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The Brown Bast Syndrome of Hevea Part I. Morphological Observations

J.B. GOMEZ* AND H. GHANDIMATHI*

From a study of several cases of long rested brown bast trees by visual examination, scoring using a sharp instrument, looking at sectional views and by histological examination of the tissues, it is found that excessive meristematic activity is a predominant feature which leads to formation of tumorous tissue. Both the vascular cambial activity and the activity of adventitious meristems surrounding previous 'nuclei' of necrotic activity resulting in the formation of nodules which finally form the so-called occluded xylem in the bark are responsible for the eventual manifestation of tumours. In some cases however, the nodule formation is not evident and the affected bark dries, cracks up and sloughs off. In such cases, smooth renewal of bark results from the activity of the vascular cambium alone. The implications of these findings are discussed.

Brown bast is a well known physiological disease of *Hevea*¹. It was known in Malaya in 1912 and in Java since 1912 although it was confused with other tapping panel diseases. According to Sharples¹, Gallaher had commented on such a disease as early as 1909. Reports by Petch^{2,3} indicate that there is some confusion between brown bast and abnormalities of trees exhibiting nodules and burrs. The disease reached alarming proportions in Malaya¹ in the period 1917-23. Investigations carried out at that time resulted in the characterisation of this disease as of physiological origin and planters were advised to use reduced intensity of tapping to curb the percentage of incidence.

Researchers on exploitation of *Hevea* by modern methods of excision tapping have repeatedly confirmed the relation between intensity of exploitation and the incidence of dry trees. They have also observed clonal differences in susceptibility. A notable case from historical records is the plight of RRIM 500, which, when tested in small-scale clone trials exhibited high incidence of dryness⁴. Seedling trees in Java on daily tapping had 50%-85% incidence of brown bast⁵ (perhaps cumulative). In more recent

times, researchers have connected the relationship between agroclimatological regions and the degree of incidence of dryness⁶. Furthermore, recently De Fay⁷ recognised the need to distinguish between reversible and irreversible forms of dryness.

Burr formation as reported by Petch^{2,3} and description of cases of woody nodules embedded in the bark of *Hevea* can be associated with brown bast. Tapping wounds caused by the pricker used for extraction of latex in earlier days before the advent of excision tapping were probably the causative factors for burr formation in those trees although later researchers, particularly Rhodes⁸ pointed out that nodules formed in early stages of brown bast trees that he examined. Gomez⁹, in reviewing the anatomy of diseased brown bast cases remarked on the frequency of meristematic activity and the formation of occluded xylem in long rested brown bast trees.

Perusal of old pictures of trees mutilated by 'machadinho' tapping indicates very clearly that the wound reaction in *Hevea* is of a severe nature and even today burred trees can be associated with poor standards of excision tapping.

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

In the present and a subsequent paper¹⁰, an attempt will be made to distinguish between the major types of morphological variants of brown bast reaction in trees continuously tapped despite the incidence of partial dryness and trees rested from tapping for various periods of time from the onset of dryness.

MATERIALS AND METHODS

In a research station such as the RRIM Experiment Station at Sungei Buloh, there are many trees in various fields, which are resting due to brown bast. The authors made a survey of such trees to secure samples for histological examination; some of the results are reported in this paper as far as the morphological types are concerned. Although many photographic records were obtained, this paper gives only a brief summary. The trees examined were of various clones, ages, tapping history and other agri-horticultural differences and hence no attempt was made to describe morphological variations arising from these sources of variation. Visual observations, often aided by a scoring instrument such as a tapping knife were all that was required for characterisation in the field for testing whether the affected bark was yielding latex or was dry; and, if there was yield, which part of the bark yielded latex and so on.

Histological observations, when required were made on samples fixed in formalin acetic alcohol¹¹ for several days before sectioning using a hand microtome or sledge microtome or by paraffin wax embedding techniques¹¹.

Whole trees were examined by sectional view in a number of instances to observe gross histology.

RESULTS AND DISCUSSION

Figure 1 shows a long rested brown bast tree showing many protuberances characteristic of malformed brown 'bast' or bark. Many of the burrs contain woody tissue embedded in the phloem and often these are connected to the main xylem. *Figure 2* shows a cross-sectional

view of another brown bast tree with xylem nodules embedded in the phloem. *Figure 3* shows spiral burr formation in a long rested brown bast tree showing a trunk which is not readily amenable for further exploitation. *Figure 4* shows a longitudinal section of such a stem showing that the occluded xylem has in fact fused with the main xylem although traces of phloem can still be seen by the expert eye. Some of this phloem is occluded in the adventitious xylem. Occasionally, dry rubber is present in such cell debris (indicated by arrows).

Figure 5 shows a section through the bark revealing the characteristic brownish streaks visible to the naked eye on the surface of the cut in selected trees affected by early stages of brown bast. The name of the disease originates from this phenomenon. In the example shown, two latex vessel rows are affected. *Figure 6* shows a higher magnification of such an affected zone showing evidence of necrosis, gummosis and unusual cell division. *Figure 7* shows the zone of necrosis in finer detail. Eventually, a nodule which is embedded in the phloem is formed as seen in *Figures 8* and *9*. *Figure 10* shows evidence of gummosis in sieve tubes and the intercellular spaces surrounding the medullary rays.

Figure 11 shows a case of brown bast of a distinctly different variety. In this case, the meristematic activity is smooth, so much so that the renewed bark is without major protuberances causing a visible bulge. The affected external phloem has however, cracked and is in the process of sloughing off.

The usual current procedure in plantations is to rest dry trees once they are found to be nearly dry and not worth while to tap. Such trees, when examined after a period of time reveal drying of the panel, cracking of the bark and sloughing off of the bark which has been affected by the condition of dryness. However, in many cases, there is a kind of tumour formation at the site of original disease or in a spiral fashion extending downwards or upwards, following the usual alignment of bark tissues and conducting xylem tissues, thus clearly indicating that agents causing meristematic activity were actively transported



Figure 1. A long rested tree suffering from brown bast. Several nodules are visible.

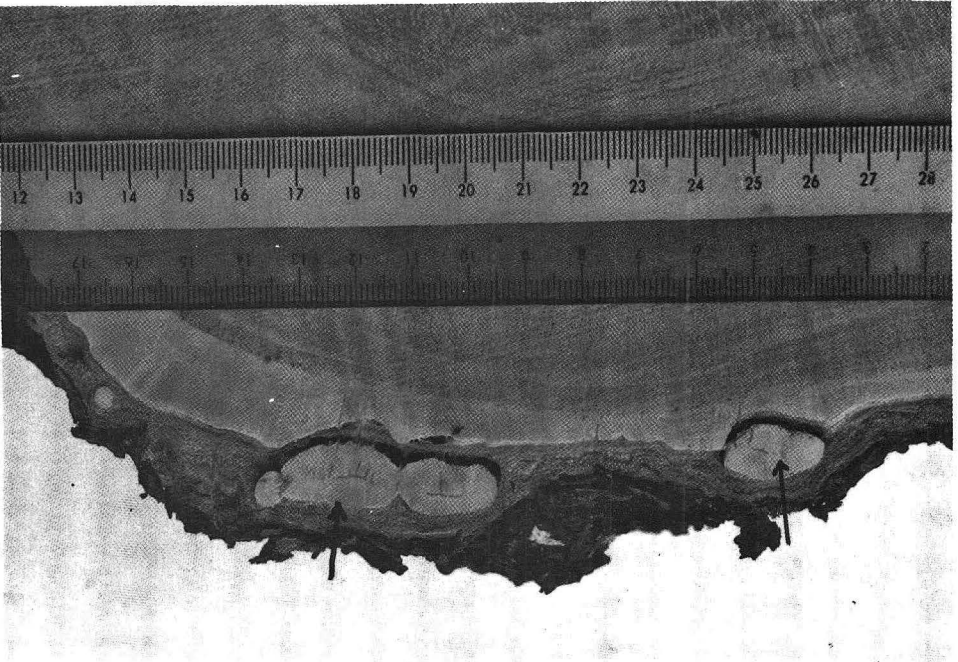


Figure 2. Cross section through stem of brown bast affected tree showing embedded nodules in the bark, i.e. occluded xylem (arrows). Section was painted with phloroglucinol.

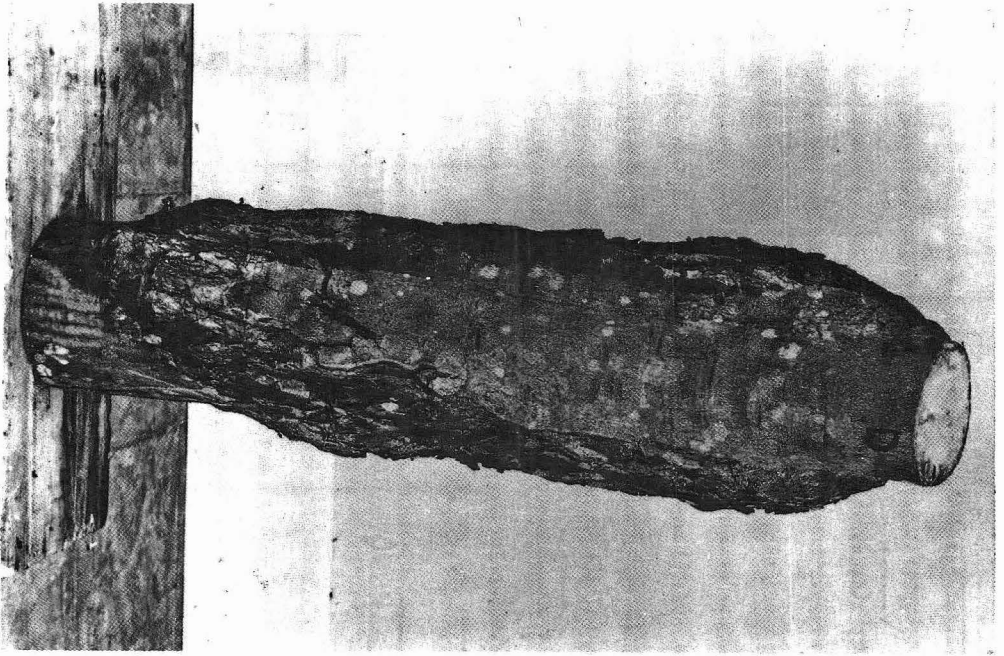


Figure 3. Spiral burr formation in long rested brown bast tree.

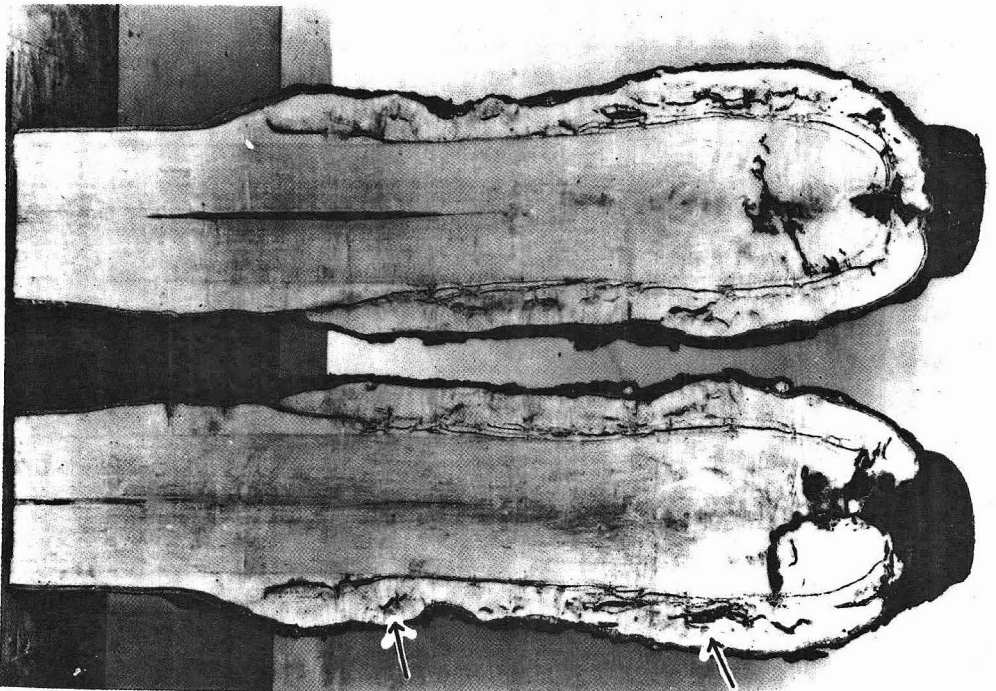


Figure 4. Sectional view of a long rested brown bast tree. Note that the occluded xylem has fused with the main xylem. Streaks of phloem can be seen embedded in the adventitious xylem (arrows).



Figure 5. Cross section through bark showing the brownish streaks along two rows of latex vessels. Stained in Sudan III. Magnification 20X.

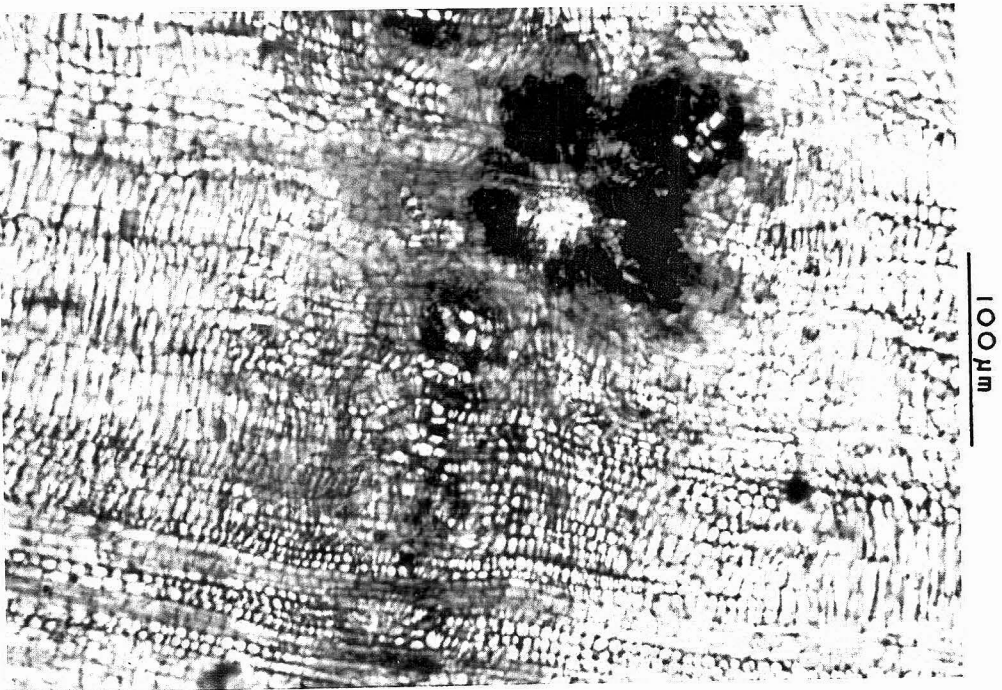


Figure 6. Section passing through a brown streak showing necrosis, gummosis and increased meristematic activity. Stained in safranin. Magnification 256X.



Figure 7. Section through a necrotic zone indicating cellular disruption and the beginning of tissue repair. Stained in safranin/fast green. Magnification 50×.

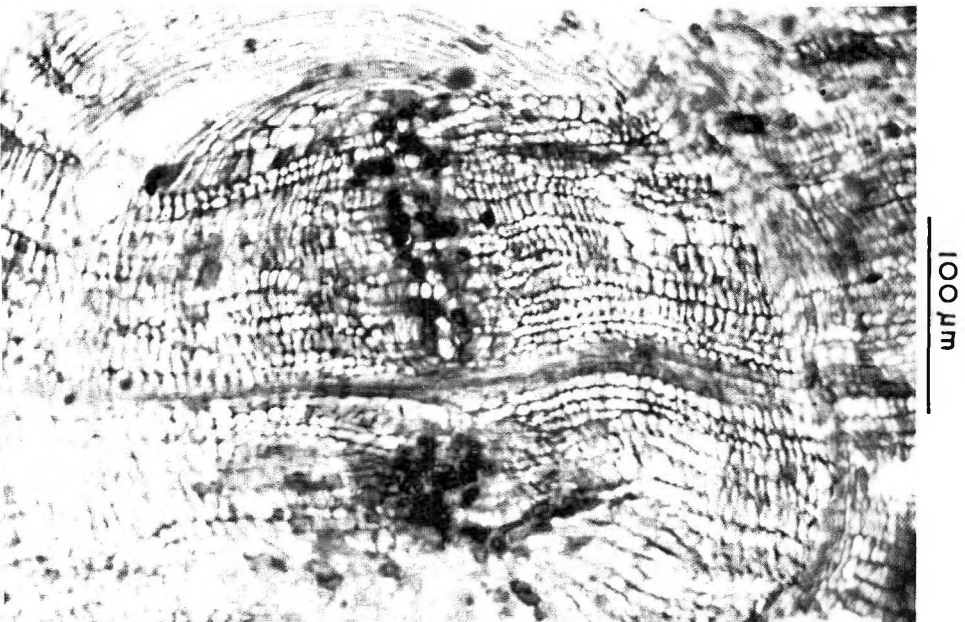


Figure 8. Section through a nodule embedded in a long rested diseased tree showing xylem elements surrounding the necrotic spot. Stained in safranin/fast green. Magnification 256×.

