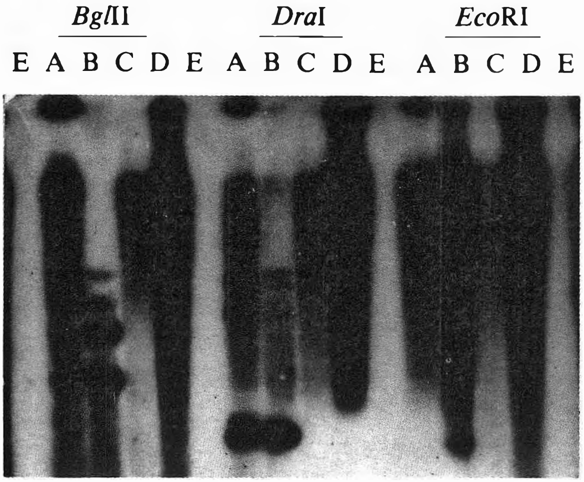
Screening of the rest of the genomic and cDNA libraries has just been completed and will be discussed elsewhere.



M = Molecular weight marker (λDNA/*Hind*III digest containing *p*UC18 DNA)

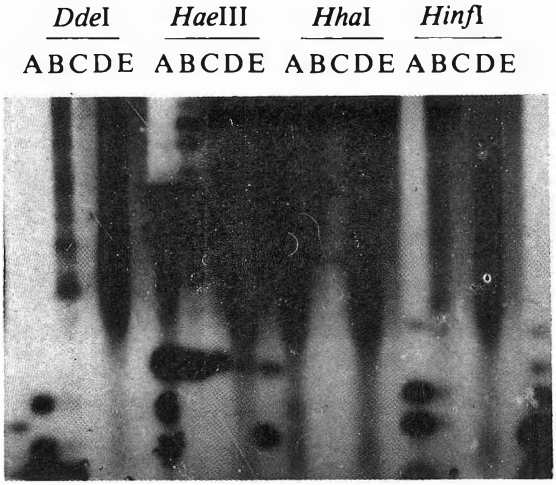
1–14 = *p*UC18 recombinants harbouring cDNA inserts

Figure 1. Size determination of cDNA clones.



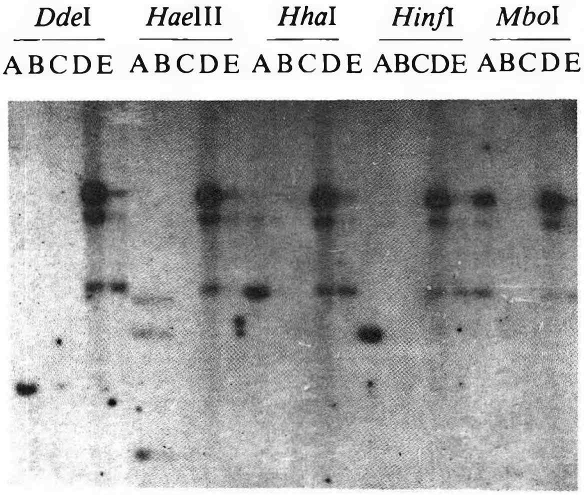
A = RRIM 600
B = RRIM 628
C = *H. camargoana*
D = *H. pauciflora*
E = Barley (control)

Figure 2. Hybridisation of a Hevea *gDNA clone with* Hevea *genomic DNA digested with RE containing six-base recognition sites.*



A = RRIM 600
B = RRIM 628
C = *H. camargoana* (T4)
D = *H. pauciflora*
E = *H. camargoana* (T5)

Figure 3. Hybridisation of a Hevea *gDNA clone with* Hevea *genomic DNA digested with RE containing four-base recognition sites.*



A = RRIM 600
B = RRIM 628
C = *H. camargoana* (T4)
D = *H. pauciflora*
E = *H. camargoana* (T5)

Figure 4. Hybridisation of a Hevea *gDNA clone with* Hevea *genomic DNA digested with RE containing four-base recognition sites.*

Preliminary results suggested that polymorphisms could be detected between *Hevea* clones and possibly between *Hevea* species. These results are encouraging but need confirmation. If RFLP in *Hevea* are confirmed, then their usefulness as a selection tool for the *Hevea* breeder could be exploited.

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Kinetics of Decomposition of Tert-butyl Peroxyisobutyrate During Vulcanisation of Natural Rubber Latex

MA'ZAM MD. SAID*, T.D. PENDLE** AND D.C. BLACKLEY***

The development of a modified iodometric method of estimating the concentration of tert-butyl peroxyisobutyrate (tBPIB) in natural rubber (NR) latex is described. The decomposition of tBPIB in NR latex, in the presence or absence of fructose was found to be a first-order reaction with respect to tBPIB concentration. The initial rate of tBPIB decomposition, however, was found to be half order with respect to initial tBPIB concentration. The effect of reaction variables on the rate of tBPIB decomposition is discussed. The activation parameters are calculated from the rate measurements. The significance of the kinetics of tBPIB decomposition in relation to tBPIB reaction and the kinetics of crosslinking is discussed.

In an earlier paper[1], the tert-butyl peroxyisobutyrate/fructose system was shown to be an effective prevulcanising system for NR latex. In this paper, the investigation on the kinetics of tBPIB decomposition during vulcanisation of NR latex is reported. No work has been published so far on the kinetics of peroxide reaction during vulcanisation of NR latex. This paper also describes a modified iodometric method developed to determine tBPIB concentration in NR latex. Development of the modified iodometric method requires the establishment of a suitable reaction medium and conditions for dispersing NR latex and fast peroxide-iodide and iodine-thiosulphate reactions. In addition, factors influencing blank titration volume need to be studied since the 'actual' blank titration volume of samples taken during the course of prevulcanisation cannot be determined.

EXPERIMENTAL

The material and the procedure for prevulcanisation of NR latex were the same as described earlier[1]. The materials, apparatus and procedure used for development of the modified iodometric method for determination of peroxide in latex were generally the same as described in the standard method[2]. Analar toluene was added in the reaction mixture to help disperse NR latex. Potassium iodide was replaced with saturated sodium iodide. Sodium iodide was found to be more soluble in a reaction mixture of isopropyl-acetic acid-autoxidised olefin than was potassium iodide[3]. This allows for a higher concentration of sodium iodide to be used, resulting in an increase in the rate of reaction and a decrease in the possible addition of iodine to unsaturated

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*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia
**Malaysian Rubber Producers' Research Association, Brickendonbury Hertford SG13 8NL, United Kingdom
***London School of Polymer Technology, Holloway Road, London N7 8DB, United Kingdom

substances[3,4]. Copper chloride was used as a catalyst for the peroxide-iodide reaction. The liberated iodine was titrated with a standard thiosulphate to a colourless end-point. In the standard method, water (50 ml) is added before titration to speed up the iodine-thiosulphate reaction[3].

Development of a Modified Iodometric Method

Using the standard iodometric method of determination of peroxyester content[2], it was found that the blank titre is not affected by the levels of fructose, toluene, isopropanol and acetic acid. The result of the effect of fructose on blank titre is significant since the concentration of fructose would decrease during prevulcanisation. In the presence of acetic acid, fructose does not appear to react with the liberated iodine. It has been found that reducing sugars react with iodine under alkaline condition[5]. The blank titre increases proportionately with the amount of copper chloride, that is 6 ml of 0.01*N* sodium thiosulphate per 1 ml of 1% copper chloride solution. Texofor FP170 is a non-ionic surfactant used for preparing the peroxide emulsion. The blank titre increases with increasing amounts of Texofor FP170 and standing time *(Figure 1)*. However, the effect of Texofor FP170 on determination of tBPIB in latex would not be important since the amount used was small[1]. When determining the contribution of latex to blank titre or determining the tBPIB concentration in latex, a known amount of latex was injected into the reaction medium using a graduated syringe. The reaction medium was stirred using a magnetic stirrer during the addition of latex. A solvent mixture of toluene (70 ml)/isopropanol (30 ml) dispersed latex (2 ml at 50% d.r.c.) very satisfactorily. In the presence of acetic acid (5 – 15 ml), a mixture of toluene (60 ml)/isopropanol (40 ml) produced a satisfactory medium for dispersing latex. The acetic acid, however must be added slowly after the latex has been dispersed in toluene/isopropanol mixture to avoid coagulation of latex. In the absence of acetic acid in the reaction mixture, the blank titre was found to decrease with increasing amounts of latex *(Figure 2)*. This is probably as a result of the addition of iodine to polyisoprene. In the presence of acetic acid in the reaction mixture, the blank titre increases very slightly with increasing amounts of latex. This is probably due to the increasing inhomogeneity of the reaction mixture with increasing amounts of latex, which tends to lead to over-stepping of the end point. Further evaluation of the method was carried out using latex containing a known concentration of tBPIB. Accurate determination of tBPIB in latex (2 ml at 50% d.r.c.) was made using reaction mixture containing toluene (60 ml), isopropanol (40 ml), acetic acid (15 ml), 1% copper chloride solution (1 ml) and saturated sodium iodide (4 ml). However, water must not be added into the reaction mixture and the normality of thiosulphate should be adjusted to avoid excessive dilution. The formation of an inhomogenous reaction mixture which tended to produce higher results, would then be avoided. The above modified iodometric procedure was used to determine the concentration of tBPIB remaining in latex during prevulcanisation. The concentration of peroxide was calculated using,

Peroxide concentration (g mol/g rubber)

$$= \frac{(a-b)\times N\times 8\times}{c\times \varrho\times D}\;\frac{M}{16}\times 100$$

where a is the volume of thiosulphate (ml) required to titrate the sample

b is the blank titre (ml)

N is the normality of sodium thiosulphate

M is the molecular weight of peroxide

c is the volume of latex (μl)

ϱ is the density of latex

D is the dry rubber content of latex

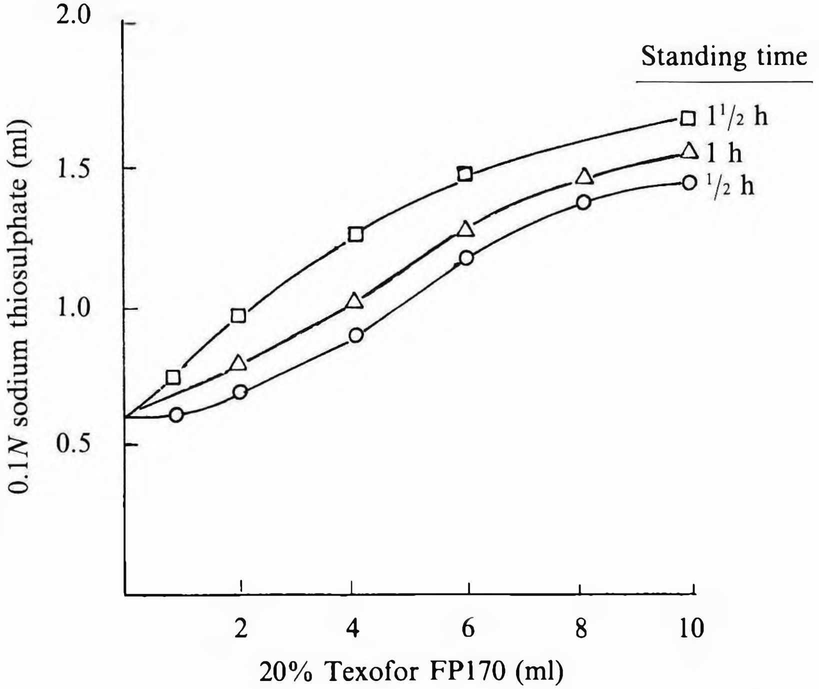

Figure 1. Effect of Texofor FP170 and standing time on titration volume of thiosulphate using the Akzo Chemie method of iodometric analysis.

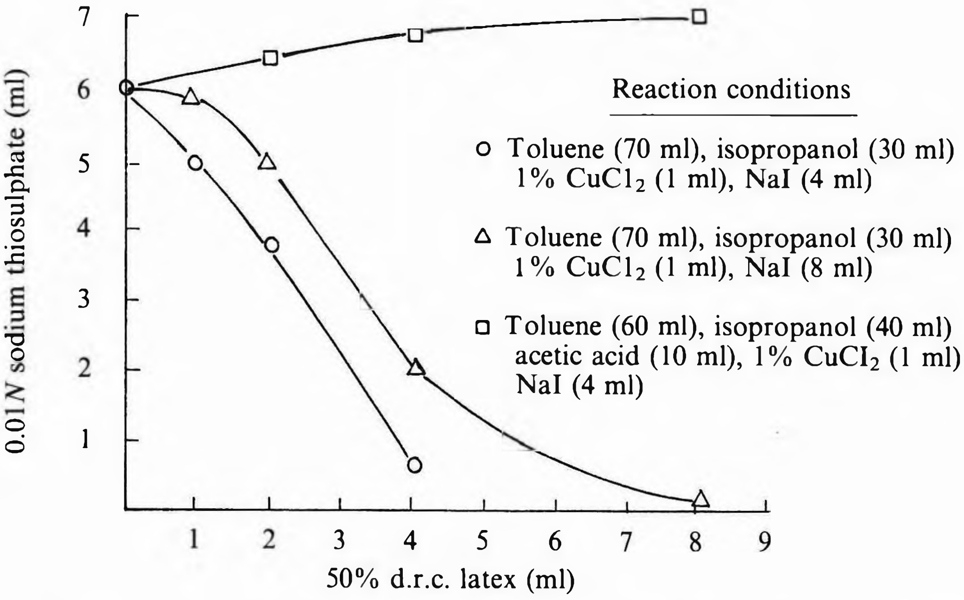

Figure 2. Effect of NR latex and reaction conditions upon titration volume of thiosulphate. Standing time was 1 h at room temperature.

The blank titre of a reaction mixture containing prevulcanised latex was assumed to be the same as that of a reaction mixture containing unvulcanised latex.

RESULTS AND DISCUSSION

Rate of Reaction

Figures 3, 4 and *5* show straight line plots of $-\ln$ [tBPIB] *versus* prevulcanisation time, where [tBPIB] is the concentration of the undecomposed tBPIB in latex. The results suggest that the decomposition of tBPIB in NR latex is a first-order reaction satisfying the following first-order rate equation:

$$-\ln [\text{tBPIB}] = k' t - \ln [\text{tBPIB}]_o$$

where k' is the rate of coefficient for tBPIB decomposition
t is the prevulcanisation time
[tBPIB]$_o$ is the initial concentration of tBPIB.

The slopes of the lines in *Figures 3, 4* and *5* give the various values of k'. First-order decomposition of tBPIB in NR latex was also observed when using other reaction conditions, both for fructose-activated and non-activated tBPIB systems.

The value of k' remains fairly constant over a range of initial tBPIB concentration for systems containing equimolar initial concentrations of tBPIB and fructose at 60°C *(Figure 6)*. At constant initial tBPIB concentration and at constant temperature, the value of k' increases with increasing initial fructose concentrations *(Figure 7)*. The value of k' increases with temperature, more rapidly for fructose-activated systems than for non-activated systems *(Figure 8)*. *Figures 7* and *8* also show the effect of reaction variables on the value of k'', the rate coefficient for crosslink formation[1]. Although the patterns in which k' and k'' are affected by the ratio of initial fructose concentration to initial tBPIB concentration, and temperature are generally similar, under certain reaction conditions, the values of k' and k'' are not equal. Thus, for instance, for non-activated systems, k' is greater than k'' over a wide temperature range. The value of k'' becomes significantly greater than k' at temperatures greater than 80°C, particularly when using a high ratio of initial fructose to initial tBPIB concentration. According to the simple mechanism of peroxide vulcanisation, it ought to be impossible for k'' to exceed k'. Hummel and Scheele[6] stated two conditions for k'' to be equal to k'. Firstly, the intermediate reactions during vulcanisation must be fast so that the concentrations of their products are very small. This condition is likely to be satisfied by a peroxide vulcanising system. The second condition is that the instantaneous crosslinking efficiency (F_t) must be constant throughout the vulcanisation reaction. The value of F_t can be obtained by plotting the concentration of crosslinks formed against the concentration of tBPIB decomposed. The slope taken at a point corresponding to time t gives the F_t value. It is found that F_t increases with prevulcanisation time, for various systems regardless of whether k'' is equal or not equal to k' as shown by the examples in *Figures 9, 10* and *11*. Thus, the variation of F_t with prevulcanisation time only partly explains the inequality of k'' and k'. Perhaps, differences in the temperature coefficients for the various competing reactions that occur during peroxide prevulcanisation of NR also influence the relationship between k'' and k' and the variation of F_t with prevulcanisation time. The increase of F_t with prevulcanisation time is probably also a result of depletion of free radical scavengers as prevulcanisation progresses. The results in *Figure 11* show that the value of F_t exceeds 50% towards the end of the reaction. This probably suggests that at high temperatures, both alkyl and butoxy radicals generated from the decomposition of tBPIB participated in the crosslinking reaction.

