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Frey-Wyssling Complex in Hevea Latex — Uniqueness of the Organelle

J.B. GOMEZ* AND SAMSIDAR HAMZAH*

Frey-Wyssling (FW) complexes, the third most numerous major organelle in Hevea latex, is examined by electron microscopic techniques to unravel the morphological variability with respect to developmental states and sedimentation characteristics. In examples drawn from tissue sections and from electron microscopy of ultra-centrifuged fractions of latex, it is shown that the FW complexes have characteristic complexity in morphology arising from the constituent lipid globules, vesicle membrane configurations and a grey body which may or may not contain embedded ropey tubes.

Latex contains three principal types of particles which make up the major volume of the dispersed solid phase. Rubber particles are the most numerous. Next in abundance is lutoids and then Frey-Wyssling (FW) complexes. In centrifuged latex, the proportions of these three particle types are reflected somewhat by the dimensions of *Zone 1*, *Zones 6-11* and *Zone 4* respectively. However, the fact that FW complexes are present in *Zones 3, 4* and *6-11* is an observation which has not been adequately recorded in literature¹⁻⁴. The presence of FW complexes in *Zone 3* may be a matter of contamination of the zone from the neighbouring *Zone 4* while sampling for electron microscopy, whereas the presence of FW complexes in *Zones 6-11* indicate that these complexes occur in a range of densities and their sedimentation behaviour might be due to the small differences in inherent densities. It was thought in earlier literature⁵ that FW complexes are 'trapped' by the bottom fraction particles in their journey downwards under the influence of the centrifugal forces; but the integrity of the particles when examined by electron microscopy in fact reveals that they belong to different density classes and this difference is adequate to explain their sedimentation in various zones.

Frey-Wyssling⁶ observed shiny yellow globules in latex by light microscopy, which were clarified to be a complex particle by Southorn¹ by light microscopy and Dickenson^{7,8} by elec-

tron microscopy. The original yellow globules discovered by Frey-Wyssling were found to be an integral part of the FW complexes, which were described in greater detail by Dickenson⁸ and Gomez and Moir⁵.

The present investigation covers a range of observations from tissue sections and preparations of latex fractions using the refrigerated ultra-centrifugation method⁹.

MATERIALS AND METHODS

Latex was collected under chilled conditions from ten trees per clone from each of five clones, RRIM 501, RRIM 600, GT 1, PB 86 and Tjir 1. The trees were tapped on *Panel BO-1* under $\frac{1}{2}$ S d/2 tapping system. Samples for electron microscopy were secured every three months for three or four occasions for the various observations made in this study.

The latices were centrifuged under refrigerated conditions in the Spinco L ultra-centrifuge for 1 h at 59 000 g (max). The latex was always kept chilled prior to centrifugation if short durations of such storage was necessary to execute the procedures. The tubes were cut after centrifugation to secure samples for fixation in chilled fixative soon after centrifugation.

Samples were numbered according to our earlier terminology of the zones as adopted in the examination of various fractions of latex^{3,4}.

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Each sample was fixed in 1% osmium tetroxide buffered with phosphate at pH 7.0 and with 0.35 M sucrose added for tonicity control. Fixation was for 2 h at 0°C–5°C after which the samples were dehydrated in graded series of ethanol before infiltration and embedding in styrene/methacrylate using low speed centrifugation method to concentrate the material from liquid media. Sections were double stained with uranyl acetate and lead citrate before examination with the Philips EM 300.

Results are based on several samplings made during different parts of the year. Thus, seasonal differences if any were largely ignored for this study. Consistent clonal differences were not noted except in the frequency of occurrence and the morphological nature of some of the components of the organelles, but this paper cannot do justice to such variation of structure.

Tissue sections were also used in the study. Young green tissue from trees were fixed in 2% osmium tetroxide in phosphate buffer (pH 7.0) with added sucrose. Other details of preparation were as for centrifuged material.

RESULTS

Complete Frey-Wyssling Complexes

Preparations from *Zone 4* generally revealed incomplete FW complexes and hence the results related to complete FW complexes will be presented from mainly *Zones 6–11*.

Figures 1–5 illustrate some of the FW complexes seen in median section. The contents include prominent large lipid globules ranging in size from 0.3–3 μ , contained inside the complex measuring 4–7 μ in the figures shown. There are some vesicles which appear electron-lucent (*Figure 2*); there is a grey body which is amoeboid in shape in *Figures 3* and *4* and embedded in the grey body are ropey membrane configurations which occasionally appear free in the ground plasm of the organelle.

From correlated light and electron microscopical studies, the shiny yellow globules (under the light microscope), described originally by Frey-Wyssling, are lipid inclusions which are

orange-yellow, presumably due to carotene (absorption peak at 450 nm).

The presence of the membrane configurations indicate an intricately complex role for the grey body organelle which has not been unfolded as yet by biochemical studies which are necessary to show the function of these organelles.

Developmental States

In some FW complexes, from young latex vessels, vacuoles are seen. Often they have peripheral electron density indicating the early stages of lipid synthesis in such vesicles.

Figures 6, 7 and *8* illustrate various developmental states of FW complexes from young latex vessels. *Figure 9* illustrates a more mature FW complex with various stages of lipid synthesis in the lipid vesicles of the organelle.

Sedimentation Behaviour

In latex subjected to ultra-centrifugation, the principal orange-yellow layer is *Zone 4*. FW complexes in this zone are often fragmented. Previous biochemical studies aimed at this fraction therefore are subject to the deficiencies caused by disruption of the organelles.

Figures 10–14 show organelles and fragments of organelles as they appear in *Zone 4*. There is a preponderance of osmiophilic lipid globules or fragments of them in these complexes. However, when they occur in *Zones 6–11*, they are intact and display various characteristics indicative of their higher density.

Figure 15 is an example from *Zone 10*. The density of this particle is high due to the greater occurrence of membranes and a lesser number of lipid inclusions in the complex. *Figure 16* is an example found in *Zone 11*.

As FW complexes are found in all zones of the bottom fraction and in *Zones 3* and *4* of the top fractions, it is evident that they occur in a range of densities. Generally, the particles in the top fractions contain larger quantities of lipid material and various complexes of higher densities are sedimented in different bottom regions of the tube.

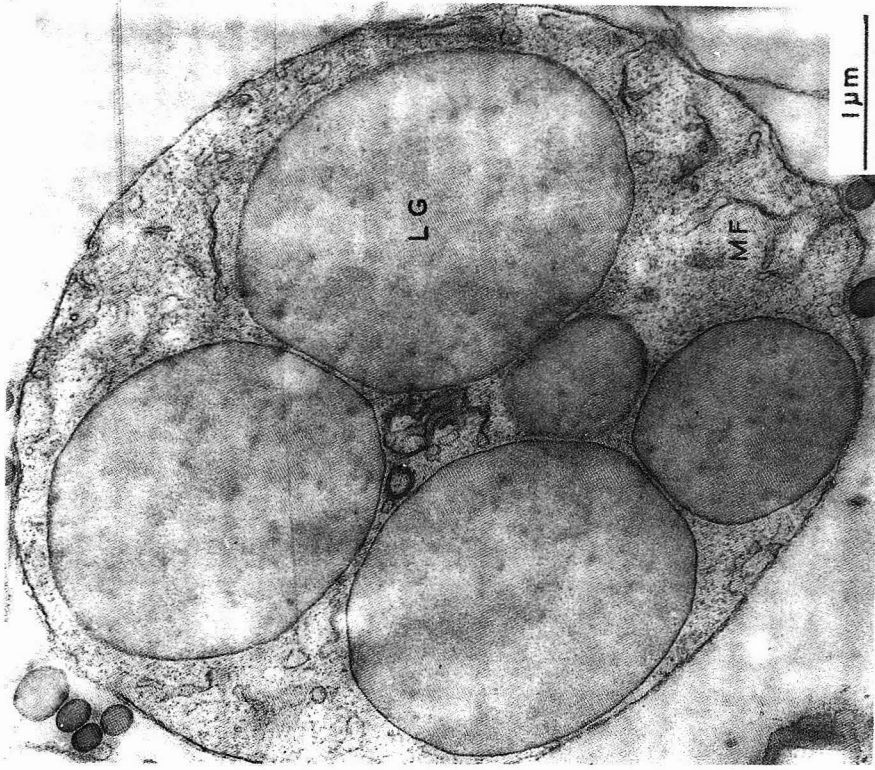


Figure 1. Median section through a FW complex which shows lipid globules (LG) and some membrane fragments (MF). Magnification 20 000 \times .

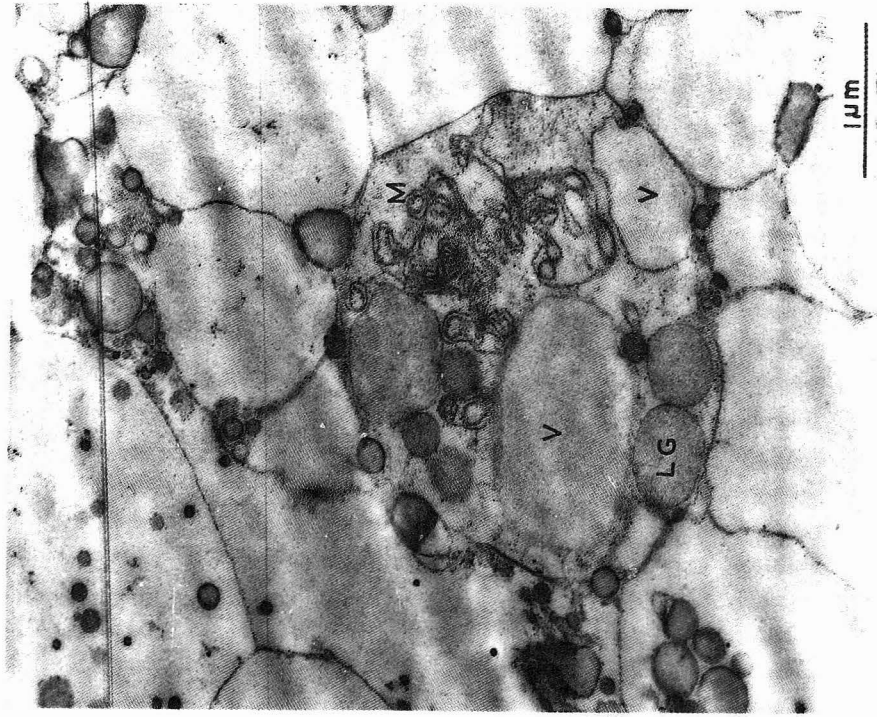


Figure 2. Section through FW complex among luteoids from Zone 8 indicating lipid globules (LG), vesicles (V) and membrane (M) configurations. Magnification 20 000 \times .

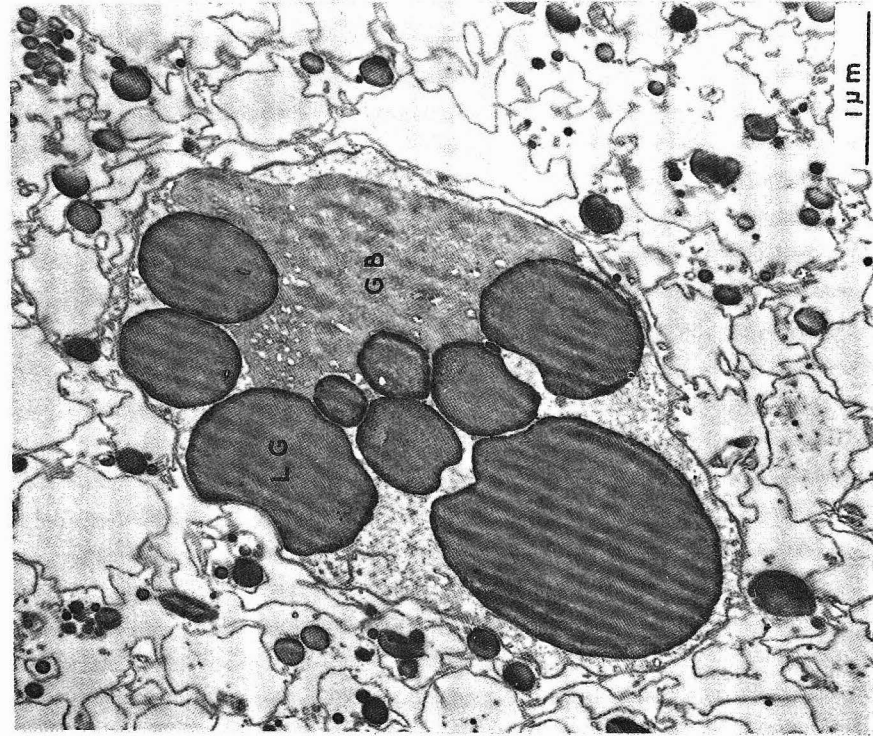


Figure 3. FW complex from Zone 8 showing many osmiophilic lipid globules (LG) and a grey body (GB). Magnification 20 000 \times .

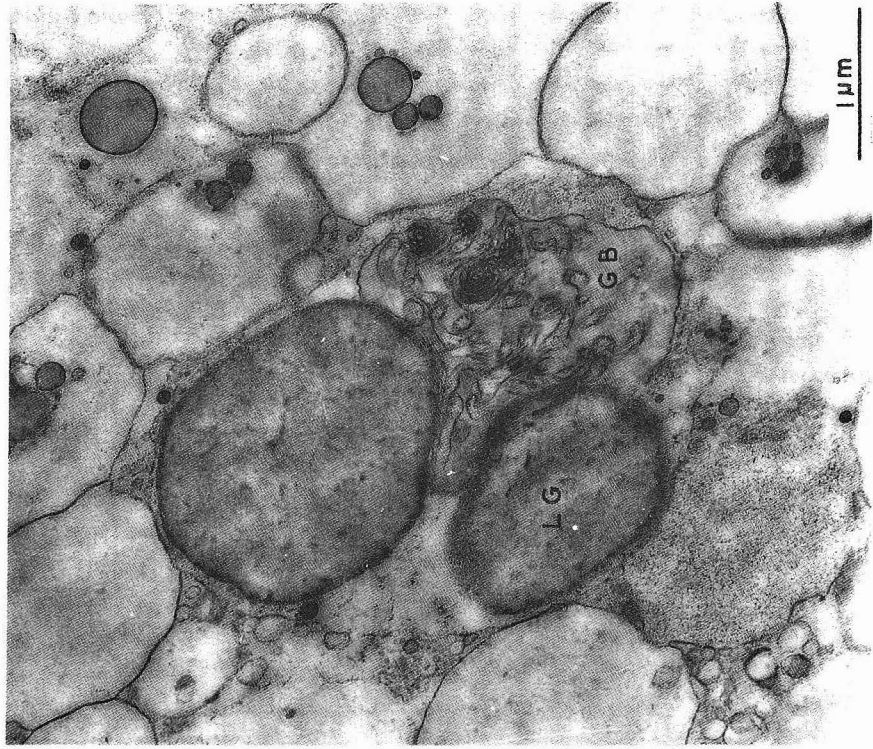


Figure 4. FW complex from Zone 8 showing lipid globules (LG) and a grey body (GB) which includes membrane configurations. Magnification 20 000 \times .

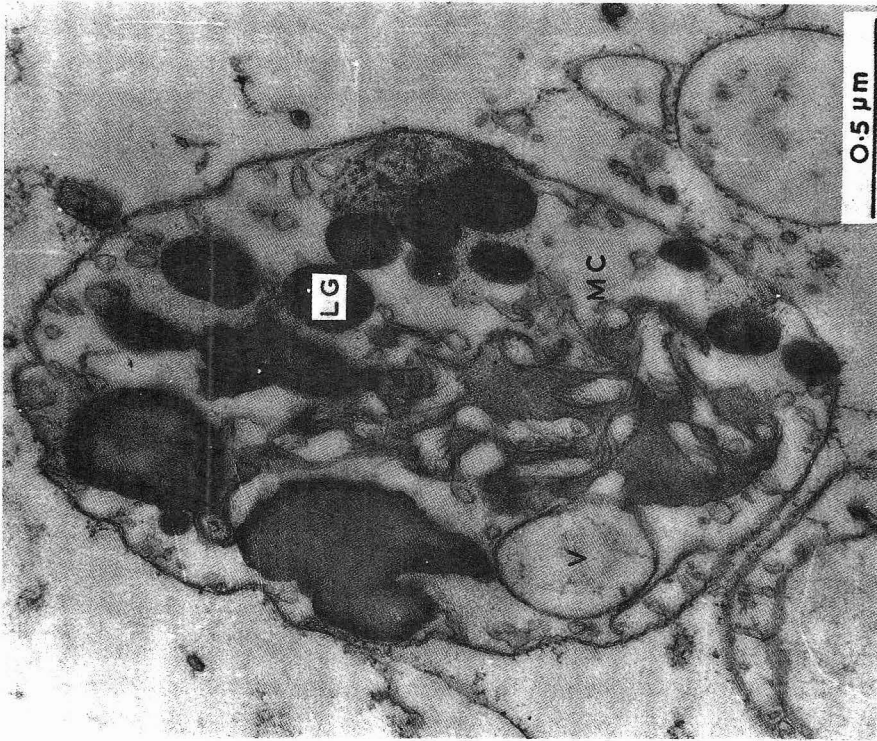


Figure 5. FW complex in Zone 10 showing lipid globules (LG), vesicles (V) and membrane configurations (MC). Magnification 52 000 \times .

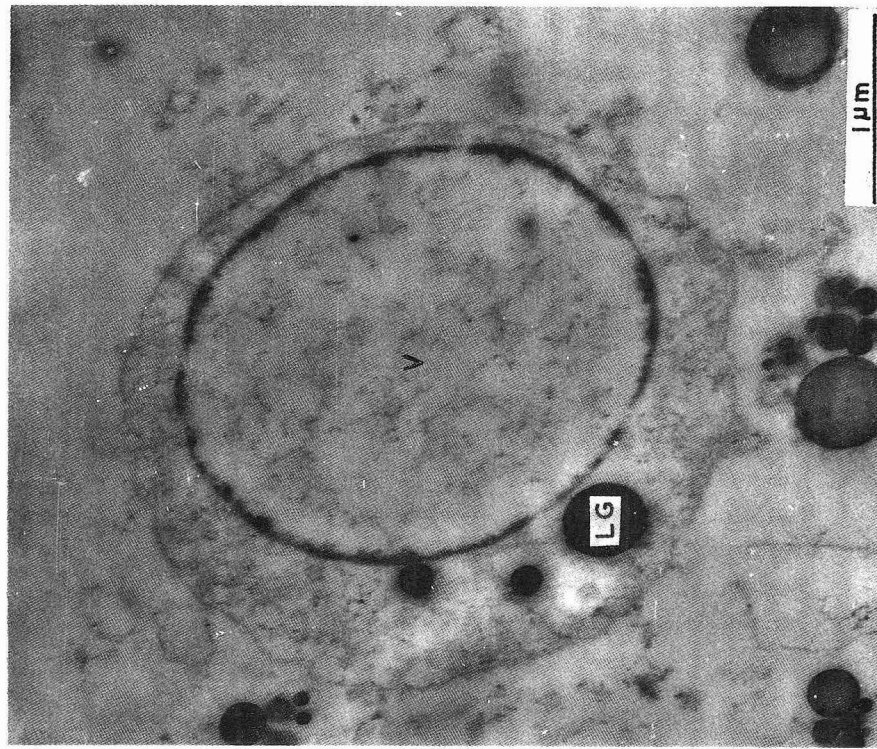


Figure 6. Young FW complex in latex vessel showing lipid globules (LG) and vesicles (V). Magnification 25 000 \times .

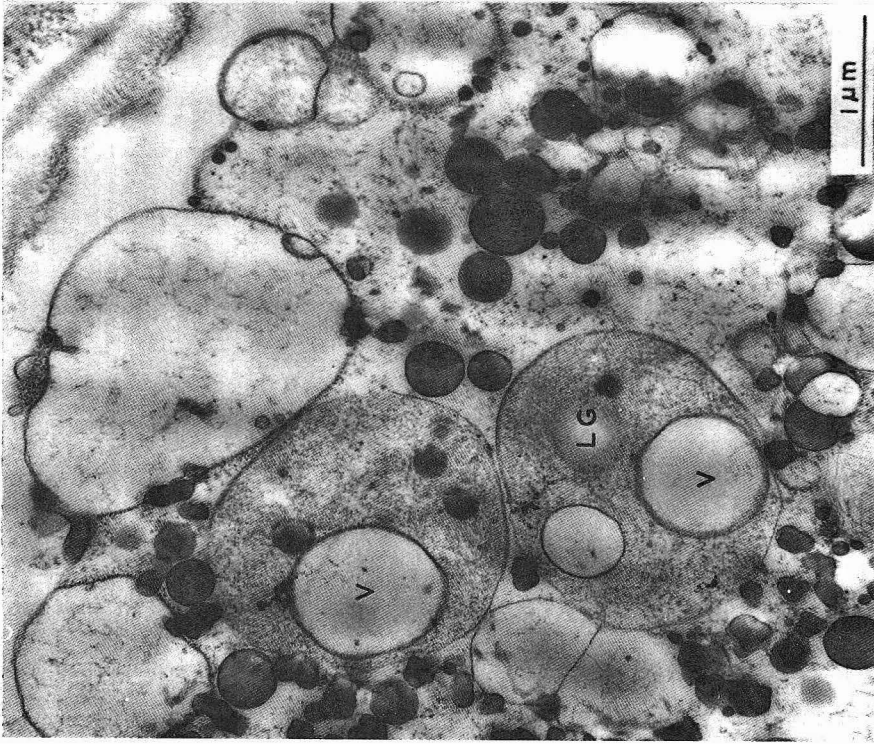


Figure 7. Young FW complex from latex vessel showing lipid globules (LG) and vesicles (V). Magnification 20 000 \times .

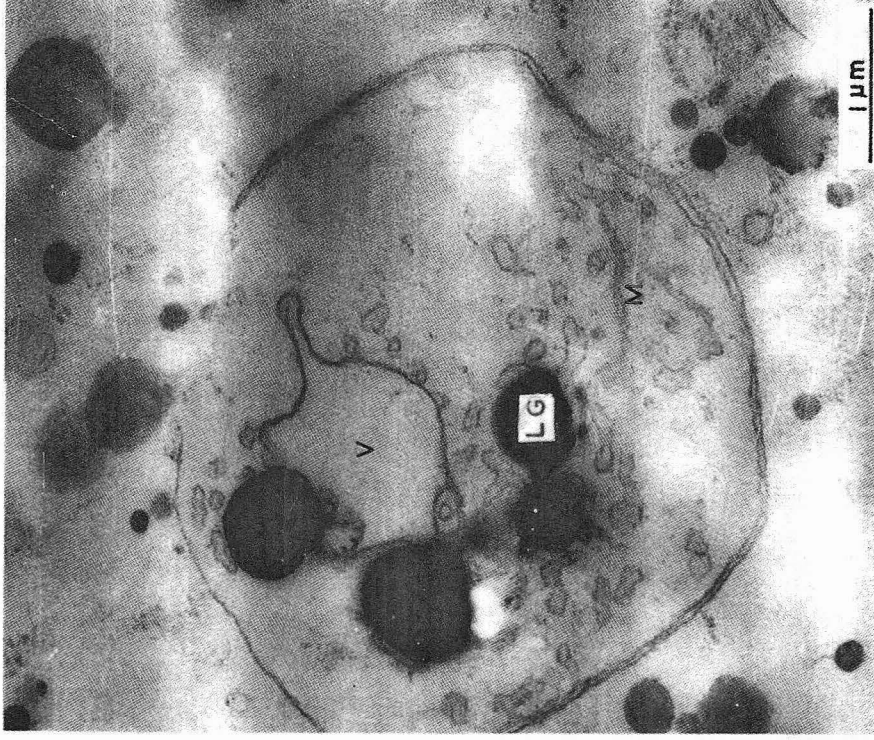


Figure 8. Young FW complex from latex vessel showing lipid globules (LG), vesicles (V) and membranes (M). Magnification 20 000 \times .

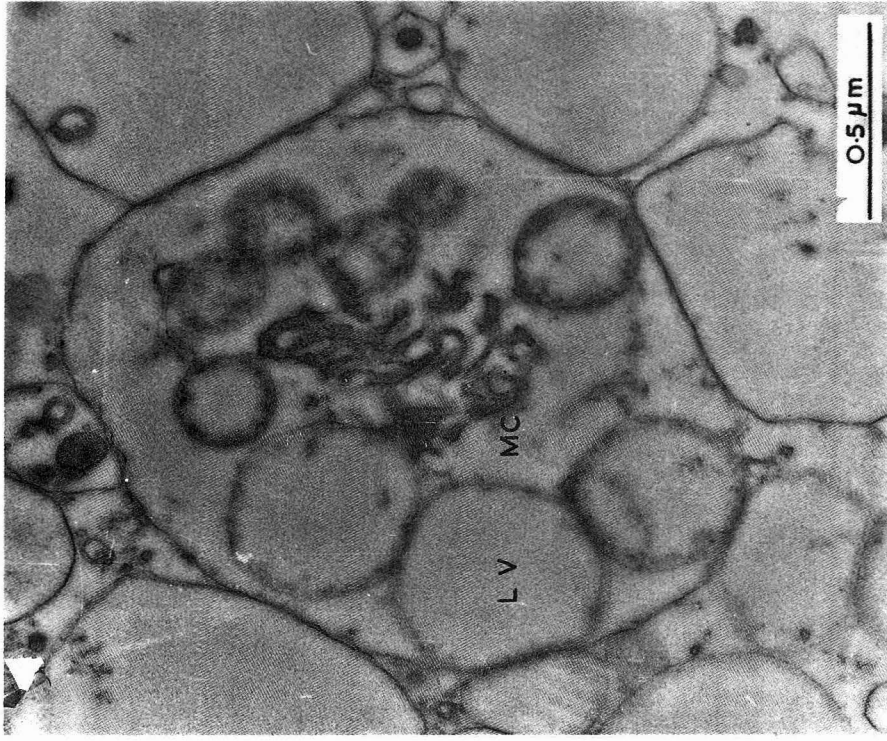


Figure 9. FW complex in Zone 10 showing lipid vesicles (LV) and membrane configurations (MC). Magnification 52 000 \times .

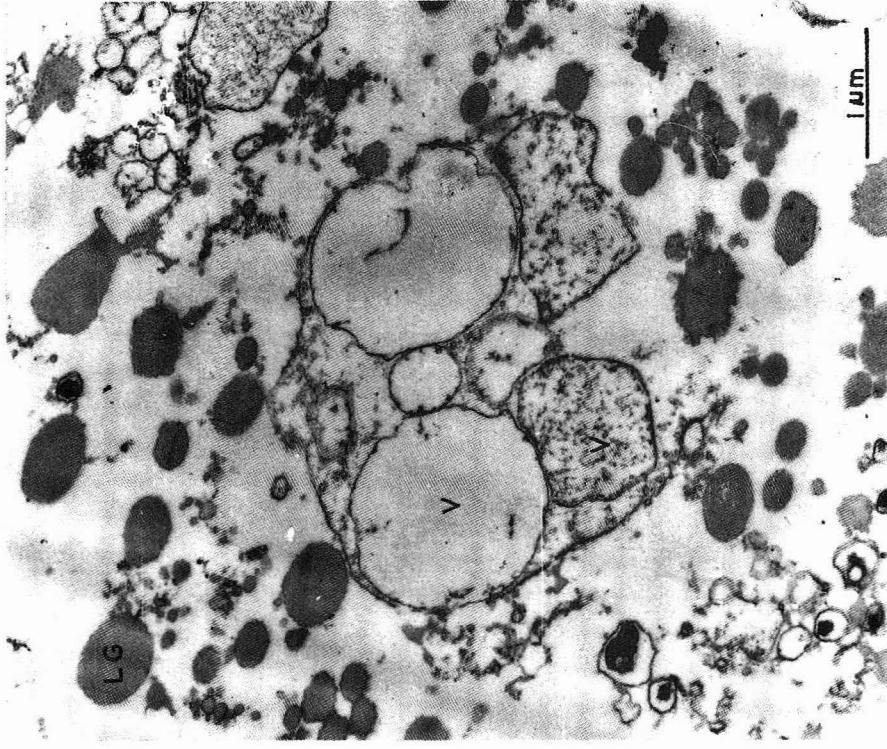


Figure 10. Broken FW complexes from Zone 4 showing vesicles (V) and liberated lipid globules (LG). Magnification 16 300 \times .