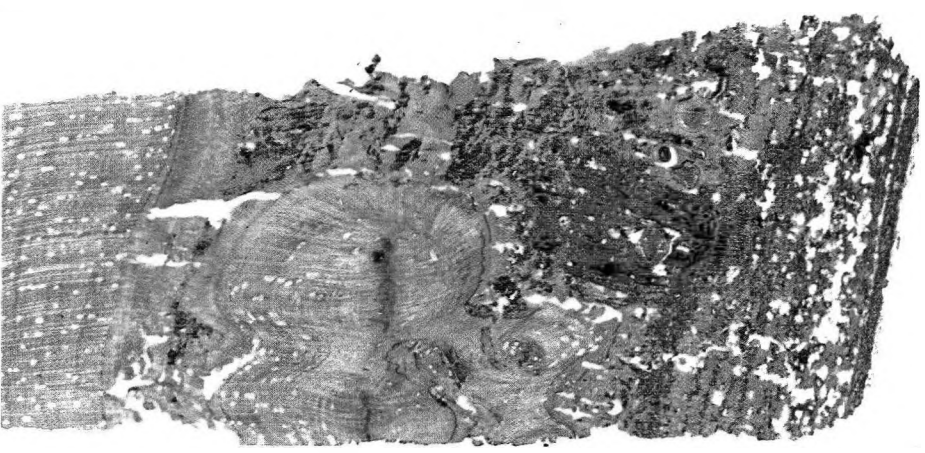


Figure 9. Occluded xylem in the long rested bark of brown bast affected tree. Stained in safranin/fast green. Magnification 4×.

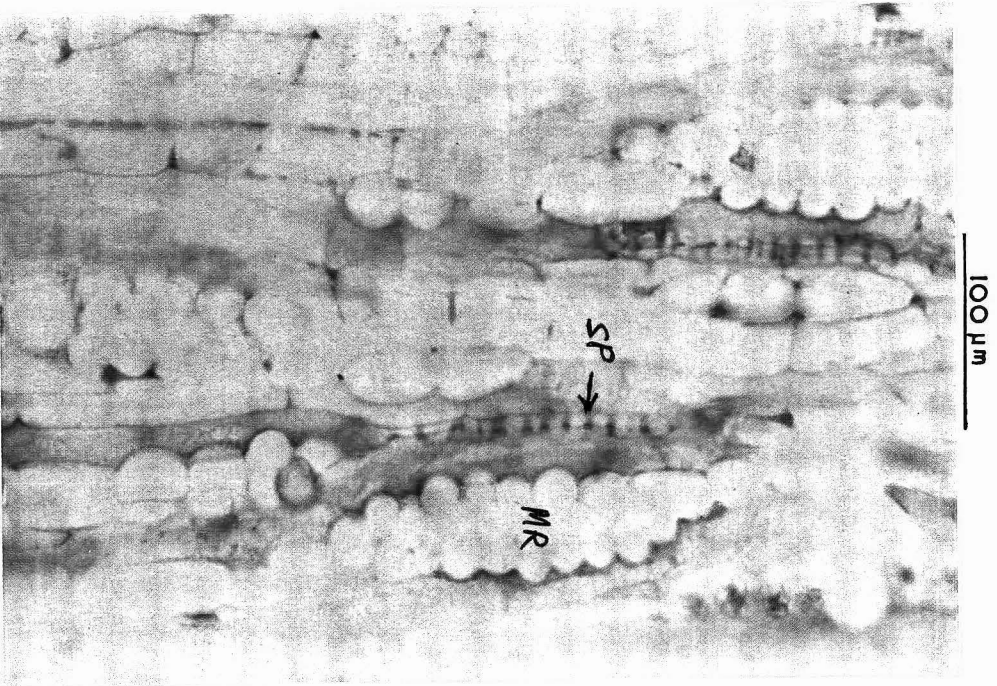


Figure 10. Gummosis in sieve tubes and the intercellular spaces of medullary ray boundaries. Stained in safranin. Magnification 256 X.
MR: Medullary ray SP: Sieve plate



Figure 11. A long rested brown bast affected tree showing bark cracking and sloughing-off reaction.

in this tissue or were synthesised in the tissue due to factors which triggered such physiological activity.

The results reported in this study show that in cases of nodule formation, the nodules contain remnants of necrotic tissue and hence by surmise indicate the presence of necrosis preceding nodule formation.

The characteristic zone of brownish discolouration of inner bark which gave the disease its name from olden times indicates not only the presence of a brownish substance which appears to be a tannin-like material as far as histological techniques can tell, but also shows evidence of increased adventitious cell division surrounding such brownish spots. Presumably these zones of meristematic activity result in the ultimate formation of nodules except when the histological changes take other directions¹⁰. Evidence that a spot of necrosis is immediately surrounded by a meristem is also an indication that primary stages of nodule formation followed cell death in a limited area and the trees' reaction to this form of danger was to form a woody nodule which would embed this debris inside it and protect the surrounding tissue from further damage.

What then, was the primary cause? The authors tend to agree with Rhodes⁸ that brown bast is essentially a wound reaction of the tree to the repeated and frequent wounding inflicted on it by the tapping process. Most researchers would agree that tapping is controlled wounding and that the severity of the reaction to wounding can depend on many aspects such as vigour of the tree, susceptibility of the clone to wounding in terms of physiological capacity for reaction, perhaps nutritional status or other hitherto not understood immunological phenomena. It is possible to conclude that when wounding exceeds a threshold level, other physiological mechanisms intervene.

The authors are also in agreement with Paranjothy *et al.*¹² and Jacob and Prevot¹³ on the question of which tissue is most affected due to reasons which are best discussed in a subsequent paper¹⁰. However, it may be

mentioned that the key to further discoveries related to brown bast and control of it lies in the physiology of the laticiferous system despite the fact that associated tissue also shows reactions characteristic of brown bast. In the view of the present authors, the most detectable primary histological symptoms are seen in the laticiferous system.

CONCLUSIONS

Morphological examination of trees rested due to the onset of dryness generally shows the sloughing off reaction in the external bark, a feature in which the tree discards dead tissue external to an underlying meristematic zone or retains the affected bark in which various malformations occur during a period of time. Hyperplastic development of tissue due to higher activity of the vascular cambium and activity of several meristems surrounding necrotic spots in the tissue is most noticeable. Histological observations of the affected tissue reveal a brown streaky region in the inner bark in the early stages of the disease and signs of meristematic activity peripheral to it. Ultimately, nodules are seen embedded in the surviving bark, resulting in the formation of occluded xylem. Obviously in cases where the bark sloughs off, these processes need not occur.

Other changes noticed in the laticiferous system and adjacent tissue will be reported in a forthcoming paper¹⁰. All these developments in the hyperplastic tissue indicate that the tree is reacting to some form of physiological stress and creates new tissue suitable for overcoming the stress. These observations are consistent with earlier findings of other researchers who concluded that brown bast is essentially a wound reaction of the trees and that the earliest relevant principal changes occur in the laticiferous system.

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The Brown Bast Syndrome of Hevea Part II. Histological Observations

J.B. GOMEZ*, SAMSIDAR HAMZAH*, H. GHANDIMATHI* AND L.H. HO*

Histological observations on trees suffering from brown bast were made on bark samples from partially dry trees and dry trees which showed external symptoms of dryness or malformations typical of brown bast. The histological behaviour of tissue is microscopically examined to reveal peculiarities evident in the brown bast syndrome.

Formation of tyloses in latex vessels, their ultimate lignification and the significance of these are considered in the paper.

Although histological changes are evident in the laticiferous system and associated tissue, it is shown that the earliest symptoms are evident in the laticifer and hence, the causative mechanism should be sought in the physiology of the laticiferous system.

The brown bast syndrome is a well known physiological disease of *Hevea* which has presumably existed since the inception of the rubber industry. There are schools of thought which favour a physiological explanation for the disease and an older school of thought which considered it to be of pathological origin¹. More recently, opinion has shifted in favour of the physiological cause and many researchers have put their thoughts on paper.

This paper attempts to bring to focus the various histological symptoms associated with diseased trees. It is expected that such a consideration would highlight the basic nature of the problem — that the tissue is reacting to a problem and tries to cope with the danger it faces by various techniques of defence known in the plant world. From the nature of the reaction in the tissue, some light can also be thrown on the causative mechanism.

Work on the histology of brown bast affected trees is not new. Rands^{2,3}, Sanderson and Sutcliffe⁴ and Rhodes⁵ are some of the researchers who have worked on the problem in detail. These authors have described the anatomy of *Hevea* bark affected by the disease.

Gomez⁶ has briefly reviewed the earlier findings on histological changes occurring in the affected tissue.

Many cells become meristematic, especially those in the vicinity of latex vessels. This meristematic activity partially contributes to the displacement and disorganisation of latex vessels in affected zones in the inner bark of *Hevea*. The latex in such vessels is often coagulated (there is no flow of latex when bark samples are taken from the affected tissue except from yielding vessels). Wound gum formation in the discoloured tissues has been reported^{3,4,5}. Paranjothy *et al.*⁷ have investigated the general nature of the spread of brown bast and concluded that it is a disease of the laticiferous system. More recently, the histological, biochemical and physiological phenomena⁸⁻¹¹ associated with the brown bast syndrome, have been further investigated.

This paper examines some of these histological features in greater detail with illustrations from many cases of dry trees or partially dry trees examined in our laboratories. A recent paper on the subject by Gomez and Ghandimathi¹² describes the morphological observations.

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

MATERIALS AND METHODS

Tissue samples were secured from trees which had a history of brown bast whenever tumorous abnormalities were investigated. In cases of incipient dryness or early stages of dryness, tissue samples were secured from partially dry zones of the bark indicated by the lack of latex flow along certain regions of the otherwise normal tapping cut. Field experience shows that such trees may continue yielding from the unaffected parts of the bark. A spiral orientation of the abnormal bark arising from excessive meristematic activity along the tissue orientation path is a well-known phenomenon among field workers.

Samples were taken with a bark punch and dropped into formalin-acetic-alcohol fixative¹³ and fixed for several days before sectioning. Free-hand sections using a bench microtome were prepared for routine examination of the tissue. Sledge microtome was used to tackle larger pieces of tissue excised from the tree whenever a gross feature was investigated. Finer sections were made by the paraffin wax embedding procedures¹³.

The staining technique employed depended on the nature of the sample and investigation required. When rubber was required for *in situ* observations on latex vessels, rubber solvents were avoided in the preparation procedures. Subsequently, rubber stains were employed for investigations¹⁴. Paraffin wax embedding procedures usually removed rubber from latex vessels and in some instances provided greater clarity for photographic purposes. Thick sections were often first examined by the Sudan III staining method and later by the safranin/fast green method after dissolving the rubber.

For conventional electron microscopy, the procedures used were those normally employed in our laboratories. Fixation of small segments of tissue was carried out in 2% osmium tetroxide solution in phosphate buffer at pH 7.0 and containing 0.35M sucrose for tonicity control. Such tissue was dehydrated and embedded in styrene methacrylate for preparation of ultra-thin sections. Sections

were stained in uranyl acetate and lead citrate before examination in a Philips EM300.

In addition to conventional electron microscopy, some unconventional electron microscopy was also done to observe particular features such as tyloses quickly and effectively. Tylose-containing latex vessels were first recognised in 50 μm thick sections prepared for light microscopy and selected areas of sections were then re-fixed in osmium tetroxide in the manner earlier described for the electron microscopic examination of such features. Such sections did not provide useful preservation of cellular elements as in conventional electron microscopy but served the purpose of preparing tyloses for electron microscopy.

RESULTS

Tyloses and their Influence on Latex Vessels

Figure 1 shows a widespread occurrence of tyloses in laticifers in a tissue taken from partially dry bark. It is important to retain the rubber in the tissues to recognise these structures readily when tissue samples are routinely scanned for the presence of tyloses. Artefacts related to latex coagulation have to be eliminated by micro-chemical tests if necessary.

If the phloroglucinol test¹³ is applied, the contrast between the red coloured lignifying elements and the remaining laticifers is quite clear (*Figure 2*).

Figure 3 shows lignified tyloses embedded in the rubber in laticifers. *Figure 4* shows a laticifer, at the upper part of the photograph, there is a latex vessel with many compartments. Whether this vessel has been invaded by tyloses or whether a process of de-differentiation is occurring is still doubtful. Coagulated rubber is seen in the periphery of the vessel; calcium oxalate crystals are plentiful in the section and lignified tyloses are present in latex vessels, shown in the lower left section of the same photograph.

Figure 5 shows a fine section of a latex vessel which includes a group of tyloses. Three or four

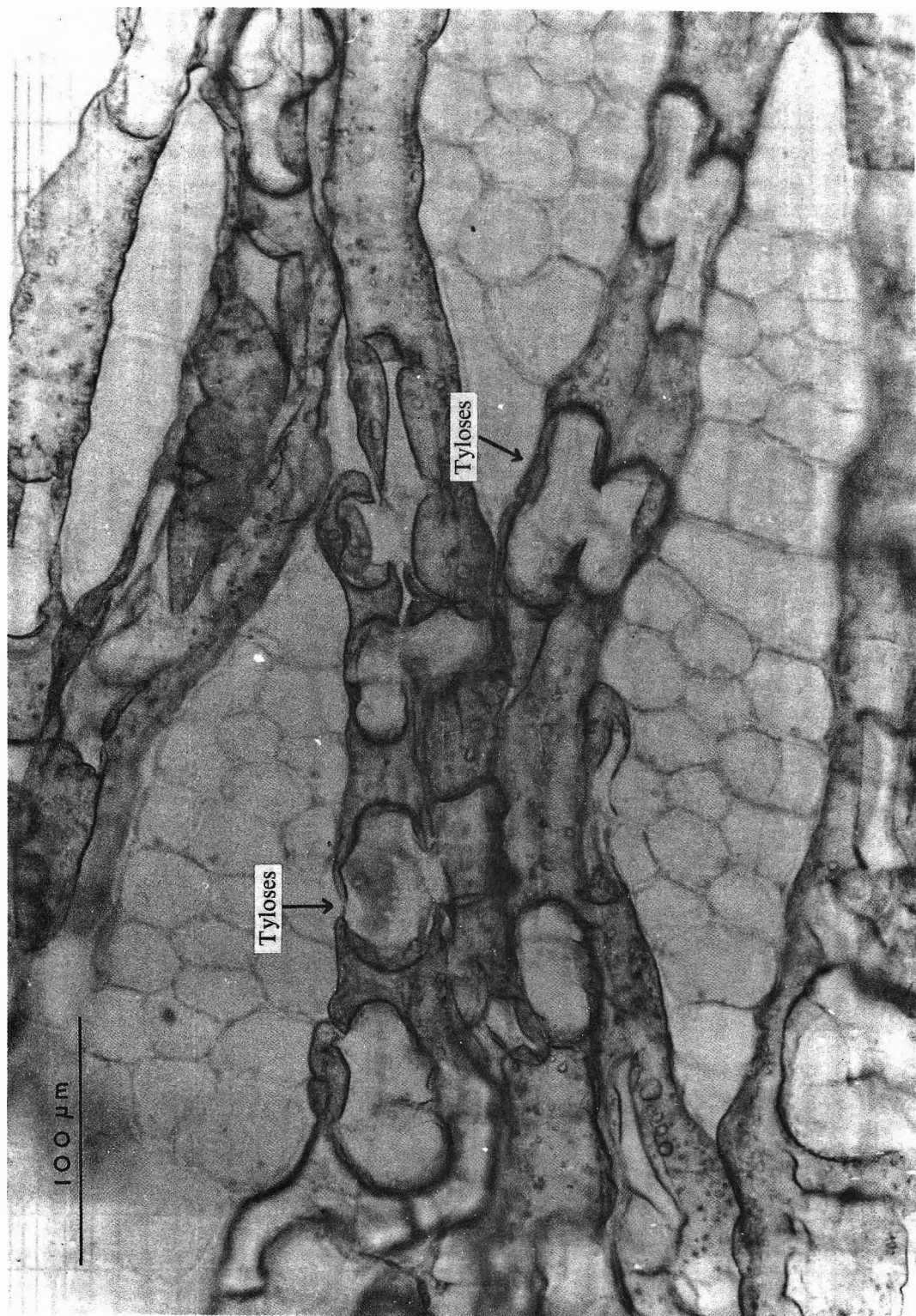


Figure 1. Section through dry bark showing profuse occurrence of tyloses. Magnification 385 ×.