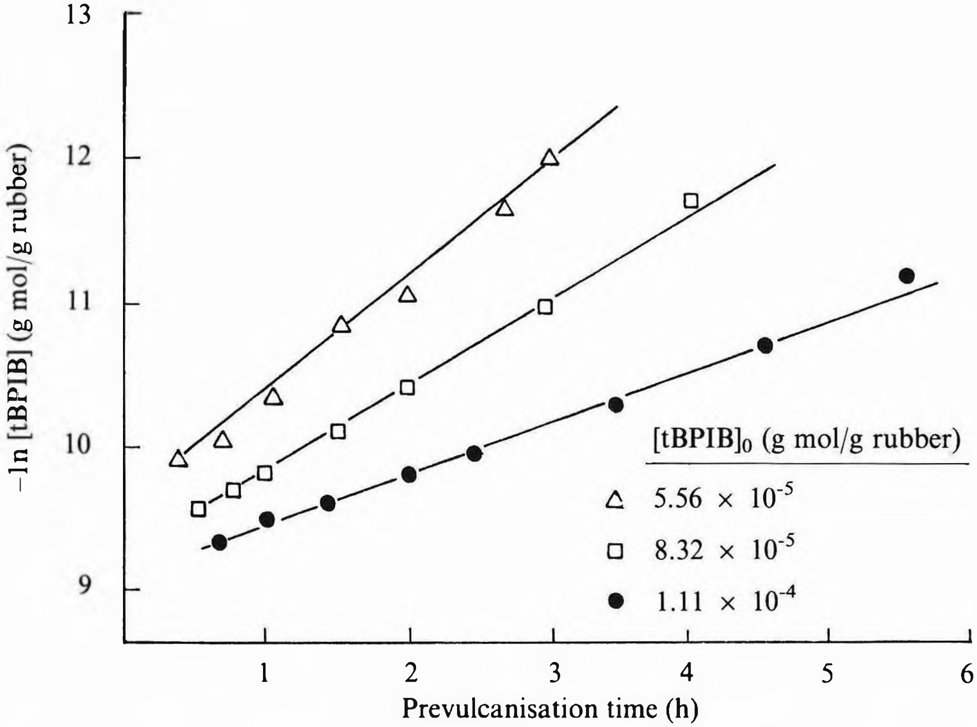

Figure 3. First-order plots for tBPIB decomposition in NR latex at 60°C for systems which initially contained 1 p.h.r. fructose and different concentrations of tBPIB.

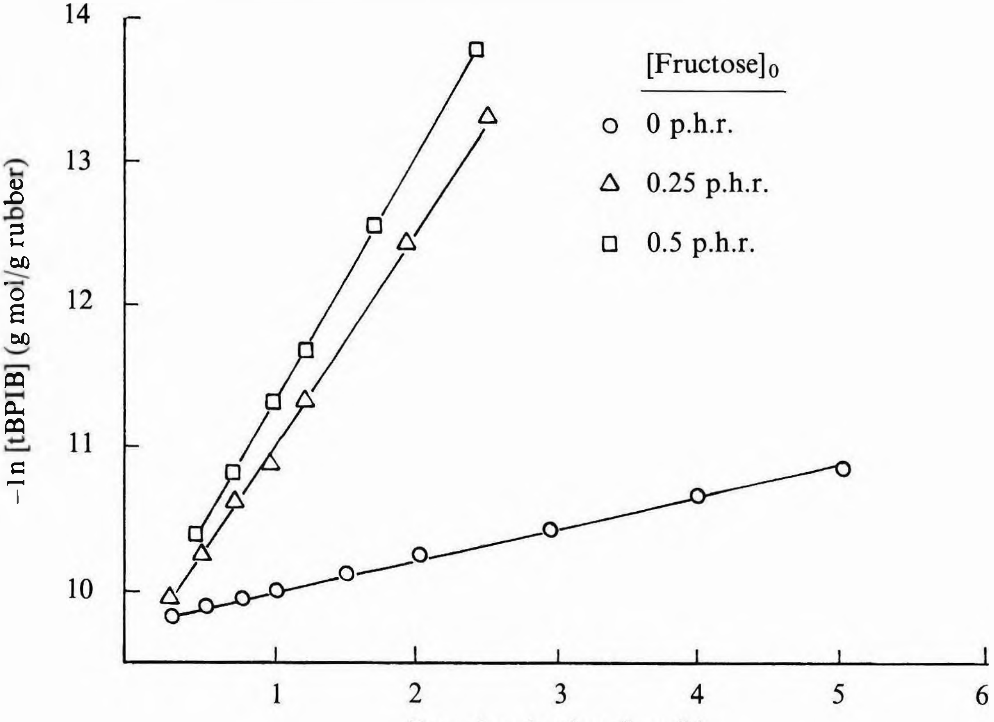

Figure 4. First-order plots for tBPIB decomposition in NR latex at 80°C for systems which initially contained 5.56 × 10^{-5} g mol/g rubber tBPIB and different concentrations of fructose.

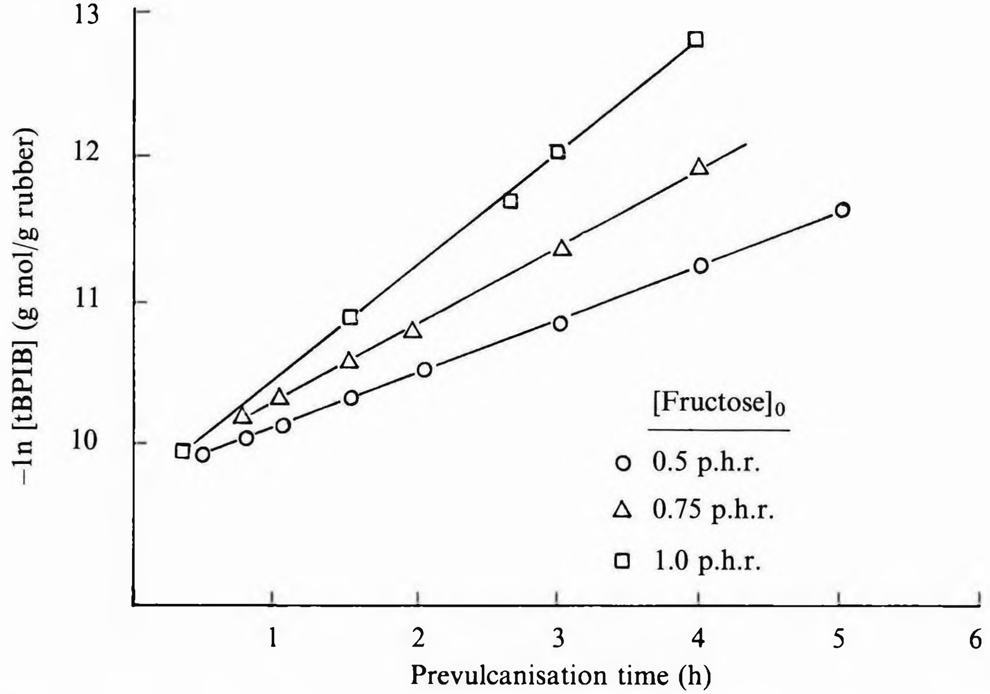

Figure 5. First-order plots for tBPIB decomposition in NR latex at 60°C for systems which initially contained 5.56 × 10^{-5} g mol/g rubber tBPIB and different concentrations of fructose.

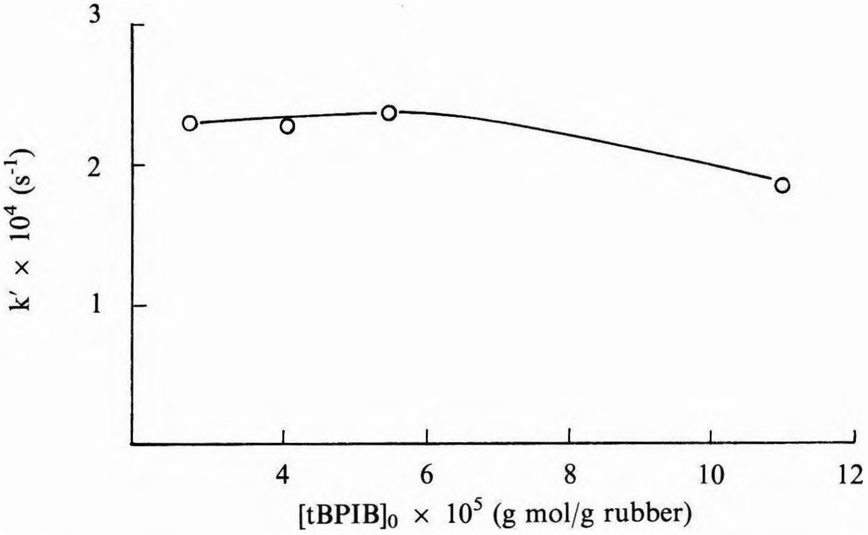

Figure 6. Effect of initial tBPIB concentration on rate coefficient k′ for decomposition of tBPIB in NR latex at 60°C using equimolar tBPIB and fructose concentrations.

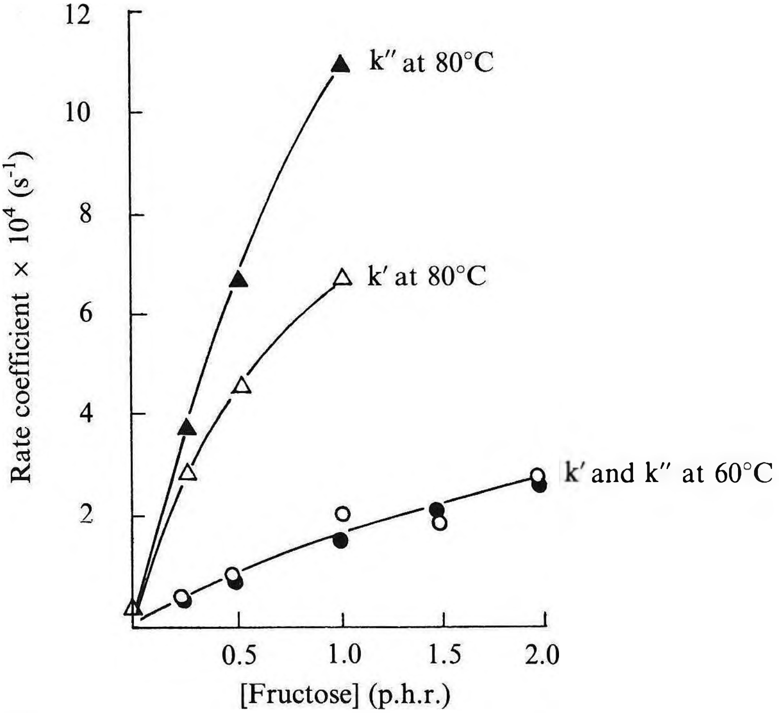

Figure 7. Effect of fructose concentration and prevulcanisation temperature on rate coefficients for tBPIB decomposition (k′) and crosslink formation (k″) at 60°C and 80°C using 5.56 × 10^{-5} g mol/g rubber tBPIB.

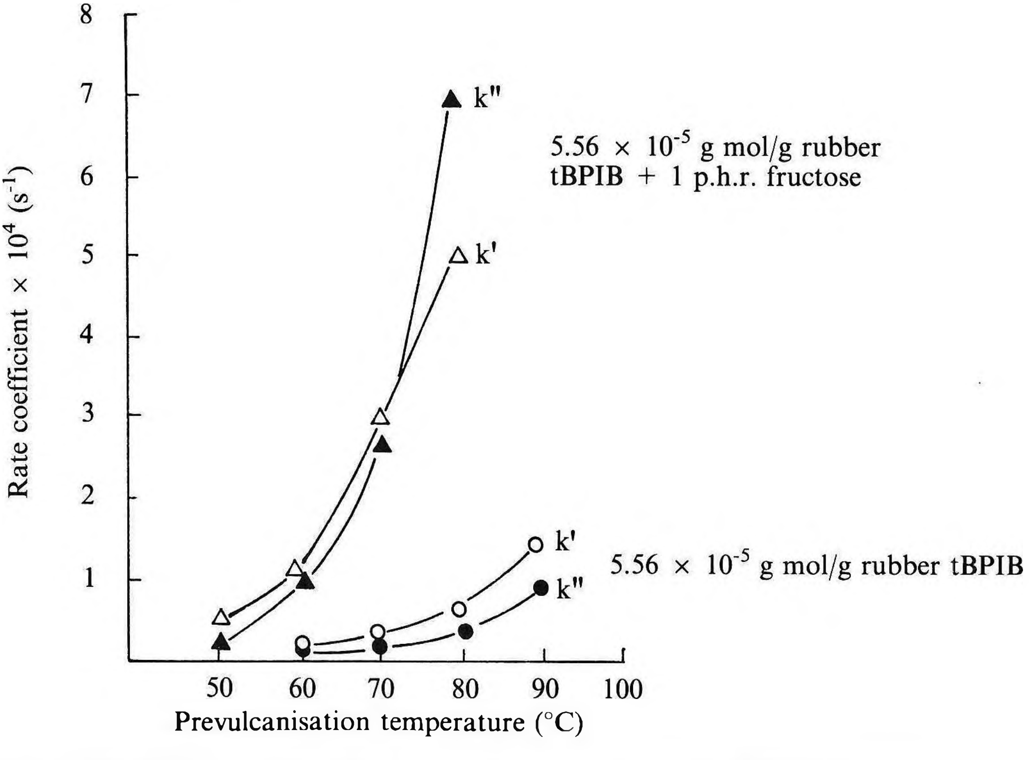

Figure 8. Effects of prevulcanisation temperature and fructose/tBPIB concentrations on the values of k′ and k″.

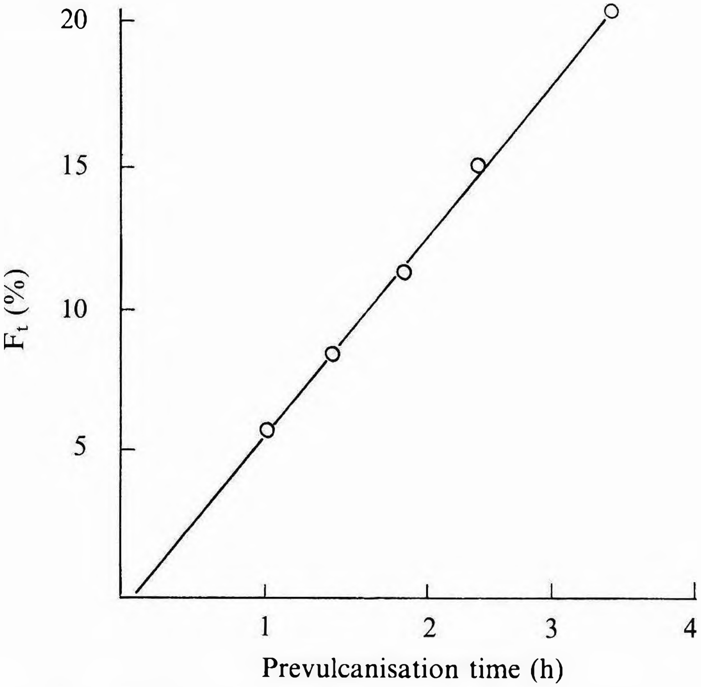

Figure 9. Variation of crosslinking efficiency F_t with prevulcanisation time at 60°C for a system which initially contained 1.11×10^{-4} g mol/g rubber tBPIB and 1 p.h.r. fructose.

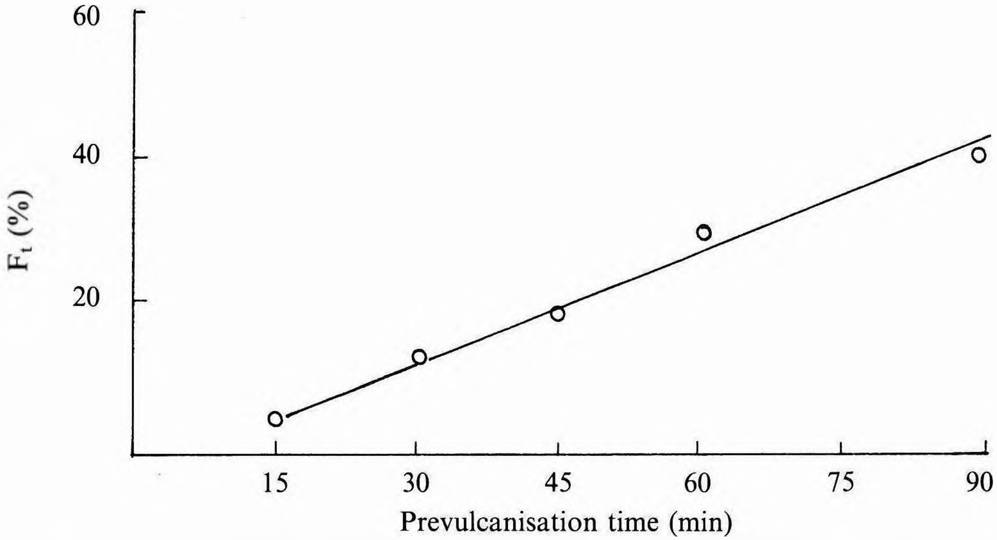

Figure 10. Variation of crosslinking efficiency F_t with prevulcanisation time at 60°C for a system which initially contained 5.56×10^{-5} g mol/g rubber tBPIB and 2 p.h.r. fructose.