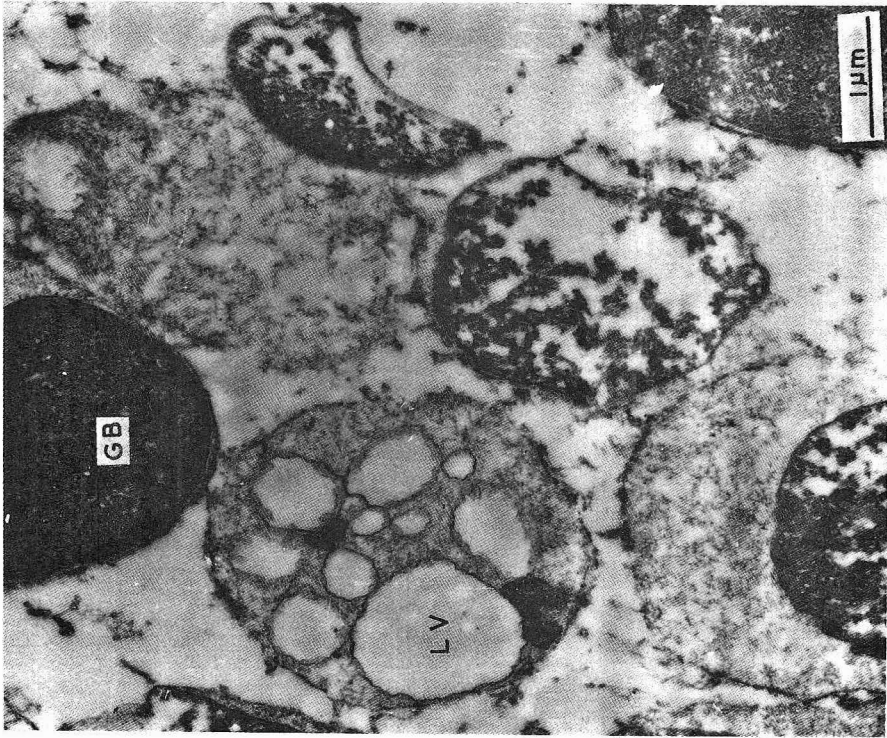


Figure 11. Broken FW complexes from Zone 4 showing grey bodies (GB) and lipid vesicles (LV). Magnification 16 300 ×.

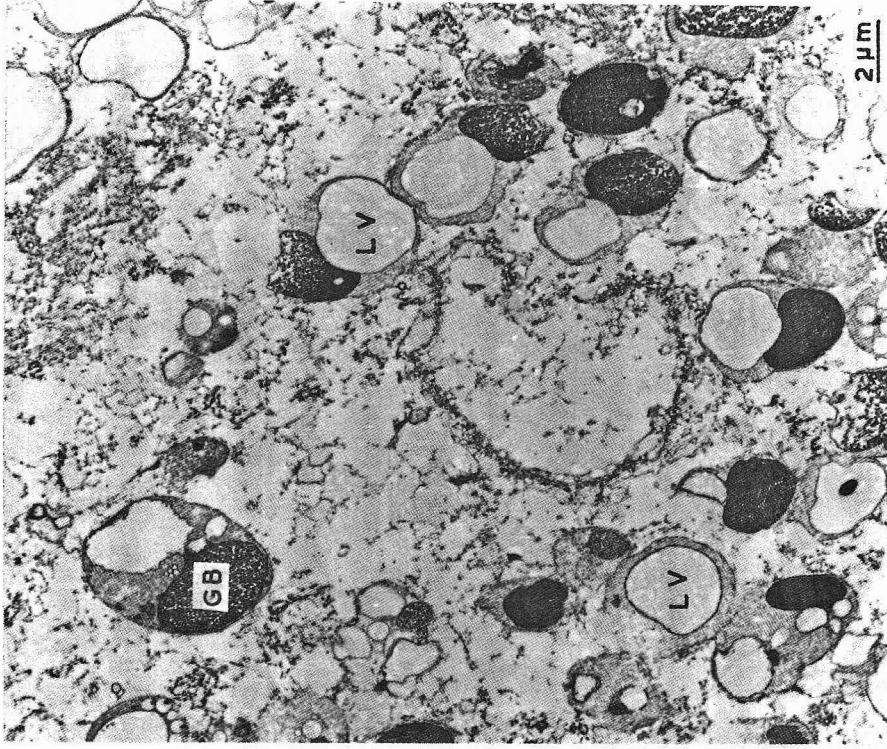


Figure 12. Broken FW complexes from Zone 4 showing grey body (GB) and lipid vesicles (LV). Magnification 4200 ×.

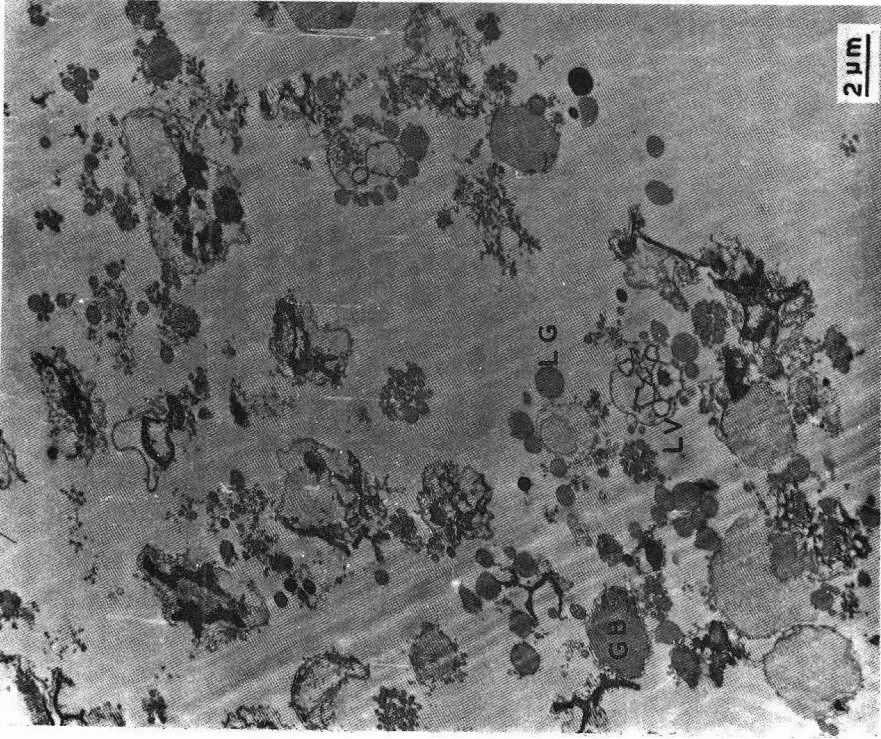


Figure 13. Broken FW complexes from Zone 4 showing grey bodies (GB), lipid globules (LG) and lipid vesicles (LV). Magnification 4200 \times .

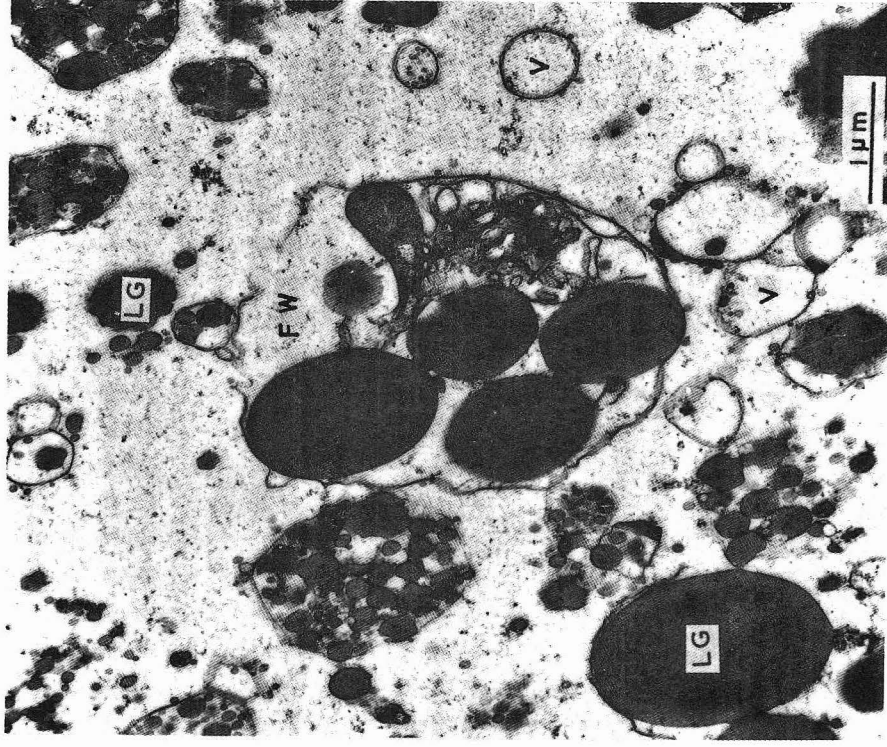


Figure 14. FW complexes from Zone 4 showing liberated lipid globules and an intact FW complex. Liberated vesicles (V) can also be seen. Magnification 16 300 \times .

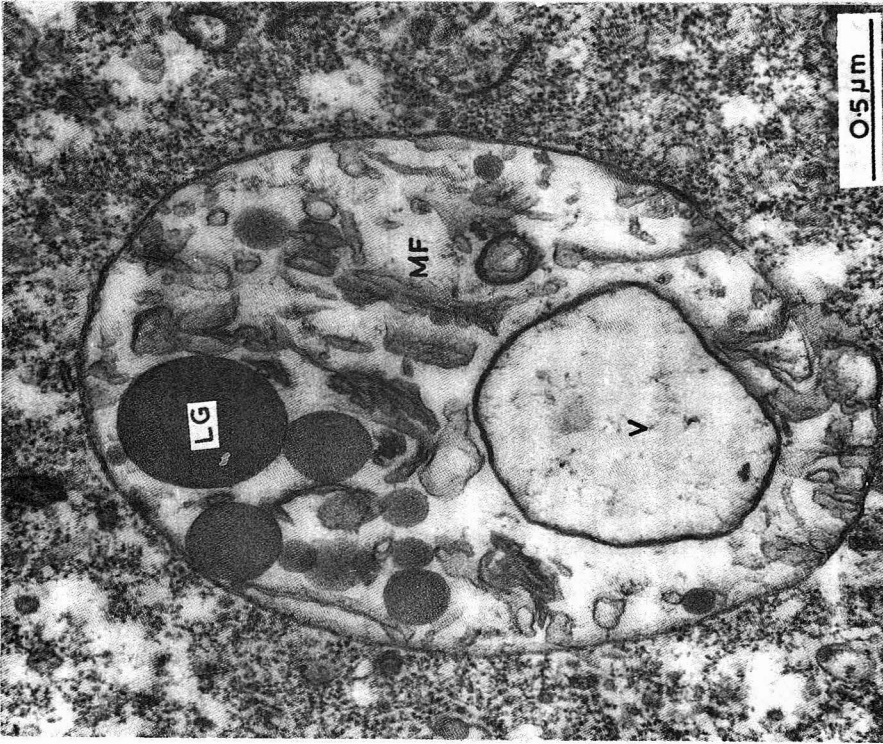


Figure 15. FW complex from Zone 10 showing few lipid globules (LG), vesicles (V) and membrane fragments. Magnification 42 000 ×.

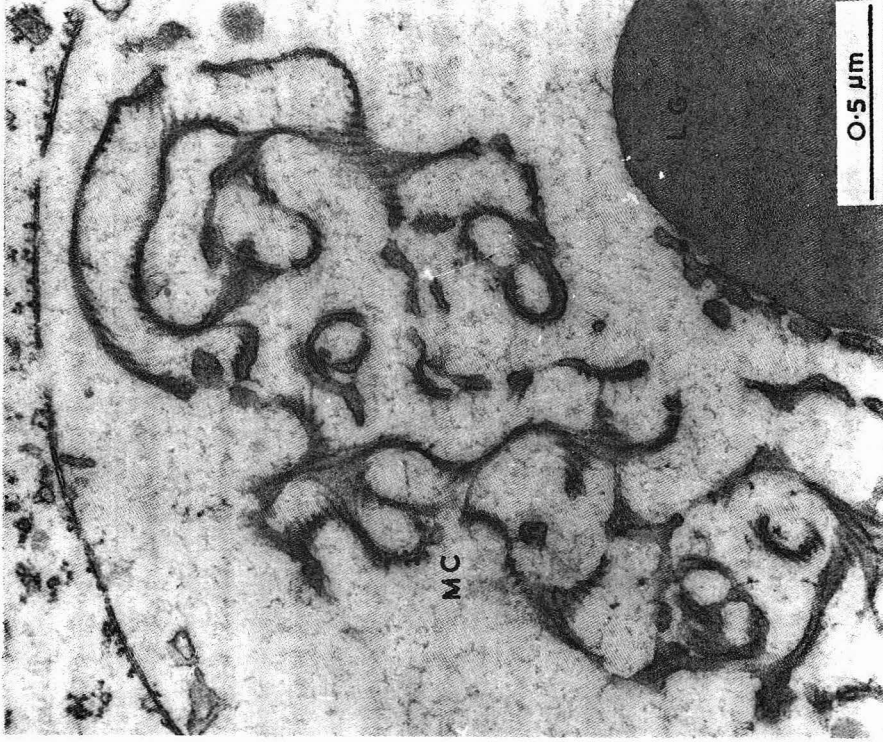


Figure 16. Part of FW complex from Zone 11 showing membrane configurations and lipid globules (LG). Magnification 52 000 ×.

DISCUSSION AND CONCLUSION

The variety of particle types identified as FW complexes differ in morphology, chemical composition, size, and electron density, due to inherent differences in lipid content or quality; an enormous array of patterns can be visualised. There are at least three or four component units, the grey body, the lipid globules, the vesicles preceding lipid synthesis and a tubular matrix which may or may not be embedded in the grey body. The FW complex is indeed a complex body.

The FW particles were originally noted to occur in clusters. Light microscopy at that time did not permit the finer resolution of the bounding membranes. Southorn¹, by use of phase contrast microscopy, confirmed that the globules tend to occur in clusters and noted that they were often associated with a vacuolar body. He suggested the occurrence of membranes surrounding the particles and this was later confirmed by electron microscopic techniques^{3,4,7,8}. Dickenson, after electron microscopic characterisation of the particles^{7,8}, concluded that the larger structure is complex in character and named it after Frey-Wyssling.

The FW complexes are found in *Zones 3-4* in the top and *Zones 6-11* in the bottom fraction of ultra-centrifuged latex. They are largely responsible for the yellow colour of latex. Even in white latex, FW complexes are present; their lesser yellow colour might be due to the presence of lesser amount of β -carotene or to the presence of colourless polyenes which are associated with the lipid particles of the FW complexes.

The FW complexes are more or less spherical, range in size from 3-7 μ , and are bounded by a double membrane. The grey body itself in certain stages can be shown to have a distinct limiting membrane. The number of osmiophilic globules in cases we have examined range from three to twelve. A system of rope-like tubes is

present; it may be free in the ground plasm of the complex or may be embedded in the grey body, which is less osmiophilic than the lipid globules.

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September 1988

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The Concept of Harvest Index as Applied to Hevea

J.B. GOMEZ*, K. SIVANADYAN*, S.K. LEONG* AND H. GHANDIMATHI*

The concept of 'harvest index' for measuring productivity of Hevea has not been generally used hitherto. In the present study, an attempt is made to obtain and compare values of harvest indices for various Hevea species, a series of Hevea brasiliensis clones and finally for a specific high-yielding Class I clone. Some physiological and structural parameters related to yield and hence ultimately to the harvest index are also considered.

From the study, it is apparent that among the Hevea species, the harvest index is highest for Hevea brasiliensis. Individuals in a population of seedling trees of Hevea also vary in their harvest indices. Clonal variation and annual variation are clearly evident. Variation due to age is also apparent. Competition between trees and the partition of assimilates between the competing physiological sinks within trees are factors which affect tree growth and hence productivity of rubber. The efficiency of the source may be assumed to be variable, especially as influenced by clonal character, age and perhaps other physiological parameters including those influencing tree-to-tree competition. It is noted that the variability of the sink may also influence these physiological parameters, through the influences on water turn-over and the variability in biosynthetic capacity of the laticiferous system. Exploitation procedures can also be expected to influence the behaviour of the sink and its efficiency.

The concept of harvest index therefore might be a very useful property not only for comparison of clones but also to measure sensitivity of the clone to exploitation procedures and other environmental factors.

For cereals and other crops where the crop is harvested along with the whole plant, the concept of harvest index is applied to represent the proportion of economic crop harvested as a proportion of total dry matter^{1,2,3}.

For a perennial crop like *Hevea*, the concept may be expressed in more than one form. Previous researchers have used terms such as 'partition of assimilates' rather than 'harvest index' to represent the ratio between dry rubber yield and observed or calculated shoot weight^{4,5}. This empirical ratio was further examined in relation to tapping experiments by Wycherley⁶.

In one of the above studies, a group of tapped trees was compared with a group of untapped trees, before commencement of tapping and two years after tapping, to obtain data on 'shoot loss' due to tapping. In another

study, the effects of tapping were systematically examined in a number of tapping trials distributed throughout the country and representing various frequencies of tapping and clone combinations, to arrive at a generalisation related to the physiological performance of clones of *Hevea*. Thus, in previous studies, the value of the regression equation relating shoot weight to girth of trees as originally obtained has been well established⁷. However, one important difference between the practice of the crop physiologists and the above studies is in the consideration of the calorific value term in the equation used in the calculation of harvest index as theoretically defined later⁸.

It is well known that a crop is rarely limited in its yield by only a single environmental or genetic factor. The progressive improvement of economic yields in crops has been brought about by improvements in numerous co-limiting

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factors or phenomena such as improvement of genetic yield potential; improvement in management inputs and practices; introduction of chemical means of yield stimulation; improvement in chemical practices of pest and disease control; improvements in weed control; degree of response to fertiliser application, *etc.*

In rubber, it is generally claimed that yield improvement since the inception of rubber research in Malaysia is of the order of five- to seven-fold (unselected seedling yield compared to experimental yield of partly proven material) and there is a promise of a further 30%–60% increase from expectations in the next two decades⁹. No doubt the improvements have been due to the multiple factors mentioned earlier.

The vexing physiological question which is still unanswered is the proportion of the fixed carbon harvested in the economic crop yield compared to the total amount of fixed carbon. As the rubber tree yields liquid latex from its reservoir of the laticiferous system, and as at least 65% of the harvested matter is water, there is no doubt that the water relations of the tree influences production to a great extent. Furthermore, it has been abundantly shown that plugging indices influence latex flow pattern and ultimate yield¹⁰. It can be stated that while the solar energy is abundant in regions grown with rubber, it has not been shown whether the utilisation of solar energy by the clones of *Hevea* and the yield of economic crop are related in a manner that can be exploited for further yield improvement. In other words, whether efficiency of the source (photosynthesis) or efficiency of the sink (laticiferous system) is more important in realising genetic potential, has not yet been decided.

Templeton's earlier studies have shown that tapped trees undergo a 'shoot loss' of 2.3–45.5 kg/tree when compared to the increment of dry weights of 59.5–112.2 kg for the untapped trees amounting to percentage shoot losses of 4% to 52%. In the same populations, the percentage ratio of rubber weight to dry weight increment ranged from 3% to 11%. Wycherley observed

that during the early years, there is a negative correlation between growth and yield, *i.e.* shoot loss is a function of yield between years and experiments. He further observed that tapping in itself, irrespective of yield, may depress growth, in addition to the shoot loss which is proportionate to the diversion of assimilates from accumulation of dry matter into yield.

This paper re-examines the efficiency of rubber extraction in the form of harvest indices, for a few *Hevea* species, a number of clones in large-scale trials (RRIM 700 series) and finally for a specific high-yielding clone, RRIM 600. Some other factors closely related to biomass production and economic (dry rubber) yield are further examined through simple correlations between some observed (structural, physiological and other yield related) properties, in a group of unselected seedlings and in RRIM 600.

EXPERIMENTAL

Various species of *Hevea* growing in *Field 67* of the RRIM Experiment Station at Sungai Buloh were used in their seventh year of tapping for the determinations on species. Data from the RRIM 700 series (second selections) were used for the comparisons of clones. Five age-classes of RRIM 600 were also utilised from the RRIM Experiment Station at Sungai Buloh (*Fields 64A, 53, 48C, 48E and 69C*). Unselected seedlings in the fifth year of tapping, growing in *Field 68* of the RRIM Experiment Station at Sungai Buloh were used for some of the determinations.

Conventional techniques of yield recording and other physiological and structural measurements as currently practised in Malaysia were followed. The term 'micro-yield' denotes yield obtained from a 1 mm puncture on the bark¹⁰.

Annual harvest index was derived as a percentage of the annual rubber harvest in calorific terms against the calculated shoot weight of the trees using the Shorrocks formula⁷.

RESULTS

Figure 1 shows the frequency distribution of dry matter in an unselected seedling population which was in the fifth year of tapping. The population has a skewed distribution with a mode around 500 kg/tree. The range in values observed for the first year of observation (fifth year of tapping) was 104 kg to 1312 kg and for the second year of observation (sixth year of tapping) was 107 kg to 1630 kg. The dry matter increment varied from a low 1 kg value to a high 318 kg/tree/year. Although the high value coincided with that of the tree with the highest dry matter on first observation, the low value did not coincide with the tree with the lowest dry matter.

Table 1 shows the mean rubber yield per tapping, mean shoot weight and annual harvest index calculated from these figures for eighteen-year-old trees of seven species of *Hevea*. As expected, the highest harvest index was found in *H. brasiliensis*, despite its fifth ranking in

shoot weight. This is due to the known higher yield potentials and partitioning coefficient in favour of economic yield.

Annual harvest index figures for clones in the fifth year of tapping, examined for the 700 series clone trial are given in Table 2. The above-average nature of RRIM 712 in this group of clones, for the whole period, is evident from the table. Annual harvest indices vary from about 2.2 to 9.3; there is an increasing trend with age upto the third or fourth year, and then there is a decline.

When the variability of annual harvest index was examined in relation to age classes within the same clone, RRIM 600 (Table 3), it was found that the indices declined from a high value of 16.2 in the first year to a low value of 4.7 in the tenth year. Furthermore, the differences between age-classes three, five, seven and ten years were not significant, indicating that the harvest index is a reliable property for evaluation purposes.

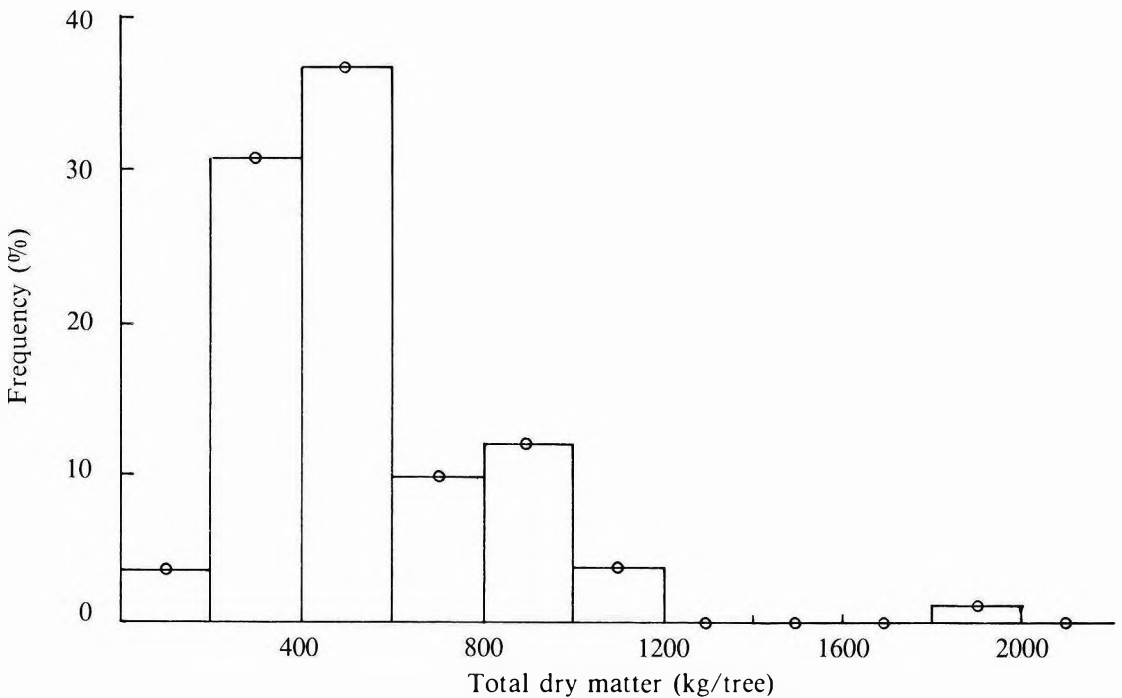


Figure 1. Dry matter distribution in unselected Hevea seedlings.

TABLE 1. YIELD, SHOOT WEIGHT AND ANNUAL HARVEST INDICES OF SEVEN SPECIES OF *HEVEA* (SEVENTH YEAR OF TAPPING)

Species	Mean yield (kg/tree/year)	Mean shoot weight (kg/tree)	Harvest index
<i>H. brasiliensis</i> (RRIM 605)	99.5	646	6.21
<i>H. pauciflora</i>	28.9	708	1.69
<i>H. benthamiana</i>	25.1	792	1.31
<i>H. guianensis</i>	5.3	380	0.45
<i>H. rigidifolia</i>	3.8	235	0.20
<i>H. spruceana</i>	2.4	1 009	0.20
<i>H. nitida</i>	1.1	802	0.14
S.E.	1.21	90.9	0.15
L.S.D.	3.36	263.3	0.45

TABLE 2. ANNUAL HARVEST INDICES FROM FIRST TO FIFTH YEAR OF TAPPING OF SOME CLONES IN LARGE-SCALE TRIALS (RRIM 700 SERIES — SECOND AND THIRD SELECTIONS)

Clone	Harvest index					Mean	S.E.
	1st year	2nd year	3rd year	4th year	5th year		
RRIM 709	3.60	6.61	7.88	6.87	5.42	6.07	0.73
RRIM 710	3.60	7.55	9.25	7.72	6.18	6.86	0.95
RRIM 711	3.49	5.33	6.28	5.66	4.70	5.09	0.48
RRIM 712	4.26	7.56	8.98	9.33	7.98	7.62	0.90
RRIM 713	3.79	4.80	4.98	4.65	3.49	4.34	0.30
RRIM 714	3.99	4.75	4.94	4.85	4.30	4.56	0.18
RRIM 715	2.53	3.07	3.22	2.85	2.60	2.85	0.13
RRIM 716	3.05	4.70	5.24	5.00	4.29	4.45	0.39
RRIM 717	5.43	6.61	6.08	5.35	4.70	5.63	0.33
RRIM 718	2.63	4.84	5.49	5.10	4.96	4.60	0.51
RRIM 719	3.19	4.43	5.28	5.45	5.19	4.70	0.42
RRIM 720	3.16	4.55	4.31	5.08	4.80	4.38	0.33
RRIM 721	4.15	6.72	7.46	6.44	5.15	5.98	0.59
RRIM 722	3.71	4.82	5.52	4.52	4.05	4.52	0.31
RRIM 723	2.31	3.44	4.68	4.53	4.24	3.84	0.43
RRIM 724	2.22	5.26	7.00	5.02	5.72	5.04	0.78
RRIM 725	3.42	5.79	6.76	5.95	4.70	5.32	0.58
Mean	3.44	5.34	6.07	5.55	4.85		
S.E.	0.19	0.31	0.40	0.35	0.28		

TABLE 3. YIELD, SHOOT WEIGHT AND ANNUAL HARVEST INDICES OF FIVE GROUPS OF RRIM 600 TREES AT DIFFERENT AGES^a

Age (years)	Mean yield (g/tree/tapping)	Mean shoot weight (kg/tree)	Harvest index
1	4.9	5	16.2
3	9.7	45	5.3
5	20.6	105	4.8
7	72.1	251	4.7
10	89.0	302	4.7
S.E.	2.44	14.1	0.58
L.S.D.	6.76	39.7	1.63

^aYields of untapped stands were obtained by test tapping alternate daily for one month.