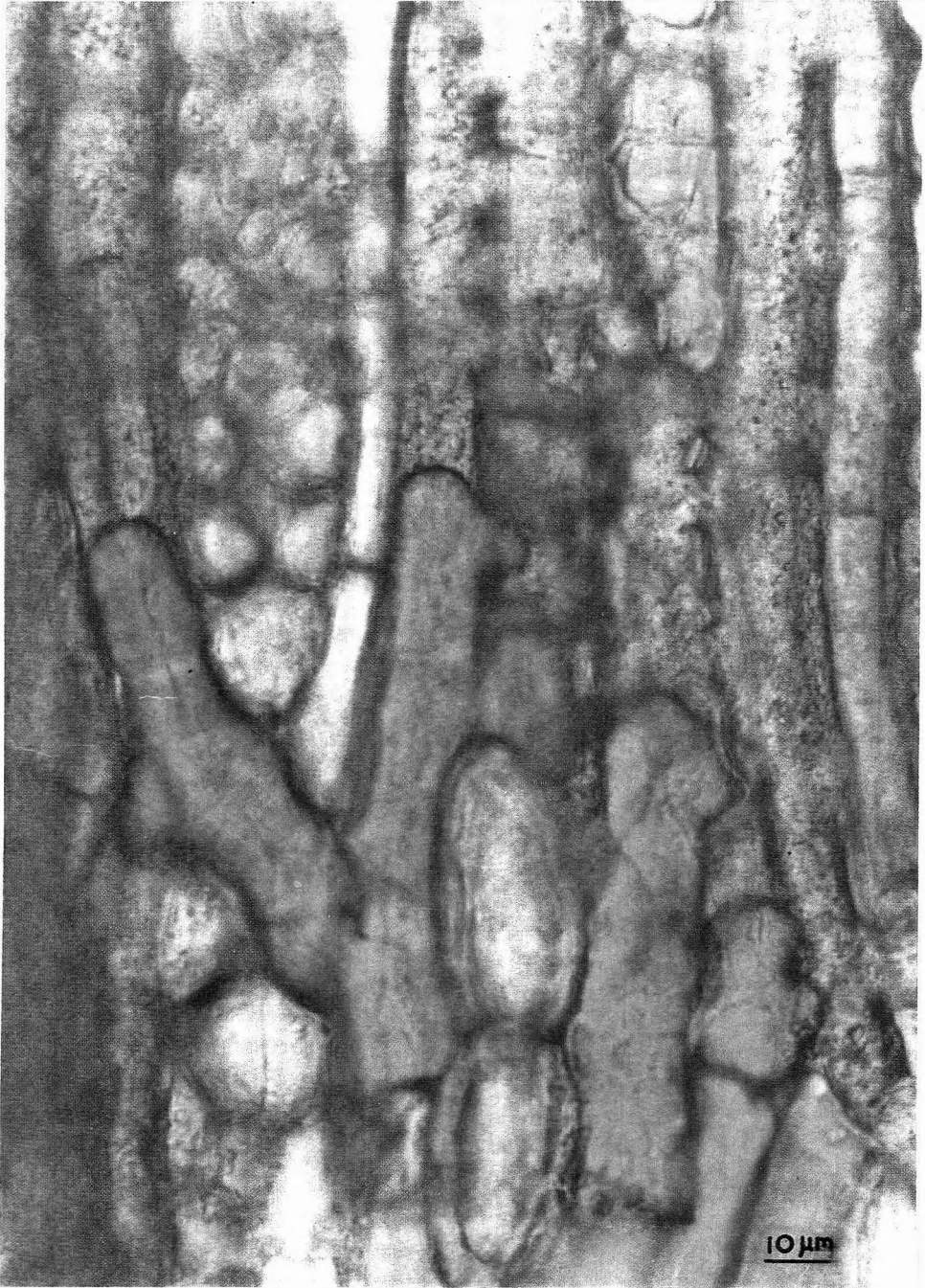


Figure 2. Application of phloroglucinol test to dry bark. Note that the latex vessels are brownish whereas the lignified tyloses are reddish. Magnification 960 \times .

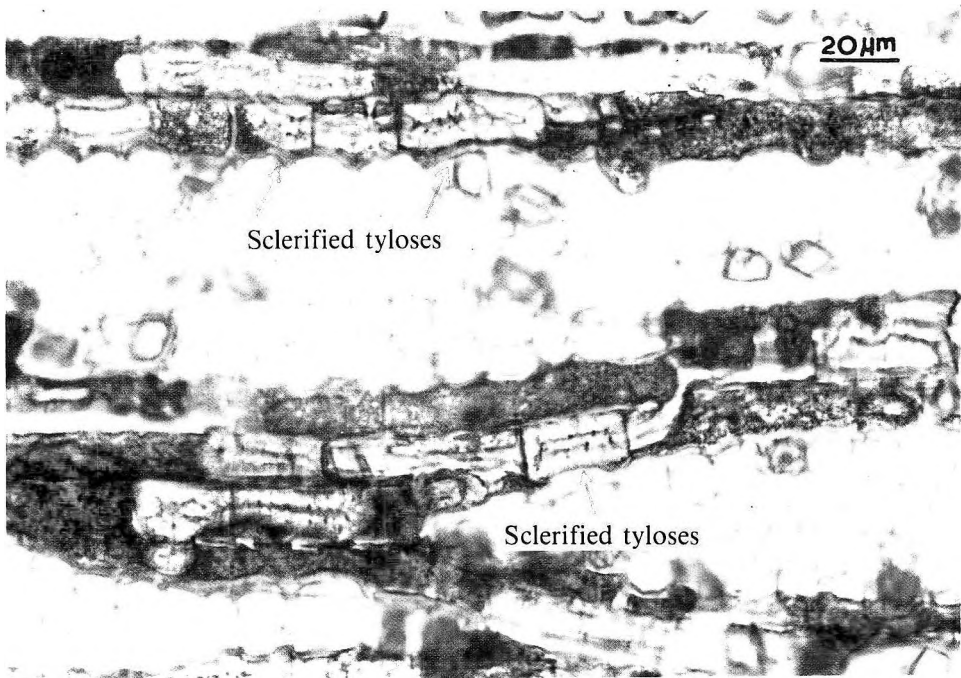


Figure 3. Section through tylose-bearing laticifer zone stained in Sudan III and fast green. Magnification 500 \times .

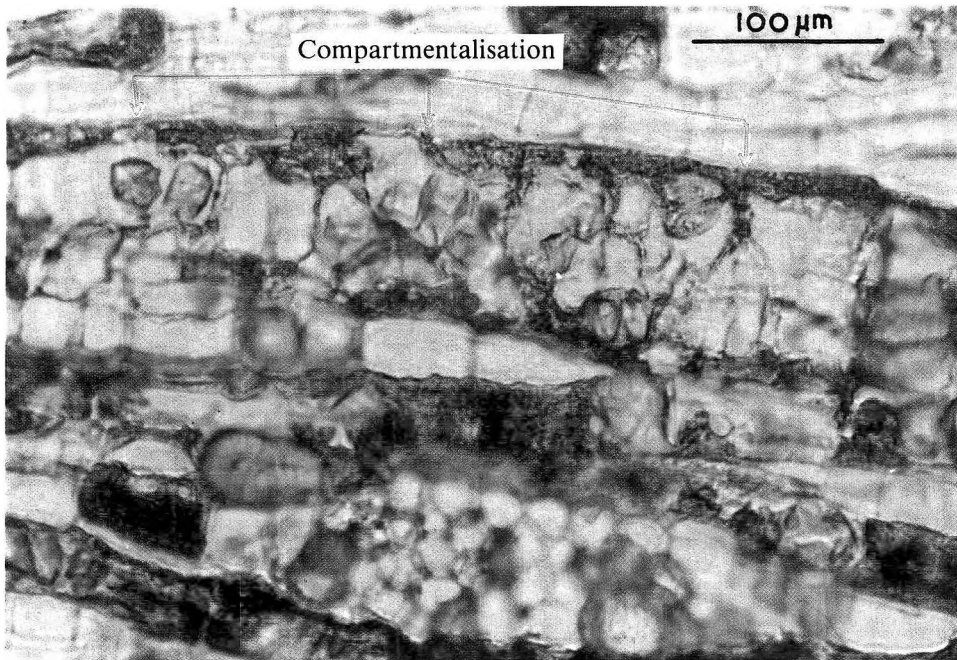


Figure 4. Section through tylose-bearing laticifers showing one vessel with compartmentalisation reflecting de-differentiation. Note the occurrence of brownish material (rubber) in the periphery of the laticifer. Stained in Sudan III and fast green. Magnification 256 \times .

units are clearly visible and the tylose wall is only beginning to thicken. Nuclei are seen in two units. Note that the neighbouring tannin cells do not show any abnormality.

Figure 6 illustrates macerated latex vessels containing bag-like tyloses fitting the lumen of the vessel and as yet showing no signs of lignification. *Figure 7* shows another example of macerated latex vessels showing a group of tyloses which are already lignified.

Figure 8 shows the occurrence of globules in tannin cells from affected tissue. The globules are white in colour in this kind of preparation and give a vacuolated appearance to the tannin cells showing this phenomenon. Normal tannin cells found in the same section do not exhibit this phenomenon.

Electron Microscopic Observations

Figure 9 shows a mosaic montage of latex vessels from a tree which was showing a depression of turgor pressure and low rates of latex flow¹⁵. The partial emptiness of the vessel is interesting. Rubber particle stability is high and destabilisation phenomena are not easily visualised.

Figure 10 shows a mosaic montage of a latex vessel from bark which was already showing tylose formation. Three tyloses can be seen in the section. Their lignified walls indicate continuous growth of the wall over a period of time. The latex in the vessel however, is coagulated.

Figure 11 shows a typical sign of latex instability frequently observed in trees showing signs of partial dryness or pre-coagulation phenomenon on the tapping cut. The individual integrity of the rubber particles has been in jeopardy. The region adjacent to the wall also shows some cytological depletion of normal constituents of the laticifer.

DISCUSSION

It has been argued by Paranjothy *et al.*⁷ that brown bast is a disease of the laticiferous system. Since then further investigations⁸⁻¹¹

have shown that tylose or tylosoid formation is observed in bark showing partial dryness and irreversible forms of dryness.

Indications of cell division, the presence of nuclei in tylosoid units and their gradual lignification are evidence presented in this paper pointing to the activities in the living tissue. A question related to de-differentiation of laticifers into smaller units which then re-differentiate into sclerified elements is worth keeping in mind for further investigations as it is not clear that all sclerified elements formed in the latex vessels arise through tylose formation.

From the growth of the multi-layered wall of the tyloses as seen in electron micrographs, the question of latex vessel death has to be raised and approached with caution. Although these vessels contained coagulated latex, the tyloses were able to secrete many layers in their walls which indicated an open supply line for wall-forming materials. However, in those trees where affected bark sloughs off, these phenomena may go unnoticed or may even be absent.

In the xylem, tyloses are well known to occur as a response to injury or water stress and occasionally as a response to infection^{16,17,18}. Perhaps current research on *Hevea* would throw further light on the problem.

Tyloses in the latex vessels of *Hevea* trees suffering from dryness were discovered in our laboratories in 1962¹⁹ but it remained obscure till 1975⁷. Since then, more work has been carried out on the subject⁸⁻¹¹.

Our histological studies were plagued by problems related to technical difficulties in the demonstration of these structures in delicate diseased tissue and by now most of the technical problems have been overcome as illustrated in this paper. However, the mode of origin, frequency of occurrence and the triggering factors remain as the three main problems related to tylose formation in latex vessels requiring further study and analysis. That the tyloses would form effective blockages in the laticiferous system still containing at least some

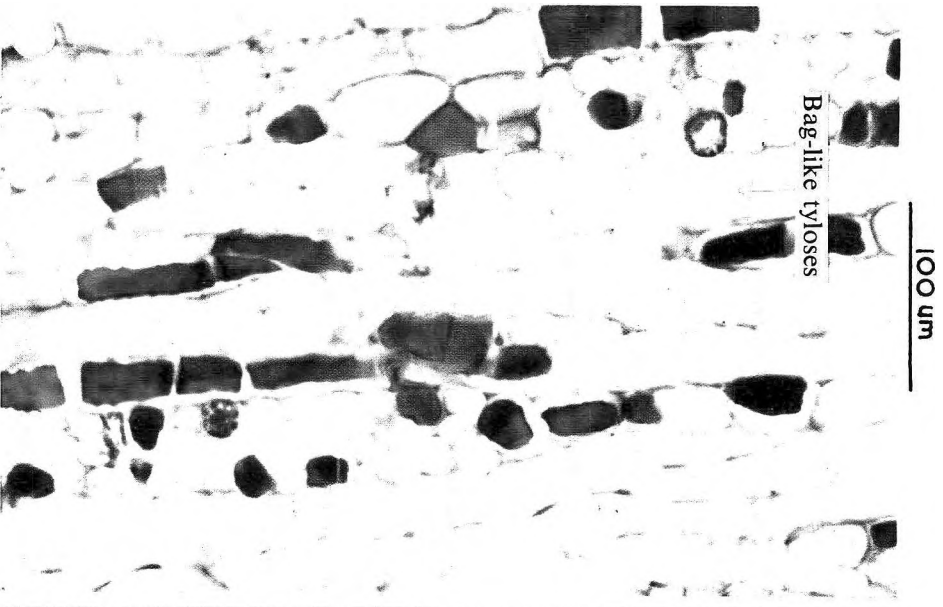


Figure 5. Section through lignified tyloses in latex vessels. Note nuclei in them. Safranin and fast green technique. Magnification 256 \times .

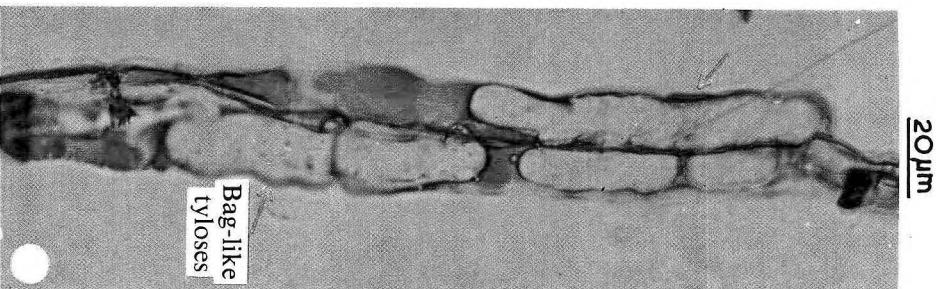


Figure 6. Macerated latex vessels showing bag-like tyloses. Stained in Sudan III after maceration in sodium hypochloride solution. Magnification 500 \times .



Figure 7. Macerated latex vessels showing sclerified elements. Stained in Sudan III. Magnification 100 \times .

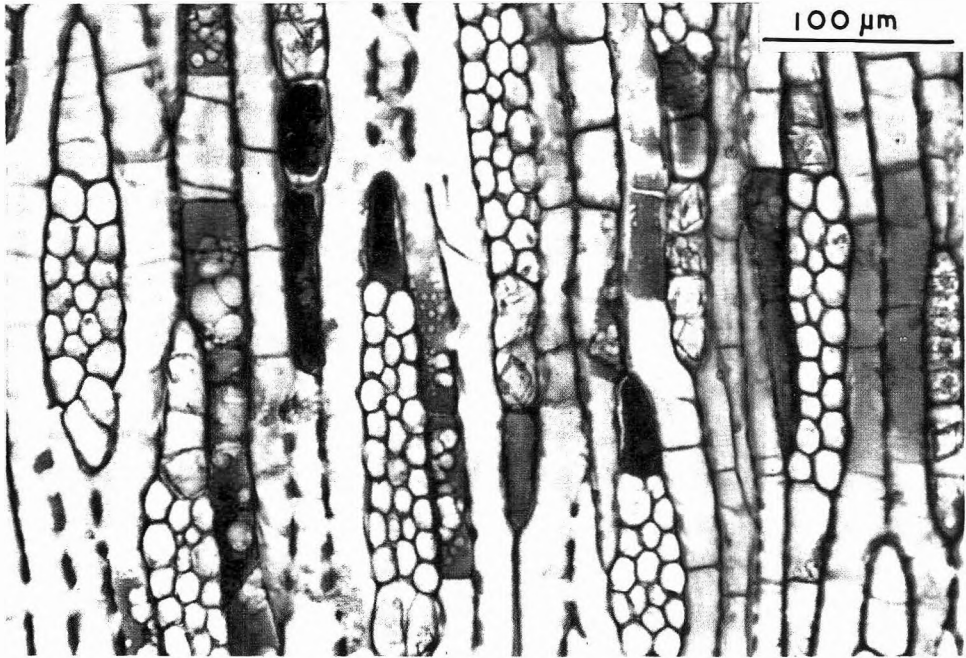


Figure 8. Occurrence of clear globules in tannin cells from affected tissue. All tannin cells do not display this phenomenon. Stained in safranin and fast green. Magnification 256 \times .

liquid latex is fairly certain. That they sclerify to form lignified elements in the tissue is very evident. It can be considered that the purpose of tylose formation is to prevent fluid loss from the laticiferous system. Questions such as to whether these are formed as a response to repeated, frequent injury, water stress or infection as in the case of xylem^{16,17,18} require further experimental investigation and study to elucidate.

Once tyloses are formed in the latex vessels, the latex contained in those vessels are found to be destabilised and coagulation *in situ* and blocked vessels result. Therefore, it is obvious that preventive measures should be aimed at events preceding tylose formation in the tissue. As far as we can surmise from present data, the instability of latex *in situ* is a matter for consideration *a priori*.

Evidence from electron microscopy indicates that in some latex vessels, a partial emptiness develops which manifests itself in the form of

low turgor pressure. It is possible that the turgor generation mechanism which involves the general ionic balance in the fluid contents of the tissue and the transportation phenomena in latex-bearing tissue is irreversibly impaired in such instances. From the observation of a low dry rubber content in such latex vessels, it may even be surmised that the biosynthesis of latex is perhaps adversely affected.

Factors leading to instability of latex may arise from perpetual deficiencies of water in the phloem tissue or the excessive presence of destabilising molecules or the absence of stabilising molecules in the colloidal system of latex. More research needs to be done but a start has been made in the recognition of the differences in levels of incidence in various precocious clones in certain agroclimatological regions²⁰. Considerable information exists on the vacuo-lysosomal complex of *Hevea* latex, the lutoids¹⁰. Although a theoretical connection exists between these factors, practical demonstrations are still lacking.