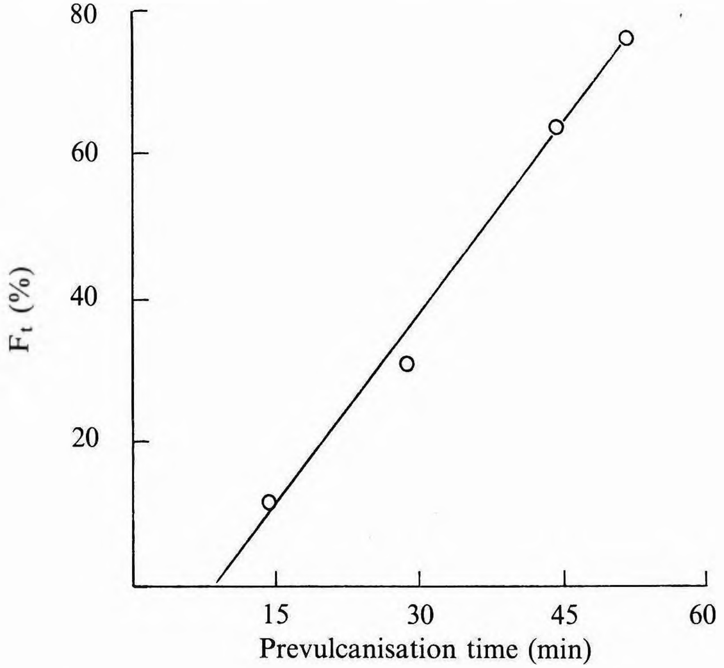

Figure 11. Variation of crosslinking efficiency F_t with prevulcanisation time at 80°C for a system which initially contained 1.11×10^{-4} g mol/g rubber tBPIB and 1 p.h.r. fructose.

Activation Parameters

The experimental activation energy E' of tBPIB decomposition is obtained using the Arrhenius equation:

$$k' = A_e{}^{-E'/RT}$$

where A is a constant
R is the gas constant (8.313 J/K)
T is the temperature.

E' is obtained by multiplying R by the negative slope of the line obtained from the plot of ln k' *versus* $1/T$ *(Figure 12)*. The experimental activation energy E'' of cross-link formation is obtained in a similar way *(Figure 13)*. Other activation parameters of tBPIB decomposition are obtained from the value of E' using the following equations:

$$\Delta H^{\ddagger} = E' - RT$$

$$\Delta S^{\ddagger} = R\{\ \ln \frac{k'h}{kt} + \frac{\Delta H^{\ddagger}}{RT}\}$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

where, $\Delta H^{\ddagger}$ is the activation energy
$\Delta S^{\ddagger}$ is the activation entropy
$\Delta G^{\ddagger}$ is the activation free energy
h is Planck constant
k is Boltzman constant.

The relationship between ln k' and $1/T$ apparently shows a strong departure from linearity at temperatures greater than 70°C for systems containing more than 1 p.h.r. fructose *(Figure 12)*. This departure is partly due to the temperature dependence of the experimental activation energy, but the major factor is probably the occurrence

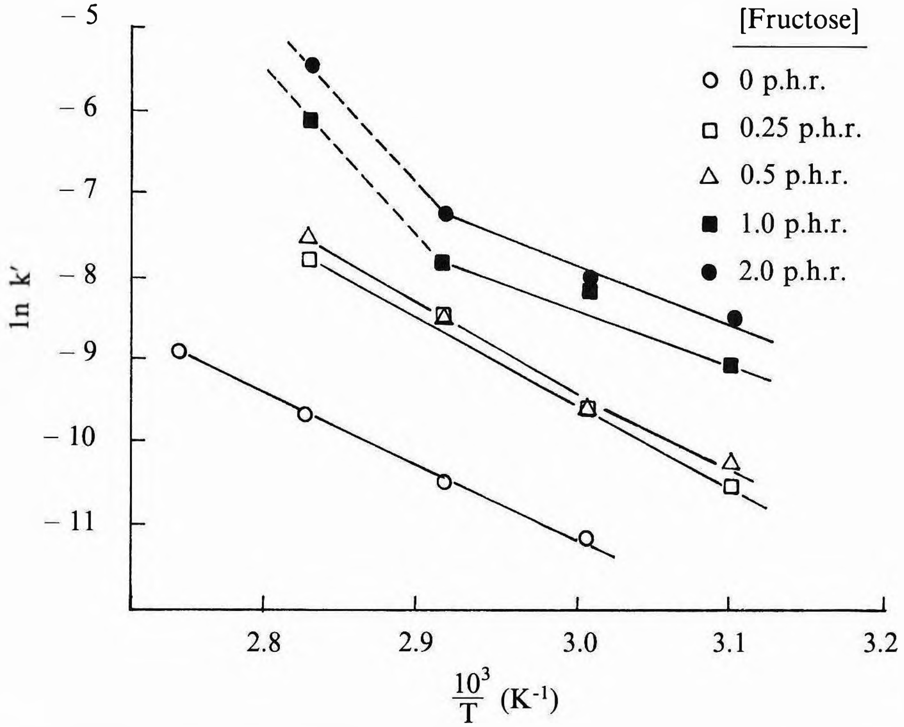

Figure 12. Plots of ln k′ against T^{-1} for prevulcanisation using 5.56 × 10^{-5} g mol/g rubber tBPIB and various fructose concentrations.

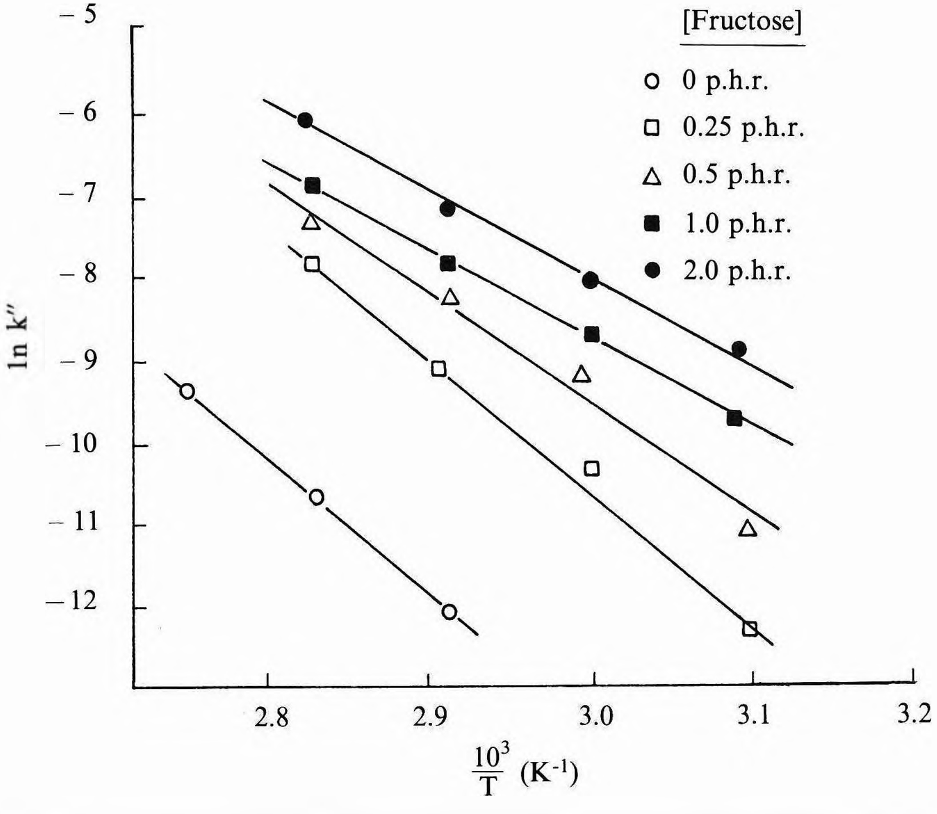

Figure 13. Plots of ln k″ against T^{-1} for prevulcanisation using 5.56 × 10^{-5} g mol/g rubber tBPIB and various fructose concentrations.

of two competing reactions[7]. In the present case, these reactions may be those of activated and non-activated decomposition of tBPIB and the latter reaction probably predominates at the higher temperatures. Calculation of the E' value in the temperature range, 70°C to 80°C for the system containing 2 p.h.r. fructose produced an E' value of 135 kJ/mol, which is approximately equal to the activation energy of non-promoted decomposition of tBPIB in chlorobenzene[8].

The value of E' for the decomposition of tBPIB in NR latex without the addition of fructose was found to be 79 kJ/mol *(Table 1)*. The lower activation energy for the decomposition of tBPIB in NR latex compared to that in chlorobenzene probably suggests that some of the non-rubber substances activate the decomposition of tBPIB. The E' and $\triangle H^{+}$ values increase and then decrease with increasing fructose concentrations. However k' was shown to increase with increasing fructose concentrations *(Figure 7)*. Thus, the rate of tBPIB decomposition appears to be influenced by both the activation energy and activation entropy of decomposition, that is the activation free energy which decreases with increasing fructose concentrations *(Figure 14)*. A higher value of $-\triangle S^{+}$ for the decomposition of tBPIB in NR latex compared to the decomposition in chlorobenzene[8] suggests the formation of a more rigid tBPIB-activator(s) complex in NR latex. The activation energy for crosslink formation decreases and then becomes constant with increasing fructose concentrations (0 to 2 p.h.r.) The activation energy for crosslink formation is higher than that for tBPIB decomposition, for all the systems studied. For comparison, the activation energy[9] for the decomposition of dicumyl peroxide in *cis*-1,4-polyisoprene and the activation energy for the crosslink formation are both the same, 150 kJ/mol.

Initial Rate of tBPIB Decomposition

The dependence of the initial rate of tBPIB decomposition, $(d[P]/dt)_o$, on the initial concentrations of tBPIB, $[P]_o$, was analysed. The value of $(d[P]/dt)_o$, was obtained from the slope of the concentration of residual peroxide, $[P]$, *versus* time curve at the initial stage of the reaction. Plotting $\ln\,(-d[P]/dt)_o$ against $\ln\,[P]_o$ for reaction systems for which $[F]_o$ is kept constant, a straight line with slope n is obtained *(Figure 15)*. Plotting $\ln\,(-d[P]/dt)_o$ against $\ln\,[F]_o$ for reaction systems for which $[P]_o$ is kept constant, a straight line with slope m is obtained at the higher range of initial fructose concentrations *(Figure 16)*. The value of n is approximately equal to 1/2 for both the systems shown in *Figure 15*. The value of m shows a temperature-dependence, being equal to approximately 1.0, 0.7 and 0.6 at 50°C, 60°C and 80°C respectively.

TABLE 1. ACTIVATION PARAMETERS OF tBPIB DECOMPOSITION AND CROSSLINK FORMATION FOR PREVULCANISATION USING 5.56 × 10^{-5} G MOL/G RUBBER OF tBPIB AND VARIOUS CONCENTRATIONS OF FRUCTOSE

[Fructose] (p.h.r.)	E' (kJ/mol)	$\triangle H^{+}$ (kJ/mol)	$\triangle G^{+}$ ((kJ/mol)	$-\triangle S^{+}$ (J/mol/K)	E'' (kJ/mol)
0	79	76	110	102	142
0.25	93	90	106	48	139
0.5	87	84	105	64	112
1.0	62	59	103	131	92
2.0	65	62	101	118	92

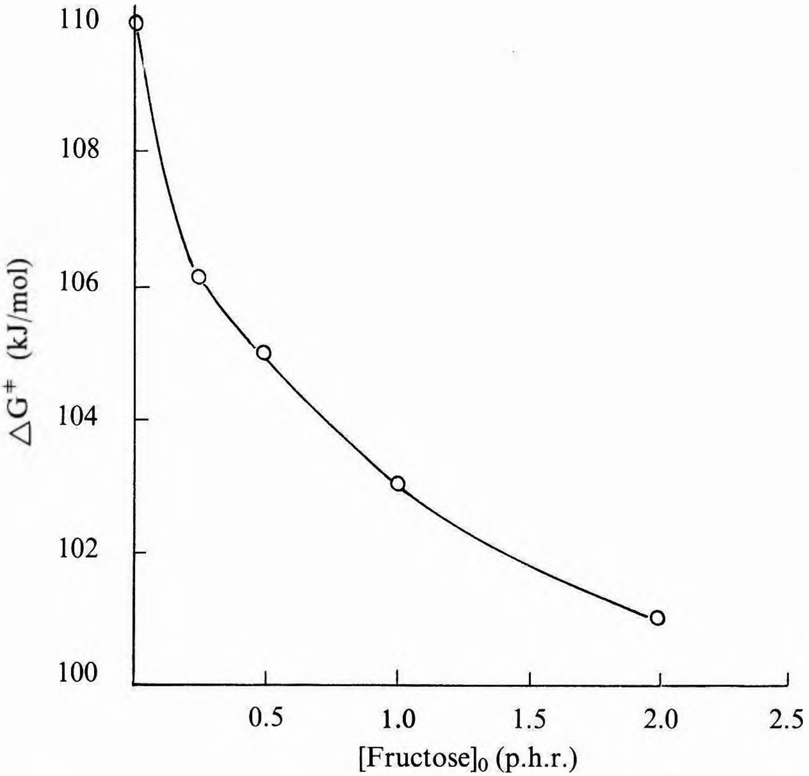

Figure 14. Effect of initial fructose concentrations at constant tBPIB concentration of 5.56×10^{-5} g mol/g rubber on $\triangle G^{\ddagger}$.

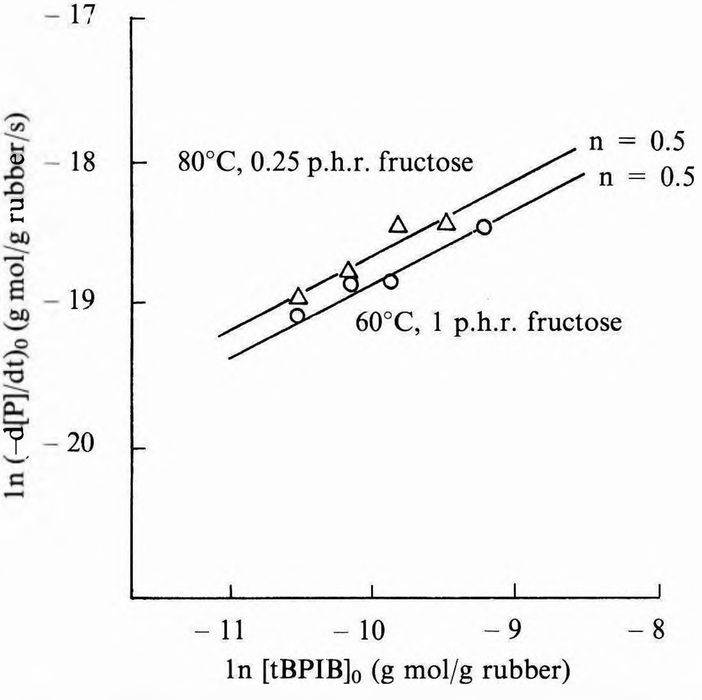

Figure 15. Plots of ln $(-d[P]/dt)_0$ against ln $[tBPIB]_0$ using two different initial fructose concentrations and temperatures.

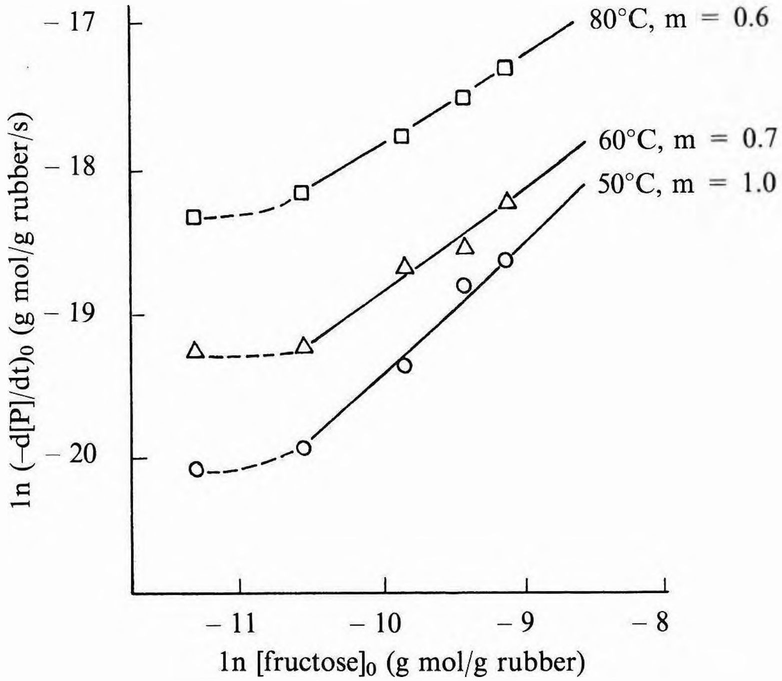

Figure 16. Plots of ln $(-d[P]/dt)_0$ against ln $[fructose]_0$ using initial tBPIB concentration of 5.56×10^{-5} g mol/g rubber at various temperatures.