Simple Correlations between Yield and Some Yield-related Parameters

Simple correlations were derived for yield per centimetre of cut and annual harvest index, yield per centimetre of cut and latex vessel index, yield and dry matter, dry matter and dry matter increment, latex vessel ring number and dry matter, and plugging index and annual harvest index for unselected seedlings. These are given in *Table 4*. Most of the values are very

TABLE 4. SOME SIMPLE CORRELATIONS BETWEEN OBSERVED PROPERTIES IN UNSELECTED SEEDLINGS (n = 53)

Correlation between	r
Yield/cm of cut and annual harvest index	0.6186***
Yield/cm of cut and latex vessel index	0.1834 ^{NS}
Yield and dry matter	0.6007***
Dry matter and dry matter increment	0.7492***
Latex vessel ring number and dry matter	0.4335**
Plugging index and annual harvest index	-0.3878**

NS: Not significant

*P < 0.05

**P < 0.01

***P < 0.001

highly significant. In this experiment, the yield per centimetre of cut and the latex vessel index were not significant; an unusual result.

Simple correlations were also computed for yield and micro-yield, yield and plugging index, micro-yield and micro-plugging index, yield and latex vessel ring number, micro-yield and latex vessel ring number and yield and dry matter, for five phases of growth of clone RRIM 600. The results are given in *Table 5*. The most consistent results are obtained for correlations between yield and dry matter for all the age-groups. Other results did not show clear trends.

Other Physiological Indicators

Table 6 gives details of physiological indicators which are linked to yield, and hence would be expected to be related to the harvest index, for the same groups of trees of RRIM 600. All three measures of yield show increasing trends with age, a property also reflected in the plugging index. Micro-plugging index, on the other hand, shows a reverse trend; dry rubber content (d.r.c.) shows a peak value before tappable age and then decreases, turgor pressure, bark thickness, latex vessel ring number, girth and dry matter show increasing trends.

DISCUSSION AND CONCLUSION

The desirability of having an index such as harvest index to measure the ratio between crop

TABLE 5. SIMPLE CORRELATIONS BETWEEN SELECTED PROPERTIES OF RRIM 600 FROM DIFFERENT PHASES OF GROWTH

Properties	Correlation				
	1 year	3 years	5 years	7 years	10 years
Yield and micro-yield	0.5764**	0.1837 ^{NS}	0.6214**	0.4930*	0.3050 ^{NS}
Yield and plugging index	-0.2482 ^{NS}	-0.5524*	-0.5109*	-0.8083***	-0.6488**
Micro-yield and micro-plugging index	-0.6027**	-0.6180**	-0.4509*	-0.6067**	-0.6212**
Yield and LVR number	0.4556	-0.0349 ^{NS}	0.4622*	0.4678*	0.5199*
Micro-yield and LVR number	0.4455*	0.2145 ^{NS}	0.7103***	0.1707 ^{NS}	0.4875*
Yield and dry matter	0.8804***	0.6031**	0.6535**	0.8657***	0.8564***

NS: Not significant

*P < 0.05

**P < 0.01

***P < 0.001

TABLE 6. PHYSIOLOGICAL AND ANATOMICAL CHARACTERS OF RRIM 600 FROM DIFFERENT PHASES OF GROWTH^a

Property	Value of property measured					S.E.	L.S.D.
	1 year	3 years	5 years	7 years	10 years		
Yield (ml)	4.9	9.7	20.6	72.1	89.0	2.44	6.76
Initial yield (ml)	0.5	4.8	9.5	16.0	25.2	0.36	0.99
Micro-yield (ml)	0.01	0.28	0.41	2.63	4.11	0.08	0.23
Plugging index	2.3	6.6	6.8	10.1	10.4	0.16	0.44
Micro-plugging index	70.3	44.9	44.0	30.4	30.3	0.7	1.9
D.r.c. (%)	39.5	47.7	54.9	44.5	44.5	0.34	0.93
Turgor pressure (atm)	0	8.7	10.4	11.4	12.8	0.09	0.25
Bark thickness (mm)	2.5	4.4	5.2	6.6	7.5	0.16	0.44
Latex vessel ring	3	5	8	16	21	0.6	1.8
Girth (cm)	14.5	32.4	44.2	60.6	64.6	1.40	3.94
Dry matter (kg)	5	45	105	251	302	14.1	39.7

^aThe untapped stands of one, three and five years were test-tapped on fifteen days during a month for determination of these values. Other determinations were obtained from one whole year of alternate day tapping.

harvested and dry matter production has been appreciated by crop physiologists around the world for many years. However, it is surprising that such an index has not been generally used in *Hevea* research since the inception of research on rubber as a crop. The partition of

assimilates has been investigated earlier and a theoretical derivation of the concept of harvest index in *Hevea* has been available to us⁸ since 1981. As far as the authors are aware, this is the first instance where experimental data have been utilised to compute harvest indices in

Hevea. The computations were based on certain assumptions and derived formulae of previous investigators^{8,11}, and they may be further improved and made more precise by future investigations. Nevertheless, the values obtained in the present work indicate some very pertinent trends.

It has been demonstrated in this study that individuals in a population vary in their harvest indices. Clonal variation and annual variation are also features clearly evident. Variation due to age is also apparent. Competition between trees and competition within trees (*i.e.* through partition of assimilates) are factors which affect tree growth and consequently productivity. Assuming that efficiency of the source is variable, as influenced by clonal character and age and perhaps other physiological factors related to tree-to-tree competition, it has also to be admitted that the sink is also variable because the latex flow characteristics are affected by water turn-over and biosynthetic capacity of the laticiferous system and by the demands made on this capacity by the exploitation procedures. Therefore, computations of harvest indices would be very useful for measuring the sensitivity of clones to exploitation regimes which in practice may be varied as much as four-fold in intensity. Hence, breeders and selectors would be advised to consider the value of employing harvest indices to compare not only the performance of genotypes *per se*, but also the genotype-environment interactions which affect performance.

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Creep Behaviour of Rubbers Subjected to Repeated Loadings

T.J. POND*

The creep behaviour of various rubbers has been studied when subjected to repeated loading conditions (cyclic creep), and compared to the creep behaviour under equivalent constant load conditions. It has been found that the repeated loading of strain crystallising rubbers under high stress levels can produce a substantial enhancement of creep rates over that observed in the static loading condition. The presence of crystallisation during stressing is thought to induce high stresses in the rubber network near the boundary region of the crystal sites and that these high stresses lead predominantly to the breakage of crosslinks. It appears from swelling and set measurements that crosslink breakage is responsible for approximately half of the total cyclic creep with visco-elastic effects accounting for the remainder.

The creep of a rubbery material subjected to repeated loadings would normally be expected to be less than the creep of that rubber under the same load continuously applied. A load applied for half the time, for example, should produce approximately the same amount of creep as half the load applied continuously. This behaviour would be shown by a material which is visco-elastically simple, that is, one obeying approximately the Boltzmann superposition principle for linear visco-elastic systems. Previous work^{1,2} have shown that for certain rubber vulcanisates, the creep under repeated stressing can in fact be considerably greater than the creep under a static load. It was suggested that this cyclic creep behaviour was partly due to the ability of these rubbers to strain crystallise. Further work is reported here using a greater range of materials than previously investigated and confirms the importance of crystallisation in producing the observed cyclic creep behaviour. Although the cyclic creep behaviour is most predominant in the tensile mode, the effect is also shown to be present in compression. The contributions of visco-elastic flow and mechanical rupture of bonds during repeated stressing of a vulcanisate are discussed in this paper together with the relative effect these two components have on the overall cyclic creep behaviour.

EXPERIMENTAL

The tensile creep measurements were conducted on strips of rubber about 100-150 mm long, 6 mm wide and 1-2 mm thick depending on the desired loads and strains. The test pieces were firmly clamped at each end to eliminate slippage and the desired strain (typically 50%-750%) achieved by applying a suitable dead load.

The static creep measurements were conducted by applying a dead load to the test piece. The resulting extension after 1 min of loading is termed the initial extension. The creep is expressed as a percentage of this initial extension. With creep defined in this way, a plot of creep against the logarithm of time is shown to produce a straight line. The creep rate can therefore be quoted as so many percent per decade, that is the amount of creep that occurs during any factor of ten in time.

The cyclic creep measurements were conducted under a cyclic load, that is a load which is repeatedly applied and removed. The loading schedule is illustrated in *Figure 1*. The creep is fairly rapid immediately after the initial loading (*A,C*), but progressively reduces. The creep is measured at the same position during each loading cycle, (e.g. D_1 , D_2 etc.), when the rate

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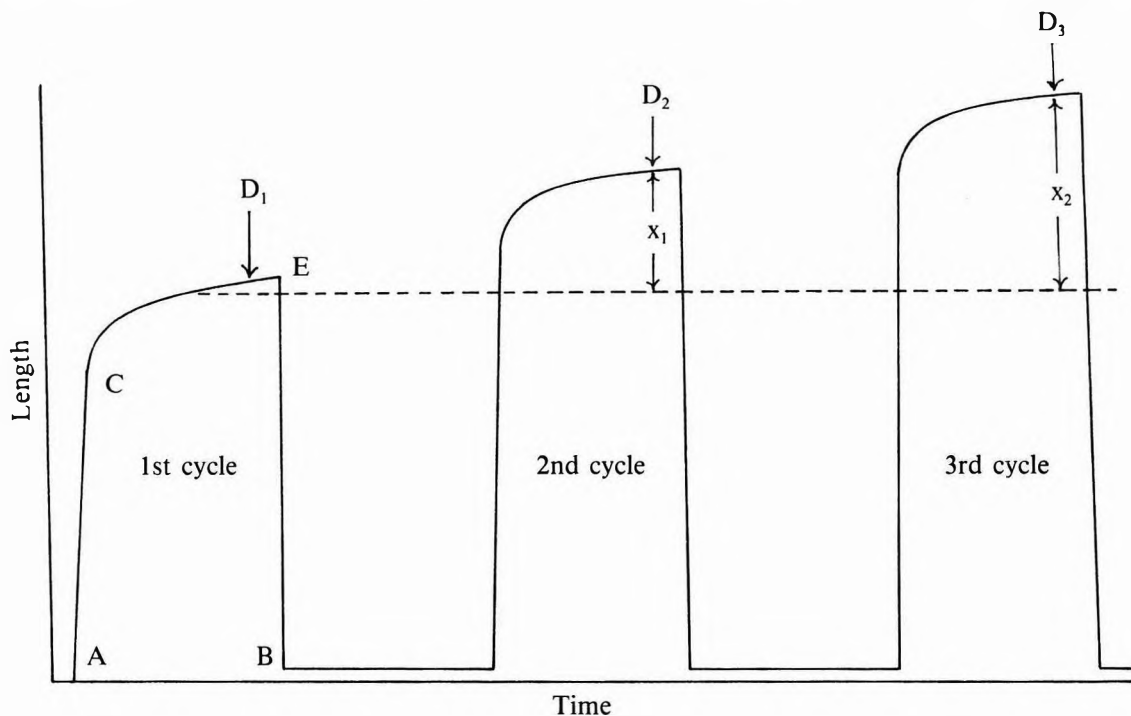


Figure 1. Schematic diagram of length versus time relation showing times at which the increases in length x_1 , x_2 , etc. are measured.

is sufficiently slow to allow good accuracy in the length measurements. The creep (x_1 , x_2 etc.), is calculated as a percentage of the initial displacement which took place in the first cycle (e.g. at Position D).

All the measurements were carried out at a temperature of 22°C except where otherwise stated.

Table 1 shows the formulations of the various rubbers used.

RESULTS

Since the amount of cyclic creep gives a linear dependence with the logarithm of the number of cycles of loading, and the static creep behaviour a linear dependence with the logarithm of time after loading, the two rates can both be expressed as percentage creep per decade of number of cycles and time respectively. As these rates have similar physical dimensions,

they can legitimately be compared. The absolute values would not be expected to be identical. As previously mentioned, in general, the cyclic rate should be less than the static rate as the load is only applied for a fraction of the time, about half in most of the following experiments. In fact, in many of the cases studied, the cyclic rates are substantially greater than the static ones. The numerical values of the cyclic and static creep rates can be realistically compared since the loading schedule is performed in a regular manner.

Figure 2 shows the static and cyclic creep behaviour of black filled natural rubber using three different vulcanising systems (Compounds A, B, C). It can be seen that the cyclic creep behaviour produces a linear dependence with the logarithm of the number of cycles for each of the vulcanising systems shown. A substantial increase in the magnitude of the cyclic creep rates, due to repeated stressing, over that of the static creep rates can be seen.

T.J. Pond: Creep Behaviour of Rubbers Subjected to Repeated Loadings

TABLE 1. FORMULATIONS OF VARIOUS RUBBERS USED

Item	Compound									
	A Cons	B SEV	C Dicup	D Gum NR	E Gum NR	F SBR	G EPDM	H P.C W	I P.C WRT	
Natural rubber, SMR 5	100	100	100	100	100					
Intol 1500						100				
NPR (WRT)									100	
NPR 4628 (W)								100		
Nordel 1470							100			
Zinc oxide	5	5		3	5	3.5	5	5	5	
Stearic acid	2	2		2	2	2.5	1	0.5	0.5	
CBS	0.6			0.3	0.6	1.1				
Sulphur	2.5	0.3		1.4	2.5	2	1.5			
Dicumyl peroxide			1.5							
Carbon black (Magecol 888)	30	30	30			30				
Nonox ZA									1.0	
Nonox HFN						1				
Flectol H									1.0	
TMTD		1.3							1.0	
MOR		2.75								
HAF							80			
Magnesium D								4	4	
Oktomine								2		
NA22								1	1	
Circosol 4240							55			
TMTM							1.8			
MBT							0.6			
Cure time (min)	60	60	60	30	40	60	35	35	35	
Cure temperature (°C)	140	150	150	140	140	140	150	153	153	
Vulcanisate hardness (IRHD)	50	47	47	43	44	47	50	44	44	

A factor of about 4 is found at this particular strain level (initially 150%), the value depending only slightly upon the vulcanising system used. Thus, the nature of the crosslinks, predominantly monosulphidic in the efficient vulcanising system (EV), and polysulphidic in the conventional sulphur system (CV), appear not to be a major factor in influencing the cyclic creep behaviour at these intermediate strain levels.

Previous work^{1,2} have shown that a limited change in the loading schedule of a repeatedly loaded natural rubber gum vulcanisate does not produce a significant change in the cyclic creep rate. Some further measurements over a greater range of loading/unloading times have been conducted, and the results are shown in *Table 2*. The results confirm that the loading schedule can be considerably altered without greatly influencing the cyclic creep rate and that

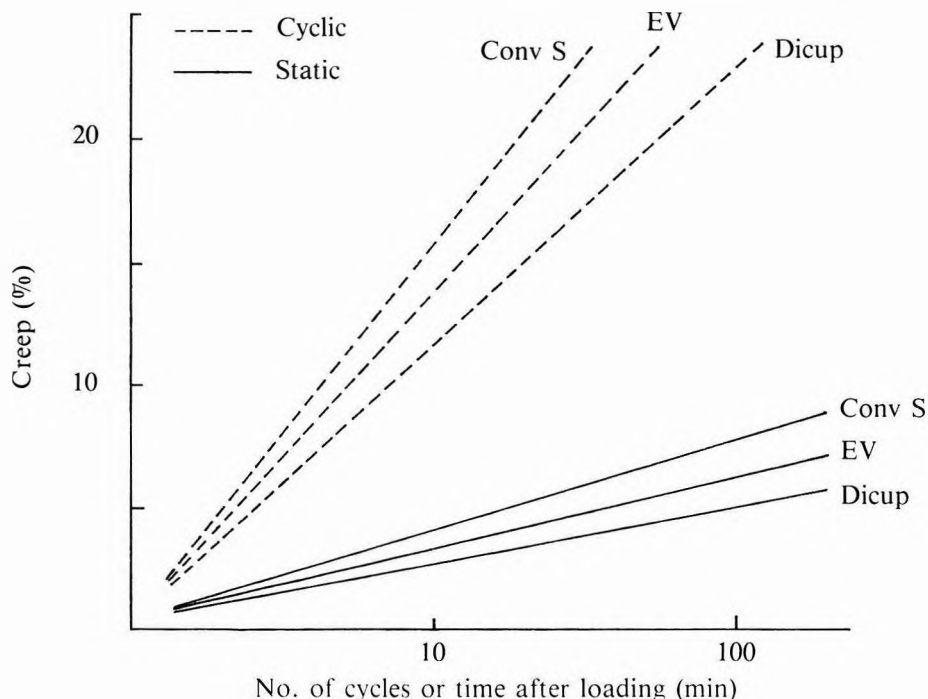


Figure 2. The static and cyclic creep behaviour of three natural rubber vulcanisates containing 30 parts of carbon black filler (Magecol 888). Compound A uses a conventional accelerated sulphur system (Conv S), B a soluble EV system (EV) and C dicumyl peroxide (Dicup). The initial test piece strain is 150%.

TABLE 2. EFFECT OF LOADING SCHEDULE (COMPOUND E)

Time loaded (min)	Time unloaded (min)	Creep (% decade)	Load/unload ratio
Continuous		3.6	
1	1 440	11.9	0.0007
1	10	13.6	0.1
1	1	14.0	1
10	0.16	16.3	60
40	0.16	17.2	240

Initial test strain 350%
Temperature 22°C

it is the process of cycling itself which produces the increased cyclic creep when compared to that of the static creep behaviour. As the unloading period becomes increasingly longer however, the cyclic creep rates can be seen to

reduce. This reduction in creep is probably due to recovery within the rubber network, the more recovery allowed to take place as the unstrained time period increases, resulting in the reduction of the overall cyclic creep rate.

Earlier work¹ has shown that the cyclic creep of a natural rubber gum vulcanisate can substantially increase with increasing applied stress. Further cyclic creep measurements have been conducted using a range of stress levels (strain 50% to 750%), and some results are shown in *Figure 3*. It can be seen that at low stress levels (below 200% strain) the cyclic creep rate falls below that of the static value, as expected, assuming the material behaves as a linear visco-elastic system, however, as the applied stress increases a substantial increase in the cyclic creep rate takes place. This increase in the cyclic creep rate¹ appeared to reach a plateau, but the results reported here, which were continued to a somewhat higher stress level, indicate the creep rate continues to increase with increase stress.

At the stress levels and subsequent strains associated with the rapid increase in the cyclic creep rate, as shown in *Figure 3*, strain-induced

crystallisation is known to develop significantly. This suggests that the presence of crystallite development and melting during the repeated stressing process may play an important role in producing the observed increase in creep at higher stress levels. Thus subsequent work reported here has further investigated the role of strain crystallisation on the cyclic creep behaviour of various rubbers.

Figure 4 shows the cyclic creep behaviour of a carbon black filled natural rubber vulcanisate (*Compound A*) repeatedly loaded until failure. The linear dependence of creep with the logarithm of the number of cycles of loading continues until a little before the failure of the sample. During the accelerating creep rate period, and just after the departure from the linear creep behaviour, cracks could be seen developing along the edges of the test pieces. The crack growth development usually took the form of a number of 'smaller' cracks growing

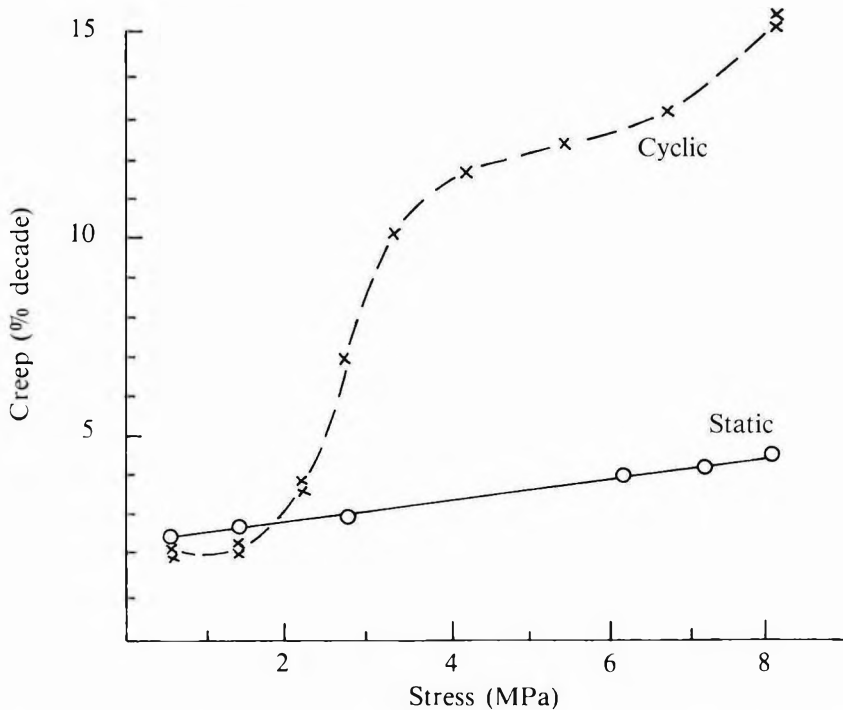


Figure 3. The effect of increasing stress on the static and cyclic creep rates of a natural rubber gum vulcanisate (Compound E). The initial strain range is 50% to 750%. Similar creep rates occur at approximately 200% strain.

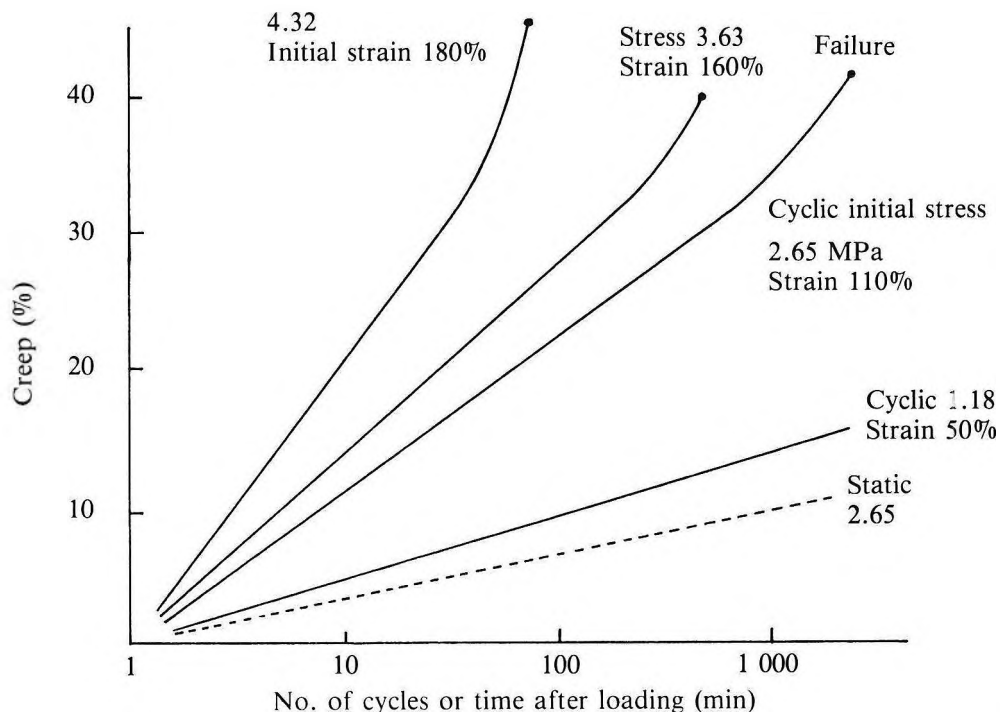


Figure 4. Static and cyclic creep measurements on a natural rubber vulcanisate containing 30 parts of carbon black, Compound A. The limit of time for the static measurements is minutes.

intermittently along the entire length of the test piece with a single dominant crack propagating until it caused the test piece failure.

If strain-induced crystallisation is contributing to the mechanism producing the enhanced cyclic creep behaviour it could be expected that a non-crystallising rubber should produce reduced cyclic creep rates. A 'well behaved' rubber *i.e.*, one following approximately the Boltzmann superposition principle, should produce cyclic creep rates which are lower than the creep rates produced under equivalent static loading conditions.

Figure 5 shows the cyclic and static creep behaviour of two non-crystallising polymers. Generally, the cyclic creep rates of both materials are considerably less than those found in the crystallising rubber, however, it is of interest that the cyclic creep rates are still a little greater than those measured in the static creep condition. Figure 6 shows the cyclic and static creep behaviour of two types of crystal-

lising polychloroprene rubber. The *W* type polychloroprene is known to readily strain crystallise, thus it could be expected that the cyclic creep rates would be considerably greater than the static creep rates if strain crystallisation played a major factor in producing the large creep rates, as found in the strain crystallising natural rubber vulcanisate. It can be seen that the cyclic creep rates are considerably enhanced, even at the moderately elevated test temperature of 35°C, where crystallite formation will be somewhat inhibited and crystallite melting encouraged. The *WRT* type polychloroprene vulcanisate is known to crystallise less readily than the *W* type, and this is reflected in the somewhat reduced cyclic creep rate of the *WRT* material.

It is known that the process of isomerising natural rubber considerably suppresses the development of strain-induced crystallisation³. Isomerised natural rubber could, therefore, be expected to act 'well behaved' in the manner of

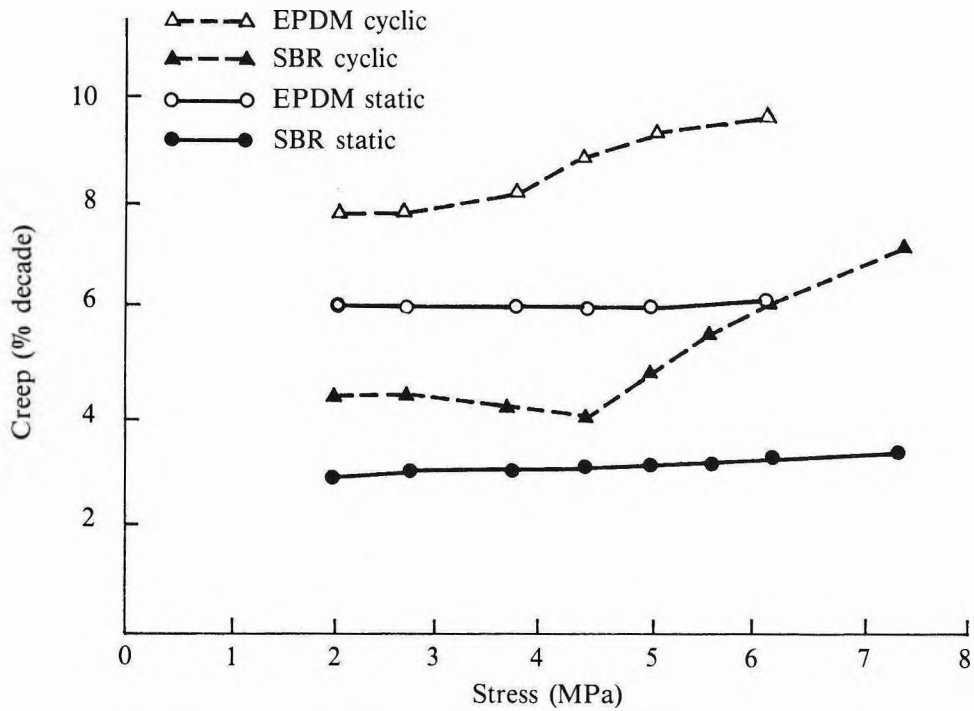


Figure 5. Static and cyclic creep rates of two non-strain crystallising polymers containing carbon black filler. The initial strain range is 110% to 280% for Compound G (EPDM) and 90% to 260% for Compound F (SBR).