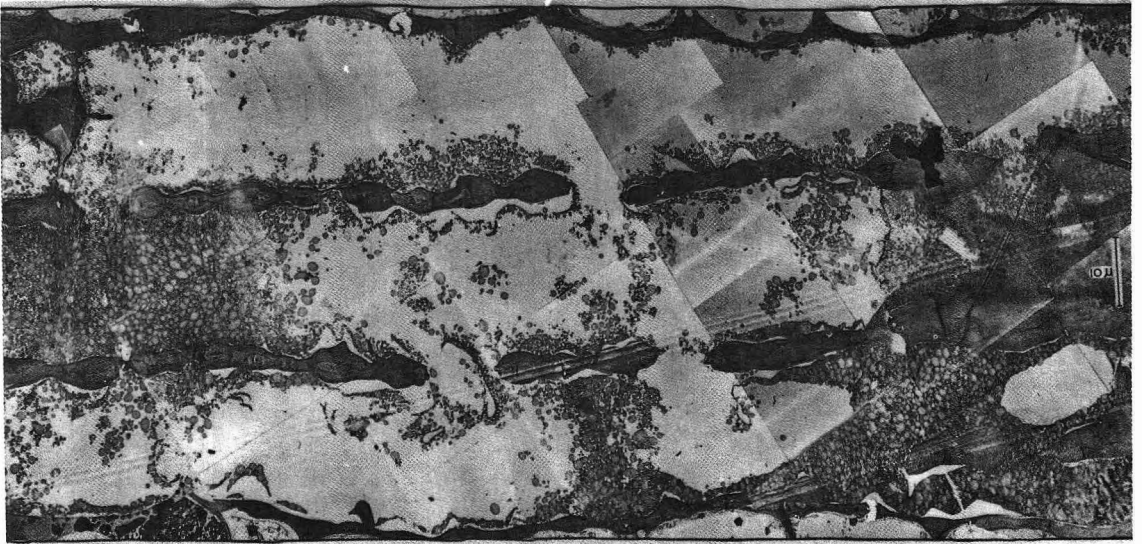


Figure 9. Montage of electron micrographs from a tree showing low turgor pressure. Note the partial emptiness of the vessel. Magnification 850 \times .



Figure 10. Montage of electron micrographs from a latex vessel with tyloses. 'C' denotes a calcium oxalate crystal. Magnification 1500 \times .



Figure 11. Electron micrograph of a latex vessel from a tree showing partial dryness. Note the instability of the rubber particles. Magnification 50 000 \times .

As discussed in an earlier paper¹², the primary causation for brown bast may be a wound reaction as the severity of the disease is related to the intensity of repeated wounding of the tree. The expression of the trauma is seen

in long rested brown bast trees in the form of excessive meristematic activity, adventitious xylem formation and certain changes in the laticiferous system and adjacent tissue. From all studies conducted so far, the basic change

in the laticiferous system appears to be the development of latex instability prior to the formation of anatomical symptoms of the disease. Admittedly, tylose formation, gummosis and other phenomena are triggered by physiological changes in the tissue, which are yet to be discovered.

Jacob and Prevot¹⁰ take the view that bark dryness can be due to many causes. While they accept that over-stimulation and over-exploitation can cause bark dryness, the histologic symptoms are those caused by traumatic or infectious attack.

Events such as acceleration of phenolic metabolism, cell necrosis and wound gum formation, sclerification of certain cells, adventitious xylem formation, general increase in meristematic activity can all be caused by changes in basic hormone levels or induced enhancement of hormone levels or metabolic levels and this in turn can be accentuated by the wound reaction the tree is subjected to. It would therefore be possible that the entire latex outflow area may not be affected in the expression of the wound reaction but an intensively regenerating zone of bark in the drainage area may be the central point from which the wound reaction phenomena emanate. Investigators of brown bast physiology are therefore advised to look for changes in the 'maximum regeneration zone' for the earliest signs of change.

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Breeding Horizontal Resistance to South American Leaf Blight of Rubber

N.W. SIMMONDS*

A scheme to breed polygenic (horizontal) resistance (HR) to South American Leaf Blight (SALB) of rubber is proposed. It is based upon biometrical genetic principles and analogy with successful HR to diverse diseases in other crops. There is already some experimental evidence of the existence of low levels of HR to SALB in rubber and fairly rapid response per generation could reasonably be expected. The objective would have to be concentrated on breeding resistant crown clones and the work would have to be done in the field in a place where SALB was reliably epidemic.

Of all the diseases of rubber, South American Leaf Blight (SALB), due to the Ascomycete fungus *Microcyclus ulei*, is potentially the most damaging. However, because it is yet absent from South-east Asia, it is of little direct economic importance. The history of the disease in its native haunts in the Amazon and of the several failed efforts to control it by breeding have been well documented^{1,2,3}. In anticipation of its possible introduction to Asia, the Rubber Research Institute of Malaysia (RRIM), many years ago, initiated research in South America, which continues today and has recently yielded some results⁴ highly germane to the present paper. Previous breeding efforts have all failed because they employed Vertical Resistance (VR) which failed under the evolution of new pathotypes and was genetically quite inappropriate to the circumstances^{1,5,6}. The biologically sensible response is to exploit instead Horizontal Resistance (HR), a fact which has had limited appreciation for some years^{6,7} but the practical, genetical and economic implications of which have never been explored.

The purpose of this article is to use our developing understanding of HR in crops in general and of new information on rubber research to propose an outline of a breeding strategy against the disease.

HORIZONTAL RESISTANCE

General Features

The main features of HR have been stated by the original inventor of the term, Vanderplank^{8,9}; his ideas have been extended and many extra examples adduced by authors of diverse books^{10,11,12} and review articles^{13–17}. It is now, in effect, conventional wisdom that HR is essential for countering most mobile airborne, fungal pathogens because, against these, VR has, with few exceptions, failed. SALB has, of course, been no exception^{1,5} and the necessity for HR has been clear for some years⁶.

To generalise (and accepting that many minor qualifications could be made) our understanding of HR yields, the following points relevant to rubber breeding are made:

- HR is polygenically controlled, subject to environmental errors, continuously distributed and can only be analysed by biometrical methods.
- ‘Polygenic’ does not have to imply ‘many’ and, indeed, what evidence there is (none of it really critical) suggests quite few, generally less than ten often less than five, genes.

*Edinburgh School of Agriculture, West Mains Road, Edinburgh EH9 3JG, United Kingdom

- The polygenic HR tends to be quite highly heritable (h^2 is often about 0.5–0.8, meaning that genetic variance is large relative to environmental variance), variance is largely additive and response to selection is good. Clonal propagation is technically favourable because it permits good control of error and therefore efficient selection.
- HR has diverse physiological components, including resistance to infection, prolonged latent period, slow lesion growth, reduced sporulation, *etc.* but, whatever the components, the outcome is simply ‘less disease’, rarely or never ‘no disease’ (= immunity).
- In practice, quick visual scoring is, indeed must be, employed and refined tests are rarely either practicable or necessary.
- If laboratory/glasshouse tests are used, they *must* be statistically validated against field experience; the field is the ultimate arbiter.
- All tests, of whatever kind, must incorporate control varieties that preferably span the range from very resistant to very susceptible; this is because seasons and sites vary and environmental variance may be substantial.
- There may well be interactions in mixed plantings^{8,9} leading to what has been called ‘representational error’, ‘cryptic error’ or ‘interference’; thus the more resistant entries may be subjected to more severe infection pressure than they would suffer in a pure stand and the more susceptible entries to less severe infection; therefore there is a risk of biased means and variances and accurate judgements can sometimes be made only on large plots.
- Ideally, selection for HR is carried out in the absence of VR genes but it is rarely feasible wholly to purge a population of them, so it is often necessary to ensure that virulent pathotypes are available and encouraged to spread.
- Test sites must be carefully chosen; the ideal (rarely exactly achieved) is a reliable, regular, middling-severe epidemic every year. A common jargon word for a good site is ‘hot-spot’ but it should be recognised that there is initially a risk of choosing too hot a spot and killing everything; later in a programme, very severe selection may be appropriate.
- Much experience with many crops says that, if a new HR is needed, it may initially be hard to find more than traces of it but that effective genetic variability is always there and well-judged selection will be effective in constructing HR. The emphasis is nearly always on constructing rather than on finding.
- HR, once constructed, is stable/durable indefinitely and is not subject to the disastrous boom-and-bust cycles that have characterised misused VR; whole crop populations that have come into equilibrium with a disease, following wide exploitation of HR, need little further attention in that respect. Predominant genetic additivity ensures that quite weak selection against the most susceptible segregates suffices to maintain equilibrium.

HR to SALB in Rubber

There is yet no genetical evidence for HR to SALB in rubber but there is persuasive evidence of variation in components of HR such as those listed above. Hashim and Pereira⁴ have examined lesion size, latent period and sporulation on leaf discs *in vitro* of numerous clones tested against several SALB

isolates/pathotypes. VR is plainly recognisable (and discountable) and clones demonstrably differ in expression of non-VR components of attack. Most strikingly, all three components are correlated across clones and four clones stand out on every criterion examined (Figures 1–3 of Hashim and Pereira⁴). They are GT 711, RRIM 501, CNSAM 7701 and SIAL 842. The first two clones are Asian, the second two are Brazilian and the latter carry R-genes already nullified by virulent pathotypes used in these experiments. Nevertheless, there is plainly HR concealed beneath the ineffective VR (and same could well be true of other clones in the material).

Elsewhere, Darmono and Chee¹⁸, studying lesion size on leaf discs, identified SIAL 263 (illegitimate progeny of RRIM 501) as outstandingly resistant but lacking detectable VR. There is clearly, therefore, immediate evidence of HR in Asian *Hevea brasiliensis* material and an indication that an orderly search of RRIM 501 relatives could be profitable. Results obtained by Hashim and Pereira⁴ are so striking that a composite diagram based on their data seems worthwhile (Figure 1). The four leading clones are plotted and the distribution of the rest indicated by the 'envelopes'. RRIM 600 has been added to the clones specifically identified because it is consistently among the best and was remarked upon years ago in Trinidad as probably having a little HR^{3,6,7}.

The evidence for *some* HR in *Hevea* clones is therefore good but the level of it as judged by field performance in substantial clonal blocks is not known. It is doubtful whether the available HR is yet good enough to be practically useful. Material to start a programme to construct HR exists and more must surely be discoverable.

Assuming, therefore, that traces of HR already exist and that a supply of starting material is assured, several assumptions must be made before a broad breeding strategy can be stated. They are as follows:

- The objective of SALB resistance breeding must be the production of

crown clones that have enough resistance for practical purposes; immunity is both infeasible and unnecessary. The main genetical and statistical features of crown breeding have been stated elsewhere¹⁹⁻²³ and one recalls that crown effects are strongly additive while disease resistance is tissue-specific. Hence there is no reason to fear conflict between the components of crown performance; indeed HR would normally be essential for good performance.

- From the literature survey above, it is reasonable to assume fair heritability, relatively small numbers of additive genes and good response to selection.
- Since the population is starting from, in effect a zero position, it would be prudent to assume that resistance genes will be rare and that statistical thought must therefore be given to population sizes.
- From the preceding, it also follows that the starting population should be on a wide genetic base and that fairly quick, rough means of handling large numbers must be invented. Certainly, a simple and repeatable field assessment system must be developed and validated as to economic implications; also, acceptable standards must be critically identified, as soon as possible.

GENETIC FEATURES

Assumptions

There are three points to make; two are concerned with developing disease resistance and one is of a more general nature.

First, the breeder seeks to assemble into single clones on increasing sample of five different + alleles, two at each of five independent loci, therefore 10 in all. It is assumed further that the + alleles are

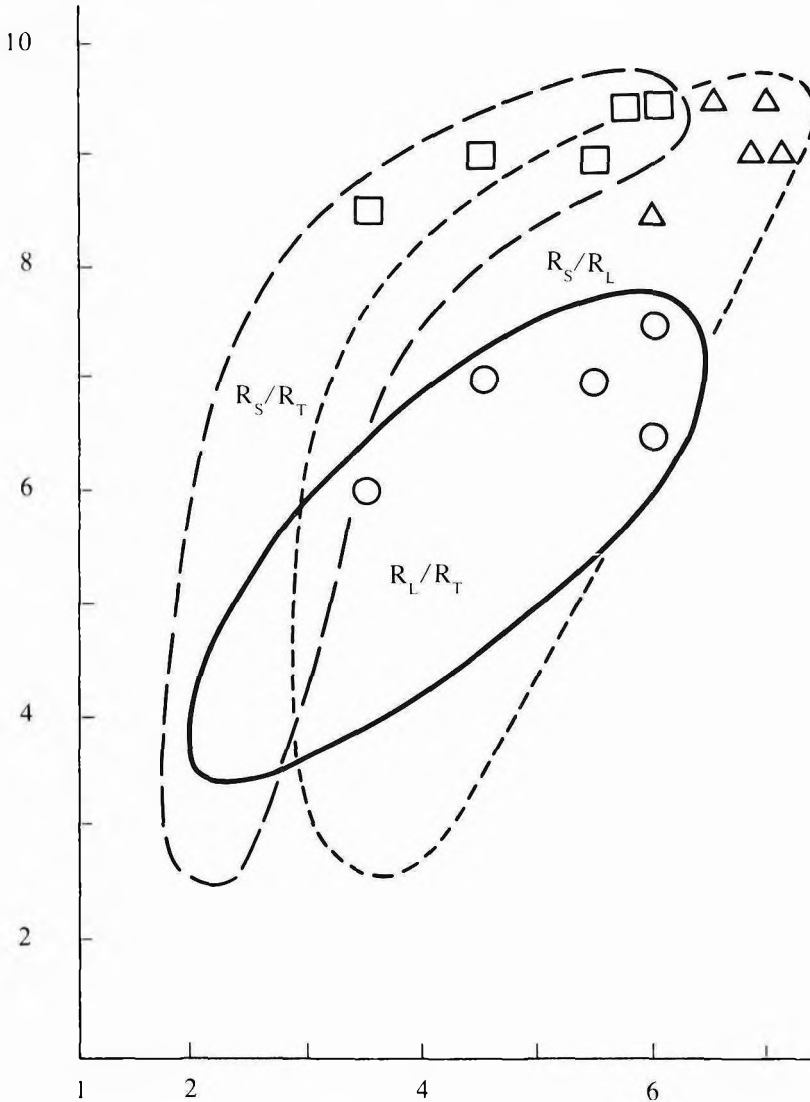


Figure 1. Correlations between components of horizontal resistance. Original data from Hashim and Pereira⁴ converted to arbitrary scales of resistance (R): R_s sporulation, R_l lesion size, R_t latent period. The four leading clones identified in the text and RRIM 600 are plotted explicitly and other points are indicated by the envelopes.

additive in action and that each contributes one unit of resistance. The range of resistance is therefore 0 (nil, very susceptible) to 10 (very resistant). Allele frequencies are denoted $f_+ = 0 \dots 1.0$. The genetic variance of resistance will be zero at both ends of the range

(when $f_+ = 0$ or 1.0) but in mid-range, $f_+ = 0.5$ and genetic variance (V_G) will be given by $npq = 10 \times 0.5^2 = 2.5$ and $\sigma_G = 1.58$. Assume also that the error variance (V_e) is unity so that, at mid-range, heritability is high: thus $h^2 = 2.5/3.5 = 0.71$ or 71%.

But it will, of course, be much less if f_+ is near 0 or 1.0. Progress under selection is therefore easily calculated or simulated.

Second, consider the matter of gene frequencies and population sizes necessary to give reasonable confidence of not losing desirable + alleles which may start at very low frequencies. We wish to define a sample size, N , such that we have a good chance (say 95%) of retaining at least one sample of each of $r +$ alleles. For necessary simplicity, suppose that all r alleles share a common low frequency, f_+ . Then it can be shown that:

$$(1 - f_+)^N = (1 - \sqrt[r]{0.95})$$

$$N = \frac{\ln(1 - \sqrt[r]{0.95})}{\ln(1 - f_+)}$$

We are assuming $r = 5$ loci, therefore:

$$N = \frac{-4.59}{\ln(1 - f_+)}$$

For $f_+ = 0.5\%, 1\%, 2\%$ we have $N = 915, 456, 227$ respectively. The numbers do not change much in the range $r = 3$ to 6 so the choice of $r = 5$ is not critical. Therefore, an initial random sample of only a thousand or so alleles should be adequate, or about 500 plants, since each plant has two alleles. A sample of 1000 plants should suffice for $r = 10$ and $f_+ = 0.5\%$. The initial needs are therefore quite modest but they are not in fact critical, as we shall now consider.

Having established that small initial samples would do, the more difficult question is to look for the size of the *selected* sample to preserve all $r (= 5) +$ alleles. Clearly, if selection is effective then f_+ rises and numerical demands are eased; and if it does not, we are wasting our time anyway. We are assuming fairly high heritability and, under the stated assumptions, simulation shows that any low f_+ is at least doubled by a cycle of selection of intensity in the range 1%–20%. To assume doubling is therefore conservative and we can conclude that even if initial f_+ were as low as about 0.5%, selected samples as small as 200–300 should

suffice to preserve all the desired alleles. This conclusion can, of course, be inverted to calculate a limiting selection rate for resistance which it would be prudent to adopt given an initial randomly selected population. Thus, if the population were 10 000, it would be wise to keep at least 250 (or 2.5%) selections but a subsample could well be selected more intensely without greatly increasing the chance of loss. After some progress had been made and f_+ had risen to 5%–20%, intense selection (< 1%), keeping selected samples of size about 20–100 would generally be quite safe for allele conservation.

To conclude, therefore, the time to be cautious is in the first cycle. It would be prudent to preserve a generous sample of selections from it but selection could become more stringent as soon as there were good evidence of progress.

The third point is rubber is an outbreeder that suffers severe inbreeding depression but is, nevertheless, quite often self-pollinated. The one available estimate suggests about one-quarter selfed seedlings at the nursery stage¹⁹. These would have to be discarded as ‘runts’ because, whatever SALB resistance they might have, selfs would be most unlikely to make acceptably vigorous seed parents or crown clones. Allowance for such discards should in principle be made in calculating numbers to be planted but in practice, the point is quite non-critical.

Model

The results of simulating selection at five rates from 1% to 20%, are shown in *Figure 2*. In the early generations, population sizes big enough to ensure that no + alleles were lost, were chosen. Obviously, the more intense the selection, the faster the progress and any decision to select intensely would have to be balanced by the use of large populations and numerous selections, as discussed above. Even at 1%–2% selection rates, it looks as though five generations might be necessary before high resistance was closely approached. Sustained responses of this order of number of generations are reported in the literature¹⁷.