The values of *m* obtained for reactions carried out at 60°C and 80°C are kinetically not rational numbers. The results probably suggest that the initial rate of tBPIB decomposition comprises more than one term containing the fructose concentration:

$$(-d\,[P]/dt)_o = [P]_o^{1/2}\,(k_1 + K_2\,[F]_o^{1/2} + K_3\,[F]_o + \ldots\ldots)$$

where k_1, k_2, k_3.... are the rate coefficients for tBPIB decomposition, associated with the appropriate terms.

The decomposition of peroxide has seldom been found to be half order with respect to peroxide concentration. The decomposition of peroxide can be half order with respect to peroxide concentration if the decomposition is induced by solvent radicals and the termination reactions involve recombination of radicals derived from the peroxide[10]. Such reactions, however, are perhaps not important for the reaction systems investigated in this report. However, under certain conditions, induced decomposition of tBPIB may be significant[10,11]. It was shown earlier that the overall rate of tBPIB decomposition is first order with respect to peroxide concentration. It is not clear why the reaction orders with respect to peroxide concentration at the initial stage of reaction and during the course of the run are different. The results suggest that the initial rate of decomposition is faster than the subsequent rate of decomposition. Perhaps the concentration of agents that accelerate the initial rate of tBPIB decomposition depletes rapidly so that the subsequent reaction would be first order with respect ot tBPIB concentration.

CONCLUSION

Decomposition of tBPIB in NR latex was found to be first order with respect to peroxide concentration. However, an investigation of the initial rate of tBPIB decomposition in NR latex revealed a more complex rate expression than a simple first-order formulation. The rate coefficients for tBPIB decomposition and crosslink formation were generally found to increase with increasing fructose concentrations and temperatures. It is the activation free energy rather than just the activation energy that determines the rate coefficient of tBPIB decomposition. At high prevulcanisation temperatures, the rate coefficient of crosslink formation tends to be significantly greater than the rate coefficient of tBPIB decomposition. The instantaneous crosslinking efficiency of tBPIB systems was found to increase with prevulcanisation time, suggesting that the concentration of free-radical scavengers decreases with prevulcanisation time. In some reaction systems, the instantaneous crosslinking efficiency tends to be greater than 50%, suggesting that both the alkyl and alkoxy radicals generated from the decomposition of tBPIB participate in the crosslinking reaction.

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Ultrastructure of the Principal Extrafloral Nectaries of Hevea brasiliensis

SAMSIDAR HAMZAH* AND ABU BAKAR ATIM*

The structural changes leading to nectar secretion in the extrafloral nectaries of Hevea *were examined by light and electron microscopy. The nectary is served by vascular tissues which arise from the branch supplying to the leaves. Only the phloem traverses up to the sub-secretory cells. Ultrastructural evidence support an energy-requiring, eccrine mode of secretion, while the pathway taken by the nectar can be both apoplastic and symplastic. Release of nectar is by means of the cuticle which ruptures under pressure. The significance of nectar production to latex flow physiology is also discussed.*

The extrafloral nectaries described in this paper refer to the structures/glands, normally three in number but varying from two to four, that are borne at the point of attachment of the stalks (petiolules) of the three leaflets. Nectar is secreted from these glands exclusively during refoliation. There are also other extrafloral nectaries in *Hevea*, e.g. on the leaf axils, flowers and abaxial leaf surfaces, but their nectar secretion is minimal. A brief description of the structure of these nectaries has been given by Heusser[1] in 1920 and Frey Wyssling[2] in 1933 gave an account of their morphology, anatomy and physiology.

The recent interest in the nectaries in *Hevea* is due to the increased importance of bee keeping under rubber trees. The bees particularly depend on nectar from these extrafloral nectaries. Studies carried out in the Rubber Research Institute of Malaysia (RRIM) have shown some inter-relationship between nectar flow, development of the bee colony and honey yield[3]. In the field of ultrastructure, many workers[4-7] are also interested in establishing the various methods of nectar secretion based on cytology of the secretory cells.

This paper traces the ultrastructural changes leading to nectar secretion with special attention to the mode of secretion. The association of the latex vessel system and phloem in relation to nectar secretion is also discussed.

MATERIALS AND METHODS

Observations of nectaries were made from leaves of mature and untapped RRIM 600 trees grown in the RRIM Experiment Station at Sungei Buloh. Nectaries of various secreting stages corresponding to the different colours of the leaf related to the developmental stages, *i.e.* bronze for pre-secretory, light green for secretory and dark green for post-secretory, were sampled from three trees. These were fixed in a mixture of 3% paraformaldehyde and 2.5% glutaradehyde in 0.1 *M* phosphate buffer (pH 7.3) with 0.15 *M* sucrose added, for 2 h and then post-fixed in buffered 2% OsO_4 for another 2 h. Dehydration was in the graded ethanol series. Tissues were embedded in Epon-araldite according to Mollenhauer[8]. Ultra-thin sections were double-stained with saturated uranyl acetate and lead citrate and examined on Philips EM 300.

For light microscopic studies, semi-thin sections made from the above resin-embedded blocks were stained with 1% toluidine blue. Paraffin-embedded sections were also examined and these were stained with safranin and fast green[9].

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*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

OBSERVATIONS

Light Microscopy

The extrafloral nectary tissue is composed of two groups of cells distinct from the neighbouring parenchyma cells *(Figure 1)*. The secretory layer, which is a modified epidermis, is made up of two to three tiers of dense columnar cells. Below them, the one to two layers of sub-secretory cells, are arranged according to the contour of the secretory layer. The other secretory cells are randomly arranged among the parenchyma cells, and are distinguished by their dense cytoplasm *(Figure 2)*.

The vascular system supplying the nectaries arises from the branch of the vascular system which supplies to the leaves *(Figure 1)*. However, only the phloem traverses as far as the sub-secretory cells, the xylem stops at the boundary between the parenchyma and the sub-secretory cells *(Figure 2)*.

The nectaries are covered with a thin cuticle which becomes more noticeable when nectar is being secreted, that is when the cuticle is detached from the surface at some points forming 'balloons'. Latex vessels have also been observed to traverse up to the sub-secretory cells and are closely associated with the phloem *(Figure 3)*.

Electron Microscopy

Pre-secretory stage. The secretory cells have very dense cytoplasm due to heavy deposits of granular material which sometimes mask the organelles (*Figures 4* and *5*). These columnar cells have thin walls, large nuclei, abundant mitochondria and dense amoeboid plastids containing very few thylakoid membranes. Endoplasmic reticulum of both the smooth and rough types are present and are mostly found close to the cell wall. Dictyosomes are relatively rare.

Few vacuoles are found in the secretory cells and they are small and often filled with stainable material of various densities and structures. Sometimes the vacuoles are completely filled with electron-dense material, possibly tannin. Plasmodesmata are common between adjacent secretory cells and between sub-secretory and secretory cells.

The sub-secretory cell is similar in appearance to the secretory cell except that the sub-secretory cell has larger and empty vacuoles and plastids containing starch grains *(Figure 6)*.

Secretory stage. The general impression given by the secretory cells during secretion is the reduction of cytoplasm, due to the presence of large vacuoles (at least one per cell). These are always filled with electron-dense material either granular in appearance or as thick deposits scattered or lining the periphery of the vacuoles *(Figure 7)* and are possibly tannins.

Besides these types of large vacuoles, smaller ones are also common and these are present in clusters or merging into bigger ones. The smaller ones are always filled with lighter stainable material. The cytoplasm remains dense as in the pre-secretory stage. Mitochondria are abundant and some plastids contain numerous plastoglobuli.

Endoplasmic reticulum is more prominent than in the pre-secretion stage but does not seem to show very much dilation. Even though sometimes located parallel to the plasmalemma, there appears to be no association with them. Dictyosomes are also rare.

An interesting feature to note at this stage is the appearance of prominent intercellular spaces especially in between the longitudinal walls of the secretory cells *(Figure 8)* and seldom between the sub-secretory cells. Some spaces would persist right up to the free surface of the secretory cells *(Figure 7)*. Stainable material is always observed in these spaces which could either be the cuticle or the nectar itself, but at a higher magnification, this material resembles the cuticle taken from the secretory cell of a bronze leaf, *i.e.* before secretion *(Figure 9)*. The cuticle is shown to be fibrillar in nature, loosely arranged unlike the cellulose walls below it. The swelling of the cuticle as observed under the light microscope

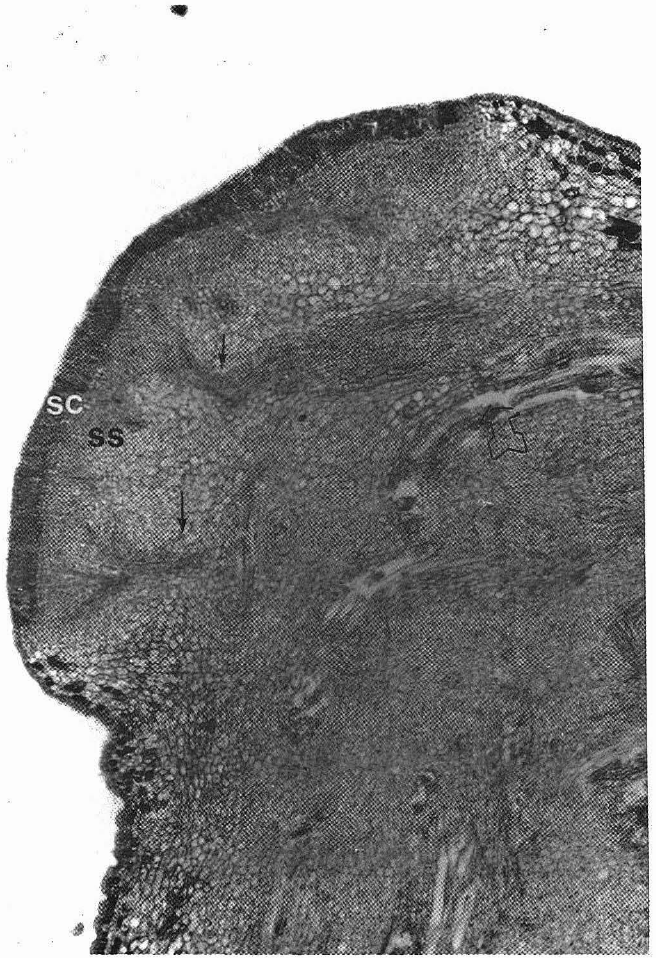

Figure 1. Nectary gland showing secretory cells (sc), sub-secretory cells (ss), vascular system supplying leaf (large arrow) and a branch of it supplying to the nectary (small arrows). Magnification 40 ×.

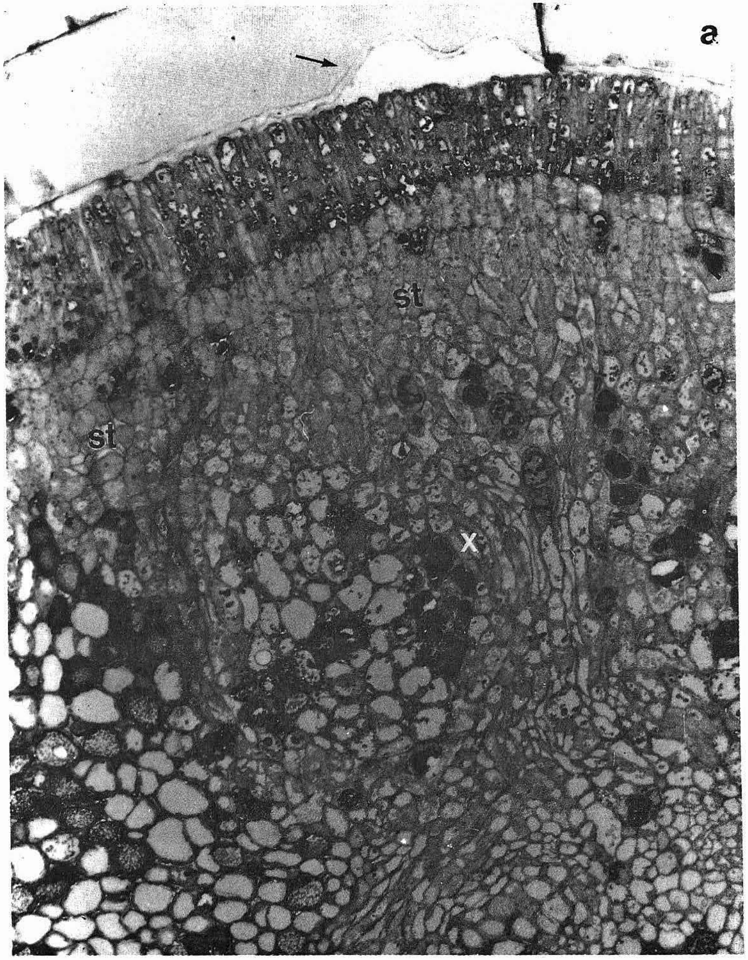

Figure 2. Nectary gland during secretion showing cuticle ballooning (arrow). Note relative position of sieve tube (st) and xylem (x). Magnification 160 ×.

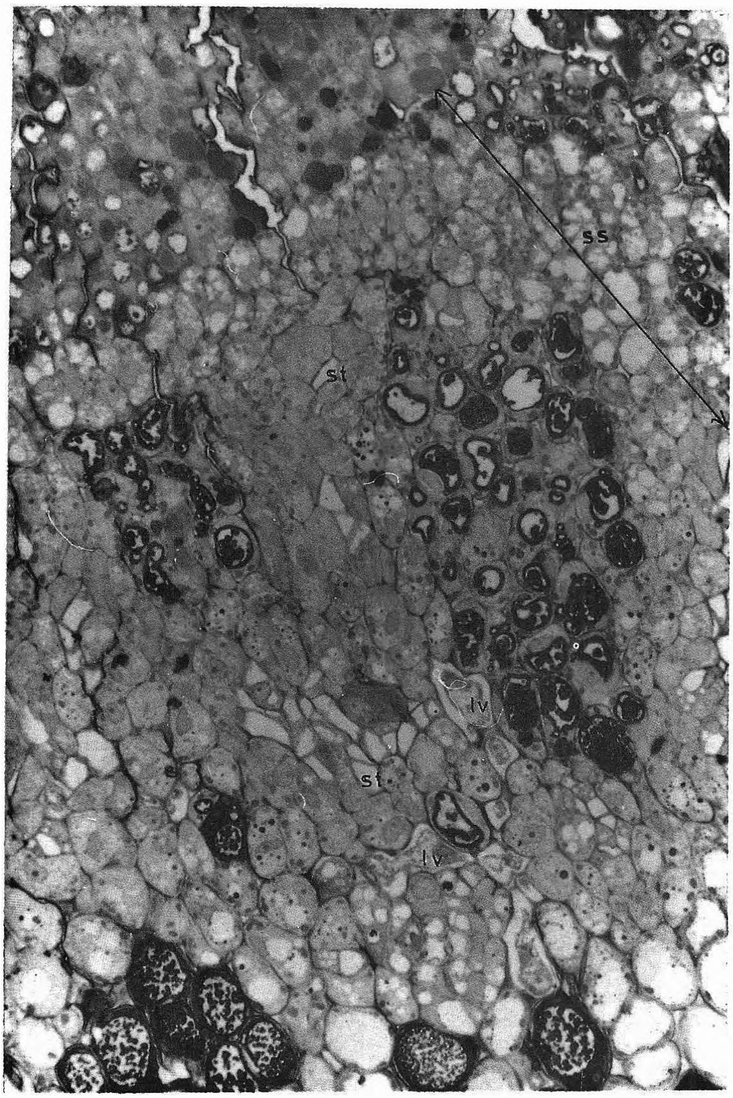

Figure 3. Sieve tube (st) and latex vessel (lv) distribution in the sub-secretory area (ss). Magnification 330 ×.

and in the scanning electron microscope *(Figure 10)* was never observed at the ultrastructural level.

Figure 11 shows a sieve tube in relation to its neighbouring cells. In most observations, the sieve tubes are about the same size or never larger than the companion cells (see *Figure 3* for overall view). Companion cells are characterised by the dense cytoplasm and smaller vacuoles compared to the parenchyma cells. Plasmodesmatal connections between sieve tubes and companion cells have also been observed *(Figure 12).* Latex vessels are also usually located within the vicinity of the sieve tubes. In this sample preparation however, the rubber particles appear to be rather unstable.

The sub-secretory cells during secretion have smaller vacuoles and there is an increase of

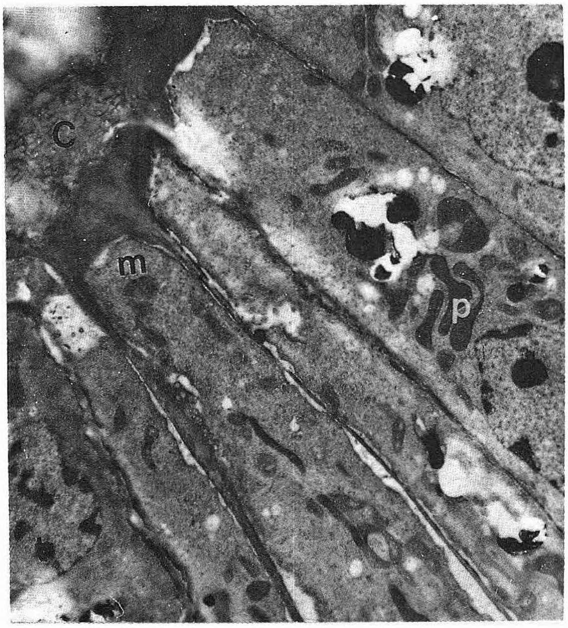

Figure 4. Secretory cells at pre-secretion showing dense cytoplasm, plastids (p), mitochondria (m) and cuticle (c). Magnification 1800 ×.