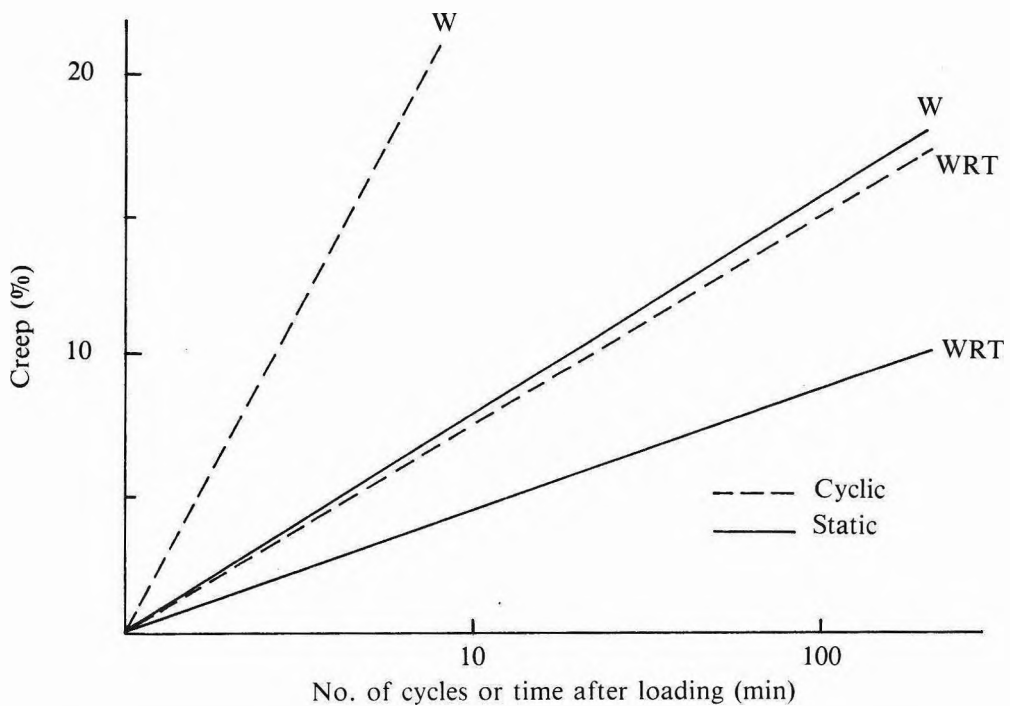


Figure 6. Static and cyclic creep behaviour of two types of strain crystallising polychloroprene rubber. Compound H (W) initial strain 230% and I (WRT) initial strain 240%.

a linear visco-elastic material whereby the cyclic creep rate behaviour should be less than the normal static creep behaviour. Some results are shown in *Figure 7* of isomerised gum and black filled rubbers subjected to cyclic and static loading conditions. From *Figure 7* it can be seen that the materials do show a cyclic creep rate below that of the static creep rate, and therefore behave in the expected well behaved manner, indeed these rubbers are the only materials tested here where the cyclic creep is appreciably less than in the static creep condition. Thus, these results further indicate that the presence of strain-induced crystallisation contributes to the observed increase in creep under repeated loading conditions.

The work described so far has been confined to creep behaviour in tension, because this mode is where the effect of cyclic creep would be expected to be most prominent and therefore easiest to study. However, the cyclic creep

behaviour would also be expected to be present under compression and shear deformations although to a lesser extent. Since in practice the majority of manufactured rubber articles will operate in some combination of compression and shear modes, it is of interest to know the degree by which the enhanced cyclic creep rate behaviour measured in tension occurs in these other modes of deformation. Some results of the stress relaxation of a natural rubber vulcanisate with two carbon black filler loadings is shown in *Figure 8*, as a function of the applied compression. It can be seen that at smaller compressive strains (less than 30%), the cyclic stress relaxation is less than that of the ordinary static conditions but as the compressive displacement increases the cyclic creep becomes greater, a behaviour similar to that found in tension. The particular value of compressive strain when the cyclic creep rate becomes greater than the static creep rate will depend on the filler loading. Since the filler

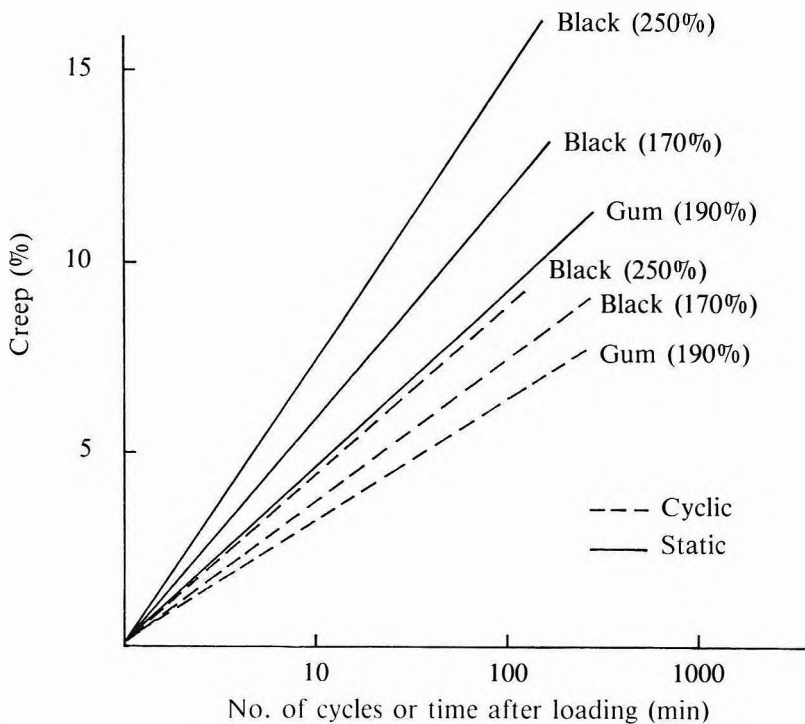


Figure 7. Static and cyclic creep behaviour of two isomerised natural rubber vulcanisates. The filled material contains 30 parts HAF carbon black. Figures within brackets indicate initial strain.

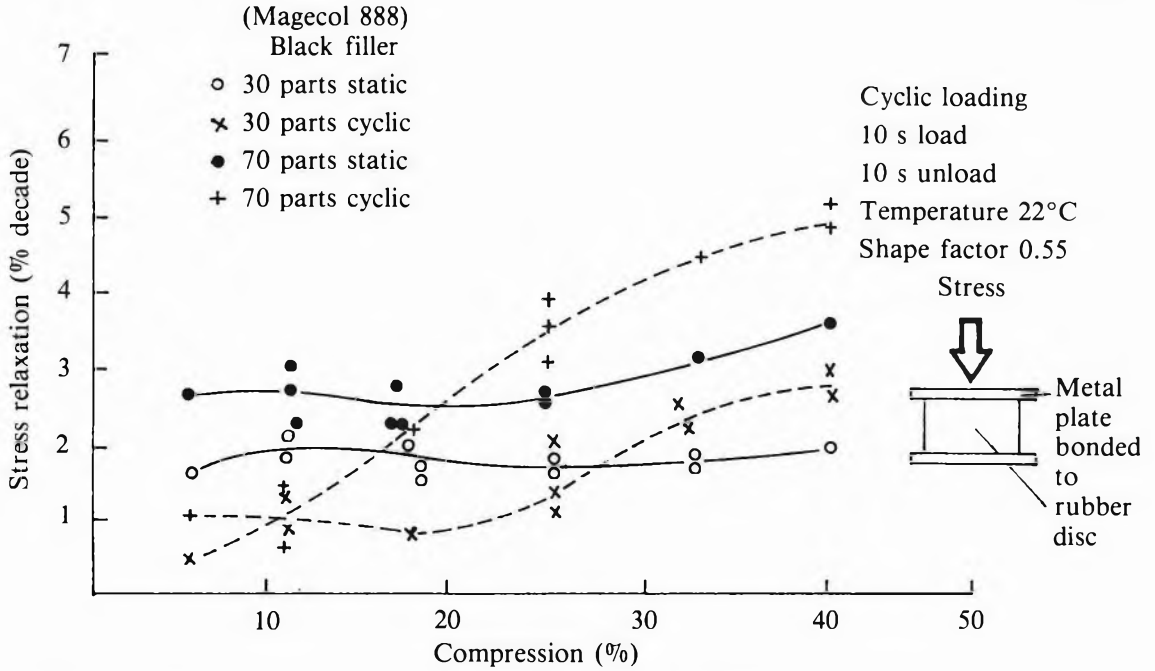


Figure 8. Static and cyclic stress relaxation of plate bonded natural rubber discs in compression. Compound E plus 30 or 70 parts carbon black filler.

loading determines the proportions of the elastic rubber phase to the inelastic carbon black phase 'strain amplification' effects will influence the cyclic creep rate values.

Set and Bond Breakage on Repeated Stressing

Ordinary creep at room temperature is regarded as a visco-elastic mechanism. Previous work using natural rubber has shown that set, resulting from ordinary creep is recoverable by swelling and deswelling the rubber in a good solvent. Measurements of cyclic creep have however shown that there is considerable permanent set, that is set that cannot be recovered even by swelling and deswelling. The presence of this permanent set suggests that there is some form of network breakdown occurring due to the repeated stressing applied to the rubber. Table 3 shows an example of the permanent set on a gum natural rubber worked for twenty cycles as a function of the applied stress. At the lowest strain shown, which is a little below the strain level when strain-induced

crystallisation is known to become significant (approximately 200%), little permanent set occurs, however, as the strain increases the permanent set likewise increases.

Previous work has shown that high stress, even at room temperature can produce rupture of chemical bonds, probably mainly crosslinks, in natural rubber vulcanisates⁴. Some recombination of crosslinks occurs while the rubber is in the strained state, and this leads to changes in the equilibrium swelling of rubber and the observed permanent set. Swelling techniques can in fact be used to detect the breakdown of bonds in a quantitative manner, however, sample weighing and length measurements normally require a high level of accuracy. The question concerning the cyclic creep behaviour is whether cyclic creep is related to the reduction in the number of molecular chains produced by stress-induced bond breakage, or whether the cyclic creep effect is predominantly visco-elastic and hence recoverable with swelling and drying, as in the static creep case, and not determined

TABLE 3. SET OF A GUM NATURAL RUBBER (COMPOUND E)

Number of cycles	Load/unload schedule (s)	Test stress (MPa)	Test strain (%)	Permanent set due to stressing (% of original length)	Total set at end of cycling (%)
20	15/15	1.32	170	0.1	2.2
20	15/15	2.65	360	1.3	7.1
20	15/15	5.30	580	7.4	17.0
20	15/15	6.62	640	11.3	18.2
20	15/15	7.95	750	17.4	24.6
20		6.62	640	10.3	18.1
20		6.62	640	11.3	19.6

by any irreversible effects. Thus to investigate this, a series of measurements were carried out in which strips of gum natural rubber *D* and *E* were repeatedly stressed, the cyclic creep being monitored in the usual way. Portions of the test pieces were cut and their lengths and weights accurately measured and then swollen to equilibrium in n-decane. The changes in equilibrium swelling are normally quite small, of the order of a few percent in the moderately stressed test pieces, so that good accuracy is necessary in these measurements. Generally, there is some extractable material present in the test pieces and therefore each sample was swollen in a container with an unstressed control sample cut adjacently from the same sheet. This procedure also allowed for any inhomogeneity in the rubber sheet. The swollen samples were weighed, and the decane evaporated off, after which the sample dimensions and final weights

were measured and allowances made for any extractable material. These measurements were used to calculate the equilibrium volume fractions of rubber in the control and stressed samples V_1 , and V_2 , and the fractional permanent set $(\lambda_0 - 1)$. During the repeated stressing process some recombination of crosslinks takes place which leads to the observed permanent set discussed earlier. This crosslink recombination produces an additional complication when interpreting the swelling measurement results, however, assuming the Tobolsky two-network theory, the fraction of bonds broken and the fractional recombination of crosslinks can be calculated^{2,4}.

Assuming there are initially N network chains per unit volume of rubber of which n_1 break and n_2 recombine during the strained state

at extension ratio λ' , $\frac{n_2}{N-n_1}$ ($= \alpha$) is

given by

$$\alpha = \frac{\lambda_0^3 - 1}{\lambda' - \lambda_0^3 \lambda'^{-2}} \quad \dots 1$$

and

$$1 - \frac{n_1}{N} = \left(\frac{v_1}{v_2} \right)^{1/3} \left(\frac{\ln(1 - v_2) + v_2 + \chi v_2^2}{\ln(1 - v_1) + v_1 + \chi v_1^2} \right) \quad \dots 2$$

$$\left[(1 + \alpha \lambda')^2 (1 + \frac{\alpha}{\lambda'^2}) \right]^{-1/3}$$

These equations make use of the Flory-Huggins relation between modulus and equilibrium swelling using a value of $\chi = 0.41$. Figure 9 shows the percentage of broken crosslinks calculated from Equations 1 and 2, plotted against the percentage creep of a natural

rubber gum vulcanisate. The results include data on test pieces repeatedly loaded for twenty cycles at various stress levels, test pieces held at a fixed stress level of 1.77 MPa and loaded over various numbers of cycles, and test pieces which have undergone the various loading schedules shown in Table 4. From Figure 9, the number of broken crosslinks can be seen to correlate with the amount of creep taking place in the rubber. The number of crosslinks which recombine during the strained state has also been calculated for the test conditions discussed and results indicate that between 20% and 30% of these broken crosslinks recombine in the natural rubber vulcanisate studied.

DISCUSSION

Evidence suggests that the presence of strain-induced crystallisation within a rubber can produce an increase in creep under cyclic loading conditions.

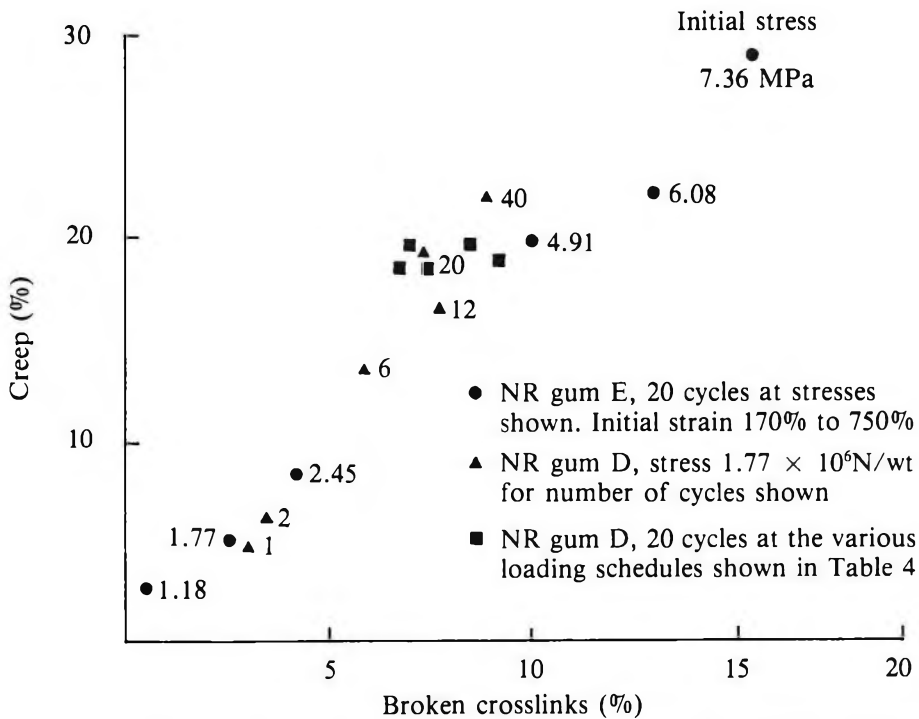


Figure 9. Percent creep variation with percent broken crosslinks deduced from set and swelling measurements of two natural rubber gum vulcanisates (E and D).

TABLE 4. NATURAL RUBBER GUM
(COMPOUND D), INITIAL STRAIN 550%

Time under load (s)	Time unloaded (s)	Cyclic creep rate (% per decade)
30	15	12.3
5	5	13.4
5	20	12.2
15	15	12.4
20	5	12.5

The varying quantities of crystallisation present in the three crystallising rubbers discussed, natural rubber and polychloroprene types *W* and *WRT*, appear to influence the degree by which the cyclic creep rate behaviour is enhanced over that of the static creep rates. The greater degree of strain-induced crystallisation present in the rubber, the greater becomes the cyclic creep rate. The much smaller cyclic creep shown by the normally non-crystallising SBR, EPDM and isomerised natural rubber suggests that the absence of significant strain-induced crystallisation produces cyclic creep rates of a magnitude similar to those of the static creep condition. The SBR and EPDM rubbers still, however, show cyclic creep rates somewhat greater than in the static condition. This may indicate that there is something akin to crystallisation taking place even in these rubbers to a limited extent. Some evidence of this has been found in stretched SBR using X-ray technique⁵. The cut growth behaviour of SBR can also show a dependence with the number of cycles of deformation rather than the time under load⁶, somewhat like a strain crystallising rubber but much less pronounced. This behaviour also further suggests that there may be a modest amount of crystallisation or crystal-like development taking place during the stressing of SBR.

The results of the swelling and set measurements indicate that part of the cyclic creep phenomenon, due to repeated stressing, can be ascribed to the breakage of crosslinks or equivalent primary bonds. It can be seen from *Figure 9* that the percentage creep is numerically

greater than the percentage of broken crosslinks, in fact it is about double. If broken crosslinks were the only mechanism causing cyclic creep, it could be expected that the percentage broken crosslinks, and the percentage creep would be approximately equal. The values obtained in *Figure 9* suggest that about half of the creep can be explained in terms of bond scission. The set measurements also confirm this conclusion where of the set at the end of a period of cycling, about half can be recovered by swelling and deswelling. The cyclic creep behaviour, therefore, appears to have two components. One is a non-recoverable creep which is responsible for a little over half the total creep and crosslink breakage is probably the main contributor. The second creep component is recoverable creep, this is probably associated with the normal rearrangement of the rubber network associated with the slippage of chain entanglements *etc.*, during stressing.

Although the results suggest that the mechanism causing the cyclic creep behaviour involves crystallisation, the exact mechanism is not known. A possible explanation of this cyclic creep mechanism is that rubber chains held around the perimeter of the crystallite sites are severely strained when a load is applied, and some failure may occur. Then as further regions of the rubber become crystalline and the crystallites melt and reform in different positions, due to the repeated loading process, further failure occurs around the new crystallite sites leading to the progressive creep behaviour taking place during each loading cycle.

The results indicate that for a gum rubber that does not significantly strain crystallise during deformation, which for a natural rubber under a tensile deformation is normally at strains less than approximately 200%, the cyclic creep rate will be smaller than the static rate and the creep is almost entirely visco-elastic and thus recoverable in time. At strains greater than about 200%, the non-recoverable creep component, caused by bond breakage, becomes increasingly important. In the gum natural rubber vulcanisate (*Compound E*), for example, approximately half of the total set is non-recoverable at a strain of 600%.

The inclusion of carbon black filler in a rubber has the effect of increasing the cyclic creep rate compared with the gum material when the rubber phase of the vulcanisate is cycled at a similar strain. Thus, the rubber-filler or the filler-filler interaction plays an important role in determining creep rates during repeated deformations. The repeatedly loaded carbon black filled non-crystallising rubbers (*Compounds F and G*) show approximately 50% increase in creep, due to cycling, even at modest strains. This observation suggests that some bond breakage is occurring possibly due to local stress concentrations caused by the introduction of filler. The still larger increase in creep, due to cycling, shown by the filled strain crystallising rubbers suggests that further enhancement of stress concentrations are occurring. This may be because of strain-induced crystallisation developing at relatively modest bulk strains, due to the stress concentration effect of filler, thus causing bond breakage by the mechanism already described.

Although the majority of the cyclic creep work described here has been confined to tensile deformation, the stress relaxation study in compression does indicate that the enhanced cyclic creep can still be present in the compression mode although to a lesser extent. The effect will almost certainly be present in shear deformation, probably to an extent somewhere between that of the tension and compression modes of deformation. Since many engineering components are subjected to cyclic loadings it is clearly important to be able to predict the creep that will occur under these conditions. The large amounts of creep occurring in some of the tension results reported here, will not normally be found in the majority of practical applications of rubber components because stress/strain levels are normally very much lower than those used here, and tensile deformations are normally avoided by design. In bridge bearings, for example, tensile strains occurring during shearing of a bearing, do not normally exceed 50% and often are considerably smaller. Thus the practical range of strains is generally small and the reported creep phenomena would not normally be a practical problem. However, the work indicates the increase in creep that can

occur if rubbers are used beyond normal operating stress and strain levels.

The presence of strain-induced crystallisation in a rubber, although producing increased cyclic creep rates at high strains, imparts other beneficial properties. In particular, these include excellent strength and cut growth characteristics. As is often the case, a good balance of properties is of more value to the engineer than outstanding performance in one particular aspect.

The phenomenon of the enhanced cyclic creep, and subsequent failure, in repeatedly loaded crystallising rubbers may occur in practice, however, in certain specific applications. An example of one important application may be in motor vehicle tyres, where the rubber can be locally repeatedly deformed to considerable strains upon contact with road asperities during each rotation of the wheel. The crosslink breakage and subsequent cyclic creep and failure which may take place under this repeated loading condition could partly account for the wear characteristics of crystallising rubbers not being correspondingly related to their strength properties.

CONCLUSIONS

The repeated loading of rubber samples can produce an increase in creep when compared to the creep occurring under a static load. The presence of strain-induced crystallisation is thought to produce stress concentrations in the rubber leading to breaking of crosslinks during repeated loading. While the general phenomenon of enhanced creep due to repeated loading has been known for sometime, the present investigation has led to new results suggesting that at high strains crosslink breakage is responsible for approximately half of the total creep with visco-elastic effects accounting for the remainder.

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Steam Sterilisation Resistance of Latex Films

NG KOK POON*

The steam sterilisation resistance of natural rubber latex films cured by conventional high sulphur and a sulphur-donor, dithiodimorpholine is examined. Changes in physical properties such as tensile strength, modulus and elongation at break and chemical crosslink density of the vulcanisates after steam treatment are monitored. The effect of addition of antioxidants on steam sterilisation is also investigated. A comparison is made between pre- and post-vulcanised films. The superiority of the sulphur-donor cure system is demonstrated.

Natural rubber latex which gives vulcanisates of high strength and extensibility, is widely used in the production of various medical items¹ such as surgical gloves, catheters, medical tubing, etc. Disposable medical items are normally packed and then sterilised. The pack keeps the product sterilised inside it until the product is withdrawn for use. Sterility has to be achieved to the level of less than one bacterium surviving among one million bacteria after the sterilisation process. The sterilisation can be performed in a steam autoclave at elevated temperatures, usually at 121°C or 132°C; or by gamma or electron-beam radiation, the minimum dose is 2.5 Megrads. Another method widely applied for polymer products is by bathing the product in ethylene-oxide gas.

In the case of sterilisable surgical gloves, latex formulation giving high temperature ageing resistance necessary to protect the items during sterilisation, is an additional requirement. An efficient vulcanisation (EV) system, giving mainly thermally stable monosulphidic and disulphidic crosslinks and much less main chain modification, of low sulphur/thiuram cure system can be employed².

This paper examines closely the steam sterilisation resistance of latex films cured by conventional high sulphur and a sulphur-donor cure system based on dithiodimorpholine (DTDM). The latter cure system has been claimed to be superior in steam sterilisation resistance^{3,4}. The advantages of DTDM are:

- It gives a high degree of crosslink, with disulphidic and carbon-carbon bonds which are stable to thermo-oxidation.
- It is regarded to be a low toxicity material, giving less biological activity than thiuram system and therefore it can be employed in the production of medical goods.

EXPERIMENTAL

A commercial grade of natural rubber latex concentrate of high-ammonia (HA) type was used throughout the study. Compounding ingredients added to the latex were either in the form of solutions, emulsions or dispersions. The chemical dispersions were prepared by ball-milling for at least 48 h before use.

The formulations employed are shown in *Table 1*.

Preparation of Prevulcanised Latex

The formulations used were *A* and *B* as shown in *Table 1*, except that for *Formulation B*, thiourea at 1.0 p.h.r. was added as an additional cure activator⁵.

The latex compounds were prevulcanised at 70°C for 150 min with constant stirring. After the prevulcanisation, the latex compounds were cooled down immediately and subsequently clarified before use. Clarification was done by passing the latex through a clarifier bowl of a Westfalia LWA 205-1 laboratory centrifuge machine.

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TABLE 1. COMPOUND FORMULATIONS

Compound	Formulation	
	A	B
NR latex	100	100
Potassium hydroxide	0.4	0.4
Potassium laurate	0.2	0.2
Zinc oxide	0.5	0.5
Zinc diethyldithiocarbamate (ZDC)	0.75	1.0
Zinc mercaptobenzothiazole (ZMBT)	—	1.0
Sulphur	1.4	—
Dithiodimorpholine (DTDM) ^a	—	3.0
Antioxidant 2246	1.0	1.0

All figures are expressed in dry weights.

^aSulphasan R (Monsanto)

Film Preparation and Testing

Latex films were prepared by casting the latex compounds at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ on levelled glass plates to a thickness of about 1 mm. After drying, the films were removed, talced and subsequently cured in an air-circulating oven at a temperature of 100°C or 120°C . The films were leached in cold water for at least 16 h and were air-dried at $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$ till clear, usually requiring at least another 72 h.

The stress-strain properties of the films were determined according to *BS 903 Part (A2) (1971)*, and relaxed modulus (MR100) at 100% elongation by a MOD tester. Chemical cross-link measurements were carried out using the method described earlier⁶.

Sterilisation Procedure

Steam sterilisation was performed in a commercial high pressure steam steriliser, Natal Autoclave 330, Mark III model. The temperature of sterilisation was set at either 121°C or 132°C . A 30-min cycle with a 1-h interval between sterilisation was selected for the study.

RESULTS AND DISCUSSION

Vulcanisation Kinetics of Latex Films

The vulcanisation kinetics of latex films cured by sulphur and sulphur-donor (DTDM)

systems is shown in *Figure 1*. Two different temperatures were used for the different cure systems, in view of the rather slow cure rate of sulphur-donor system at 100°C . Optimum cure time to 100% (t_{100}) was determined for each of the cure systems. These are summarised below:

Cure system	Temperature ($^{\circ}\text{C}$)	t_{100} (min)
A (S/ZDC)	100	30
B (DTDM/ZDC/ ZMBT)	120	25

All the latex films used in the study were subsequently cured with the optimal conditions determined above.