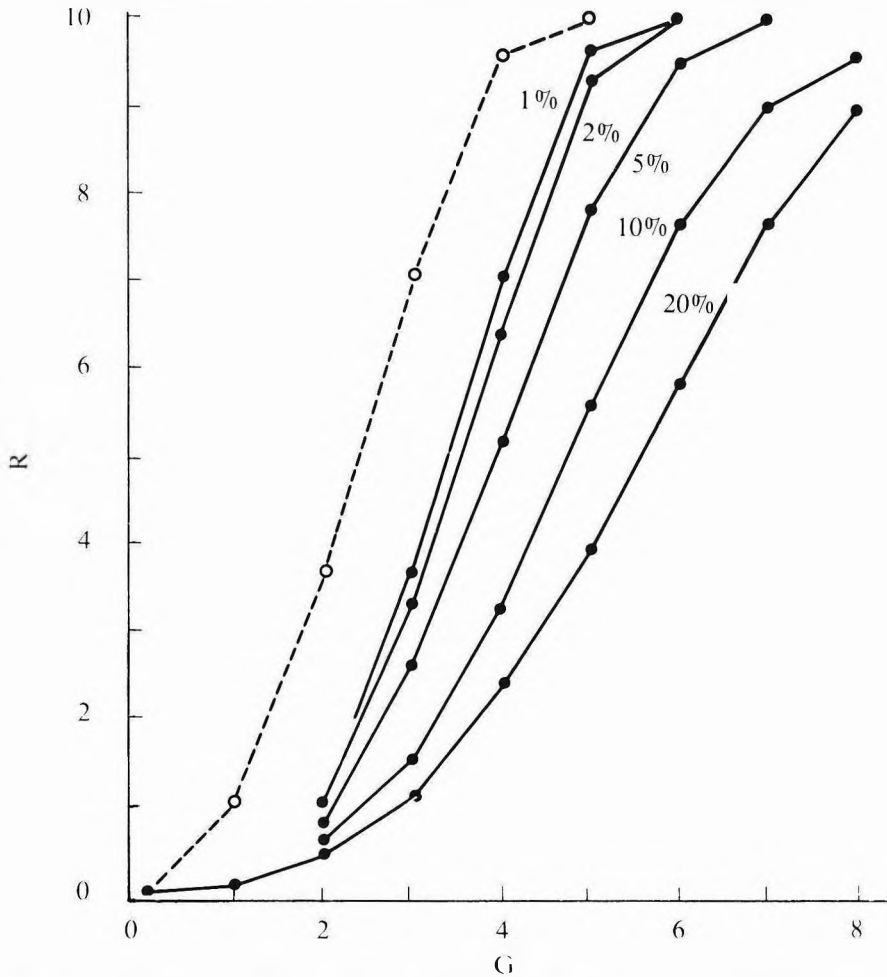


Figure 2. Simulation of response to selection for resistance (R) to SALB plotted against generations (G). Five levels of rate of selection (1%–20%) are shown. The dashed line on the left indicates the order of response that might be achieved by intense selection (1%) if initial + allele frequency were high (2%).

However, five generations of selection, though probably acceptable to a breeder of an annual crop, would be a discouraging prospect for the rubber breeder. Inspection of *Figure 2* suggests that a reasonable strategy to accelerate progress would be to try to move an intense selection curve to the left. This would imply very large initial populations, intense selection and, of course, growing of big enough parental pools to keep the risk of loss of + alleles acceptably low. If initial + allele frequencies were higher than one might guess, then early progress might be better than expected.

The curves plotted in *Figure 2* are based upon random mating among the members of each cycle of selection. Since the assumed heritability is less than unity, better progress could be achieved by cloning and re-testing each set of selections before using them as parents. This, however, would take time and it would seem preferable to do what is suggested below, namely to sacrifice efficiency for speed and intensity by using open-pollinated seed-garden seeds from the main bodies of selections and concentrating hand-pollination activities on a minority of the phenotypically best trees. In any

case, if selection were fairly intense, there would be little room for further selection and assortative mating among potential parents.

BREEDING STRATEGY

Principles

The preceding discussion leads to the following list of principles that should be observed:

- The objective is to breed vigorous and SALB-resistant crowns. Latex yields are irrelevant.
- Starting populations should be large, containing both numerous clones and random seedlings.
- Clones should be randomly replicated so that survivors can be made to yield estimates of 'clonal repeatability' (in effect broad sense h^2) of HR to SALB.
- In selection, a flexible strategy should be operated, the very best-looking selections being clonally propagated, the rest left to constitute seedling seed gardens. Thus, intense selection could be practised safely, in the knowledge that back-up populations had been preserved if it should turn out that heritability and progress were not so good as might have been hoped.
- Every cycle must start from seedlings produced by selected parents. Open-pollinated seedlings from selected clonal seed gardens should be quite good but it would be sensible to employ hand-pollination to ensure genetic recombination between any outstanding plants that might be identified. It should be noted that open-pollinated seed-progeny from an outstanding parent with not-so-good neighbours as pollinators might be superior but would be less promising than those derived from deliberate crossing. In effect, heritability would be reduced.
- As soon as possible, standard clones should be identified and planted generously in all plantings. Ideally, the standards should cover a range from highly resistant to as susceptible as will survive in the chosen site. These, however, could not become available very quickly. A start would have to be made with any available clones that lack VR and would survive. The two Asian clones, GT 711 and RRIM 501, mentioned by Hashim and Pereira⁴ and SIAL 263 noted by Darmono and Chee¹⁷ might be clones to start with.
- The scene of operations must be where SALB is reliably epidemic. A standard scale of resistance must be invented, say 0 (very susceptible, lethal) to 9 (highly resistant). The scale must be validated by reference to performance of clones in a pure stand. In particular, the scale point at which resistance was adequate for commercial cultivation would have to be explicitly identified. Obviously, a visual scale would have to be based largely on defoliation (canopy density) and lesion development.
- Plant material having VR genes should, as far as possible, be avoided, since transient immunity is the last thing that is wanted. However, some VR would probably get through, in which case the breeder would have to decide whether to destroy it or use specialised fungal races to detect it. If the latter seemed necessary, some laboratory operations would probably be essential but the breeder would recall that this is a plant breeding programme that should on no account be allowed to become a pathotype-hunting or VR study. Some back-up research would be needed in this connection if the confusing effects of useless VR were to be negated.

- There is another pathological matter which might deserve some research and of which the breeder should certainly be aware. In any stand of plants heterogeneous for a HR, there is a tendency for plant-to-plant or plot-to-plot interaction such that susceptibles are over-scored and resisters under-scored ('representational error'). This happens because plants are subject to spore loads from neighbours different from what they would suffer in a pure stand⁸. Thus 'apparent' genetic variance is diminished and discrimination is made more difficult. We at least need to know whether this happens in the case of SALB. It probably does but a good answer can only come from experiments in which extensive clonal response data from both nurseries and substantial pure-stand blocks can be compared. In the interim, the breeder might have to be prepared to try to discriminate rather finely in mixed stands.
- Finally, potential parent plants that have survived a selecting/thinning process would be required to yield seeds as quickly as possible. Therefore, the trees should be very generously treated, well cultivated and well sprayed (at whatever cost) to minimise defoliation by SALB (or other fungi). In practice, this should pose no acute problems because the trees would be young and small and required to yield only modest seed harvests before they were either discarded or placed on a 'care-and-maintenance' regime. Seeding might be expected to begin in about five years and be complete in about six.

Practice

The principles just outlined are drawn together in practical proposals, summarised in *Figure 3*.

Starting at the top left of the diagram, the basic requirement would be genetically diverse seedlings and clones from very many sources. As far as possible, VR should be avoided but this might be a council of perfection. A relatively high frequency of VR genes in at least some materials is evident in the literature^{4,7,18}.

Next, a site somewhere in the American tropics and subject to reliably epidemic SALB at high but not extreme intensity would be required. The land should be good and management should be competent to grow young rubber fast and well. Sizes of initial plantings are not accurately calculable, about 10 ha of seedlings and clones with 1000 plants per hectare would, in the light of preceding considerations, be appropriate. The plants would be selected visually and progressively thinned, leaving no more than 200 plants/ha at four to five years. These densities are based upon spacing experiments and seed garden practice reviewed by Webster and Baulkwill²⁴.

Of the 10 ha or thereabouts to be planted, most should be committed to very diverse seedlings drawn from seed gardens, genetic collections, old South American plantings, *etc.* Calculation is impossible but it can be estimated that 8 ha of seedlings and 2 ha of clones would be about right. Again, the clones should be as diverse as possible. Two thousand plants would accommodate a lot of clones reasonably well replicated to help to validate the scoring procedure.

The outcome would be at most about $10 \times 200 = 2000$ selected plants. If the populations were so susceptible or the attack so severe that large numbers of entries died, then there might be fewer than 200 seedling trees left per hectare. All especially promising looking trees would be cloned into a clonal seed garden and the very best, if sufficiently promising, would be tested as crowns in substantial blocks of commercially managed rubber.

The resulting seedling 'seed gardens' would be erratically spaced and would differ fundamentally from conventional clonal seed gardens. Orderly layouts designed on statistical principles¹⁹ are therefore not at issue.

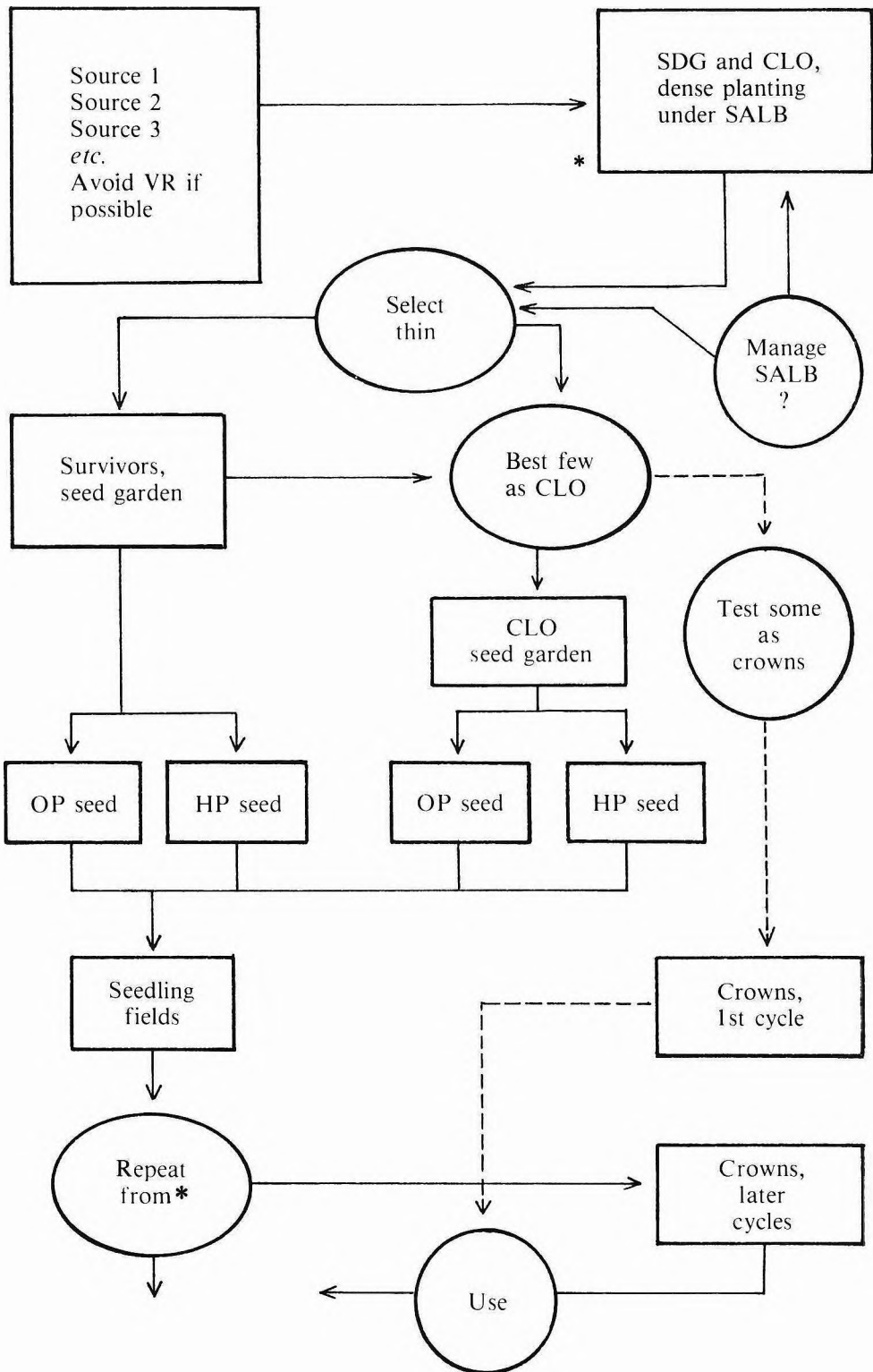


Figure 3. Scheme for mass selection of HR to SALB in rubber crown clones.

Near the top right of *Figure 3* there is reference to the management of the disease. This is a reminder that it might be necessary to disseminate pathotypes virulent to unavoidable VR in the populations. Some parallel laboratory testing might also be relevant in this context and the identification of usable standards would have to be actively pursued. But any and all such pathological activities would be subservient to the primary objective, namely breeding SALB resistant crowns.

At this point, the programme would be established and about to start on its second cycle. The seed gardens, whether seedling or clonal, would have yielded seed (some open-pollinated, some hand-pollinated) and new seedling fields would be on the way to establishment. Synchronous planting would be impossible because the several seed sources would be spread over time and rubber seed must be sown very soon after harvest. Detailed planting plans for the second cycle would have to be developed in the light of experience. In particular, improved scoring methods, and knowledge of heritability and response to selection, would affect judgments. It is not surprising to learn that first cycle response turned out to be so good as to suggest the feasibility of more strongly assortative mating, intense selection and rather high frequencies of formal crown-testing. But sensible decisions could only be made on the basis of proper biometrical analysis of first cycle results.

Though the programme described is essentially a highly practical plant breeding operation, it should go without saying that both genetic and pathological skills would be needed and that orderly records of field plans, numbers of plants, scorings and decisions should be kept. The data would be crucial for any rational biometrical calculations as to procedures to be adopted in the second cycle.

DISCUSSION

There are six points to make. First, the prospects of success must be judged to be good at the purely technical level of producing usable

crowns. From experience, effective HR to any fungal pathogen can be constructed if needed; there are no significant exceptions to this rule. In time, therefore, SALB should be reduced to the sort of status that Gloeosporium Leaf Disease (GLD) (*Colletotrichum gloeosporioides*) has long had in Malaysia^{2, 5}. It is a nuisance that can well be coped with by discarding some too-susceptible clones and using Enviromax principles²⁴ sensibly.

Second, supposing that SALB eventually becomes generally distributed then rubber agriculture would simply *have* to employ the complementary crown-trunk breeding strategy proposed here and previously outlined elsewhere²⁰⁻²³. Rubber breeders are, indeed, fortunate that they can contemplate such a venture rather than the immeasurably harder one of breeding resistant but high yielding clones *de novo*. Separate breeding of crowns and trunks is intrinsically attractive whether or not SALB is at issue²⁰.

Third, SALB-resistance can only be generated by a breeding programme conducted in the field under natural SALB attack. It is idle to suppose that any other procedure would be practically feasible. A breeding centre in the American tropics is implied and a strong international element in funding and running the enterprise for the general good is ineluctably implied too. Some political vision and resolve would be essential. Results would not come quickly if two or three (or more) cycles of selection were needed and sponsors would have to accept this fact at the outset, along with the necessity for continued expenditure. They would no doubt reflect however that such expenditure is probably an essential pre-condition for the very survival of the NR industry. As a long-term perennial, rubber poses some especially formidable problems¹².

Fourth, *apropos* the statement made above that progress (per cycle) in developing resistance is likely to be good, it is worth recalling that plant breeding history is replete with cases of spectacular successes against epidemic diseases that were at first devastating, for example: potato blight in the very susceptible Andean

potatoes introduced to Europe and North America; maize rust (*Puccinia polysora*) introduced to the African tropics from America in the 1940s; coffee berry disease that emerged from wild bush coffee in upland East Africa; a stream of damaging diseases which have gone round the world attacking sugar cane but have been almost universally (and very quickly) controlled by breeding¹².

Perhaps a closer analogy to the SALB problem, however, is offered by the *Cronartium* rusts that attack the loblolly and slash pines of the south-eastern USA. US tree breeders have had to take these diseases very seriously and have adopted a mass selection approach among thinned seedling stands rather like that proposed here for SALB^{25, 26, 27}. Both HR and VR are involved but it is not clear how the hazards of misplaced VR are to be coped with. First signs of progress look quite good.

Fifth, we have a technical point about population sizes. Calculations for the SALB problem suggest population sizes that, intuitively, might seem remarkably small. A few hundred plants to preserve a system of (presumptively) rare polygenes does seem few but the principle is long established and well explored in the literature^{28, 29}.

Sixth and finally, the correlations between the components of HR revealed by the work of Hashim and Pereira⁴ and summarised in *Figure 1* are very interesting. They would seem to imply an underlying correlation inherent in the plant's response to SALB. Such correlations have been found elsewhere and would not be surprising in genotypes that were the product of several cycles of selection for HR. Indeed, correlated responses could almost be predicted but it is perhaps surprising to find correlations there before selection. Perhaps there has already been more selection than thought. Genetic studies of HR in rubber in this context will be of extraordinary interest.