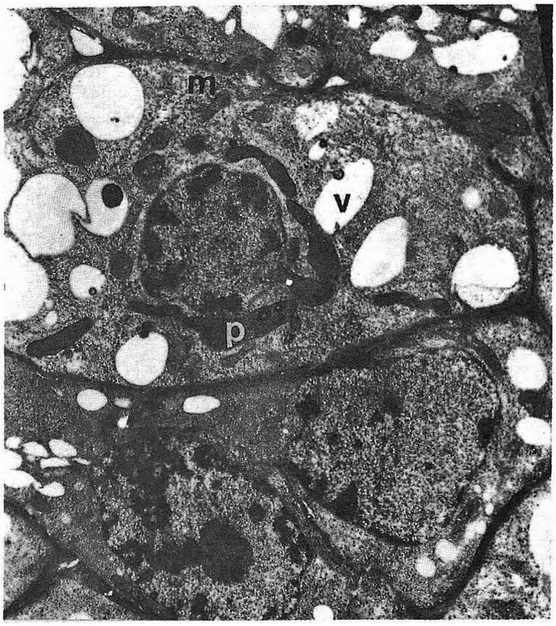

Figure 6. Sub-secretory cells at pre-secretion showing plastids (p), mitochondria (m) and vacuoles (v). Magnification 1800 ×.

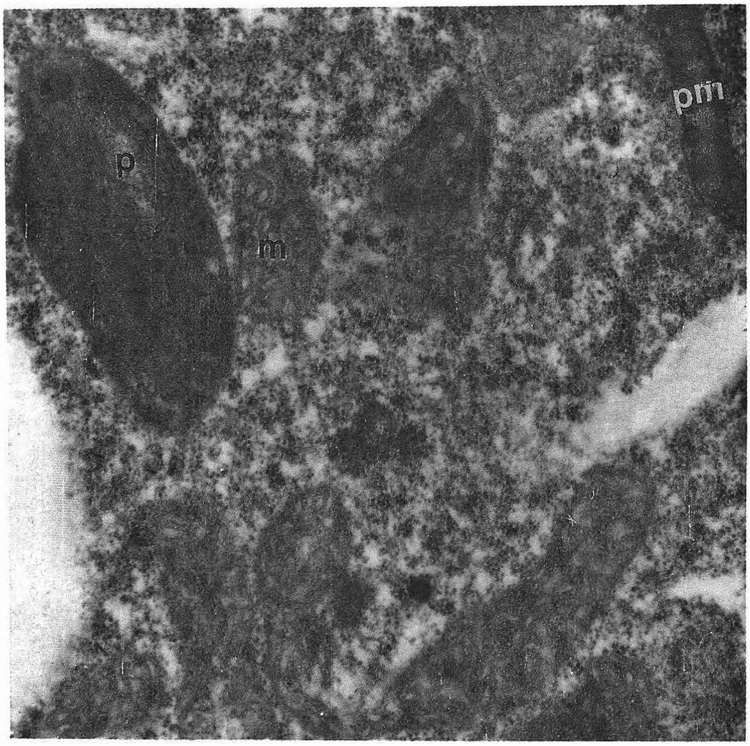

Figure 5. Cytoplasm in the secretory cell at pre-secretion masking the organelles: plastid (p), mitochondria (m). Note the plasmodesmata (pm). Magnification 27 000 ×.

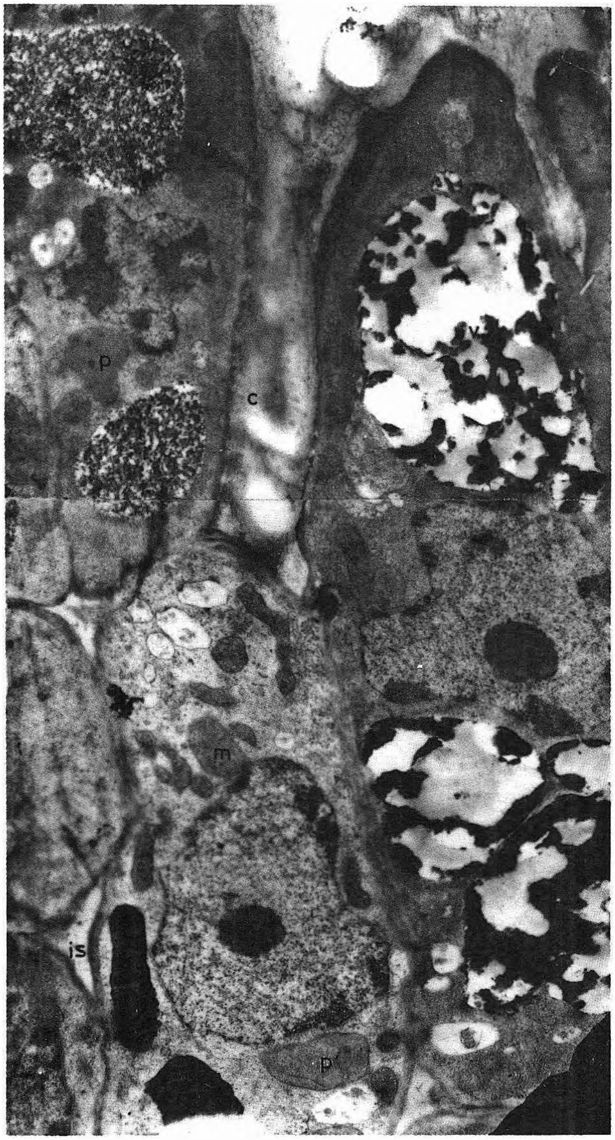

Figure 7. Secretory cells during secretion showing vacuoles (v), mitochondria (m), plastid (p). Intercellular spaces (is) lined with cuticle (c) are continuous with the external surface. Magnification 4000 ×.

endoplasmic reticulum compared to the pre-secretion stage.

Post-secretion. Since samples were taken when there were no traces of nectar observed, there is no way of determining when secretion ceased. The secretory cells may therefore appear similar to those at secretion or they may have very dark cytoplasm, normally occupying a thin peripheral layer as a result of the large vacuoles present *(Figure 13)*. Mitochondria, dictyosomes, endoplasmic reticulum and small vacuoles

Figure 8. Secretory cells showing intercellular spaces (is) in between them. Magnification 3000 ×.

Figure 9. High magnification of cuticle (c) above the cell wall (cw) (left), compared with stainable material in the intercellular spaces (right). Magnification 27 000 ×.

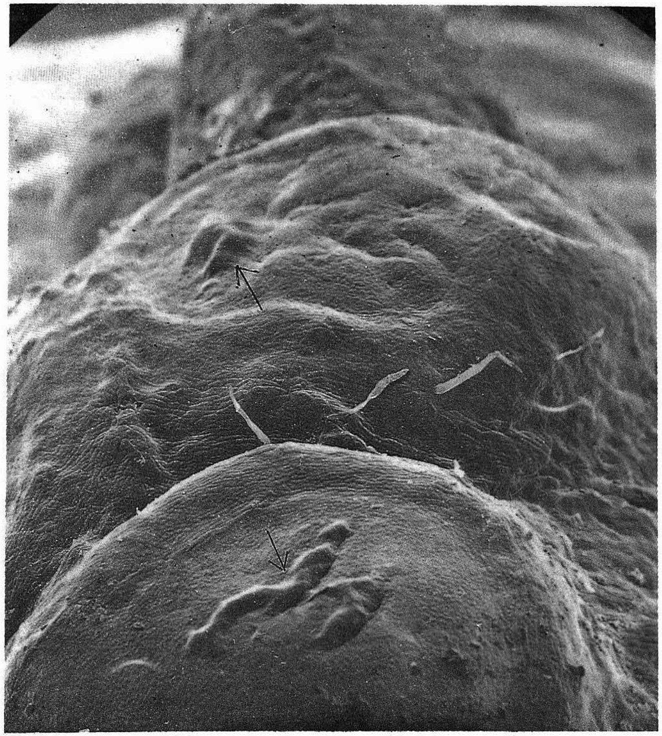

Figure 10. Scanning electron microscopy of the nectary glands showing buckling of the cuticle (arrows). Magnification 90 ×.

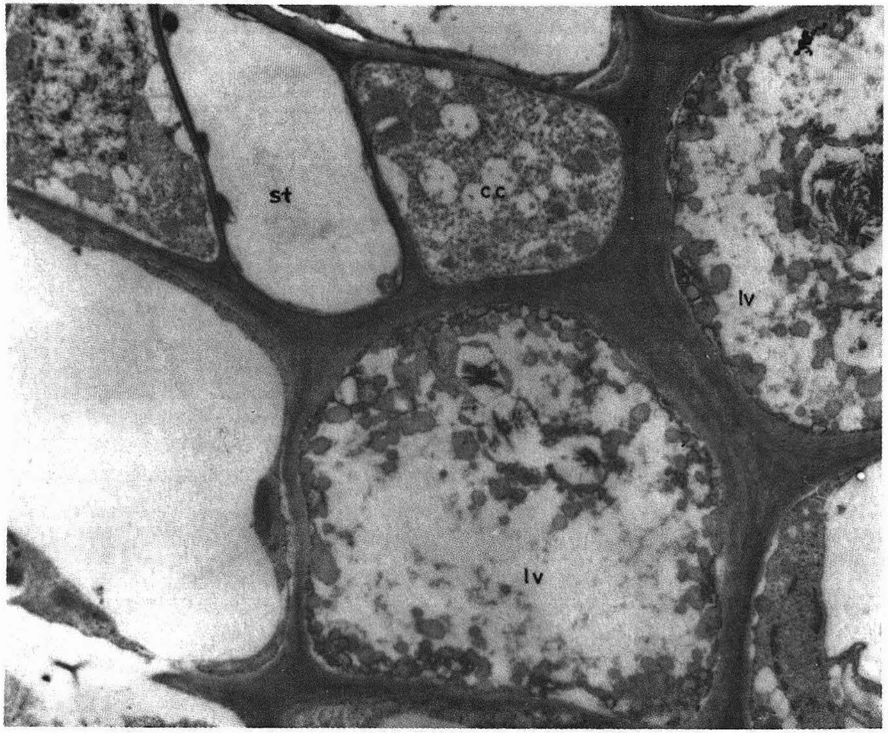

Figure 11. Sieve tube (st) in relation to companion cell (cc) and latex vessels (1v). Magnification 4000 ×.

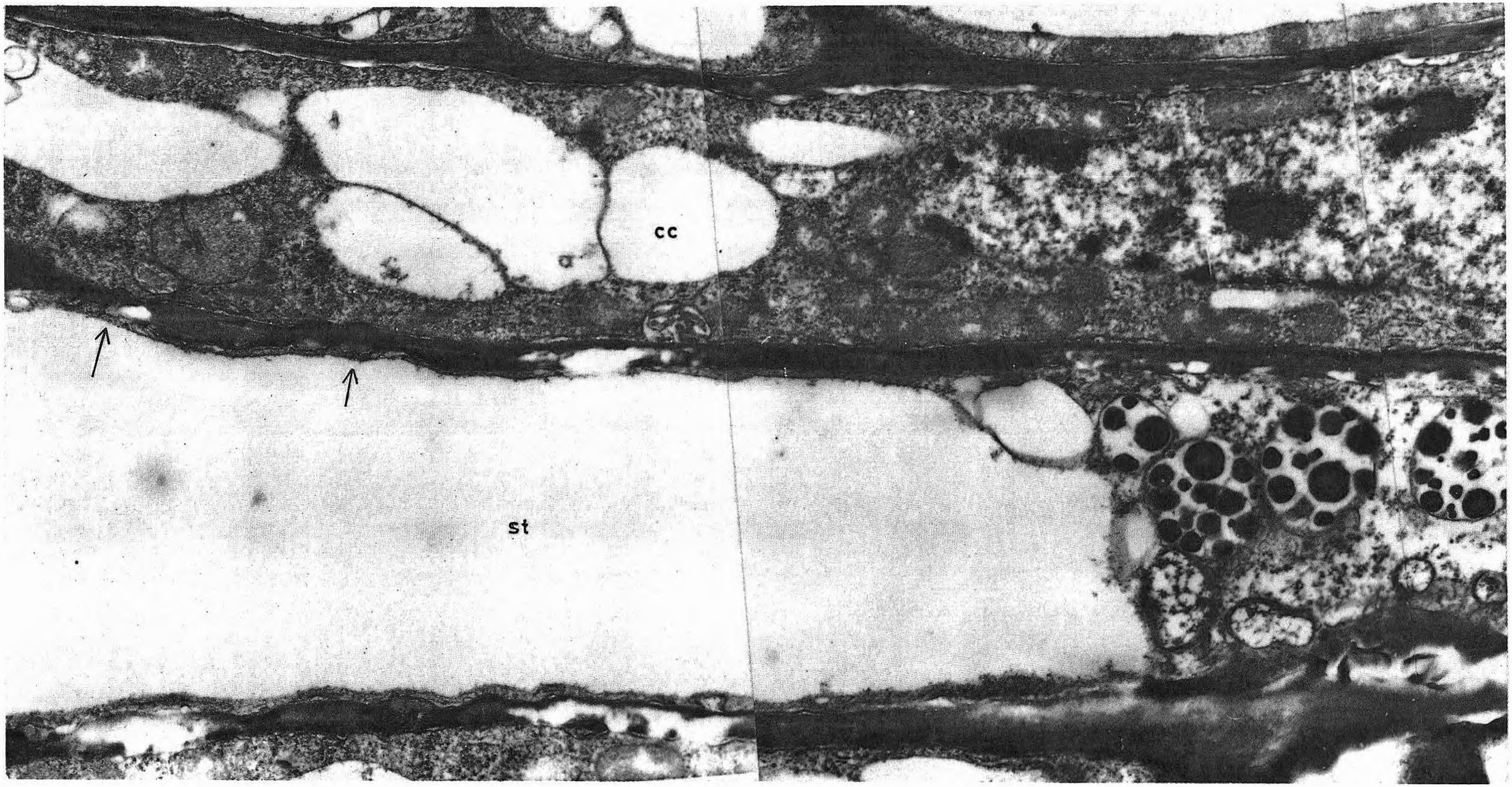

Figure 12. Longitudinal section of sieve tube (st) and companion cell (cc) showing the plasmodesmatal connection (arrow) between them. Magnification 4000 ×.

containing vesicles are also present *(Figure 14)*. Plastids have very well-developed thylakoid membranes.

The cuticle ultrastructure is no longer fibrillar but has become rather thick and dense. It is possible that the microstructure has been altered. Continuity of the cuticle is also broken in some parts of the nectary surfaces.

DISCUSSION

The ultrastructure of the nectary tissue of *Hevea* observed during secretion is typical of most nectary cells[4-7], *i.e.* dense cytoplasm, abundant endoplasmic reticulum, mitochondria, small vacuoles and plasmodesmata. Dictyosomes are also present but relatively rare. An exception perhaps is the presence of iarge vacuoles containing dark-staining material, possibly tannin, which reduces the cytoplasm. The definite role of these large vacuoles at this stage is unknown but these are perhaps a result of normal cell maturity.

The presence of intercellular spaces and plasmodesmata could indicate an apoplastic and symplastic route respectively for the nectar secretion. Nectar which has been shown to be secreted phloem sap[10] is transported through the symplasm *via* the plasmodesmatal connections that exist right through to the secretory cells. The enlarged companion cells could also play a role in the short-distance transport from the sieve tubes to the sub-secretory cells as was suggested for the extrafloral nectaries of *Passiflora*[5]. On the other hand, an apoplastic route would also be possible especially at the secretory cells where large spaces were observed during secretion. The lining of the spaces with cuticle and its continuity with the external surface have also been shown in *Brassica*[6], *Vinca* and *Citrus*[7]. In these plants however, the spaces are in continuity with the stomatal spaces, the stomata being the exit zone for the nectar. In *Hevea*, nectar is probably released through the cuticle which breaks up upon pressure building up, resulting from nectar accumulation beneath the cuticle. This is seen in the swelling of the cuticle and its discontinuity under the electron microscope.

As for the mode of secretion, the ultrastructural evidence such as abundance of mitochondria and lack of dictyosomes and dilated endoplasmic reticulum seem to indicate an active eccrine machanism rather than the granulocrine. A similar conclusion based on the above observations was also made for *Brassica napus*[6] and *Passiflora*[5]. The abundance of endoplasmic reticulum and mitochondria after the cessation of secretion however may indicate a different role for them. These may be involved in the lysis of cytoplasm as demonstrated in *Sambucus*[4], which was inferred to result in the darkening of the cytoplasm.

The occurrence of phloem and the absence of xylem in the sub-secretory cells are significant to the sugar content of the nectar. The mean of 13% sugar content obtained in an untapped ten-year-old tree[11] is quite low as compared to the values (up to 50% sugar) given by Frey-Wyssling[10] in nectaries solely supplied by the phloem. Our values obtained were measured quite early in the morning and it is possible that evaporation had not taken place yet.