Changes in Physical Properties of Latex Films on Steam Sterilisation

When latex films were subjected to steam sterilisation at 121°C and 132°C , it was observed that generally there was a reduction in tensile strength and modulus, with an increase in elongation at break. However, the extent of change was less at 121°C . *Figure 2* shows changes in tensile strength, modulus at 300% elongation (M300) and elongation at break with steam treatment for conventional high sulphur cure system (*Formulation A*), while *Figure 3* shows similar changes for the sulphur-donor cure system based on DTDM (*Formulation B*).

The sulphur-donor system was observed to give higher modulus than the conventional high sulphur cure system. The superiority of the sulphur-donor cure system could be seen, particularly at a higher temperature of steam sterilisation of 132°C . *Table 2* summarises the percentage retention of tensile strength (TS), M300 and elongation at break (EB) for both the cure systems, after five and ten cycles of steam treatment at 132°C .

The sulphur-donor cure system (*B*) retained about 80% of its original tensile strength after ten cycles of steam treatment at 132°C , while the conventional high sulphur cure system retained only about 50% of its original tensile strength.

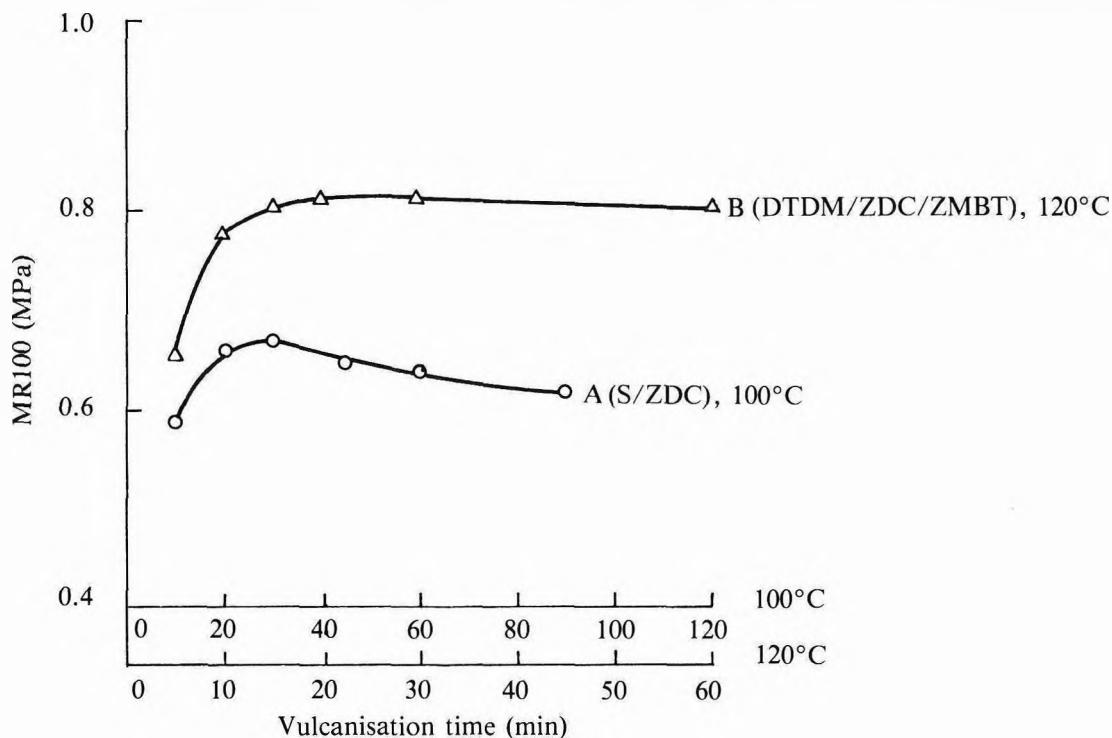


Figure 1. Vulcanisation kinetics of latex films of conventional high sulphur (S/ZDC) and sulphur-donor (DTDM/ZDC/ZMBT) cure systems.

Effect of the Presence of Antioxidants on Steam Sterilisation Resistance of Latex Films

Several commercial non-staining antioxidants, at 1 p.h.r., were evaluated for their effectiveness in protecting the latex films against steam sterilisation. Figures 4 and 5 show changes in tensile strength, M300 and elongation at break for the conventional high sulphur cure system and the sulphur-donor system, respectively.

The presence of an antioxidant did not, in general, bring about improvement in steam sterilisation resistance of the latex films. This could be probably due to the fact that the ageing under the condition of pressurised steam was closer to anaerobic ageing, due to the limited availability of free oxygen. The extent of degradation would therefore be determined by the type of cure system. Protection offered by the antioxidants would be minimal as such. Furthermore, it has been established previously⁷

that, under an anaerobic ageing condition, the peroxide and EV cure systems offer the best protection. The superiority of the sulphur-donor cure system of the latex films and the independence of antioxidant would suggest that ageing under pressurised steam was of the anaerobic type.

Steam Sterilisation Behaviour of Pre-vulcanised and Post-vulcanised Latex Films

With the frequent use of pre-vulcanised (PV) latex in the production of latex dipped goods, it is therefore useful to examine its steam sterilisation characteristics and compare its performance with a post-vulcanised (POST V) latex compound.

The MR100 values for these two types of latex films were determined and these are shown in Table 3.

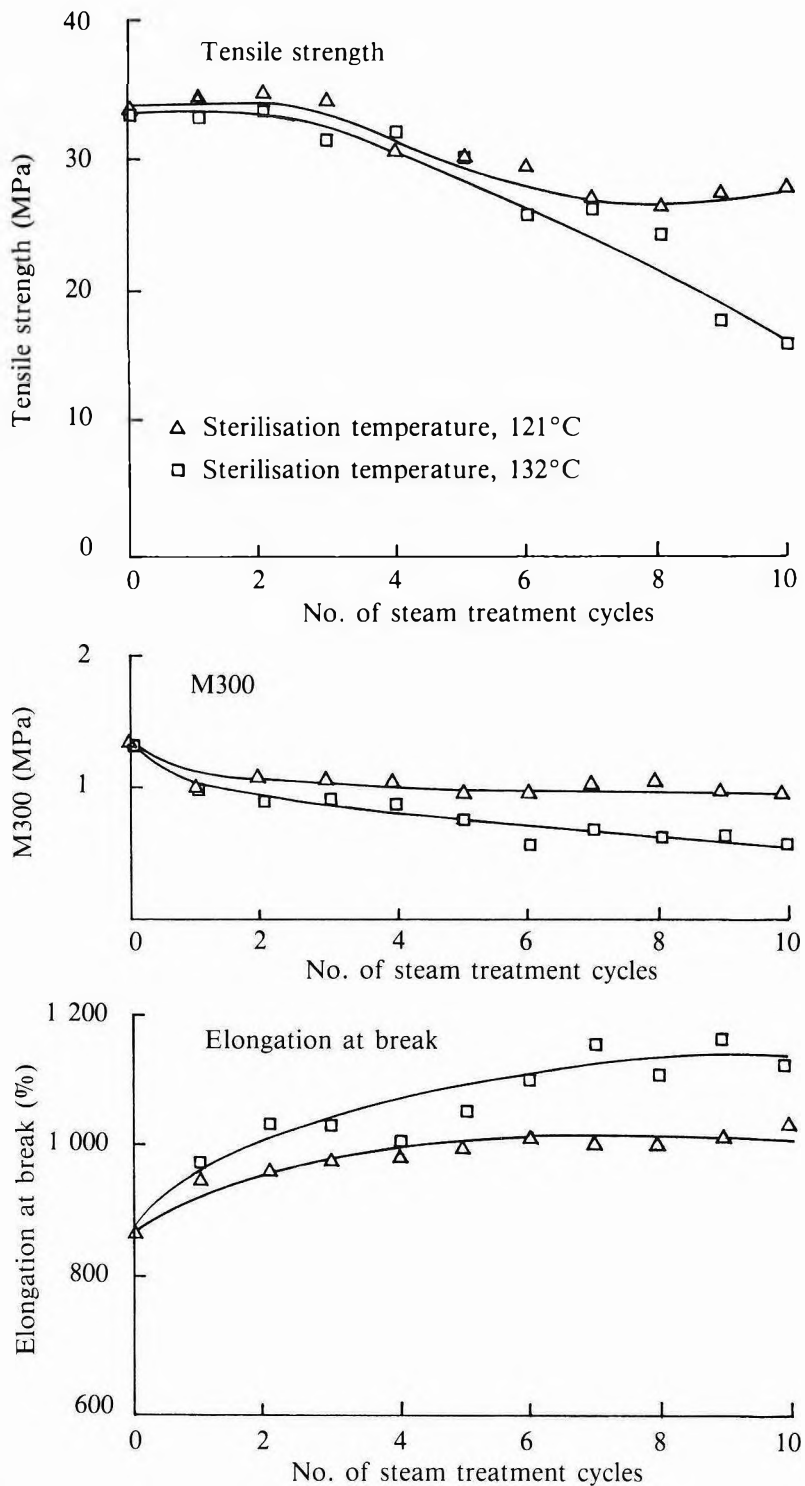


Figure 2. Effect of steam sterilisation on tensile strength, M300 and elongation at break for Cure System A.

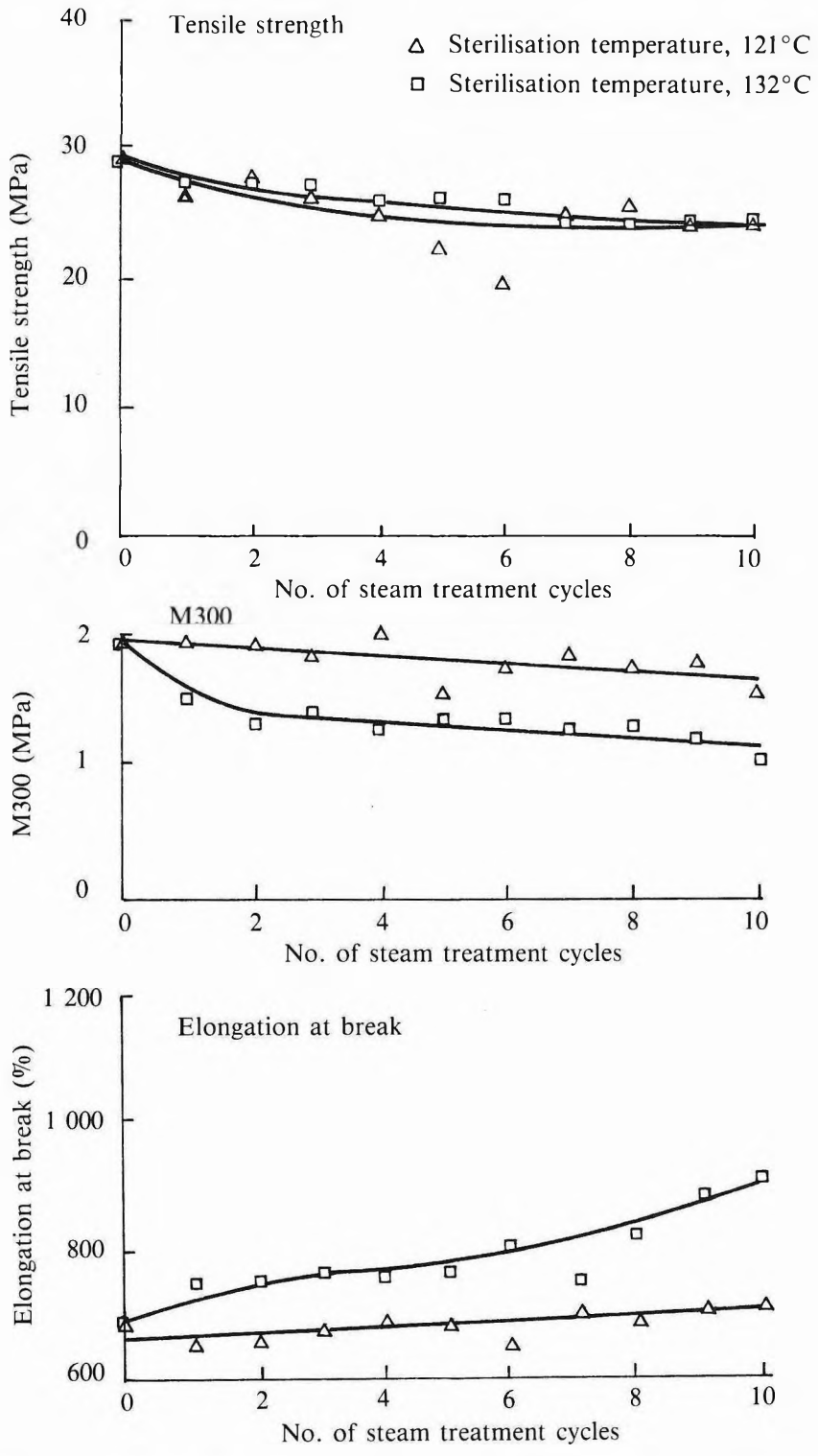


Figure 3. Effect of steam sterilisation on tensile strength, M300 and elongation at break for Cure System B.

TABLE 2. RETENTION IN PHYSICAL PROPERTIES AFTER STEAM TREATMENT

Steam treatment (cycles)	Retention in physical property (%)					
	Cure System A			Cure System B		
	TS	M300	EB	TS	M300	EB
5	91	58	122	87	68	110
10	50	44	130	81	52	130

TABLE 3. RELAXED MODULUS (MR100) OF PREVULCANISED AND POST-VULCANISED LATEX FILMS

Cure System	MR100 (MPa)
A, PV	0.74
B, PV	0.82
A, POST V	0.66
B, POST V	0.86

Higher values of MR100 were obtained for the sulphur-donor cure system for both the prevulcanised and post-vulcanised latex films, indicating the higher state of cure achieved.

The changes as a result of steam treatment in tensile strength, M300 and elongation at break are shown in *Figures 6, 7 and 8* respectively for post-vulcanised and prevulcanised latex films at 121°C and 132°C. Overall, little difference was observed between prevulcanised and post-vulcanised latex films. Reduction in tensile strength, M300 and increase in elongation at break after steam treatment were observed for both types of latex films.

Changes in Chemical Crosslink Density

The changes in physical properties as a result of steam sterilisation of latex films were expected to relate to changes in the chemical crosslink density of the vulcanisates. *Table 4* shows changes in the chemical crosslink density for the prevulcanised and post-vulcanised latex films subjected to various steam treatment.

Higher values of retention of chemical crosslink density were generally obtained for the sulphur-donor cure system, indicating the inherent stability of the crosslinks. After ten

cycles at 132°C, about 45% of crosslink density was still retained in the case of sulphur-donor system, compared to only about 13% for the conventional high sulphur cure system.

CONCLUSION

A sulphur-donor cure system based on DTDM has been confirmed to be superior in terms of steam sterilisation resistance to a conventional high sulphur cure system. A reduction in tensile strength, modulus and an increase in elongation at break have been observed, the severity of which depends on the extent and the temperature of sterilisation. There is no difference in steam sterilisation resistance behaviour between prevulcanised and post-vulcanised latex films. The presence of an antioxidant in the latex films does not give protection against steam sterilisation. This is probably due to the anaerobic nature of ageing with the limited supply of free oxygen in the autoclave.

The superiority of the sulphur-donor cure system could be explained by the higher crosslink density and the greater stability of the crosslinks when subjected to steam treatment, typical of an EV cure system.

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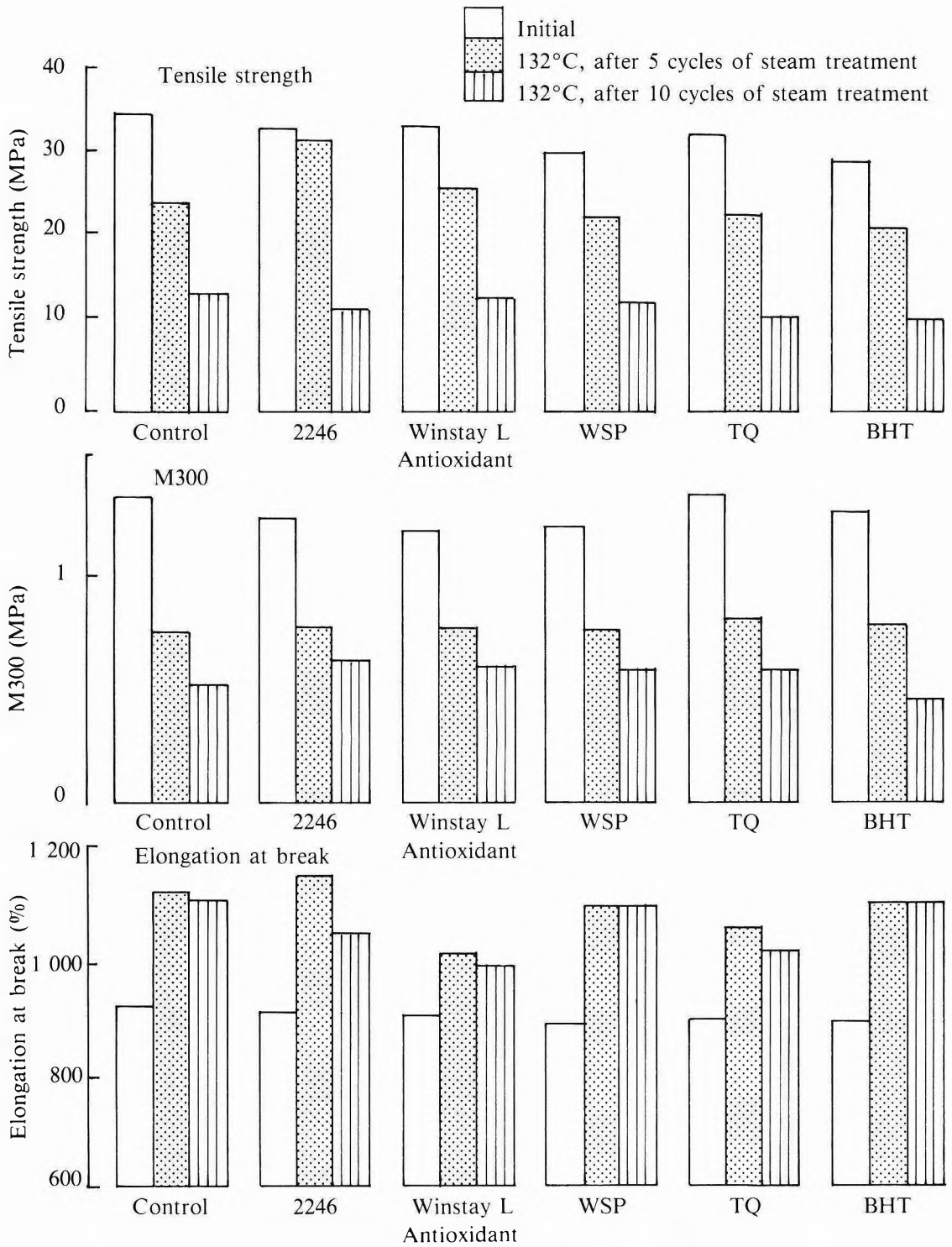


Figure 4. Variation of tensile strength, M300 and elongation at break with antioxidant type after steam treatment for Cure System A.

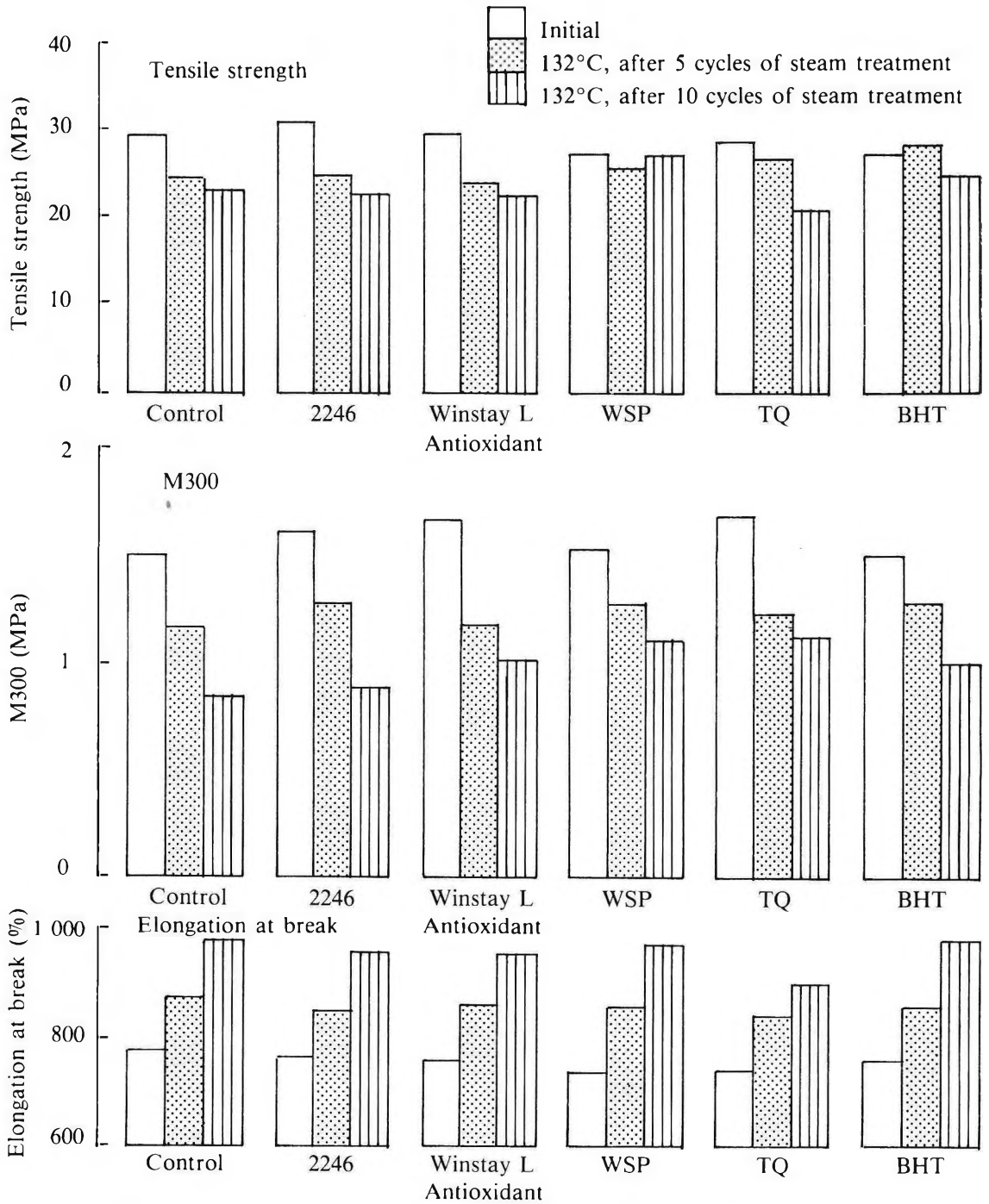


Figure 5. Variation of tensile strength, M300 and elongation at break with antioxidant type after steam treatment for Cure System B.

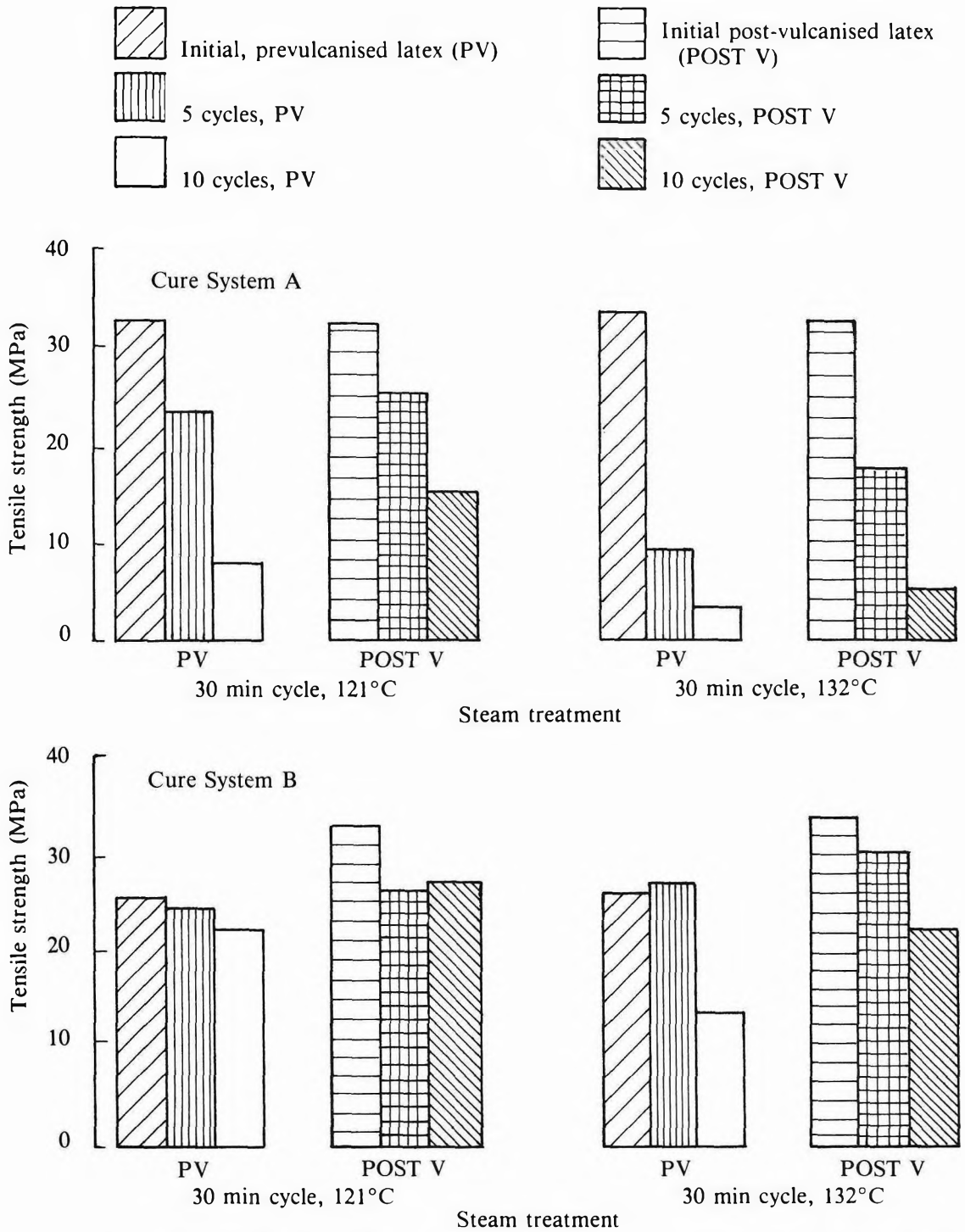


Figure 6. Tensile strength of pre-vulcanised and post-vulcanised latex films after steam treatment for Cure System A and Cure System B.