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Composition and Cure Behaviour of Skim Block Natural Rubber

G.M. BRISTOW*

Test data covering composition, cure behaviour and ageing resistance for eight samples of skim block rubber are presented. The influence of both natural fatty acid and protein content on cure behaviour is considered. The curing characteristics allow up to 20 p.p.h.r. of skim rubber to be added to normal natural rubber without addition of further curatives: a high level of vulcanisate properties is retained. For vulcanisate of comparable modulus, the ageing resistance of skim is found to be superior to that of normal natural rubber grades despite the presence of up to 30 p.p.m. of copper in the skim rubber.

Skim rubber is a material which results from the production of latex concentrate by centrifugation. After the centrifugation process, some 5% - 10% of the total rubber, together with an enhanced proportion of the non-rubber constituents of the original latex, remain in the serum phase to form 'skim latex'. Neutralisation and coagulation of this latex by appropriate methods then give 'skim rubber'. In the traditional plantation industry, skim rubber was often considered a by-product or even waste material, and was certainly regarded by most consumers as a very inferior material. In many respects, this opinion was justified. The product was variable in rubber hydrocarbon content and in the nature of the non-rubber constituents: this led to inevitable variation in cure behaviour and vulcanisate properties. Ageing resistance was often found to be very inferior. The materials also generally possessed a strong, offensive odour. Consistent with this opinion, skim rubber was specifically excluded from the 'Green Book' - the International Standards of Quality and Packing for Natural Rubber Grades and the Various Grades of SMR.

Production procedures to minimise these adverse features have been available for many years; several of these procedures are described by Edgar¹. Recently, such procedures have been applied more extensively. This, together with presentation in small (33 $\frac{1}{3}$ kg) bale form

rather than as creped sheets, has allowed the marketing of materials to be more attractive to the consumer. It must be emphasised, however, that despite the improved appearance and relatively less odour of these so-called 'skim block' rubbers, they inevitably retain many of the features of the traditional materials. In particular, the rubber hydrocarbon content is relatively low, normally about 80% compared with 93% - 94% for normal grades such as RSS, SMR L and SMR 20. Also, the type and high level of non-rubbers present give rise to rather slow, sometimes scorchy cures and to high modulus vulcanisates. The latter can be considered to arise at least in part from the protein present acting as a reinforcing filler².

Despite these potentially adverse features, skim rubber has always been favoured by some consumers. It has a low dirt content, often accompanied by light colour, and relatively low cost, even allowing for the reduced hydrocarbon content. The availability of modern skim block material is increasing and as a result of the rising demand for latex concentrate, it is likely that the supply will increase further. A review of the properties of skim rubbers therefore seems timely. This is the objective of the first part of this paper.

Blending skim rubber with normal grades of natural rubber is an obvious possible

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

approach to offsetting the adverse features of the skim material. The results of such blending are not entirely as expected, as shown by data presented in the second part of this paper.

EXPERIMENTAL

The samples of skim rubber were obtained directly from producers, from dealers' stocks or from end-users. There is no reason to suppose that they were atypical in any way. SMR L and SMR 10 were standard commercial materials, as were the various compounding ingredients. Raw rubber tests were performed using standard procedures on material mill-blended according to the method³ specified for SMR. Vulcanisate property measurements were made as specified in the appropriate British or ISO standards. Except where otherwise noted, references to vulcanisate modulus or rheometer torque are to maximum or optimum values of these properties.

Characteristics of Skim Rubber

Composition. The raw rubber properties of eight samples of skim rubber are compared with those typical of SMR L in *Table 1*. The samples show the expected characteristics: a nitrogen level indicating 10% - 15% protein content and a high level of acetone-extractable material, an appreciable proportion of which consists of a mixture of various fatty acids. These acids cover a similar range of carbon number and degree of unsaturation to those found in normal grades of natural rubber but the proportions of the various species may well be different. In terms of contaminant 'dirt' level, the skim samples are on the average substantially cleaner than SMR L but the ash content, which comprises all types of mineral matter, is some 50% greater. Another feature of skim rubber, noted many years ago⁴ is the high level of copper. This is perhaps ten to thirty times greater than that found in latex grades such as SMR L, or in centrifuged latex concentrate. Despite the high level, the copper appears to be inert as an oxidation catalyst, since, as shown in *Figure 1*, no correlation exists between copper

content and PRI, a measure of raw rubber oxidisability. Manganese is the other transition metal having potential as an oxidation catalyst and commonly present in trace amounts in natural rubber. In contrast to the high copper levels in skim rubber, levels of manganese are quite comparable to those found in normal latex grade SMR L. Presumably, the manganese is associated with the rubber phase of the latex, while the copper is present in the serum and is thus concentrated in the skim latex and finally co-precipitated with the rubber during coagulation.

Cure behaviour; ACS 1 test formulation. The cure behaviour of skim rubbers in the standard ACS 1 test formulation:

<u>Parts by weight</u>	
Natural rubber	100
Zinc oxide	6
Sulphur	3.5
Stearic acid	0.5
MBT	0.5

is rather different from that observed for normal grades of natural rubber. Typical rheographs are given in *Figure 2* and further data in *Table 2*. Vulcanisate modulus and rheometer torque are much higher than observed for even 'high modulus NR' and, though initial cure rate is relatively high, the time to maximum torque is relatively long. These features are further demonstrated in *Figure 3*. Cure rate, expressed as rheometer t_{90} , is relatively low and fails to follow the usual inverse dependence on rheometer torque or modulus. Similarly, scorch time, t_{s2} , is shorter than would be anticipated from the $t'_c(90)$ value (*Figure 3*). For the present samples, an excellent correlation exists between rheometer torque and vulcanisate modulus but there are indications, as shown in *Figure 4*, that correlation is not continuous with the less well defined correlation found for various normal natural rubber grades.

Skim rubber differs most obviously from normal natural rubber in the high levels of fatty acid and protein present. Either or both of these could be responsible for the observed

TABLE 1. RAW RUBBER PROPERTIES AND CURE BEHAVIOUR IN THE ACS 1 FORMULATION FOR EIGHT SAMPLES OF SKIM RUBBER

Property	Sample										A - H Mean C.V(%)	Typical SMR L
	A	B	C	D	E	F	G	H				
Mooney viscosity, ML 1 + 4, 100°C	91	62.5	88.5	86.5	93	100	63.5	89.5	84.3	16	90	
Wallace plasticity, P ₀	36	29.5	43	44	46	41.5	28	42.5	38.8	18	53	
Plasticity retention index, PRI	26	76	44	71	37	5	11	83	44	68	80	
Nitrogen content (%)	1.95	2.17	2.11	2.27	2.51	2.16	1.57	1.74	2.06	15	0.4	
Ash content (%)	0.42	0.33	0.42	0.27	0.53	0.45	0.32	0.44	0.40	21	0.25	
Dirt content (%)	0.002	0.017	0.002	0.002	0.002	0.012	0.037	0.036	0.014	-	0.01	
Acetone extract (%)	6.87	7.30	10.44	9.70	7.04	7.56	8.69	4.86	7.81	23	2.8	
Free fatty acid content ^b (%)	4.03	3.44	5.30	5.21	2.18	3.50	5.11	1.58	3.79	37	0.8	
Copper content (p.p.m.)	14	24	11	10	28	18	14	22	18	37	1	
Manganese content (p.p.m.)	1.0	0.2	1.4	0.6	0.3	0.3	2.0	1.4	0.9	73	0.7	
Approx. hydrocarbon content ^c (%)	81	79	76	76	77	79	81	84	79	4	95	
Cure behaviour, ACS 1 cure system	13.8	12.8	16.7	17.5	15.2	13.7	14.1	11.4	14.4	14	6	
MOD value 140°C (kg/cm ²)												
Monsanto rheometer, 160°C, ±3°arc												
M _{HR} - M _L (torque units)	60.5	58.2	65.3	66.7	63.1	60.2	58.0	56.1	61.0	6	34	
Scorch time, t ₂ (min)	0.95	1.15	1.15	1.3	0.85	1.25	1.1	0.9	1.1	15	2	
Cure time, t _c (90) (min)	8.8	10.7	8.6	8.4	8.7	11.1	8.6	8.2	9.1	12	10	

^aMaterial in crepe form

^bFree fatty acid calculated as stearic acid

^cAs the acetone extract contains little or no nitrogen, hydrocarbon content can be estimated as 100 - % extract - (6.25 × % nitrogen)

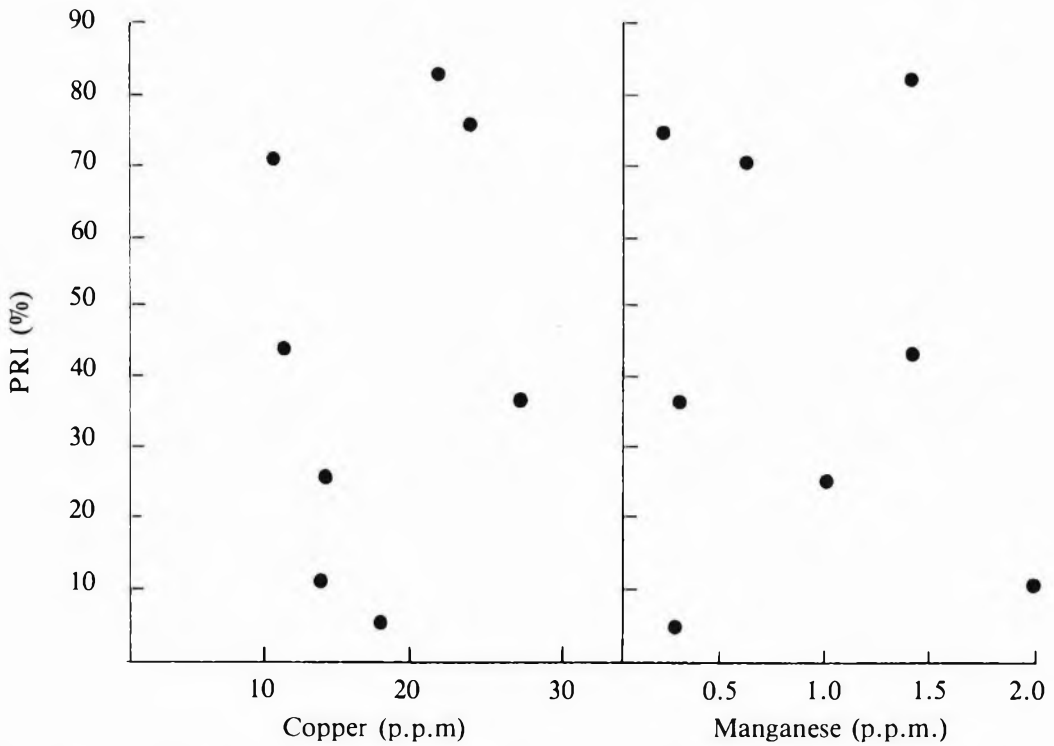


Figure 1. Plasticity retention index as a function of copper and manganese content for eight samples of skim rubber.

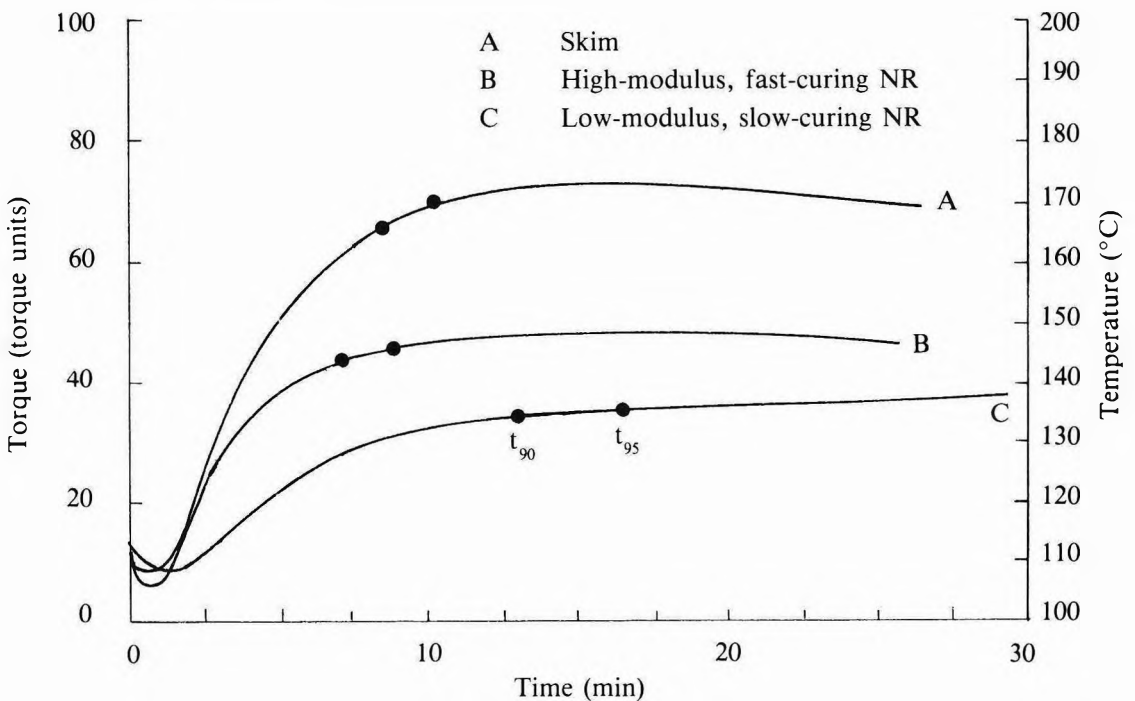


Figure 2. Rheographs for typical samples of natural rubber and skim rubber in the ACS 1 formulation.

TABLE 2. COMPARISON OF CURE BEHAVIOUR OF SMR 10 AND SKIM RUBBER - ACS 1 FORMULATION

Item	ACS 1		
SMR 10	100		
Skim A	100		
Skim D	100		
Zinc oxide	6	6	6
Stearic acid	0.5	0.5	0.5
Sulphur	3.5	3.5	3.5
MBT	0.5	0.5	0.5
Mooney scorch time, 120°C, t_{55} (min)	5.0	4.7	6.4
Monsanto rheometer, 160°C, $\pm 3^\circ$ arc $M_{HR} - M_L$ (torque units)	39.0	61.3	65.2
t_{52} (min)	1.2	1.2	1.2
t'_c (50) (min)	2.3	3.5	3.6
t'_c (75) (min)	4.5	5.9	6.0
t'_c (90) (min)	6.7	9.2	8.8
t'_c (95) (min)	8.3	11.0	10.6
t'_c (max) (min)	$\sim 13^{1/2}$	~ 16	~ 16

cure behaviour. The data of Figure 5 show that increasing the stearic acid level of the ACS 1 cure system does not reproduce the rheometer torque levels observed for skim rubber, nor is there a significant correlation between torque and fatty acid content for the various samples of skim. Similarly, while the high acid content of skim probably contributes to the relatively low cure rate, addition of stearic acid to the ACS 1 cure system in normal grades of natural rubber does not reproduce the relations observed between $M_{HR} - M_L$, t_{52} and t'_c (90) for skim rubbers (Figures 6 and 7).

There is rather more definite evidence for the participation of the protein content of skim in the vulcanisation process. Figure 8 is a log-linear plot showing the overall dependence of rheometer torque (or modulus) on nitrogen content (expressed as the typical range observed) for deproteinised natural rubber (DPNR), SMR 20, SMR L and skim. While an overall trend is evident, the significance of

the data is diminished by the lack of any standard natural rubber grade with nitrogen content in the range 0.5% - 1.0%. Within the various grades, the position is less definite; for SMR 20 and SMR L, there is no correlation between ($M_{HR} - M_L$) and nitrogen content (Figure 9), while even for the present skim samples, this correlation is of relatively low significance (Figure 10). So far as cure rate behaviour, as characterised by t_{52} and t'_c (90), is concerned, simple inspection of the data of Table 1 show there is no dependence of either of these parameters on protein content.