The presence of nectar is significant in *Hevea*. It not only provides nectar for the bees and other nectarphillic insects, but is also related to other physiological functions. Available data has shown that the volume of nectar and its sugar content were reduced when the trees are tapped[11]. It is possible that nectar production and latex flow are inter-related. Studies by Low and Gomez[12] concluded that the increase of sucrose in the second tapping of trees tapped twice daily was due to the import of sugars from remote regions of the panel. Hence, if trees are tapped, there is a possibility that sugar meant for the nectar is mobilised to the tapping panel. The reduction in volume of sugar in the nectar can also be explained by the effect caused on the phloem, as a result of the suction pressure created when turgor is lost during tapping[13].

Sections of nectary glands have also been seen to harbour fungal colonies which may cause leaf diseases[14]. It is possible that the fungi use the nectar as their substrate and hence the glands act as the point of entry of pathogenic organisms. Based on the above

Figure 13. Secretory cells at post-secretion showing both typical secretory cell (ts) and cell undergoing cytolysis (cs). Magnification 4000 ×.

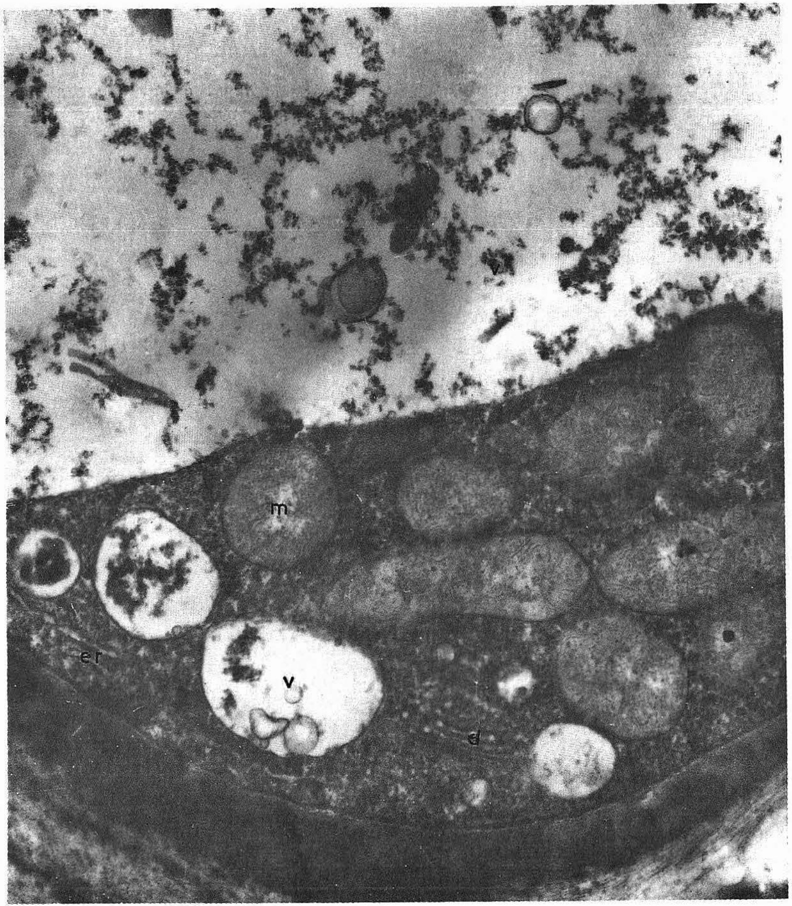

Figure 14. Secretory cell with darkened cytoplasm showing mitochondria (m), dictyosome (d), vacuoles (v) and endoplasmic reticulum (er). Magnification 27 000 ×.

observation it would be interesting to speculate whether the removal of nectar by nectarphillic insects would reduce the incidence of leaf diseases.

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Epoxidised Natural Rubber

I. R. GELLING*

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[1] 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[2,3,4] to soft rubbery polymers[5,6,7]. The epoxidation of NR and other unsaturated polymers was stated to increase solvent resistance and improve wear resistance and mechanical properties[8,9]. However, other publications have reported a reduction in tensile strength properties[10,11]. A number of epoxidised latices have also been studied[9,12,13].

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[14,15] and it is known that secondary ring-opening reactions of the initially formed epoxide group can occur[16].

A systematic study[5,17] 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[18] *(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[5,19]. This arises from the attack of a ring-opened epoxide on

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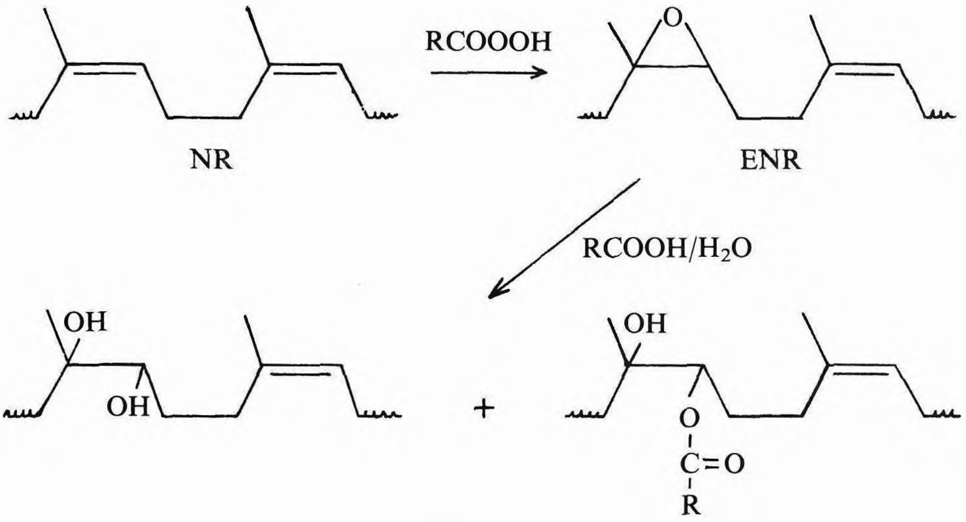
*Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford, SG13 8NL, United Kingdom



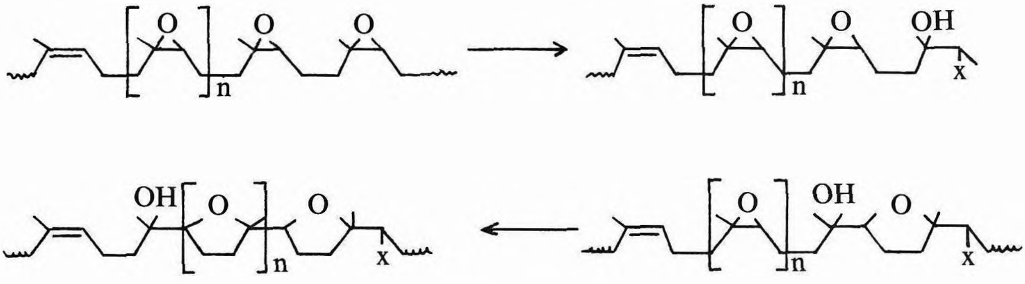
Scheme 1

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}H NMR spectroscopy and by model chemistry[5,19]. 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[4] in the epoxidation of NR latex with hydrogen peroxide and formic acid.

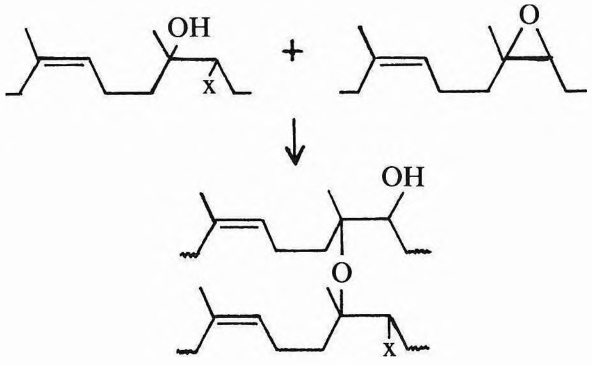
In the light of the established ring-opening chemistry that can occur during the epoxidation of NR, it is easy to understand the variety of products that were reported in the earlier literature on this topic.

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[19].

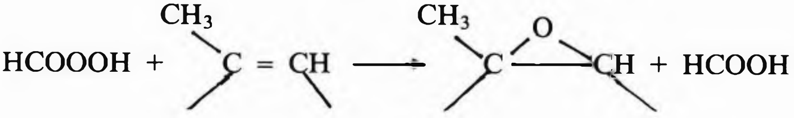
Under carefully controlled conditions, NR latex can be epoxidised to over 75 mole% without the formation of secondary ring-opened structures. Both preformed peroxyacetic acid[5,19] or the *in-situ* generation of peroxyformic acid[20] from hydrogen peroxide and formic acid can be employed *(Scheme 4)*. 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[7,21]. The major factor in controlling the *in-situ* epoxidation rate is the formation of the peroxyformic acid from hydrogen peroxide and formic acid[22]. A more detailed study[23] 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, ^1H 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

$$H_2O_2 + HCOOH \rightleftharpoons HCOOOH + H_2O$$



Scheme 4

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

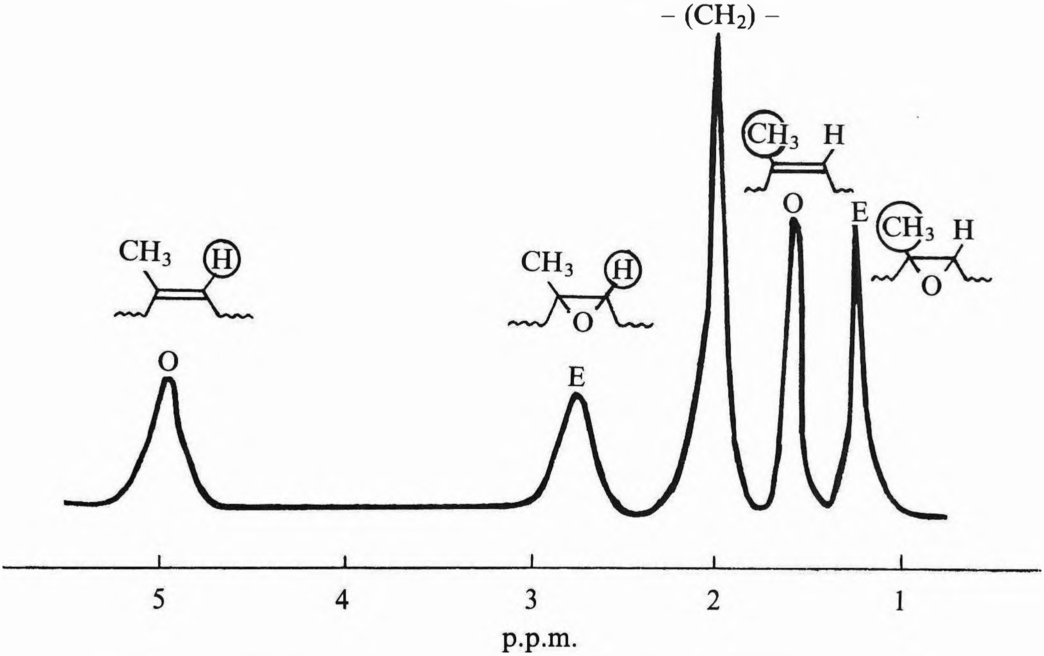


Figure 1. ^1H *NMR spectrum of 50 mole% epoxidised natural rubber.*

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[24]. 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[25]. Further confirmation is obtained from ^{13}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}C NMR and the observed sequences match those calculated for a totally random epoxidation[26]. The ^{13}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[27].

Quantitative analysis of epoxide groups utilises tetraethylammonium bromide[28], hydrochloric or hydrobromic acids, but these reagents when applied to ENR give significantly lower epoxide values than NMR or IR techniques[29]. 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[30] and thus ENR is a *cis* 1,4-polyisoprene with epoxide groups randomly situated along the polymer backbone.

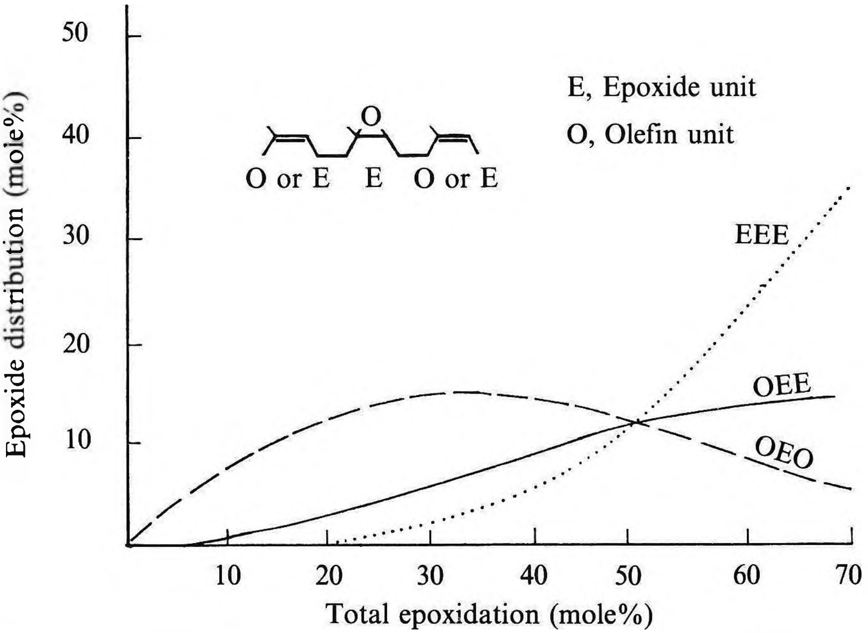


Figure 2. Calculated distribution of epoxide groups for a random epoxidation process.

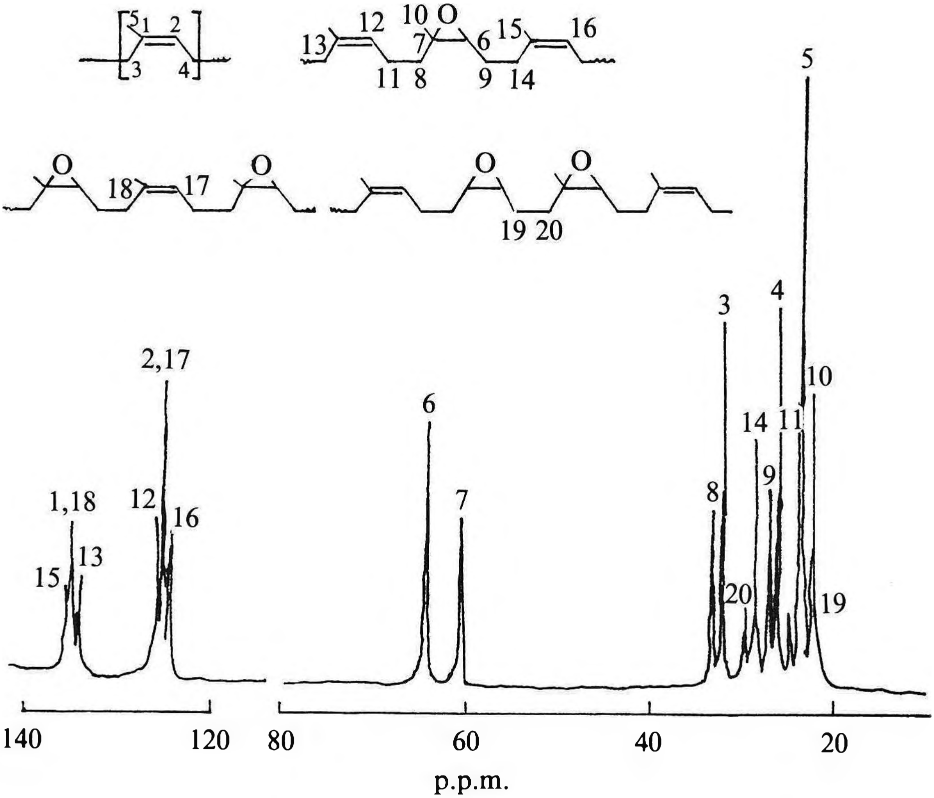


Figure 3. ^{13}C NMR spectrum of 20 mole% epoxidised natural rubber.

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 Epoxyprene 25 and Epoxyprene 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[26]. 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[24] *(Table 1)*, each 1 mole% epoxidation raises the solubility parameter by approximately 0.031 $(Jm^{-3})^{1/2}$.