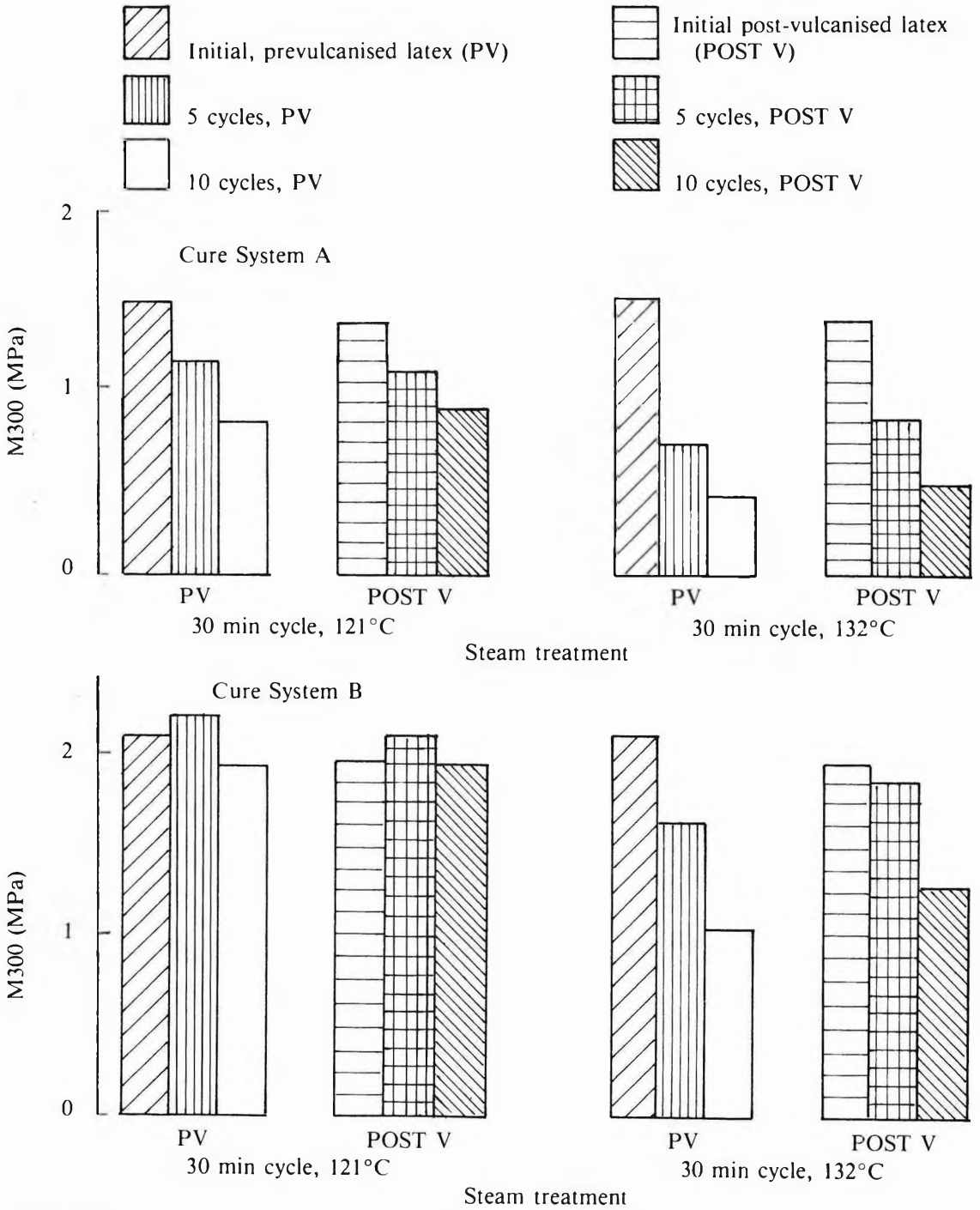


Figure 7. M300 of pre-vulcanised and post-vulcanised latex films after steam treatment for Cure System A and Cure System B.

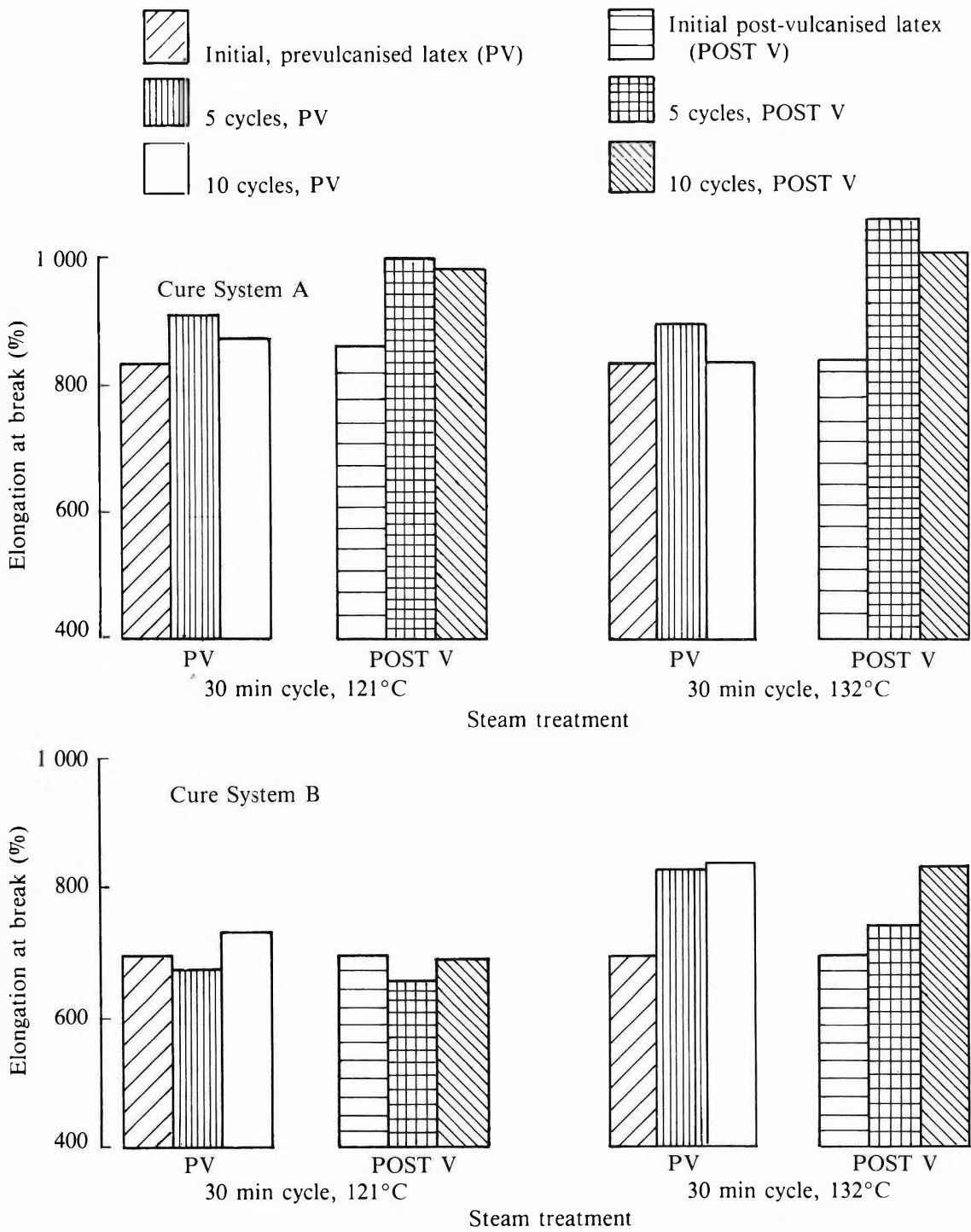


Figure 8. Elongation at break of prevulcanised and post-vulcanised latex films after steam treatment for Cure System A and Cure System B.

TABLE 4. CHANGES IN CHEMICAL CROSSLINK DENSITY OF LATEX FILMS

Steam treatment	Chemical crosslink density $\times 10^5$ (g mole/g rubber hydrocarbon)			
	A		B	
	PV	POST V	PV	POST V
Initial	3.26	3.41	5.61	4.69
121°C				
After 5 cycles	2.03 (62)	2.16 (63)	6.25 (111)	4.44 (95)
After 10 cycles	1.45 (45)	1.51 (44)	4.69 (84)	3.95 (84)
132°C				
After 5 cycles	0.65 (20)	0.99 (31)	3.91 (70)	3.34 (71)
After 10 cycles	0.40 (12)	0.47 (14)	2.40 (43)	2.18 (47)

Figures within brackets denote percentage retention in chemical crosslink density.

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Easy Processing Epoxidised Natural Rubber

ABU BIN AMU* AND SIDEK BIN DULNGALI*

The latest production technique in the preparation of epoxidised natural rubber (ENR) has resulted in a promising new form of ENR which can be easily processed in large internal mixers. The new samples of ENR (ENR 25 and ENR 50, i.e. ENR containing 25 and 50 mole per cent of epoxidation, respectively) are characterised by their significantly low gel contents and high basic nature. The commercial production of this new form of ENR by Kumpulan Guthrie Sendirian Berhad (KGSB) is anticipated in 1989.

The mill-sticking problem which was encountered when mixing ENR on small laboratory mills at high temperatures can now be avoided. The method of solving the problem involves a partial sulphur crosslinking that enhances the cohesive strength of the ENR. This improvement in the cohesive strength of ENR coupled with the incorporation of additional level of stearic acid prevents the rubber from sticking to the two-roll mill. It is to be noted that the results obtained from this study were based on small laboratory mills where high shear is created during the milling process. The results obtained may not be related to commercial operations where the magnitude of the shearing force is different from that based on small-scale operations.

Controlled epoxidation of natural rubber (NR) has been known to give a chemically modified rubber, called ENR, with improved resistance to hydrocarbon oils, lower air permeability, increased damping and good bonding properties¹⁻⁹. The changes in physical properties from the original NR have brought about some of the unique and useful features for consideration in rubber product applications which would not otherwise be possible with NR. The high damping and good wet-grip characteristics of the rubber have been found to be useful in non-slip shoe soles, floor mats and sportballs, while the good bonding property of the rubber has been shown to give potentially useful applications in sealants and adhesives^{8,9,10}. The low rolling resistance and good wet-grip of the rubber have been proven in tyre trials involving passenger car treads^{6,7}.

Earlier promotion of ENR³ to consumers has been hampered by problems of high Mooney viscosity (ML1 + 4 at 100°C of about 120) and high gel contents coupled with the

slightly acidic nature of the rubber (pH of aqueous extract 6.0-6.5). These preliminary samples had been shown by consumers to give mixing problems, particularly when large internal mixers are used. Longer mixing time, higher mixing energy and poor dispersion of fillers in the rubber were the main problems associated with the earlier version of ENR.

These mixing problems have necessitated an alternative technique to produce easy processing ENR. Presently, a new production technique has been found to give ENR with low Mooney viscosity and substantially reduced gel contents as well as of a highly basic nature (pH of aqueous extract of about 10).

The production process of ENR employing this new technique has been licensed to KGSB, and ENR produced by KGSB will be of two grades only, namely ENR 25 and ENR 50. The commercial production of ENR is anticipated in 1989.

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EXPERIMENTAL

Materials

ENR was prepared at the Rubber Research Institute of Malaysia (RRIM) pilot plant using the technique for easy processing ENR. The compounding ingredients used were of the recommended grades for rubber.

Procedure

Mastication of ENR 25 and ENR 50 was carried out on a 152 × 30 cm two-roll mill with a starting temperature of about 30°C. The batch size of the milling process was based on 12 kg of the raw rubber. During the mastication process, samples were taken at various time intervals for determination of the raw rubber Mooney viscosity in accordance with the *ASTM D1646* procedure.

In the case of mastication of ENR 25 and ENR 50 in an internal mixer, a Francis Shaw K2A mixer of capacity 27 litres was used. The conditions of mastication were as follows:

Starting temperature = 80°C and then water cooling

Rotor speed = 40 r.p.m.

Ram pressure = 0.69 MPa

Samples were dumped at various time intervals and refined on a 152 × 30 cm two-roll mill for 1 min.

Similar conditions as above were used for mixing ENR 25 and ENR 50 with carbon black and other ingredients based on formulations shown in *Table 1 (Formulations 1 and 2)*, but the schedule of mixing was as follows:

0 min — ENR 25 or ENR 50, zinc oxide, stearic acid and Santoflex 13

0.5 min — ½ Carbon black and oil

1.5 min — ½ Carbon black

3.5 min — Sweep down feeding chute

4.0 min — Dump

Refining of the above masterbatches were carried out on a 152 × 30 cm two-roll mill for 1 min.

TABLE 1. FORMULATIONS USED IN THIS STUDY

Ingredient	Formulation (parts by weight)		
	1	2	3
ENR 25	100	—	—
ENR 50	—	100	100
ISAF carbon black (N-220)	50	50	50
Dutrex 737 MB ^a	5	5	5
Zinc oxide	5	5	5
Santoflex 13 ^b	2	2	—
Permanax TQ ^c	—	—	1
Stearic acid	2	2	Variable
Sulphur	—	—	Variable

^aDutrex 737 MB — Aromatic processing oil

^bSantoflex 13 — N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

^cPermanax TQ — Poly-(2,2,4-trimethyl-1,2-dihydroquinoline)

Samples of ENR 25 and ENR 50 masterbatches prepared from a K2A internal mixer were mill-mixed carefully and cured to optimum at 150°C using a semi-efficient vulcanisation system (sulphur 1.5 p.h.r., MOR 1.5 p.h.r. and PVI 0.2 p.h.r.). It is to be noted here that excessive milling of the compounds at high temperatures can result in mill-sticking. The physical properties of these cured samples were determined according to the testing procedures normally used at the RRIM, *i.e.*

Tensile properties to *ISO 37*

Hardness to *ISO 48 (ASTM D1415)*

Compression set to *ISO 815* using small test pieces

Tear strength, trouser, to *ISO 34*

Rebound resilience, Dunlop tripsonometer, to *BS 903: Part A8*.

The study on the mill-sticking behaviour of raw ENR 50 was carried out on a 30 × 15 cm two-roll mill using a frictional ratio of 1:1.25. The mill temperature was varied by means of cooling water and steam regulation and the

temperature was determined by using a surface pyrometer.

ENR 50 masterbatches with variable concentrations of sulphur and stearic acid as shown by *Formulation 3* in *Table 1* were mixed on the two-roll mill running at low temperature and cured for 5 min at temperatures ranging from 150°C–180°C. Their respective Mooney viscosities were determined.

In the preparation of ENR 50 masterbatches in a 2-litre OOC Banbury for visual observation of the subsequent milling process, the following mixing cycle was employed.

- Starting rotor temperature — 100°C
- Rotor speed — 80 r.p.m.
- 0 min — ENR 50, zinc oxide, stearic acid, Permanax TQ and sulphur
- 0.5 min — ½ Carbon black and oil
- 1.5 min — ½ Carbon black
- 4.5 min — Sweep down feeding chute
- 5.0 min — Dump

The dump temperature was varied by means of steam regulation. Refining of the masterbatches was carried out on a 50 × 20 cm two-roll mill for 1 min before the visual observation of mill-sticking. The screening test of the respective ENR 50 masterbatches for observation of mill-sticking tendency was carried out by masticating the masterbatches on a 30 × 15 cm two-roll mill with an initial roll temperature of 75°C for 15 min. The reduction in Mooney viscosity of the masterbatches during the process of mastication was also determined.

RESULTS AND DISCUSSION

Raw Rubber Properties

Typical values of basic raw rubber properties of the two available grades of ENR are summarised in *Table 2*. The new ENR grades are characterised by their significantly lower Mooney viscosity and gel contents and higher pH.

TABLE 2. TYPICAL RAW PROPERTIES OF NEW ENR

Property	ENR 25	ENR 50
Epoxidation level (mole %)	25	50
Glass transition temperature (°C)	-45.3	-22.5
Mooney viscosity (ML1 + 4 at 100°C)	60-80	60-80
Macrogel content (weight %)	14.9	21.5
pH	10	10

Mill-breakdown Behaviour

Mill-breakdown behaviour of raw ENR 25 and ENR 50 was studied by determining the Mooney viscosity of the rubber with respect to the mastication time. Two grades of NR, *i.e.* SMR 5 and SMR CV, were chosen for comparison. As shown in *Figure 1*, there is a drastic reduction of Mooney viscosity of ENR 25 between 0 and 5 min of mastication; beyond this the reduction is gradual and tends to level off on prolonged mastication. With SMR 5 and SMR CV, the viscosity reduction is gradual throughout the mastication.

Figure 2 shows the mill-breakdown behaviour of raw ENR 50 in comparison to SMR 5 and SMR CV. A drastic reduction of Mooney viscosity of ENR 50 occurred between 0 and 10 min of mastication. Comparing the rate of viscosity reduction from 0 to 5 min of mastication, ENR 25 showed a faster rate of reduction compared to ENR 50.

Breakdown Behaviour in Internal Mixer

Breakdown behaviour of raw ENR 25 and ENR 50 in a Francis Shaw K2A internal mixer is shown in *Figures 3* and *4*. Both ENR 25 and ENR 50 of similar initial raw rubber viscosity as SMR CV gave faster rate of viscosity reduction. Considering the breakdown behaviour between 0 and 2 min of mastication, the rate of viscosity reduction of ENR 25 was faster than that of ENR 50.

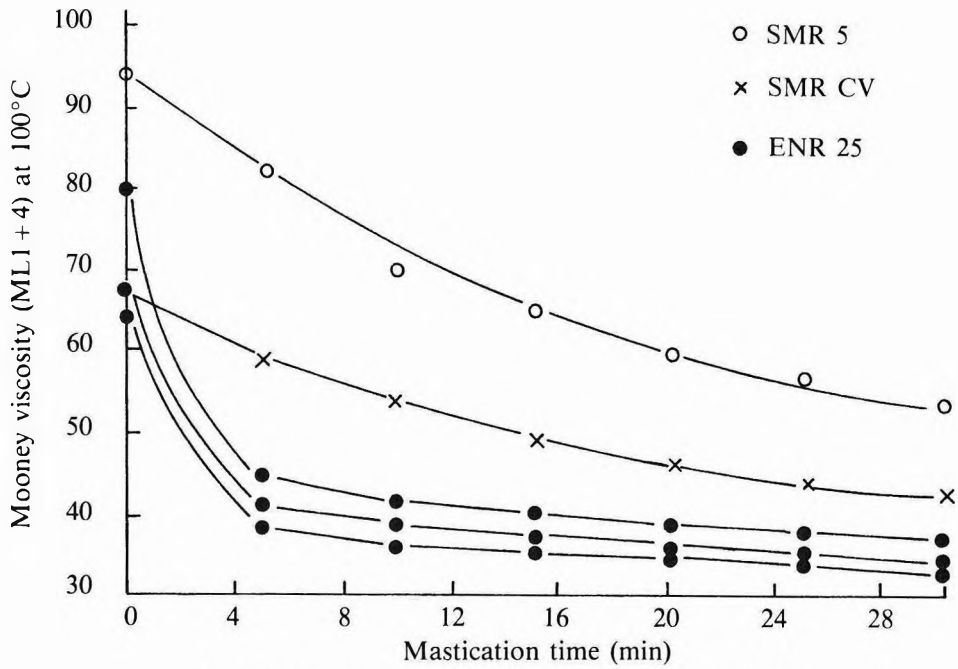


Figure 1. Mill-breakdown behaviour of raw ENR 25.

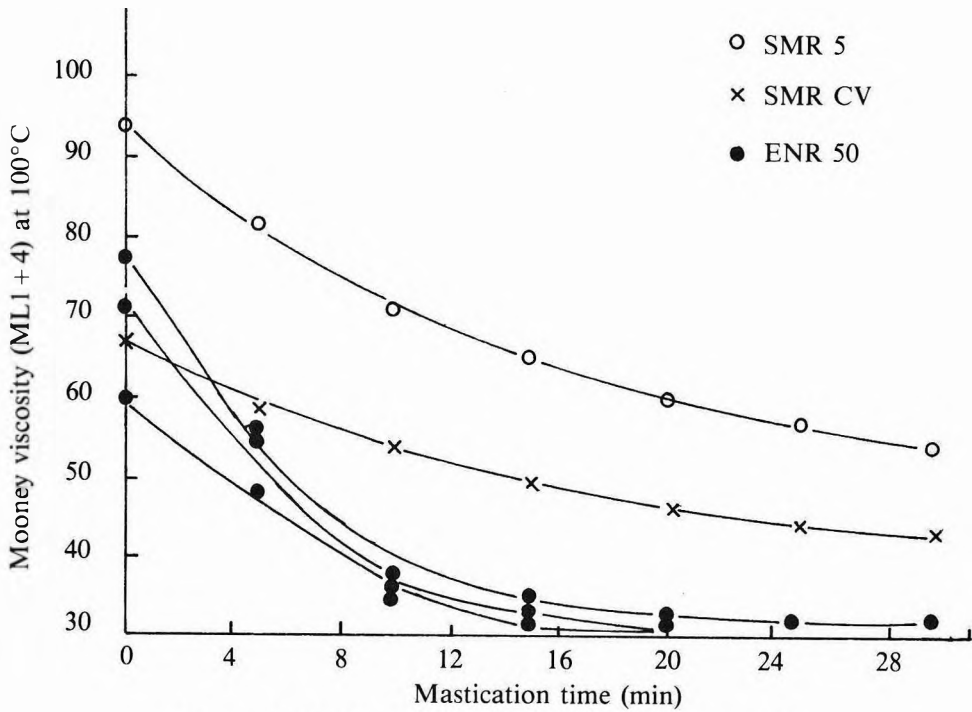


Figure 2. Mill-breakdown behaviour of raw ENR 50.

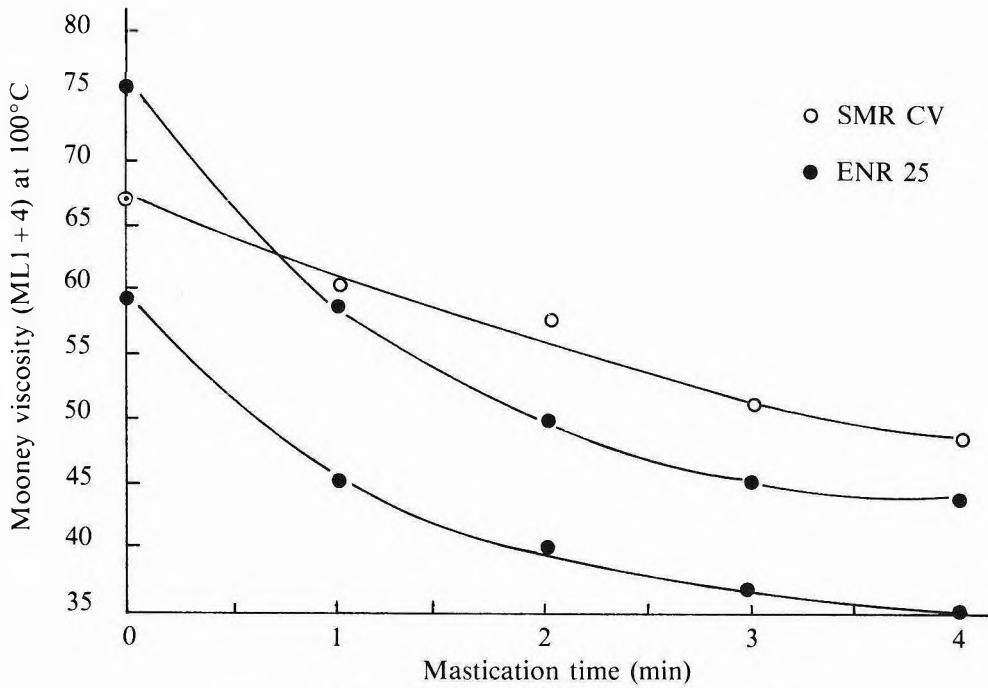


Figure 3. Mastication of raw ENR 25 in K2A mixer.

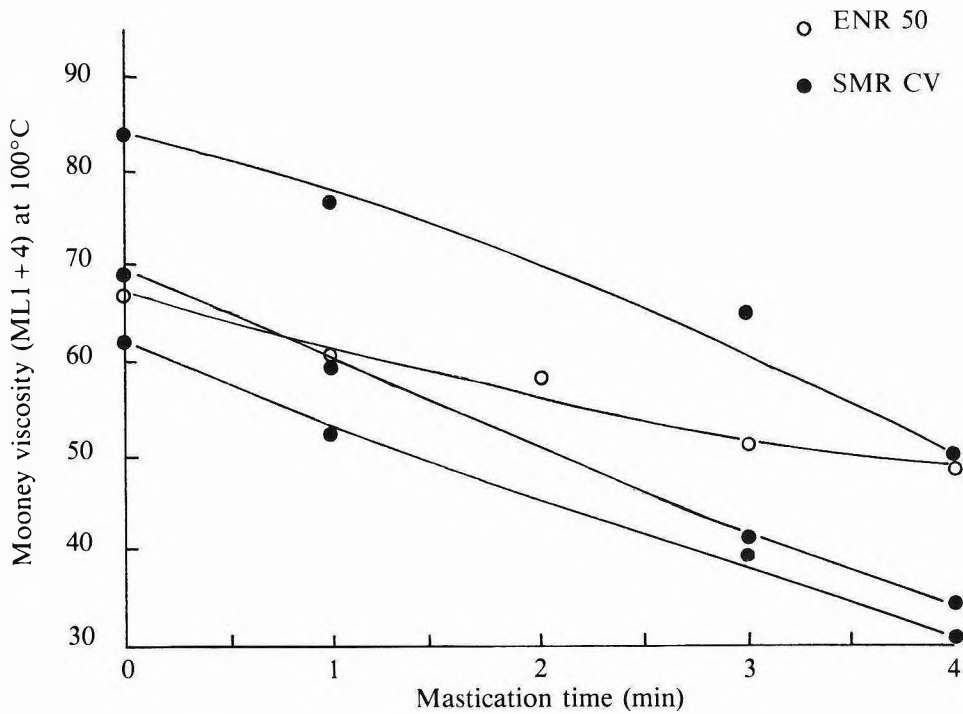


Figure 4. Mastication of raw ENR 50 in K2A mixer.

Mixing Behaviour with ISAF Carbon Black

In the majority of fabrications of rubber products, fillers are normally incorporated into elastomers for improving physical properties or for cost reduction. Thus, it is important that the ENR produced from the modified production technique can be easily mixed with fillers in internal mixers. Earlier samples¹¹ of ENR suffered from processing problems brought about by the high Mooney viscosity, high gel contents and slightly acidic character (pH of aqueous extract 6.0–6.5).

The relative ease of mixing ENR 25 and ENR 50 with filler was studied. In this study, ISAF carbon black was chosen and mixing was carried out in a Francis Shaw K2A mixer. The effect of raw rubber Mooney viscosity of ENR 25 and ENR 50 on the viscosity of the carbon black masterbatch prepared from the internal mixer is shown in *Figures 5* and *6*. The variation in viscosity of ENR 50 masterbatches prepared from samples of raw viscosity (V_R) 60–80 is significantly larger compared to those

of ENR 25. For ENR 25 with V_R 60–80, the batch viscosity (V_B) obtained ranged from 70 to 77, while for ENR 50, the V_B range was from 60 to 90. However, this large variation in viscosity for ENR 50 masterbatches could be minimised by refining on the two-roll mill (*Figure 7*). After 2 min of refining on the 152 × 30 cm two-roll mill, viscosity ranging from 47 to 58 could be obtained. Hence, to minimise batch variations in viscosities, it is advisable to use a longer milling time for ENR 50.

The vulcanisate properties of ENR 25 and ENR 50 mixes prepared from the K2A mixer are shown in *Tables 3* and *4*, respectively. These data suggested that the variation of the raw rubber viscosities of both ENR 25 and ENR 50 from 56 to 85 did not cause any significant variation in the vulcanisate properties.