Cure behaviour; practical formulations. The high modulus of skim rubber so evident in the ACS 1 formulation is also apparent in more practical cure systems. Data for typical thiazole and sulphenamide systems are given in Table 3, though the relative behaviour of skim and natural rubber is more clearly demonstrated in the corresponding rheo-

TABLE 3. COMPARISON OF CURE BEHAVIOUR OF SMR 10 AND SKIM RUBBER - PRACTICAL FORMULATIONS

Item	MBT/S		CBS/S	
SMR 10	100		100	
Skim A	100		100	
Zinc oxide	5	5	5	5
Stearic acid	3	3	3	3
Sulphur	3	3	2.5	2.5
MBT	1	1	-	-
CBS	-	-	0.5	0.5
IPPD	2	2	2	2
Mooney scorch time, 120°C, t_{55} (min)	5.1	3.6	18.8	15.5
Monsanto rheometer, 140°C, $\pm 1^\circ$ arc $M_{HR} - M_L$ (torque units)	17.7	25.8	18.4	26.1
t_{51} (min)	2.2	1.7	8.7	6.0
t'_c (50) (min)	5.6	5.7	15.8	14.6
t'_c (75) (min)	10.0	10.8	21.2	22.9
t'_c (90) (min)	15.5	16.3	25.5	30.9
t'_c (95) (min)	18.8	20.0	29.4	37.6
t'_c (max) (min)	~ 30	~ 40	~ 44	~ 65

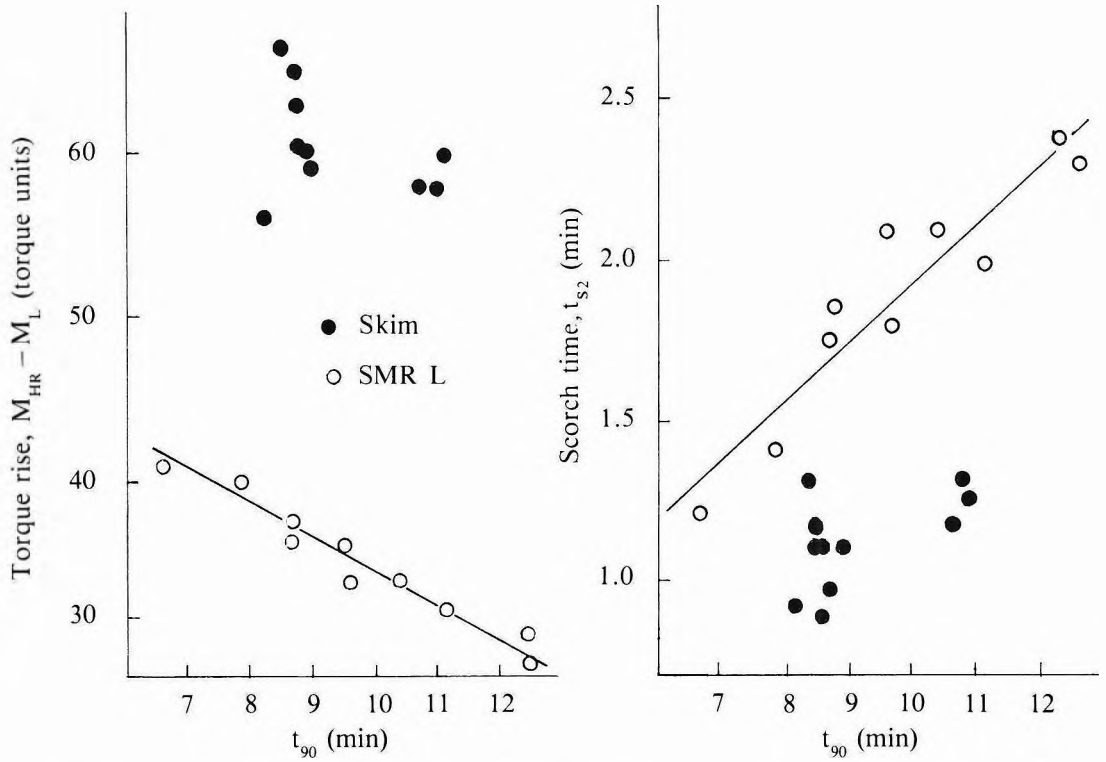


Figure 3. Rheometer torque rise and scorch time as functions of t'_{90} for samples of SMR L and skim rubber in the ACS 1 cure system.

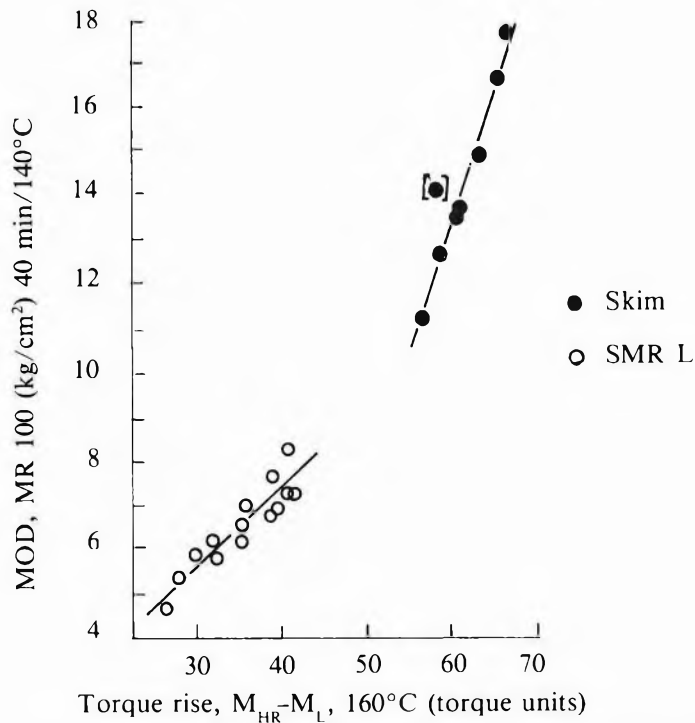


Figure 4. Vulcanisate modulus as a function of rheometer torque rise for samples of SMR L and skim rubber in the ACS 1 cure system.

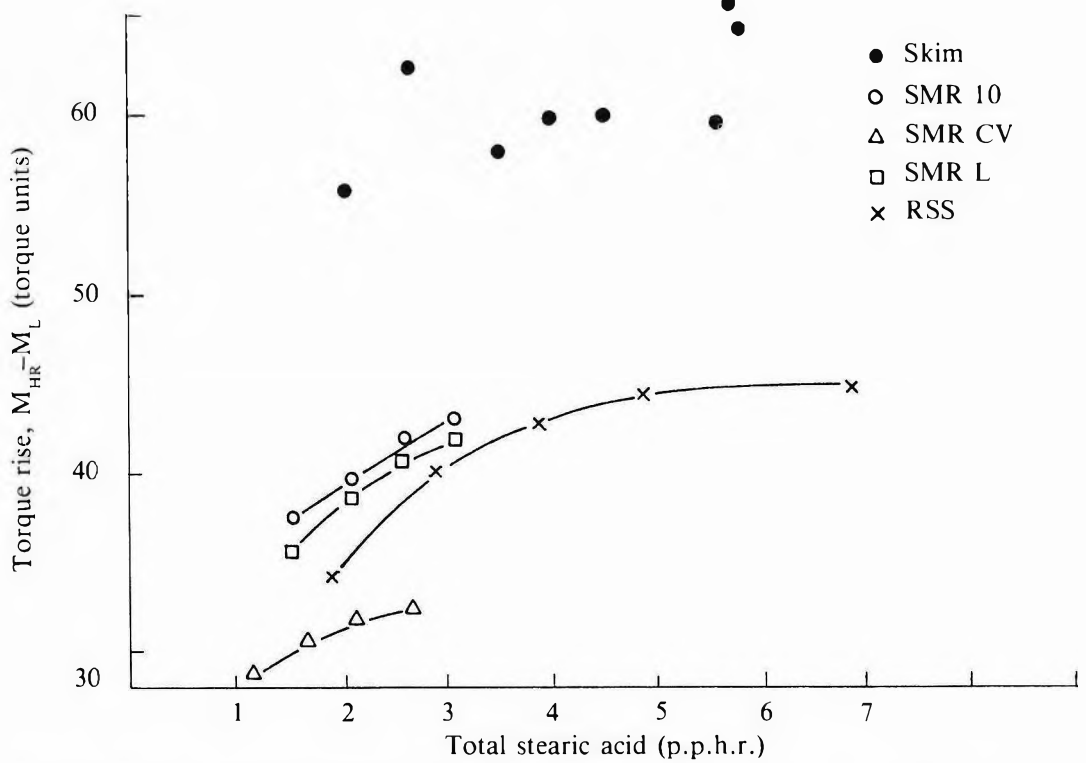


Figure 5. Effects on rheometer torque rise of the addition of stearic acid to the ACS 1 cure system.

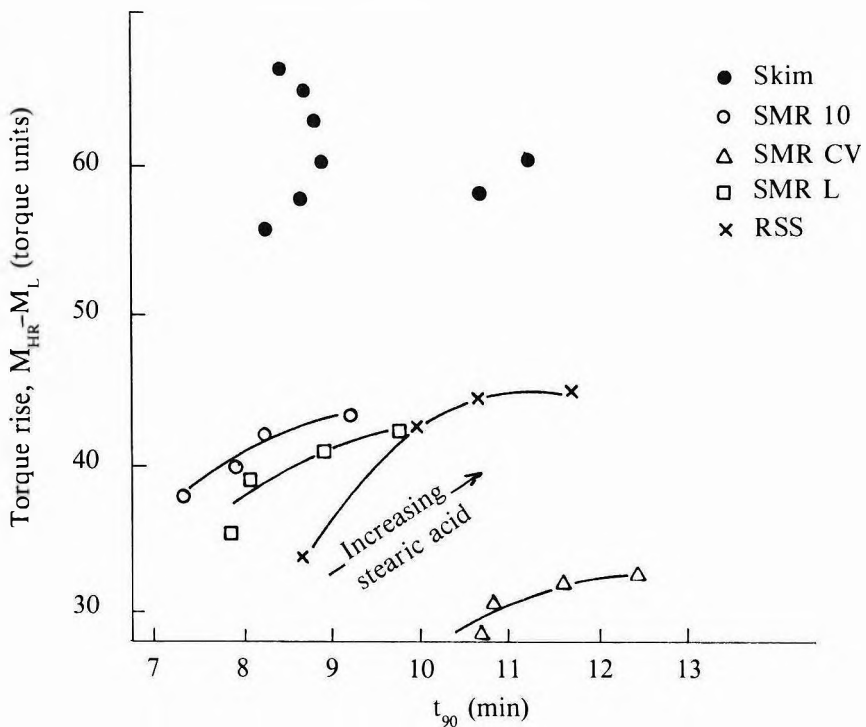


Figure 6. Correlation of torque rise and $t'_c(90)$ for ACS 1 systems containing additional stearic acid.

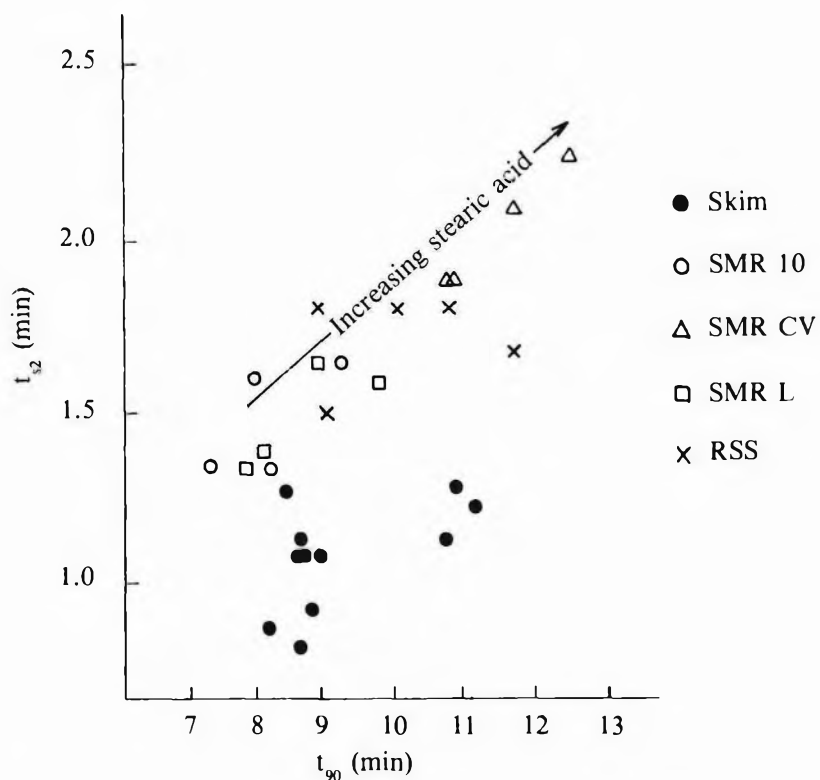


Figure 7. Correlation of t_{52} and $t'_{\zeta}(90)$ for ACS 1 systems containing additional stearic acid.

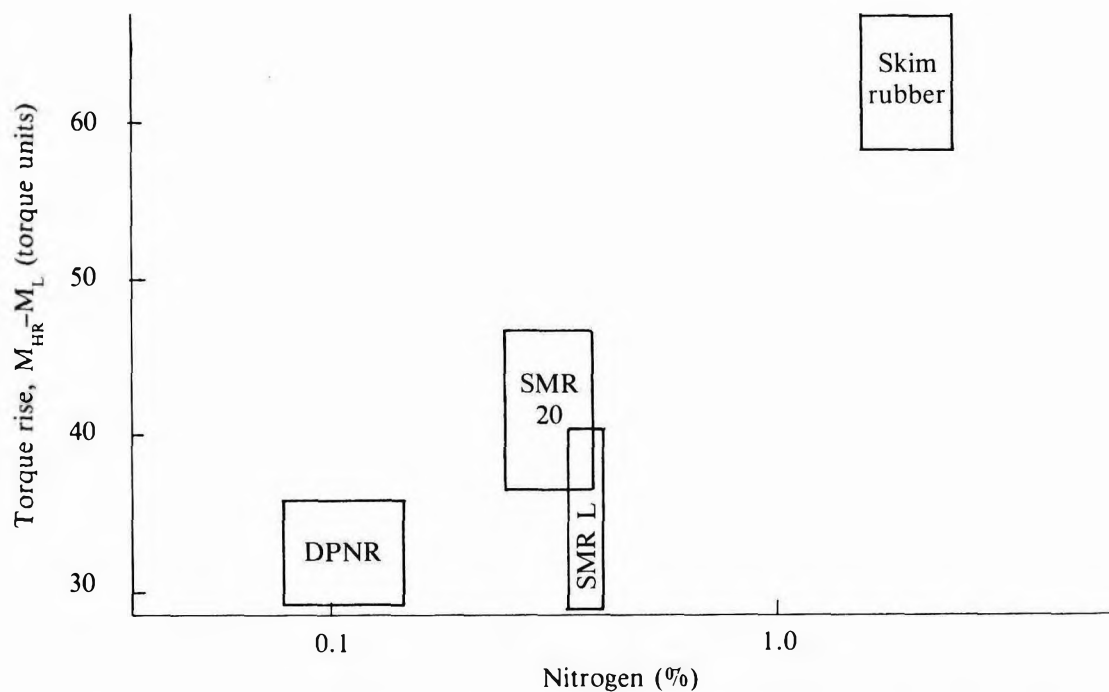


Figure 8. Dependence of ACS 1 torque rise on nitrogen content for various NR grades.

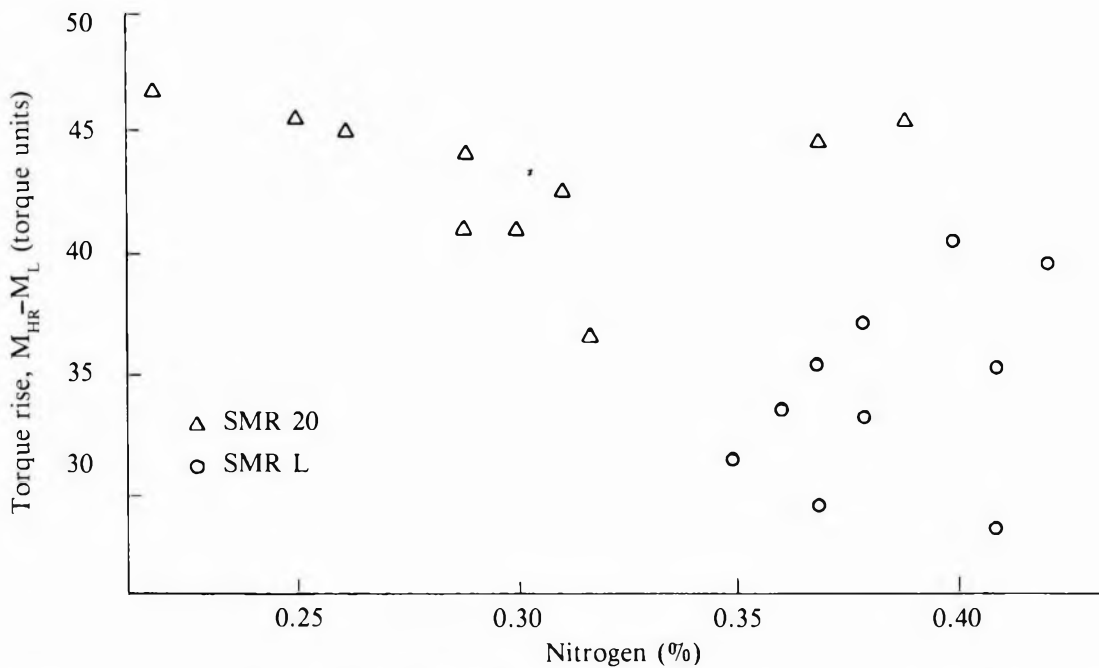


Figure 9. Dependence of ACS 1 torque rise on nitrogen content for samples of SMR L and SMR 20.

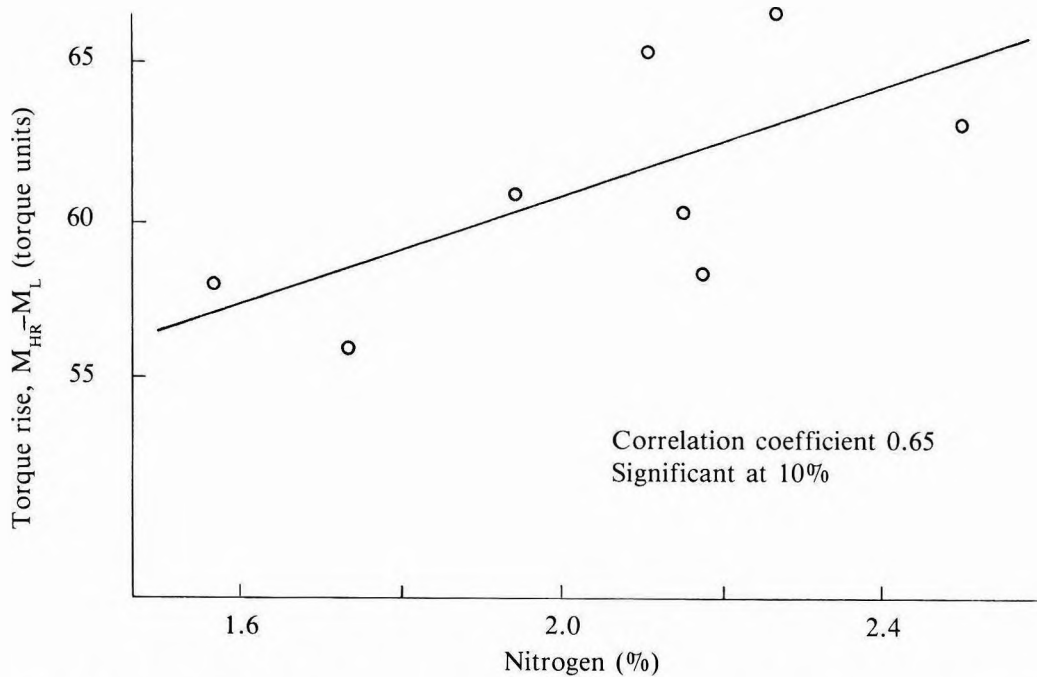


Figure 10. Dependence of ACS 1 torque rise on nitrogen content for samples of skim rubber.

graphs of *Figures 11* and *12*. More extensive data for the systems:

<u>Parts by weight</u>	
Natural rubber or skim	100
Zinc oxide	5
Stearic acid	2
IPPD	2
MBT	Variable
Sulphur	Variable

with S/MBT = 3

are given in *Figures 13 - 20*. The high hardness or stiffness of skim vulcanisates compared to SMR 10 is shown as a function of sulphur level (at constant sulphur : accelerator ratio) for rheometer torque and 100% modulus in *Figures 13* and *14* respectively. Both plots indicate that the relative stiffness of a skim vulcanisate is very dependent on sulphur level; at zero sulphur level, *i.e.* no crosslinking, SMR 10 and skim have the same apparent torque or modulus. This is consistent with the comparable viscosities of the raw rubbers and suggests that, unlike with carbon black, 'protein reinforcement' is only evident in vulcanised materials. Modulus is plotted as a function of torque rise in *Figure 15*. As with carbon black, stiffness enhancement by protein is more evident in vulcanisate modulus (at ambient temperature) than in rheometer torque at curing temperature.