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

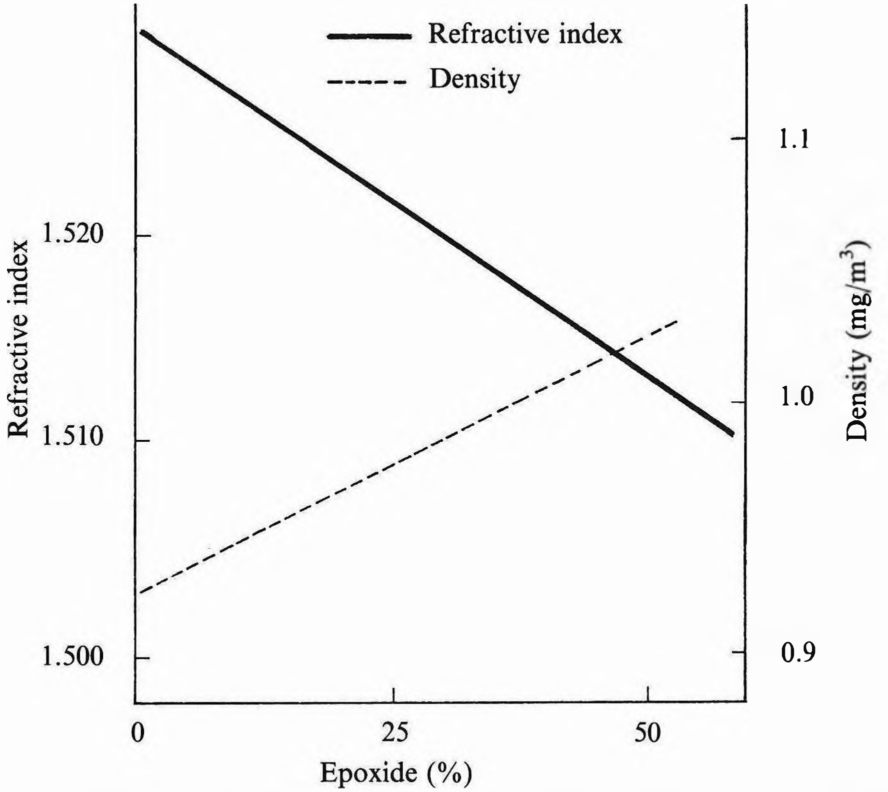


Figure 4. Variation of refractive index and density of ENR with extent of epoxidation.

TABLE 1. SOLUBILITY PARAMETERS OF ENR

ENR (mole% epoxide)	Solubility parameter $(\mathrm{Jm}^{-3})^{1/2}$
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[32] or epoxide[33] 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[34] has shown that the epoxide group is not responsible for the storage hardening of NR.

Compounding and Vulcanisation

Epoxyprene 25 and Epoxyprene 50 have Mooney viscosities in the range 70 to 100 units but break down more readily than NR of comparable viscosity[35] 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[36] 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 crosslink unsaturated polymers[37]. Dibasic carboxylic acids can also be used[38].

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[39]. 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[40]. 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[5,41] 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)*[19], peel adhesion increases[42] as does wet traction[39,42]. The latter is dealt with in more detail in the section under applications. The

TABLE 2. FORMULATIONS FOR ENR

Compound	Formulation 1 Conventional	 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[a]	2	2	2
Antioxidant[b]	1.5	1.5	1.5
Paraffinic wax	3	3	3
Sulphur	2.5	1.5	0.5
CBS[c]	0.6	–	2.5
MBS[d]	–	1.5	–
TMTM[e]	–	1.5	–

[a] N(1,3-dimethylbutyl)-N′-phenyl-p-phenylenediamine

[b] Poly-2,2 4-trimethyl-1,2-dihydroquinoline

[c] N-cyclohexylbenzothiazole-2-sulphenamide

[d] 2-morpholinothiobenzothiazole-2-sulphenamide

[e] Tetramethylthiuram monosulphide

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

Solubility parameters are also a factor in both the uncured and cured adhesion of ENR to other polymers[43].

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[a]							
	1		2			3		
	NR	ENR 50	NR	ENR 25	ENR 50	NR	ENR 25	ENR 50
Mooney scorch, 120°C,								
t_5 (min)	20	14	20	21	38	13	12	28
Monsanto rheograph, 150°C, Arc ± 1								
t_{95} (min)	16	25	10	8	13.5	24	19	15
t_{max} (min)	–	–	13	12	18	60	40	23
$\triangle T$ (d N.m.)	19.2	25.9	23.7	31.6	30.5	27.1	28.2	25.9

[a] 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.

TABLE 4. PHYSICAL PROPERTIES OF ENR VULCANISATES[a] 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[b]	11	11	10	4
Unit cell volume (mm^3)	0.955	0.985	0.999	1.036

[a] 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.

[b] 400% extension, 20°C for 1.5 h.

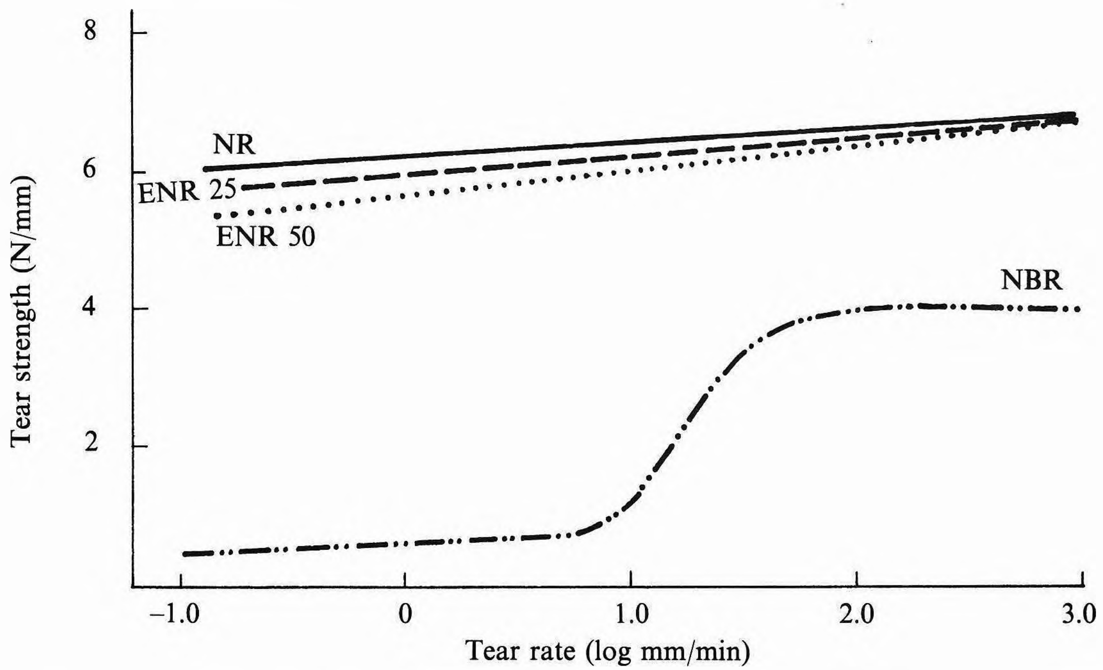


Figure 5. Tearing energies of NR, ENR 25 and ENR 50 compared to a non-strain crystallising NBR.

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[a]

Property	Vulcanisate			
	NR	ENR 25	ENR 50	NBR[b]
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, △T°C from 23°C, 30 min	44	46	52	87
Akron abrasion (mm^3/500 rev.)	45	18	12	13
DIN abrasion (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 (M^4.s^{-1}.N^{-1} × 10^{18})	27.0	8.0	1.98	2.2

[a] 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_{max} at 150°C

[b] 34% acrylonitrile butadiene rubber

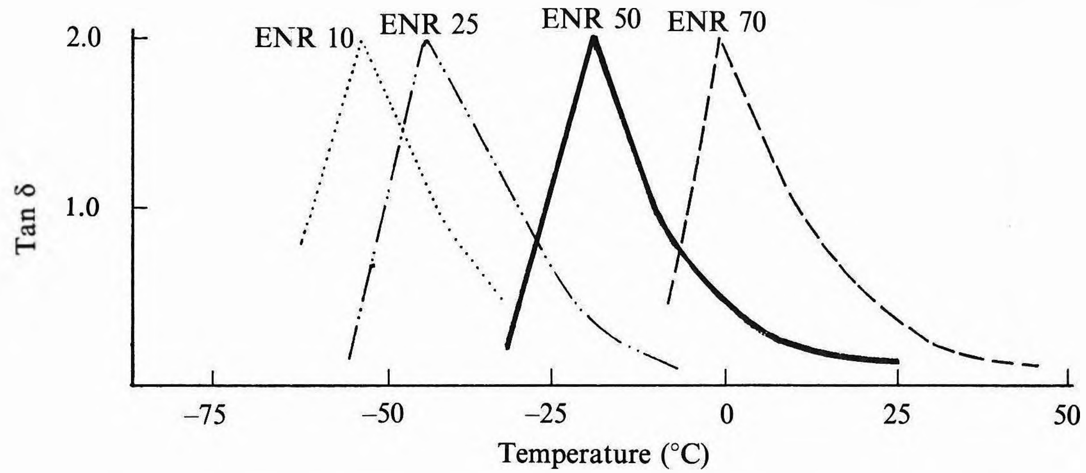


Figure 6. Effect of epoxidation level on temperature/hysteresis profile of ENR.

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

Property	50 p.p.h.r. N330 black[a]			50 p.p.h.r. silica[b]		
	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^3/500 rev)	21	14	11	63	15	14
Goodrich HBU, △T°C (30 min from 100°C)	7	7	23	47	7	19

[a] 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

[b] 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[37] 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[44]. 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)*[42], 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.

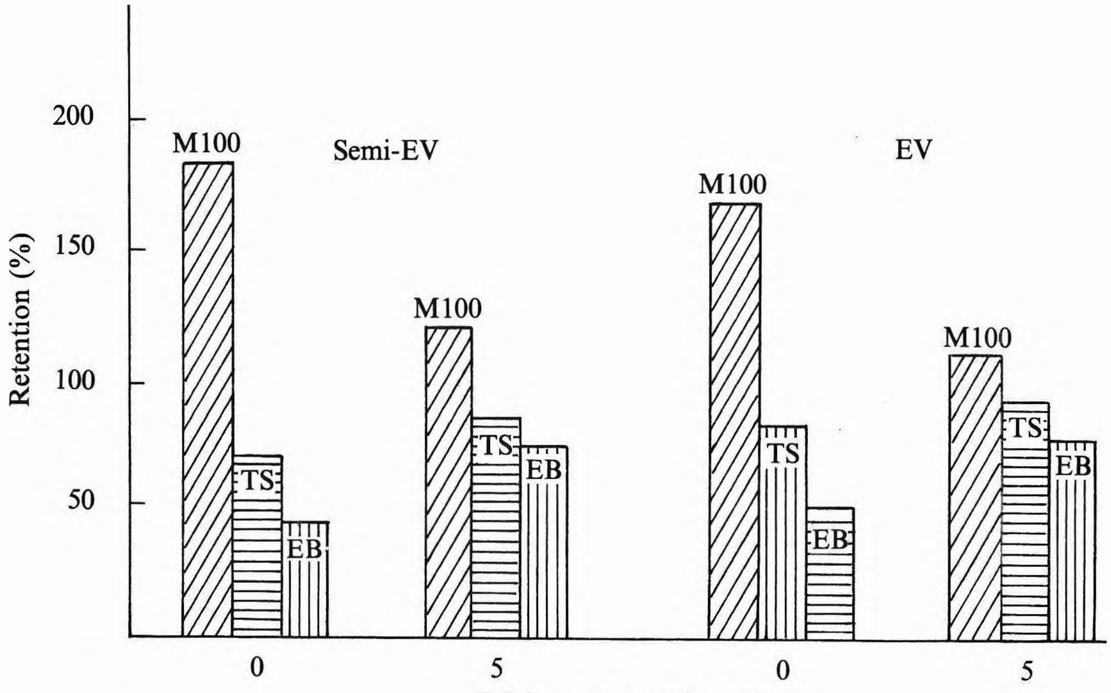


Figure 7. Air aged properties, three days at 100°C, of ENR 50 vulcanisates (50 p.p.h.r. N-330 black and 5 p.p.h.r. process oil; semi-EV Formulation 2 and EV Formulation 3 in Table 2).

TABLE 7. CURED ADHESION OF ENR TO OTHER POLYMERS

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

[a] Rubber failure

[b] Bond failure

[c] A blend of NR/ENR 50 (50:50) applied as a solvent-based adhesive

The adhesive strength to other substrates, nylon[45], brass coated steel[46] and glass[47] 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[46] and a factor of ten in that of ENR 50 to nylon[45]. 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[48] and Haidzir[49] 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[49] and this is particularly marked with regard to air permeability. Blends of ENR 50 with *cis* 1,4-polybutadiene[50] (BR) and styrene butadiene copolymer[51] (SBR) are also two-phase systems and in the former case, optimum properties are reported[51] 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[52].

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[53] on the high adhesion between ENR 50 and PVC, Margaritis *et al.*[54] 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[55] 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[56] and plasticised[57] 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[58,59]. 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.*[60] 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 crosslinked blends. The dynamic vulcanisation of PVC/ENR blends has also been reported[61].

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

The addition of PVC to ENR significantly improves ozone resistance[64]. Flame resistance is also increased[65]. 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[66].

Chlorinated polyethylene[66], chlorosulphonated polyethylene[67,68], chlorinated polypropylene[69], poly (vinylidene chloride – alkyl acrylate) copolymer[69] and chloroprene[70] 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'[71,72,73]. 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[72].

Blends of carboxylated NBR and polychloroprene are also 'self vulcanisable' but are a two-phase immiscible system[74]. 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)

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

Blend system	Property Hardness (Shore A)	M100% (MPa)	TS (MPa)	EB (%)	Resilience (%) 23°C	Tear (N/mm)
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[a]	54	1.25	22.3	634	41	38.5
50/100[a]	55	1.57	20.6	538	47	38.0
ENR 50/Hypalon						
100/100	75	6.18	10.0	205	21	12.8

[a]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[75].

The chlorosulphonyl groups in chlorosulphonated polyethylene react with ENR and blending also yields a self-vulcanising system[67,76,77]. 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[78]. TPE based on ENR, covering a range of hardnesses have been produced[79]. 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[80,81].

Thermoplastic elastomers have also been produced by blending ENR and a styrene-acrylonitrile (SAN) copolymer[82]. 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[83].

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[38], as a means of introducing rubber bound antioxidants[84,85] and as intermediates for further chemical modification[86,87].

Adhesives

Adhesive compositions based on epoxidised natural rubber have been developed for the bonding of vulcanised rubbers of differing polarity[88] 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[89]. The adhesive and sealant properties of ENR have also been utilised in the area of epoxy resin technology[90] and to develop glazing sealing systems[91].

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[92].

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[39] 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[39]. 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.

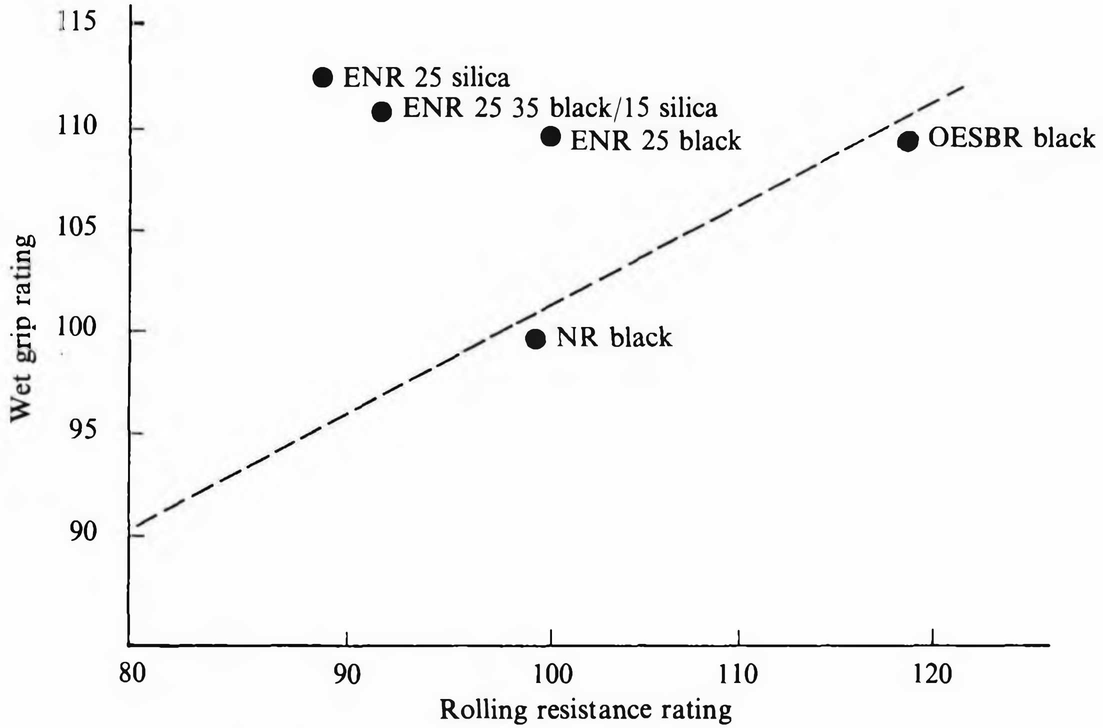


Figure 8. Plot of rolling resistance and wet traction properties of ENR 25 compared to similar NR and OESBR tyre compounds.

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[93]. Blends of ENR 50 and NR have also been evaluated with particular emphasis placed on the safety aspects of motorcycle tyres[94].

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[95]. Other publications[96,97] 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 Epoxyprene 25 and Epoxyprene 50, their use in applications and market volume are expected to increase rapidly.

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Cation Composition in Soil Solution of Two Malaysian Soils

NORHAYATI MORIS*

A study was carried out to determine the cation composition in soil solution of two soils commonly cultivated with rubber (Rengam and Munchong series) and their relationships to exchangeable cations.