Mill-sticking Behaviour

There are various factors affecting the mill-sticking behaviour of ENR, particularly

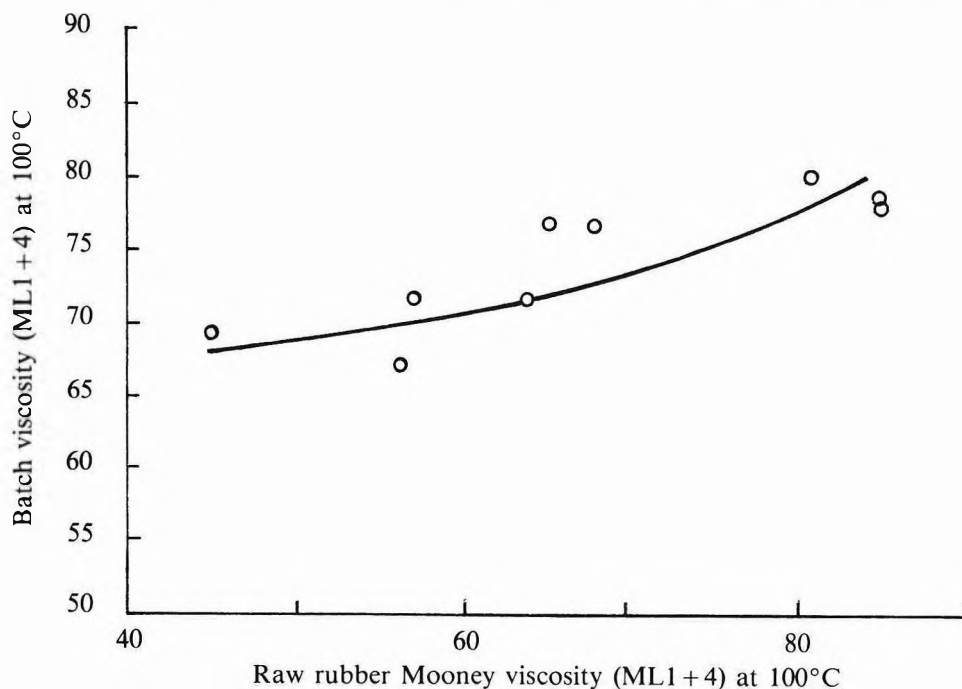


Figure 5. Effect of raw rubber Mooney viscosity on viscosity of ENR 25 batches prepared from K2A mixer. Batches prepared using Formulation 1 of Table 1.

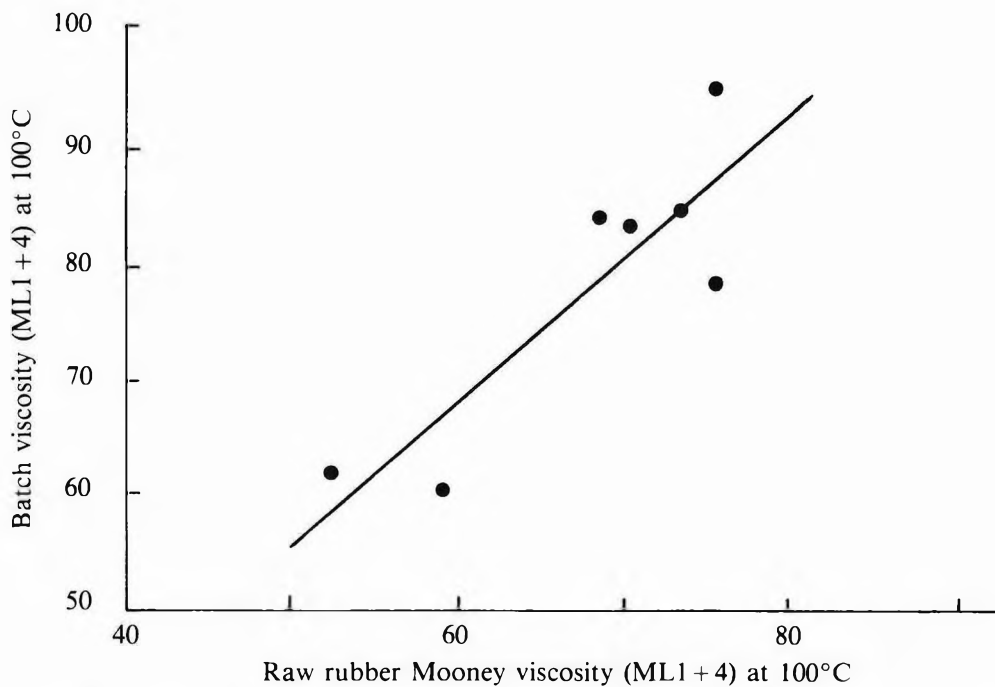


Figure 6. Effect of raw rubber Mooney viscosity on viscosity of ENR 50 batches prepared from K2A mixer. Batches prepared using Formulation 2 of Table 1.

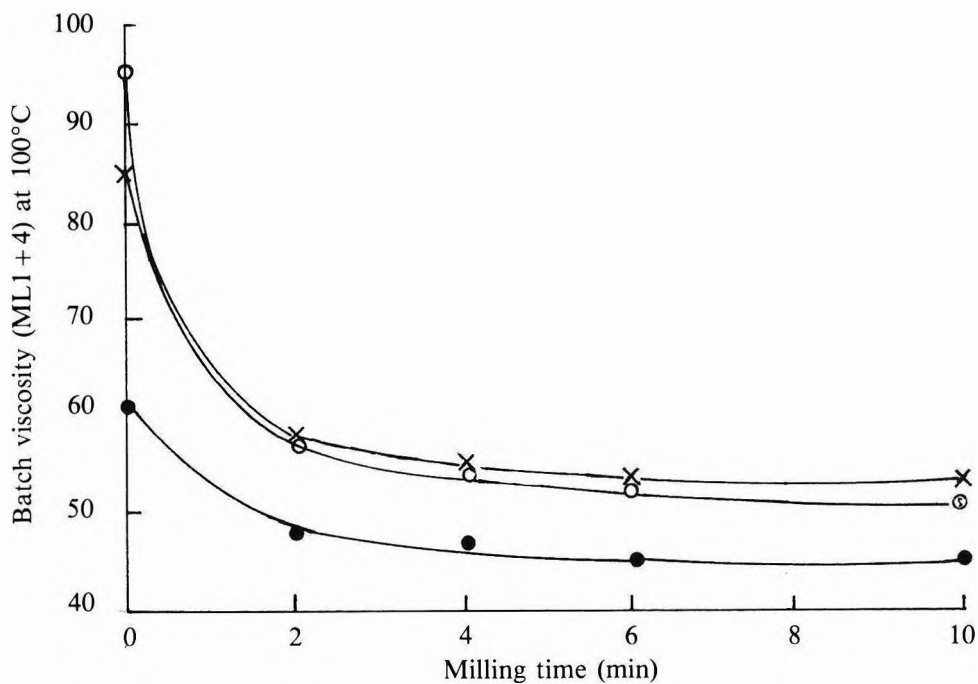


Figure 7. Effect of milling on batch viscosity of ENR 50. Batches prepared using Formulation 2 of Table 1.

TABLE 3. VULCANISATE PROPERTIES OF ENR 25^a

Property	Sample				
	1	2	3	4	5
Raw rubber viscosity MLI + 4 at 100°C	85	85	65	64	56
Power consumption (kwh/kg)	0.20	0.20	0.21	0.21	0.21
Dump temperature (°C)	152	156	159	153	161
Mooney scorch at 120°C (min)	31	35	38	34	31
Tensile strength (MPa)	27.2	27.2	27.2	27.0	27.0
Elongation at break (%)	510	495	505	500	495
M100 (MPa)	3.3	3.2	3.3	3.0	3.0
M300 (MPa)	14.6	14.7	15.2	14.6	15.0
Rebound resilience (%)	46	46	46	47	45
IRHD	71	69	70	70	70
Trouser tear (N/mm)	16	26	23	17	13
Compression set, 1 day/70°C (%)	27	24	25	24	24

^aFormulation used — ENR 25 100, ISAF carbon black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Santoflex 13 2, sulphur 1.5, MOR 1.5, PVI 0.2

TABLE 4. VULCANISATE PROPERTIES OF ENR 50^a

Property	Sample					
	1	2	3	4	5	6
Raw rubber viscosity MLI + 4 at 100°C	76	76	74	71	69	59
Power consumption (kwh/kg)	0.21	0.18	0.21	0.17	0.20	0.20
Dump temperature (°C)	156	149	158	150	160	156
Mooney scorch at 120°C (min)	38	33	30	32	30	31
Tensile strength (MPa)	26.2	23.9	24.6	25.3	25.1	24.6
Elongation at break (%)	485	455	480	490	470	490
M100 (MPa)	3.4	3.5	3.7	3.4	3.4	3.3
M300 (MPa)	15.2	14.9	15.4	14.9	15.2	14.8
Rebound resilience (%)	24	21	22	24	22	23
IRHD	75	78	74	77	75	75
Trouser tear (N/mm)	23	26	25	22	22	24
Compression set, 1 day/70°C (%)	29	31	33	31	32	34

^aFormulation used — ENR 50 100, ISAF carbon black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Santoflex 13 2, sulphur 1.5, MOR 1.5, PVI 0.2

ENR 50. Besides, Mooney viscosity, temperature and cohesive strength within the rubber itself¹², the gel content of the rubber is equally important. The presence of gel in the rubber enhances the cohesive strength of the rubber.

A Mooney viscosity-mill temperature relationship at which the rubber starts to stick on the roll for the new ENR 50 is shown in *Figure 8*. The data shown in this figure differ slightly from the original data¹². The differences in the gel contents could account for such differences. The new ENR 50 as shown in the earlier data (*Figure 2*) gave a fast breakdown characteristic on the two-roll mill and this can result in a mill-sticking tendency if the temperature is not properly controlled.

Figure 8 shows that at any given Mooney viscosity, the mill-sticking tendency of ENR 50 increases with increasing mill temperature. This behaviour may be explained by the fact that by increasing the mill temperature the cohesive strength of the rubber itself decreases while the adhesive strength between the rubber and the

surface of the roll increases. Thus, in avoiding the mill-sticking, the ENR 50 needs to be designed in a manner whereby the cohesive strength is greater than the adhesive strength at the given mill temperature.

One of the recommended methods to reduce the adhesive strength between rubber and metal surfaces during processing is to employ stearic acid. Stearic acid reduces the coefficient of friction between the rubber and the metal surfaces. We have observed that by incorporating stearic acid into the new ENR 50, even up to a level of 8 p.h.r., the mill-sticking of the rubber was not completely avoided. Although the adhesive strength was reduced in this case, the cohesive strength of the new ENR 50 was still insufficient to pull the rubber away from the metal surface.

In searching for an improvement in the cohesive strength of the new ENR 50, we looked into a possibility of introducing sulphur linkages since a reaction between the rubber and sulphur alone can occur rapidly and

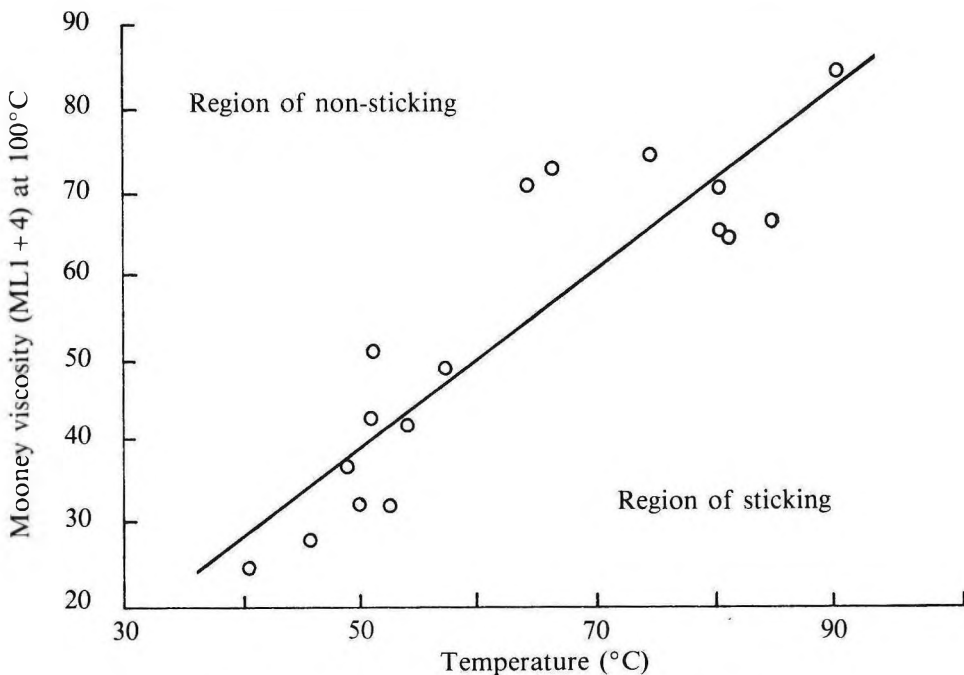


Figure 8. Mill-sticking behaviour of raw ENR 50.

efficiently^{1,10}. The effects of variation in sulphur concentration on cure characteristics and torque values are shown in *Figure 9* and *Table 5*, respectively. These data illustrate the

TABLE 5. INCREASE IN TORQUE VALUES OF ENR 50^a MIXES AFTER 5 MIN AT VARIOUS CURE TEMPERATURES

Concentration of sulphur (p.h.r.)	Cure temperature (°C)			
	150	160	170	180
0	0	0	0	0.1
0.10	0.1	0.4	0.9	1.2
0.15	0	0.5	1.1	1.8
0.20	0.3	0.8	2.0	2.7
0.25	0.3	1.0	2.5	2.8

^aFormulation used — ENR 50 100, ISAF carbon black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Permanax TQ 1, sulphur variable

effectiveness of preparing lightly crosslinked ENR 50 by incorporating a small amount of sulphur in the absence of organic accelerator. Both the sulphur content and temperature were shown to be critical in controlling the gel of the rubber as indicated by the rise in torque values.

In order to incorporate this vulcanisation process in normal processing practices, sulphur needs to be introduced into the rubber during high temperature mixing in the internal mixer. The preformed gel after the internal mixing enhances the cohesive strength of the rubber and consequently prevents sticking during the subsequent milling process. In this way, the reinforcing filler can be easily incorporated and dispersed in the rubber matrix before the formation of gel.

To obtain an indication of the increase in Mooney viscosity that is unlikely to occur after

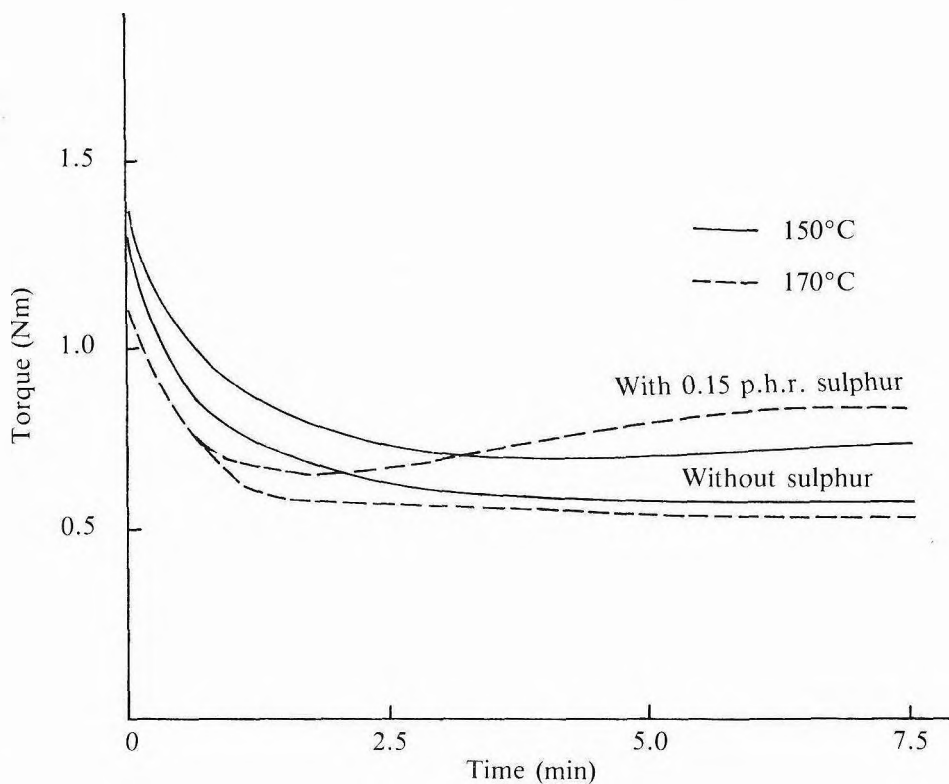


Figure 9. Cure characteristics at different temperatures. Formulation used: ENR 50 100, ISAF black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Permanax TQ 1.

the process of internal mixing, samples with various concentrations of sulphur were cured for 5 min at temperatures ranging from 150°C to 180°C. *Figure 10* shows that increasing the sulphur level at a given temperature increased the Mooney viscosity. It is therefore preferable, when mixing ENR 50 in the internal mixer, to choose the lowest level of sulphur possible in order to prevent excessive increase in Mooney viscosity for easier processing in subsequent operations. A sharp increase in the Mooney viscosity also occurred when increasing the temperature from 150°C to 170°C but at 180°C the Mooney viscosity was not much different from that at 170°C.

The actual increase in Mooney viscosity after mixing ENR 50 in the internal mixer is shown in *Table 6*. In this particular experimental design, the concentrations of sulphur and stearic acid and the dump temperature were varied. Stearic acid was included in the

formulation as a release aid for prevention of mill-sticking and more importantly, to minimise the usage of sulphur. With the lowest concentration of sulphur (*i.e.* 0.1 p.h.r.), the normal level of stearic acid (*i.e.* 2 p.h.r.) was shown to be insufficient to prevent mill-sticking even with a high dump temperature. With a higher level of stearic acid (*i.e.* 3 p.h.r.), the mill-sticking can be avoided. However, the preferred formulation from the data available would be the one based on 0.1 p.h.r. sulphur and 4 p.h.r. stearic acid since a wide range of dump temperature is applicable.

The effect of milling of some selected master-batches prepared at various dump temperatures on the Mooney viscosity is shown in *Figure 11*. Although the initial batch Mooney viscosity differed significantly with dump temperature, the difference was minimised on milling for about 5 min. This fast breakdown of initially high batch Mooney viscosity provides easier

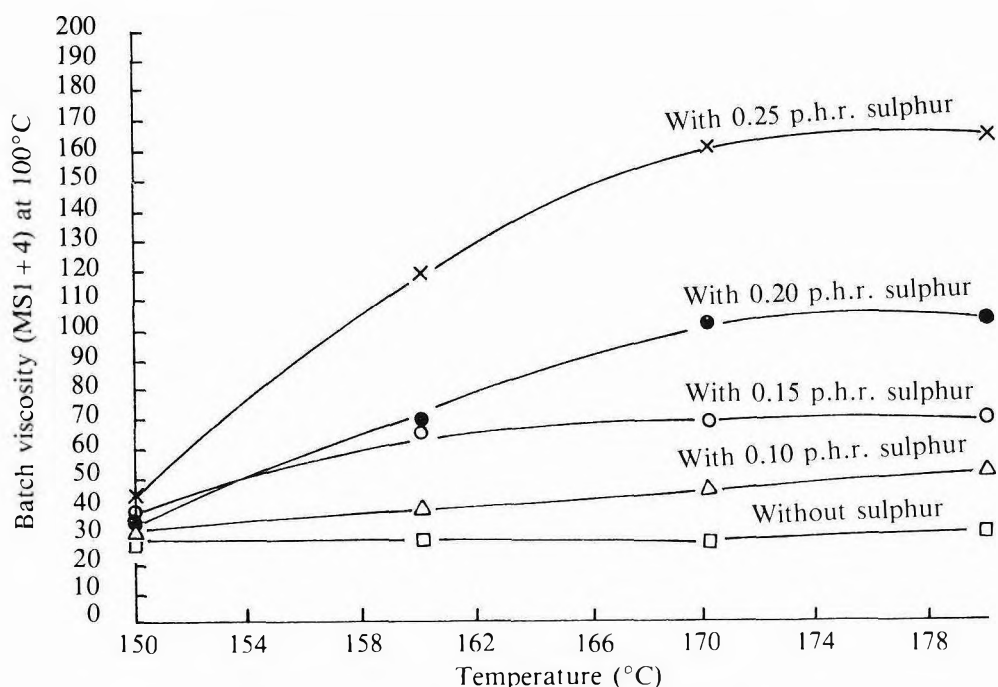


Figure 10. Effect of temperature on batch viscosity (batch viscosity taken after 5 min curing). Formulation used: ENR 50 100, ISAF black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 2, Permanax TQ 1.

TABLE 6. EFFECT OF SULPHUR, STEARIC ACID AND DUMP TEMPERATURE ON MILL STICKING BEHAVIOUR OF ENR 50^a

Sulphur (p.h.r.)	Stearic acid (p.h.r.)	Dump temp. (°C)	Initial batch viscosity ^b	Final batch viscosity ^c	Mill-sticking tendency ^d
0	2	165	35.0	—	1
0.10	2	173	82.0	—	1
0.10	3	151	50.0	—	1
0.10	3	171	73.0	35.5	2
0.10	4	155	47.5	34.0	2
0.10	4	173	75.0	36.5	2
0.10	4	180	86.0	36.5	2
0.10	5	150	52.0	28.0	2
0.15	2	185	95.0	—	1
0.15	4	158	59.0	32.0	2
0.15	4	171	75.0	32.0	2
0.15	4	178	77.0	34.5	2
0.20	2	168	119.0	—	1
0.20	4	161	78.5	38.5	2
0.20	4	172	115.0	36.0	2
0.20	5	158	74.0	31.5	2

^aFormulation used was based on *Formulation 3* of *Table 1*.

^bBatch viscosity (MS 1 + 4) at 100°C after mixing in the internal mixer.

^cBatch viscosity (MS 1 + 4) at 100°C after 15 min of milling on the two-roll mill with initial temperature of 75°C.

^d1. Adhered to the rolls.
2. No mill-sticking observed.

processing in the subsequent operations such as addition of curatives and accelerators.

Figure 12 shows the relationship between Mooney viscosities based on a large rotor and those based on a small rotor. These data are provided for the purpose of conversion as the processability parameter is normally quoted in terms of measurements based on a large rotor.

CONCLUSIONS

Both ENR 25 and ENR 50 produced from the new production technique have been demonstrated to give very satisfactory processing behaviour in large internal mixers. The mill-sticking problem associated with ENR 50

during high temperature mixing can now be avoided by incorporating a small amount of sulphur and a slightly higher level of stearic acid. However, this investigation was carried on small laboratory mills and the results may not be related to commercial operations.

ACKNOWLEDGEMENTS

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September 1988

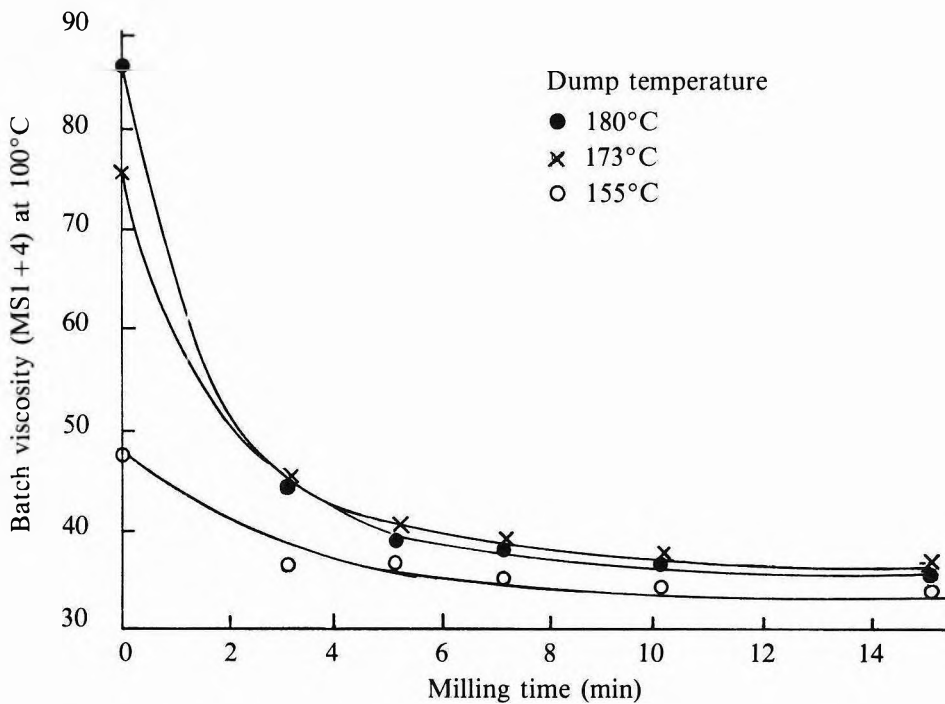


Figure 11. Effect of milling on batch viscosity (batches were obtained at various dump temperatures). Formulation used: ENR 50 100, ISAF black 50, Dutrex 737MB 5, zinc oxide 5, stearic acid 4, Permanax TQ 1, sulphur 0.1.

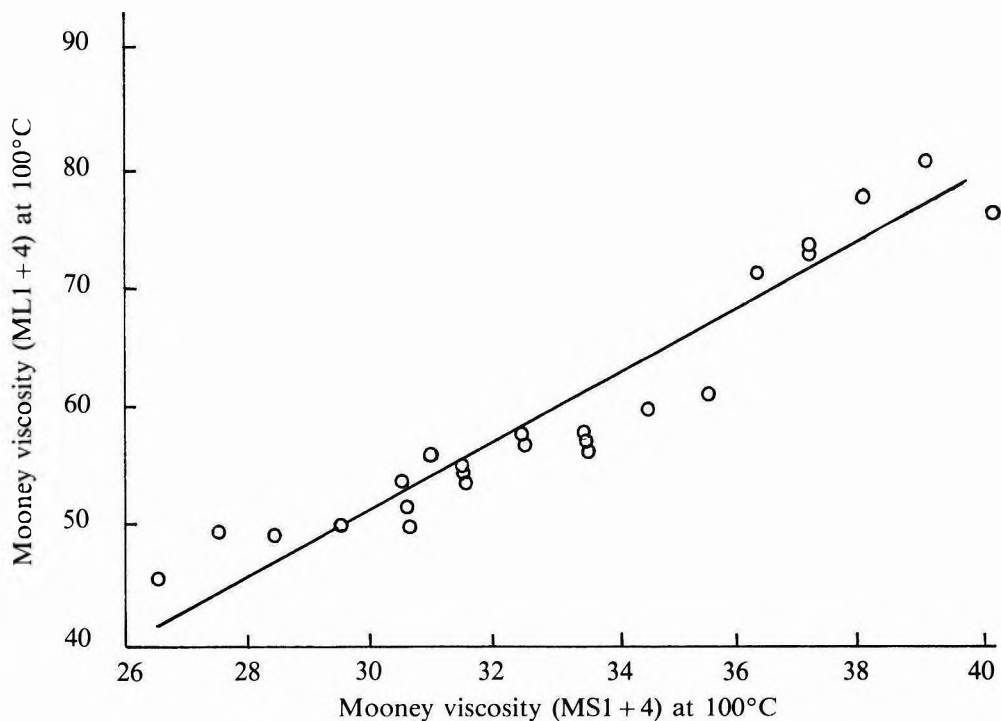


Figure 12. Relationship between (MSI + 4) and (ML1 + 4).

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An Analysis of the Plasticity Retention Index of the Standard Malaysian Rubber Scheme

M.S. SAMBHI*

Molecular degradation is the main process occurring during the Plasticity Retention Index (PRI) test of commercial grades of raw natural rubber. The relationship between Wallace plasticities and number-average degrees of polymerisation allows one to express the PRI in terms of number-average degrees of polymerisation.