The concentration of the cations in the two soil solutions is generally less than 0.5 cmol (+)/kg. The soluble cation concentrations are higher for Rengam soil, an Ultisol than for Munchong soil, an Oxisol, for all the cations studied, viz Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} *and* Al^{3+}.

Low concentrations of soluble cations result in soil solutions with low ionic strength. The ionic strength of the two soils is less than 0.008 M, with the ionic strength of Rengam soil being higher than that of Munchong soil.

A good correlation was observed between soluble and exchangeable cation concentrations. The percentage of exchangeable cation which is readily solubilised is low. The differences in availability of the cations in soil solution are attributed to the clay mineralogy of the inorganic soil colloids.

Acid soils occupy approximately 72% of the land area in Peninsular Malaysia. The two main orders of acid soils found in Peninsular Malaysia are the Ultisols and Oxisols. Acid soils are usually highly weathered and characterised by low fertility status, low pH and high exchangeable aluminium saturation.

The mineralogy of acid soils is dominated by 1:1 type clay silicates and oxides of iron and aluminium. These minerals have been demonstrated to possess both cation and anion exchange capacities which are dependent on the ionic strength of the ambient medium[1,2].

The solid-phase properties of acid soils of Peninsular Malaysia have been relatively well studied. Unlike the solution-phase, which due to the unawareness of its significance and importance and partly to the difficulty in obtaining a sufficient quantity of the soil solution itself for full elemental analysis, has not been extensively examined.

The soil solution has been defined as a quasi-equilibrium solution of electrolytes that are present in the soil under unsaturated moisture conditions[3]. It is the medium which is in contact with plant roots and is the source from which plants obtain their nutrients.

Knowledge of the characteristics of soil solution is thus essential in understanding the factors controlling the availability and reactivity of plant nutrients. A study was initiated with the following objectives:

- To determine the composition of solutions extracted from two acid soils
- To determine the relationship between the cationic concentration of the soil solution and that of the solid phase.

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*Rubber Research Institute of Malaysia, P.O. Box 10150, 50908 Kuala Lumpur, Malaysia

A great obstacle to studies on soil solutions is obtaining a sufficient and true quantity of the soil solution which is unchanged by the extraction procedure. For practical purposes, it is always easier and more convenient to extract soil solutions from air dried soil samples. Studies by Gillman and Bell[2,4], Edmeades *et al.*[5] Elkhatib *et al.*[6] and Menzies and Bell[7] have shown that the composition of soil solution extracted from pre-wetted air-dry soil is the same as that extracted from field-moist soil.

Soil solutions can be extracted by several ways *viz.* centrifugation, suction, displacement and compaction. There are advantages and disadvantages for each method. However, extraction by centrifugation is preferred because it is simple, rapid and the pressure applied is mild, well within the available moisture range.

MATERIALS

Soils

Soils used in this study were sampled at 0 – 15 cm depth from two intercropping trials at Sungala Estate, Port Dickson, Negeri Sembilan and at a smallholding in Machang, Kelantan. The treatments involved application of ground magnesium limestone (GML) at 0, 500, 1000 and 2000 kg/ha. The cropping sequence was groundnut, maize, maize and groundnut. Details of the experimental trial have been described in a paper by Mohd. Yusoff *et al.*[8] The soils studied were Rengam series (Typic Kandiudult) in Machang, Kelantan and Munchong series (Tropeptic Haplorthox) in Sungala, Negeri Sembilan. The particle size distribution and some of the chemical properties of the two soils are described in *Table 1.* Munchong and Rengam soils have 80% and 19% clay content while their cation exchange capacities are 4.69 and 2.26 cmol (+)/kg respectively. The exchange capacities of the clay fractions are 19.34 and 8.92 cmol (+)/kg for Rengam and Munchong series respectively[9].

From field observations, in the initial stage, rubber establishes easier on Rengam soil than on Munchong soil. This is attributed to the relatively good physical structure and higher nutrient contents of Rengam soil compared to Munchong soil. The clayey nature of Munchong soil gives it a more compact structure than Rengam soil, thus impeding water infiltration and root growth. However, at later stages of growth, it has been observed that the plants were able to overcome the physical and chemical constraints and growth in the two soils was comparable[10].

Soil samples were taken before and two weeks after the application of lime and after every harvest of the intercrop. The soils were oven dried at 55°C, ground and passed through a 2 mm sieve.

METHODS

Soils Solution

To extract the soil solution, 50 g of oven-dried soil was placed in a centrifugal assembly specially designed for the purpose *(Figure 1).* The centrifugal assembly is

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF SURFACE SOILS STUDIED[a]

Soil	Clay (%)	Sand (%)	Silt (%)	pH	C (%)	CEC [cmol (+)/kg]	
						Soil	Clay
Munchong	79.9	11.2	8.9	4.2	1.89	4.69	8.92
Rengam	18.9	78.6	2.5	5.3	1.76	2.26	19.34

[a]After Zainol *et al.*[9]

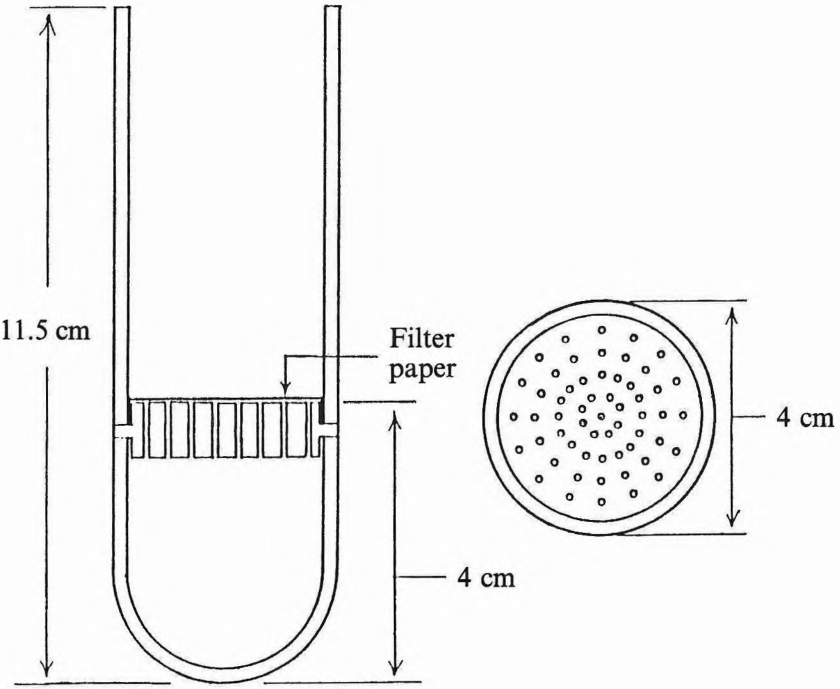

Figure 1. Centrifugal assembly used for extracting soil solution.

a modification of the one proposed by Gillman[11]. The soil was wetted to field capacity with distilled water. The amount of water added was calculated by determining the field capacity of the soil on a separate soil sample. The wetted soil was equilibrated for 24 h and centrifuged at 3000 r.p.m. for 20 min. The soil solution was passed through a Whatman filter paper No. 4.

K, Ca, Mg, Na and Al in the soil solution were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICPAES).

Exchangeable Cations

To measure the exchangeable cations, 20 g soil was placed in a glass column. Ammonium acetate at pH 7 was passed through the soil and the leachate collected over a 6-h period. The concentrations of K, Ca and Mg in the extract were determined by atomic absorption spectrometry.

Calculation of Ionic Strength of Soil Solution

The ionic strength *(I)* of the soil solution was calculated using the formula:

$$I = 0.5 \ \Sigma C_i Z_i^2$$

where C_i = ionic concentration

Z_i = ionic valency.

Statistical Analysis

Simple linear regression studies were carried out on the data using the Lotus 123 computer programme on an IBM compatible personal computer.

RESULTS AND DISCUSSION

Cation Concentrations

The concentrations of the cations in the soil solution were not corrected for ion pair formation, noting that studies by Gillman and Bell[4] showed that ion pair formation was not extensive in soil solutions extracted from some highly weathered soils of tropical North Queensland. The concentration ranges of the cations in soil solutions are presented in *Table 2*. The cation concentrations of the two Malaysian soils are generally less than 0.5 cmol/litre for Ca, Mg and K, with the concentration ranges being 0.01–0.4 cmol/litre for Ca, 0.01–0.5 cmol/litre for Mg and 0.02–0.2 cmol/litre for K. The concentrations of K, Ca and Mg in the two soils are generally low and of the same magnitude as those presented by Gillman and Bell[4] for the soils of tropical North Queensland, but are much lower than those reported for temperate soil solutions[12] (2.5–5 cmol/litre for Ca, 4–8 cmol/litre for Mg and 0.5–1 cmol/litre for K).

In addition, the concentrations of the soluble cations K, Ca and Mg are generally higher for the Ultisol than for the Oxisol.

Effect of Liming on Cation Concentration

In general, K concentration in the soil solution decreased while Ca and Mg concentrations increased with increasing rate of application of lime *(Table 3)*. However, the increases in the concentrations of Ca and Mg in the soil solution of Munchong are not as great as those in the soil solution of Rengam series. Cation ratios in soil solution influence their uptake by the plant. The activity ratio (AR) between K and the divalent cations, Ca and Mg in the soil solution can be calculated by the equation:

$$AR_K = \frac{a_K}{[a_{Ca} + a_{Mg}]^{1/2}}$$

where a_M is the activity of the cation, M.

The activity ratio of K in soil solution decreased with increasing rate of application of lime *(Table 3)*. Le Roux and Sumner[13] and Gillman and Bell[4] have reported that good correlation was obtained between the activity ratio of K in soil solution and that determined by the conventional procedure of ionic equilibra.

Ionic Strength

Ionic strength of the soil solution was calculated taking into account the cations present in significant amounts, *viz.* K, Na, Ca, Mg and Al.

The ionic strength of soil solution is generally low, being in the range of 0.002 to 0.008 M for Rengam soil and 0.001 to 0.005 M for Munchong soil *(Table 4)*. This is in accordance with the higher soluble cation concentrations present in Rengam soil compared to Munchong soil. With increasing cationic concentration in the soil solution on liming, ionic strength increased. The increase in ionic strength was higher for Rengam than Munchong. The application of lime and possibly other agronomic inputs such as fertilisers, alter the soluble cation concentrations in solution. The ionic

TABLE 2. CONCENTRATIONS OF SOLUBLE CATIONS IN RENGAM AND MUNCHONG SERIES AT 0 – 15 CM DEPTH

Cation	Concentration of cations (µm) Rengam series	Munchong series
Ca^{2+}	106 – 3630	222 – 2377
Mg^{2+}	89 – 4798	62 – 1415
K^+	210 – 2143	116 – 1111
Na^+	127 – 855	45 – 759
Al^{3+}	7 – 815	3 – 124

TABLE 3. EFFECT OF APPLICATION OF LIME ON CONCENTRATIONS OF POTASSIUM, CALCIUM AND MAGNESIUM[a]

Rate of lime applied (kg/ha)	Concentration of cation (μm)						AR_k	
	K		Ca		Mg			
	Rengam	Munchong	Rengam	Munchong	Rengam	Munchong	Rengam	Munchong
0	407	350	265	628	260	217	18	12
500	401	406	426	813	484	356	13	12
1000	394	474	486	660	631	336	12	15
2000	348	336	521	655	777	403	10	10

[a] Soil was sampled two weeks after application of lime.

TABLE 4. EFFECT OF LIMING ON IONIC STRENGTH OF SOIL SOLUTION[a]

Treatment	Ionic strength (*M*) Rengam	Ionic strength (*M*) Munchong
R_0 (0 kg/ha lime)	0.0046	0.0029
R_1 (500 kg/ha lime)	0.0062	0.0036
R_2 (1000 kg/ha lime)	0.0050	0.0040
R_3 (2000 kg/ha lime)	0.0076	0.0076

[a] Soil was sampled two weeks after application of lime.

strength of the soil solution also controls the soil pH and variable charge of the alumino silicate minerals as indicated by the double layer theory.

The ionic strengths of the soil solutions extracted from the two soil series are much lower than 0.03 *M*, the value commonly quoted for soil solutions[14]. However, they are of a similar magnitude to the ionic strengths of other tropical soils[4,13].

Relationship between Soluble and Exchangeable Cations

To relate the concentration of cation in soil solution to the routinely determined exchangeable cations, as measured by 1*N* ammonium acetate at pH 7, simple correlation studies were carried out on the data obtained *(Table 5)*.

A strong relationship exists between the cations in the soil solution and the exchangeable cations *(Table 5)*. K appeared to be more strongly correlated to the exchangeable form than Ca and Mg. Mono-valent cation concentration in the exchangeable form is more strongly related to those in the soluble form. The relationship is even better when the data for the two soils are not pooled together, thus indicating that there are certain inherent characteristics of the soil that influence solubility of the cation. In a study by Bruce *et al.*[15] on some acid soils in Queensland, it was observed that the release of Ca and Mg from exchange sites to the soil solution was affected by the relative amounts of exchangeable Ca and Mg. When the average concentrations of basic cations in soil solution were expressed as percentages of

TABLE 5. CORRELATION COEFFICIENT BETWEEN SOLUBLE CATIONS AND EXCHANGEABLE CATIONS (0 - 15 CM DEPTH)

Soil series	Correlation coefficient Ca	Correlation coefficient Mg	Correlation coefficient K
Munchong (n = 118)	0.76***	0.72***	0.84***
Rengam (n = 238)	0.57***	0.75***	0.66***
Combined (n = 358)	0.49***	0.51***	0.34***

P = < 0.001
n = degrees of freedom

TABLE 6. RELATIONSHIP BETWEEN CATION CONCENTRATION IN SOIL SOLUTION $(M)_s$ AND EXCHANGEABLE CATION $(M)_{ex}$ (0 – 15 cm DEPTH)

Soil series	Ca	Mg	K
Munchong	$[Ca]_s = 0.06\ [Ca]_{ex} + 17.32$	$[Mg]_s = 0.11\ [Mg]_{ex} + 3.99$	$[K]_s = 0.19\ [K]_{ex} + 2.46$
Rengam	$[Ca]_s = 0.17\ [Ca]_{ex} + 22.26$	$[Mg]_s = 0.51\ [Mg]_{ex} + 6.43$	$[K]_s = 0.46\ [K]_{ex} + 9.67$
Combined	$[Ca]_s = 0.06\ [Ca]_{ex} + 28.11$	$[Mg]_s = 0.49\ [Mg]_{ex} + 8.37$	$[K]_s = 0.15\ [K]_{ex} + 16.71$

the exchangeable plus soluble cations, Bell and Gillman[16] found that the release of the cations followed the order Na > K > Mg > Ca. The electrostatic affinities of the ions for the exchange sites were cited as the reason for the trend. On calculation of the data obtained in this study, a similar trend was generally observed, *i.e.* K > Ca > Mg for Rengam soil. However, for Munchong soil the order was K > Mg > Ca.

The relationship between soluble cations and exchangeable cations can be expressed as:

$$M^{+}{}_{s} = \text{Constant } x\, M^{+}{}_{ex}$$

where $M^{+}{}_{s}$ = Soluble cation
$M^{+}{}_{ex}$ = Exchangeable cation

The constant, however, has been shown to be a function of solution ionic strength[17] or electrical conductivity with which the soil solution is in contact. The relationships established for K, Ca and Mg for the two soil series are presented in *Table 6*.

From *Table 6*, it is apparent that an estimate of the concentration of cations in soil solution can be made from the exchangeable cations. The concentration of the cation in soil solution is only a small fraction of the exchangeable cations. In Munchong soil, the percentages of cations in soil solution are 6%, 11% and 19% of the exchangeable cations for Ca, Mg and K respectively. In Rengam soil, the percentages of the exchangeable cations that are soluble are slightly higher, that is 17%, 51% and 46% for Ca, Mg and K respectively. The higher concentrations of cations in the soil solution of the Rengam series compared to Munchong series can be attributed partly to the higher exchange capacity of the clay minerals of Rengam soil and also to higher concentrations of exchangeable cations[9]. Although Munchong soil has a higher clay content than Rengam soil, the exchange capacity of its clay is lower *(Table 1)*. The Clay fraction of Rengam soil is dominated by kaolinite and that of Munchong soil is dominated by goethite and gibbsite[18]. Goethite and gibbsite confer to the soil system positive charges thus lowering the net negative charge of the soil colloids and therefore the ability to retain cations in the exchangeable form.

CONCLUSION

The composition of the solution of two soils studied showed that the concentrations of the cations K, Na, Ca, Mg and Al in solution are low, that is, generally less than 0.5 cmol/kg. They are generally higher for Rengam soil, an Ultisol than for Munchong soil, an Oxisol. Ionic strength of the soil solution is also low, that is, less than 0.008 *M*.

The relative ease with which the exchangeable cation can go into solution is higher for Rengam soil than Munchong soil. The order of release of the cations into soil solution is K > Ca > Mg for Rengam soil and K > Mg > Ca for Munchong soil. The composition of the clay minerals was one of the reason for the higher cation release in Rengam soil.

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