The degradation data, for a number of commercial grades of natural rubber, can be represented by typical first-order type of kinetic equations. For such rubbers, the dependence of PRI on the initial Wallace plasticity and the chain scission rate constant is determined. A generalised treatment of the factors that influence the PRI value is presented and some of the empirical observations made with regard to the PRI are rationalised. The effectiveness of the PRI, as a measure of the susceptibility of raw natural rubber, is gauged.

The Plasticity Retention Index (PRI) of the Standard Malaysian Rubber (SMR) Scheme has been designed to provide a rapid assessment of the susceptibility of raw natural rubber (NR) to thermal oxidative degradation^{1,2}. High PRI values are generally associated with rubbers that possess good resistance to thermal oxidation breakdown^{2,3}. The PRI values are also useful in that they can be correlated with certain performance aspects of the rubbers during mastication and compounding and with the ageing performance of the derived vulcanisates^{1,2,3}.

For the majority of commercial grades of NR samples studied, the degradation as measured in terms of Wallace plasticities, can be satisfactorily represented by typical first-order type of kinetic equations, particularly for the early stages of degradation^{4,5}. It was therefore considered that PRI reflects a genuine thermal oxidative characteristic of NR and is independent of the progress of oxidation and the initial Wallace plasticity of the rubber.

A recent study⁶ has shown that NR degradation data can be satisfactorily represented by first-order type of kinetic equations if chain

scission of NR starts off with zero-order or pseudo-zero-order kinetics and becomes autocatalytic in due course of time. However, deviations are bound to occur as chain scission of NR can follow varying kinetic paths.

Experimental evidence for the independence of PRI on P_0 was obtained from mastication experiments^{3,5}. However, a more critical examination of the mastication data reveals that in some instances the differences in PRI values are significantly greater than the normal $\pm 3.5\%$ error associated with PRI measurements⁴. A recent mastication experiment conducted showed that PRI of a SMR CV rubber decreased as P_0 of the rubber was progressively lowered *via* mastication at room temperature⁷. It has been reported⁸ that rubbers with low P_0 values tend to have high PRI values and PRI values in excess of the maximum theoretical value of 100 have been quoted^{2,8}.

It seems necessary now to quantify some of the observations related to PRI and obtain a satisfactory understanding of the factors that can influence PRI values. The effectiveness of PRI as a measure of thermal oxidative degradation of NR is gauged.

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EXPERIMENTAL

The ageing of NR samples and PRI determinations were done according to the procedure laid out for the PRI test⁹. PRI is given by the expression

$$\text{PRI} = P_{30}/P_o \times 100 \quad \dots 1$$

where P_o is the initial plasticity and P_{30} is the plasticity after ageing for 30 min at $140^\circ\text{C} \pm 0.5^\circ\text{C}$.

The intrinsic viscosities $[\eta]$ of NR solutions of toluene were determined at $30^\circ\text{C} \pm 0.01^\circ\text{C}$. The number-average molecular weights (\bar{M}_n) were calculated from the expression

$$[\eta] = K\bar{M}_n^a \quad \dots 2$$

(where $K = 1.288 \times 10^{-3} \text{ dl g}^{-1}$ and $a = 0.66$) obtained from data pertaining to a set of unfractionated commercial NR samples¹⁰.

RESULTS AND DISCUSSION

The Wallace plasticity of an NR sample which has been subjected to thermal oxidative ageing for a time t is satisfactorily given by the expression⁵

$$P_t = P_o - P_d + P_{hr} + P_{hr} \quad \dots 3$$

where P_t is the aged plasticity

P_o is the initial plasticity

P_d is the decrease in plasticity due to thermal oxidative degradation

P_{hr} is the increase in plasticity due to the hardening of the rubber arising from crosslinking reactions of functional groups present in the NR system^{11,12} (of possible importance in the early stages of the ageing process)

P_{hr} is the increase in plasticity due to crosslinking of radical intermediates produced during the oxidative process¹³.

These radical reactions are generally outweighed by scission reactions and can only assume importance during the advanced stages of oxidation¹³.

Since PRI has been designed to denote the susceptibilities of NR to thermal oxidative breakdown, then naturally erroneous estimations of the susceptibilities are obtained if crosslinking reactions leading to the hardening of the rubber can occur concurrently with degradation during the PRI test. The aged Wallace plasticity after 30 min then needs to be written as

$$P_{30} = P_o - P_d + P_{hr} \quad \dots 4$$

and

$$\text{PRI} = 100(P_{30}/P_o) = 100(1 - P_d/P_o + P_{hr}/P_o) \quad \dots 5$$

Ideally P_{hr}/P_o should be negligible compared to P_d/P_o so that PRI is a reflection only of the degradative behaviour of the rubbers. While the contribution of P_{hr}/P_o may be significant for freshly prepared samples in laboratory experiments^{5,8}, its contribution to commercial grades of SMR is probably not significant⁵. We will therefore assume, in our subsequent discussions, that degradation is the dominant process occurring during the PRI test.

The thermal oxidative degradation of NR can follow varying kinetic paths⁶. However, for a number of commercial grades of NR studied, the degradation, could be represented by typical first-order kinetic equations of the type^{4,5},

$$P_t = P_o \exp - k_d t \quad \dots 6$$

where k_d is a rate constant of degradation expressed in unit of min^{-1} . PRI for such rubbers can be expressed as

$$\text{PRI} = 100 \exp - 30 k_d \quad \dots 7$$

While PRI becomes independent of the progress of oxidation on the basis of *Equations 6* and *7*, yet, one cannot infer that PRI is independent of P_o , unless one can show that k_d is independent of P_o .

For aged NR samples, $[\eta]$ of NR solutions of toluene are linearly related to Wallace plasticities (P) of the rubbers by a simple relationship of the type^{5,6,14}

$$[\eta] = bP + c \quad \dots 8$$

In view of *Equations 2* and *8*, one can write⁶

$$P_t = \bar{X}_t^a / \alpha - \beta / \alpha \quad \dots 9$$

where P_t is the Wallace plasticity at ageing time t

\bar{X}_t is the number-average degree of polymerisation at ageing time t

$$\alpha = b / KM_r^a$$

$$\beta = c / KM_r^a$$

M_r is the molecular weight of the repeating unit of NR.

Equation 9 allows us to discuss PRI either in terms of number-average degrees of polymerisation or Wallace plasticities.

Equation 6 can also be expressed on terms of number-average degrees of polymerisation according to the expression^{5,6}

$$\ln[1 - (\bar{X}_{p=0} / \bar{X}_o)^a] - \ln[1 - (\bar{X}_{p=0} / \bar{X}_o)^a (1 + s)]^a + a \ln(1 + s) = k_d t \quad \dots 10$$

where \bar{X}_o is the initial number-average degree of polymerisation

$\bar{X}_{p=0}$ is the number-average degree of polymerisation calculated from the intrinsic viscosity value $[\eta]_{p=0}$ corresponding to the zero reading on the plastimeter scale

s is the average number of chain scission events experienced by an initial NR molecule up to an ageing time t .

It has been shown⁶ that when *Equations 6* and *10* are operative,

$$k_d = ak_s / 1 - (\bar{X}_{p=0} / \bar{X}_o)^a \quad \dots 11$$

where $s = k_s t$, $k_s = k_o / N(O) = k_o M_r \bar{X}_o / \rho L$ or $k_1 \bar{X}_o$ for zero-order or pseudo-zero-order chain scission process respectively

k_o and k_1 are the zero-order and first-order rate constants of chain scission respectively

$N(O)$ is the initial concentration of NR molecules expressed usually in terms of molecule per cubic centimetre

ρ is the NR bulk density

L is the Avogadro constant.

The use of kinetic expressions that do not incorporate the diffusion parameter is justified as it has been shown that homogeneous degradation of NR pellets will occur during the PRI test⁶.

For zero-order chain scission process, *Equation 11* takes the form

$$k_d = a k_o M_r \bar{X}_o / \rho L (1 - \bar{X}_{p=0} / \bar{X}_o)^a \quad \dots 12$$

For pseudo-zero-order chain process, *Equation 11* takes the form

$$k_d = a k_1 \bar{X}_o / 1 - (\bar{X}_{p=0} / \bar{X}_o)^a \quad \dots 13$$

Equations 12 and *13* show that k_d values are dependent upon \bar{X}_o (or P_o) values and PRI cannot be considered as independent of P_o values on the basis of the observed first-order kinetics of degradation as given by *Equations 6* and *7*. The dependence of PRI on \bar{X}_o (or P_o), when *Equations 6* and *7* are obeyed, can be determined in the following manner.

For a set of rubbers differing only in \bar{X}_o (or P_o) values, one can write from *Equation 12* the following expression

$$dk_d / d\bar{X}_o = a k_o M_r / \rho L \left\{ [1 - (\bar{X}_{p=0} / \bar{X}_o)^a - a (\bar{X}_{p=0} / \bar{X}_o)^a] / [1 - (\bar{X}_{p=0} / \bar{X}_o)^a]^2 \right\} \quad \dots 14$$

for zero-order chain scission, and from *Equation 13*

$$dk_d / d\bar{X}_o = a k_1 \left\{ [1 - (\bar{X}_{p=0} / \bar{X}_o)^a - a (\bar{X}_{p=0} / \bar{X}_o)^a] / [1 - (\bar{X}_{p=0} / \bar{X}_o)^a]^2 \right\} \quad \dots 15$$

for pseudo-zero chain scission process. From *Equations 14* and *15*, one can obtain the conditions that

$$dk_d / d\bar{X}_o \text{ is } + \text{ for } (\bar{X}_{p=0} / \bar{X}_o) < 0.46 \quad \dots 16$$

and

$$dk_d / d\bar{X}_o \text{ is } - \text{ for } (\bar{X}_{p=0} / \bar{X}_o) > 0.46 \quad \dots 17$$

In the experiments conducted with commercial grades of NR so far, $(\bar{X}_{p=0}/\bar{X}_o)$ value has seldom exceeded 0.3. In view of this, Equation 16 is applicable to the degradation data. Thus, according to Equations 6 and 7, PRI decreases as \bar{X}_o (or P_o) increases. This is in consonance with the empirical observation that rubbers with high P_o values tend to have low PRI values⁸.

For a set of rubbers differing only in k_o or k_1 values, Equations 6, 7, 12 and 13 allow us to draw the inference that PRI will decrease with increasing magnitude of the chain scission rate constant. In view of the fact that it may not always be possible to represent the degradation data according to Equations 6 and 10, it is now necessary to present a generalised treatment of the factors that influence PRI and rationalisation of some of the empirical observations made with regard to PRI.

The use of Equations 8 and 9 allow PRI of NR to be expressed as⁵

$$PRI = 100 (\bar{X}_{30}^a - \bar{X}_{p=0}^a) / (\bar{X}_o^a - \bar{X}_{p=0}^a) \quad \dots 18$$

where \bar{X}_{30} is the number-average degree of polymerisation after ageing for 30 min at $140^\circ\text{C} \pm 0.5^\circ\text{C}$. The ageing period for the PRI test is 30 min and it is likely that, for the majority of NR samples, the zero-order or pseudo-zero-order chain scission kinetic model is operative^{6,15,16}. For the 30 min ageing period one can write

$$s = \bar{X}_o / \bar{X}_{30} - 1 \quad \dots 19$$

and taking into account the expressions for the zero-order and pseudo-zero-order chain scission processes, PRI can be written as

$$PRI = 100 [(\bar{X}_o / 1 + k_c \bar{X}_o 30)^a - \bar{X}_{p=0}^a] / (\bar{X}_o^a - \bar{X}_{p=0}^a) \quad \dots 20$$

where $k_c = k_1$ (min^{-1}) for pseudo-zero-order chain process and $k_c = k_o M_r / \rho L$ (molecules $\text{cm}^{-3} \text{min}^{-1}$) for zero-order chain scission process.

From Equation 20, PRI is a function of \bar{X}_o , k_c and $\bar{X}_{p=0}$ and one can write

$$\begin{aligned} dPRI &= (\partial PRI / \partial \bar{X}_o) d\bar{X}_o \\ &\quad k_c, \bar{X}_{p=0} \\ &+ (\partial PRI / \partial k_c) dk_c \\ &\quad \bar{X}_o, \bar{X}_{p=0} \\ &+ \left(\frac{\partial PRI}{\partial \bar{X}_{p=0}} \right) d\bar{X}_{p=0} \\ &\quad \bar{X}_o, k_c \end{aligned} \quad \dots 21$$

It is now of interest to explore the changes in PRI resulting from changes in \bar{X}_o , k_c and $\bar{X}_{p=0}$.

The dependence of PRI on \bar{X}_o (or P_o) is given by the expression

$$\begin{aligned} (\partial PRI / \partial \bar{X}_o)_{k_c, \bar{X}_{p=0}} &= 100 a \bar{X}_o^{a-1} / (1 + k_c \bar{X}_o 30)^a \\ &\quad (\bar{X}_o^a - \bar{X}_{p=0}^a) [1 / \bar{X}_o \\ &\quad + \bar{X}_{p=0}^a (1 + k_c \bar{X}_o 30)^2 / \\ &\quad \bar{X}_o (\bar{X}_o^a - \bar{X}_{p=0}^a) \\ &\quad - 30 k_c / (1 + k_c \bar{X}_o 30) \\ &\quad - \bar{X}_o^{a-1} / (\bar{X}_o^a - \bar{X}_{p=0}^a)] \end{aligned} \quad \dots 22$$

An examination of Equation 22 reveals that $(\partial PRI / \partial \bar{X}_o)_{k_c, \bar{X}_{p=0}}$ can take up values which can be positive or negative or zero. This is confirmed by Plots A, B and C of Figure 1.

The significance of the plots of Figure 1 can best be ascertained if PRI is firstly correlated with a fundamental parameter of degradation. The fundamental parameter that reflects the ability of a macromolecule to resist breakdown is \bar{X}_{30}/\bar{X}_o of Equation 19. The effectiveness of PRI can be gauged by determining how well it correlates with $100 (\bar{X}_{30}/\bar{X}_o)$.

Figure 2 gives the plot of PRI versus $100 (\bar{X}_{30}/\bar{X}_o)$ based on data pertaining to Plot A of Figure 1. A positive relationship exists between PRI and $100 (\bar{X}_{30}/\bar{X}_o)$ up to the maximum point of the plot. Beyond the maximum point, PRI in fact decreases rapidly as $100 (\bar{X}_{30}/\bar{X}_o)$ increases. If one accepts the established practice that high PRI values denote high resistance of NR to thermal oxidative breakdown, then PRI values beyond the maximum point would give misleading estimations of the susceptibilities of the rubbers to degradation. In view of this, the useful regions for PRI

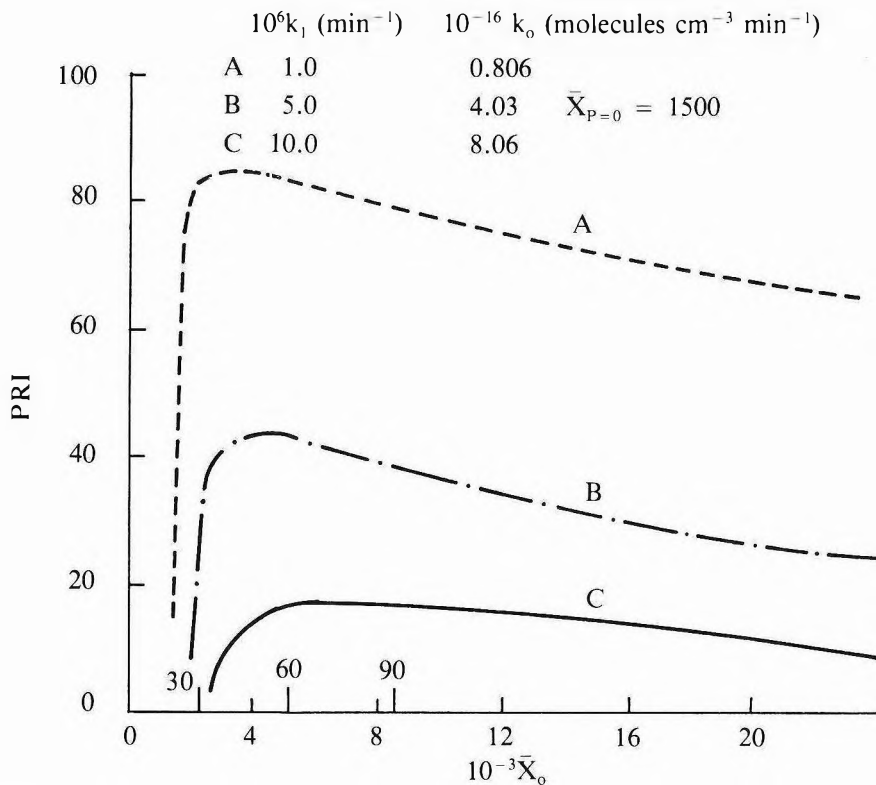


Figure 1. Plots of PRI versus \bar{X}_o (average $P = 30, 60$ and 90 are indicated).

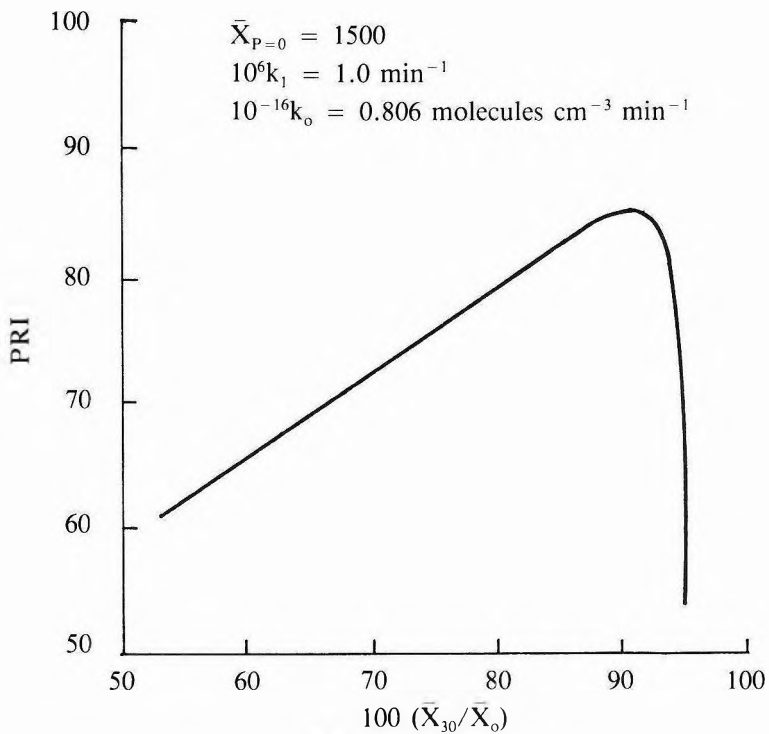


Figure 2. PRI versus $100 (\bar{X}_{30} / \bar{X}_o)$ based upon theoretical data.

are beyond the maxima of *Plots A, B and C* of *Figure 1*. This imposes the condition that below a certain P_o value of the rubber, PRI values can become misleading. The maximum points of *Plots A, B and C* of *Figure 1* occur at \bar{X}_o of 3500, 4000 and 6000 respectively. Molecular weight studies of clonal and SMR grades of rubbers^{8,10} show that \bar{X}_o varies from about 3000 to 9000 and only in a few instances is \bar{X}_o below 3500. Thus, it is likely that, in the majority of cases, quoted PRI values would provide an index of thermal oxidative degradation.

For a number of commercial grades of NR¹⁵, k_1 is in the region of $1.0 \times 10^{-6} \text{ min}^{-1}$ at $140^\circ\text{C} \pm 0.5^\circ\text{C}$ while the equivalent k_o value is $0.806 \times 10^{16} \text{ molecules cm}^{-3} \text{ min}^{-1}$. *Plot A* of *Figure 1* is based upon these values with $\bar{X}_{P=0} = 1500$. It will be shown later that the variation of PRI with the range of $\bar{X}_{P=0}$ found for rubbers is not large. In the useful region of PRI of *Plot A*, PRI decreases as \bar{X}_o (or P_o) increases. However, the decrease in $(\partial \text{PRI} / \partial \bar{X}_o)_{k_c, \bar{X}_{P=0}}$ is gradual and virtually linear. A two-fold increase in \bar{X}_o from $\bar{X}_o = 4000$ (average $P_o = 47.4$) to $\bar{X}_o = 8000$ (average $P_o = 84.4$) changes PRI from 84.9 to 80.2. This difference in PRI is not much greater than the 3.5% error involved in a single PRI determination⁴. If a rubber sample can be masticated without significantly changing the level of its hydroperoxide, then it is likely that one can observe that PRI does not significantly change as P_o decreases. For a set of rubbers from the same source material and prepared in a similar manner, magnitudes of the chain scission rate constants which reflect in the main, the levels of hydroperoxide, pro-oxidants and inhibitors present in the rubbers, are likely to be similar. If the variations in P_o are not extremely large, then PRI is likely to become independent of P_o . However, if small variations in k_1 or k_o values do occur, then the PRI values will cluster around a small range of values. This is in consonance with the observation that different grades of NR tend to have different ranges of PRI values^{2,3}.

The dependence of PRI on the chain scission rate constants k_1 and k_o is given by the expression

$$(\partial \text{PRI} / \partial k_c)_{\bar{X}_o, \bar{X}_{P=0}} = -3000 a \bar{X}_o^{a+1} / (1 + k_c \bar{X}_o 30)^{a+1} (\bar{X}_o^a - \bar{X}_{P=0}^a) \quad \dots 23$$

If chain scission of NR is a genuine first-order reaction, then at any particular temperature, PRI will be invariable as given by *Equation 23* since $k_c = k_1$. A recent kinetic study¹⁶ of degradation of NR advocates zero-order kinetics of chain scission. Chain scission is envisaged to occur between two peroxy radicals in the termination step of the oxidation mechanism. If the thermal oxidative degradation of NR is kept to the initial stages, then the overall hydroperoxide concentration of NR can be considered to remain constant during the degradation. Thus, the magnitude of the zero-order chain scission rate constant k_o will be linked to the concentration of the hydroperoxide present in the NR system. The zero-order chain scission mechanism seems plausible as there is significant variation in k_o and k_1 values¹⁵. This suggests that that chain scission rate-constant k_o is operative. Hence, according to *Equation 23*, PRI will decrease as k_o increases.

The magnitude of the chain scission rate constant k_o exerts a major influence on the PRI value. If the magnitudes of k_o for the rubbers (*Plots B and C* of *Figure 1*) are significantly greater than the value used for *Plot A* (*Figure 1*), then it is likely that SMR grades, derived from latex, sheet material and blend, will not be able to satisfy the PRI requirements¹⁷ of 60 and 50. However, SMR grades derived from field grade material, particularly SMR 20 and SMR 50 are likely to meet the PRI requirements of 40 and 30 respectively¹⁷. As mentioned before, the magnitude of the chain scission rate is mainly governed by the levels of hydroperoxide, pro-oxidants and inhibitors that are present in the NR system and it seems prudent to avoid situations that can enhance the levels of hydroperoxides and pro-oxidants in NR systems.

The dependence of PRI on $\bar{X}_{P=0}$ is given by the expression

$$\left(\frac{\partial \text{PRI}}{\partial \bar{X}_{P=0}} \right)_{\bar{X}_o, k_c} = -a \bar{X}_{P=0}^{a-1} [1 / (\bar{X}_o^a - \bar{X}_{P=0}^a) + (\bar{X}_{30}^a - \bar{X}_{P=0}^a) / (\bar{X}_o^a - \bar{X}_{P=0}^a)^2] \quad \dots 24$$

According to Equation 24, PRI decreases as $\bar{X}_{P=0}$ increases. Typical values of $\bar{X}_{P=0}$ lie in the region of 900 to 300⁶. For $\bar{X}_o = 5000$ and chain scission rate constants of Plot A (Figure 1), PRI has values of 87.0 and 89.5 when $\bar{X}_{P=0}$ changes from 900 to 300 respectively. The difference in PRI of 2.5 units is about the magnitude of the $\pm 3.5\%$ error involved in a single PRI determination⁷. Thus, it seems likely that variation of PRI with $\bar{X}_{P=0}$ may not be significant and possibly ignored for the majority of rubbers, unless one is dealing with an exceptional type of rubber.

The variations of PRI have been discussed in treating changes in \bar{X}_o , k_c and $\bar{X}_{P=0}$ separately. However, it is possible that for a set of rubbers, variations of all these parameters can exist and it is therefore possible for PRI to increase or decrease or become independent of \bar{X}_o (or P_o) according to the prevailing situation.

The effectiveness of PRI can be gauged by determining how well it correlates with the fundamental parameter of degradation \bar{X}_{30}/\bar{X}_o . A plot of PRI versus $100(\bar{X}_{30}/\bar{X}_o)$ for a number of NR samples is shown in Figure 3. It is encouraging to note that an increase in PRI corresponds to an increase in $100(\bar{X}_{30}/\bar{X}_o)$. PRI is a $f(\bar{X}_o, k_c, \bar{X}_{P=0})$, while $100(\bar{X}_{30}/\bar{X}_o)$ is a $f(\bar{X}_o, k_c)$ (see Equation 20). For the practical range of \bar{X}_o (or P_o) values, changes in $\bar{X}_{P=0}$ of the rubbers probably do not contribute significantly to changes in PRI values. If \bar{X}_o (or P_o) and k_c are independently varied, then one may or may not observe a positive relationship between PRI and $100(\bar{X}_{30}/\bar{X}_o)$.

For a set of rubbers, a positive relationship between PRI and $100(\bar{X}_{30}/\bar{X}_o)$ will definitely be observed if only one of the parameters \bar{X}_o or k_c is a variable. PRI is rather insensitive to \bar{X}_o (or P_o) and the chain scission rate constant k_o will exert a major influence in determining

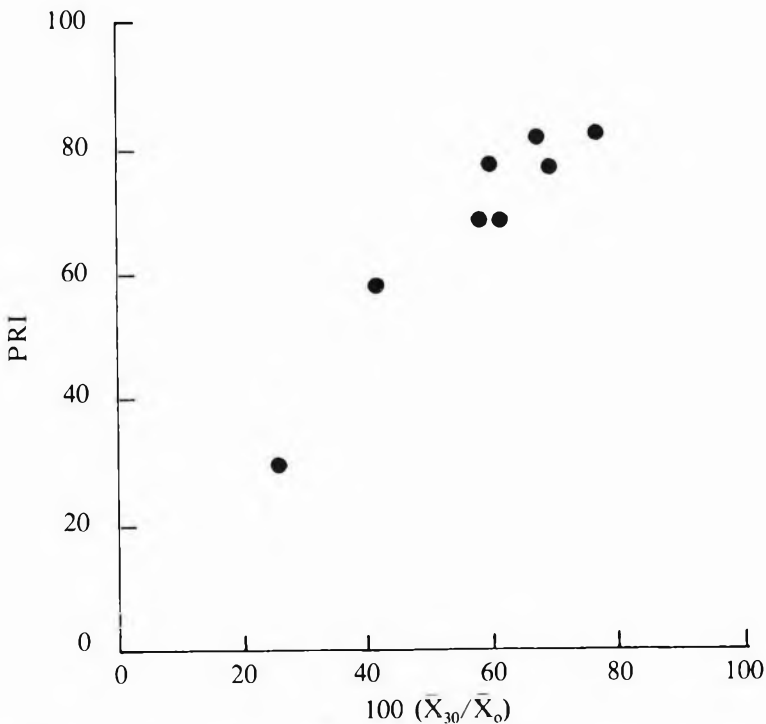


Figure 3. PRI versus $100(\bar{X}_{30}/\bar{X}_o)$ based upon experimental data.

the PRI value. In practical terms, this means that direct comparisons of PRI values are best restricted to within the individual grades of NR in order that PRI values reflect in an optimum manner the susceptibilities of the rubbers to thermal oxidative degradation.

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