Figures 13 and *14* give an immediate indication of the substantial reduction in curative level necessary if normal natural rubber is to be replaced by skim at constant modulus. As shown in *Table 4*, vulcanisates having comparable stress-strain properties are obtained, provided due allowance is made for the concurrent change in cure rate. Tensile strength tends to be higher for skim though, possibly owing to the reinforcing influence of the protein. This parity disappears on ageing; after two days at 100°C, the tensile properties of the skim vulcanisate are far superior. This is evident in the data of *Table 4*, plotted in *Figure 16*, and the data for a pair of more lightly crosslinked materials, plotted in *Figure 17*. The advantages for skim are more

evident in the stiffer vulcanisates of *Figure 16*. Modulus changes on ageing are clearly very different for the SMR 10 and skim rubber vulcanisates and more extensive data covering a wide range of crosslinking levels are plotted in *Figures 18 - 20*.

Aged modulus (M100) is plotted as a function of sulphur level in *Figure 18*. As found for unaged modulus (*Figure 14*), the difference between skim and SMR 10 tends to zero in the absence of curatives. After ageing, however, the data appear to extrapolate to M100 = 0, rather than to M100 = *ca* 0.3MPa as found before ageing. No explanation of this difference can be offered. Relative stiffening on ageing is plotted as a function of sulphur level in *Figure 19* and, perhaps with more significance, as a function of unaged modulus, in *Figure 20*. This figure provides a rationalisation of the superior ageing performance of skim. For a given unaged modulus, normal natural rubber stiffens far more on ageing than skim rubber. Furthermore, the dependence of the extent of stiffening on unaged modulus, *i.e.* the degree of cross-linking, is far greater for normal natural rubber.

Blends of Natural Rubber and Skim

As noted above, blending normal and skim rubber is an obvious method of taking advantage of the relatively low price of skim rubber while minimising its disadvantages, not least that of possible variability. In addition, it seems possible that in such blends the curing characteristics of skim might be used to advantage. The data of *Table 5* show that this is indeed the case. The simple addition of 20 p.p.h.r. of skim to a normal rubber mix, *without further curatives*, produces only small changes in rate and state of cure as indicated by rheometry, for both CBS/S and MBT/S systems. Confirmatory data for 0 - 20 p.p.h.r. skim added to a CBS/S cure system are given in *Table 6*. Changes in scorch at 120°C and cure rate at both 140°C and 160°C are within the likely experimental error. In the important vulcanisate properties, stiffness, resilience and compression set, trends are evident but the property changes at even 20 p.p.h.r. addition are small.

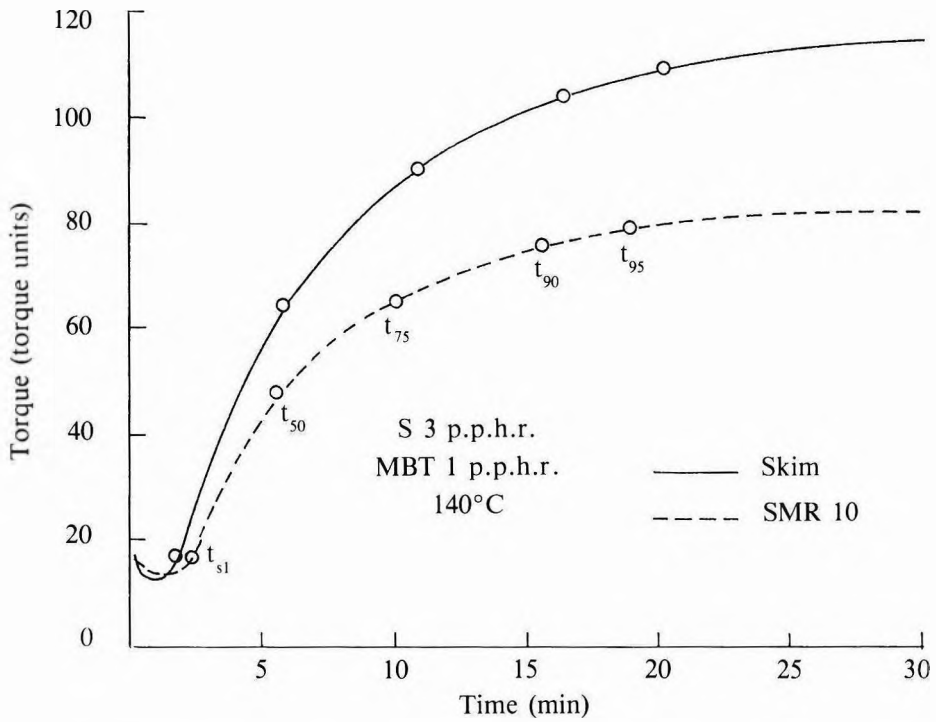


Figure 11. Rheographs for typical samples of skim rubber and SMR 10 in a sulphur-MBT cure system.

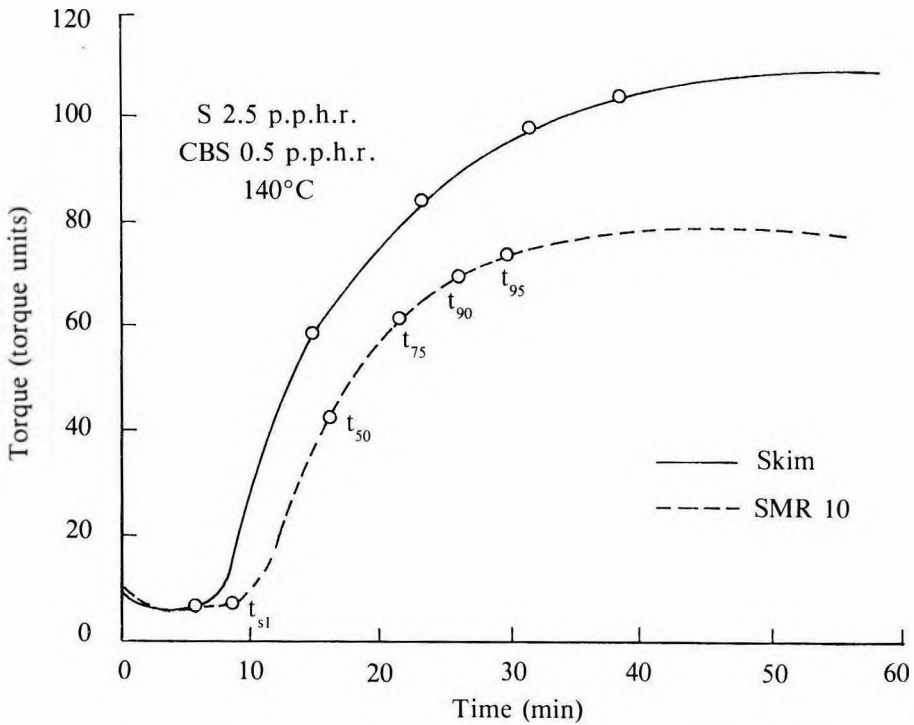


Figure 12. Rheographs for typical samples of skim rubber and SMR 10 in a sulphur-CBS cure system.

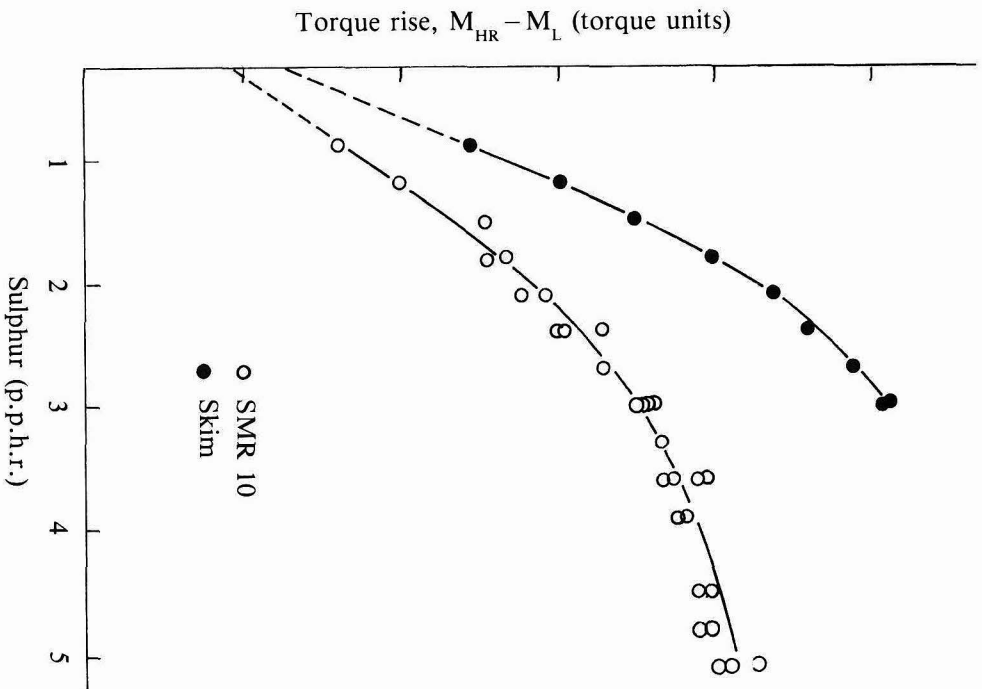


Figure 13. Rheometer torque rise as a function of curative level for skim rubber and SMR 10.

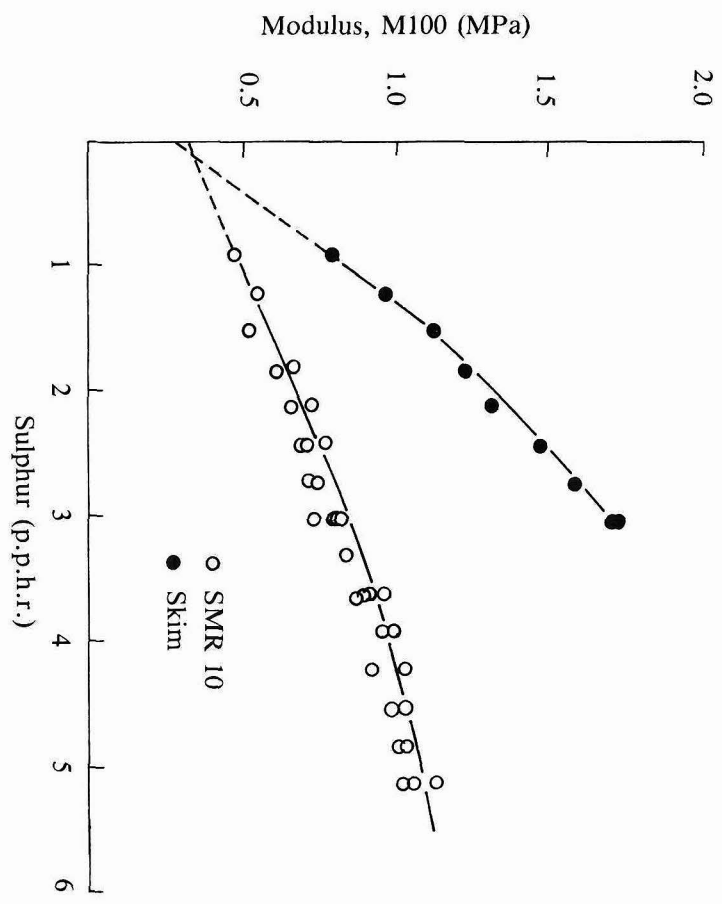


Figure 14. Vulcanisate modulus as a function of curative level for skim rubber and SMR 10.

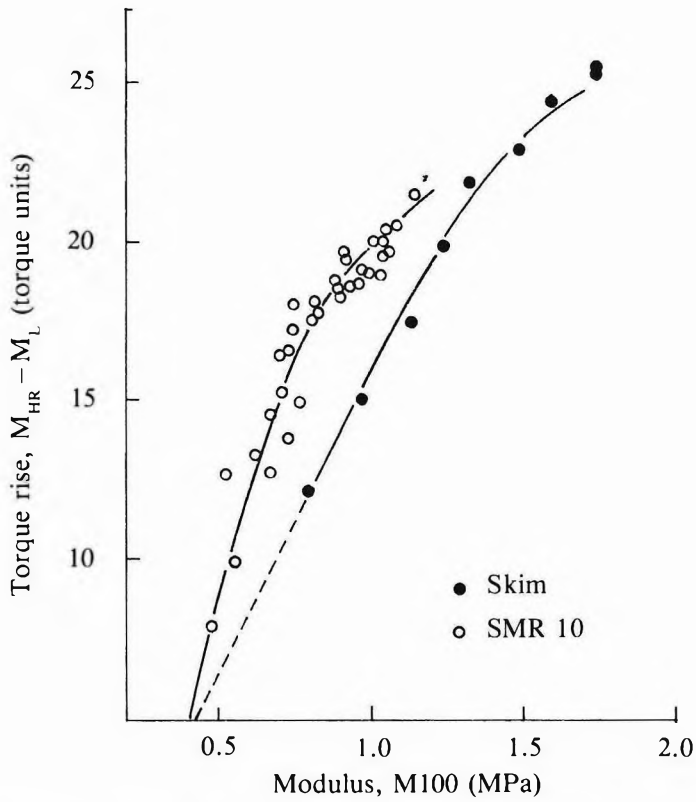


Figure 15. Rheometer torque rise as a function of vulcanisate modulus for skim rubber and SMR 10.

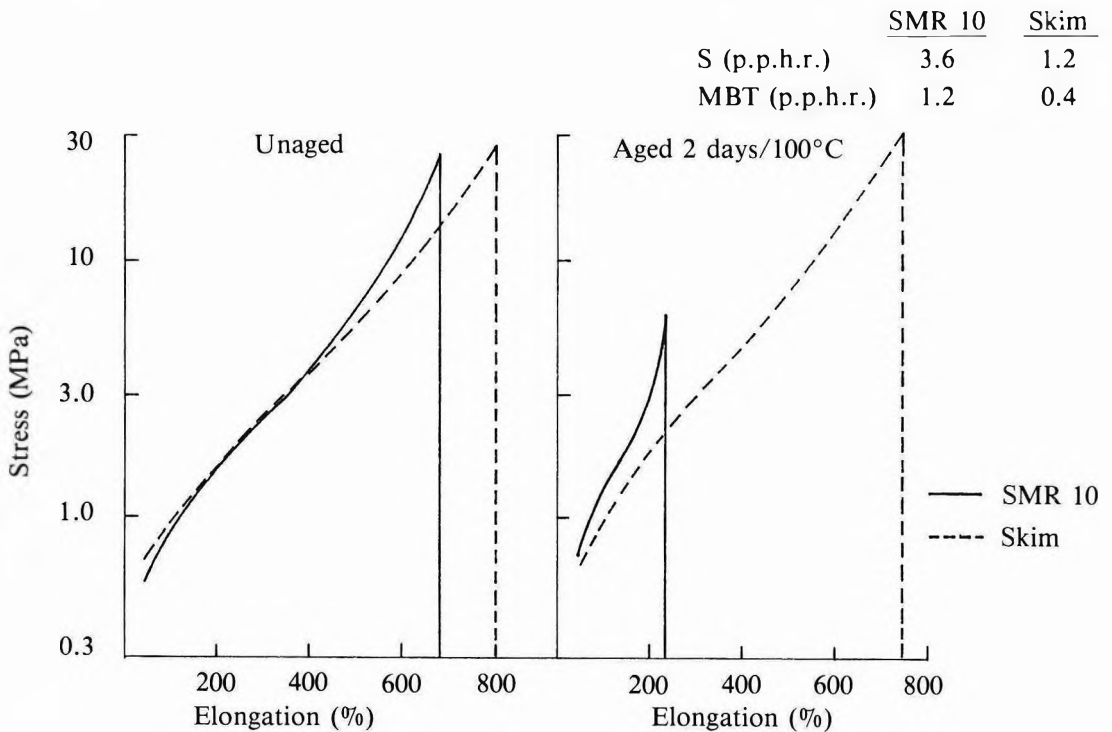


Figure 16. Stress-strain curves for high modulus vulcanisates of skim rubber and SMR 10 before and after ageing.

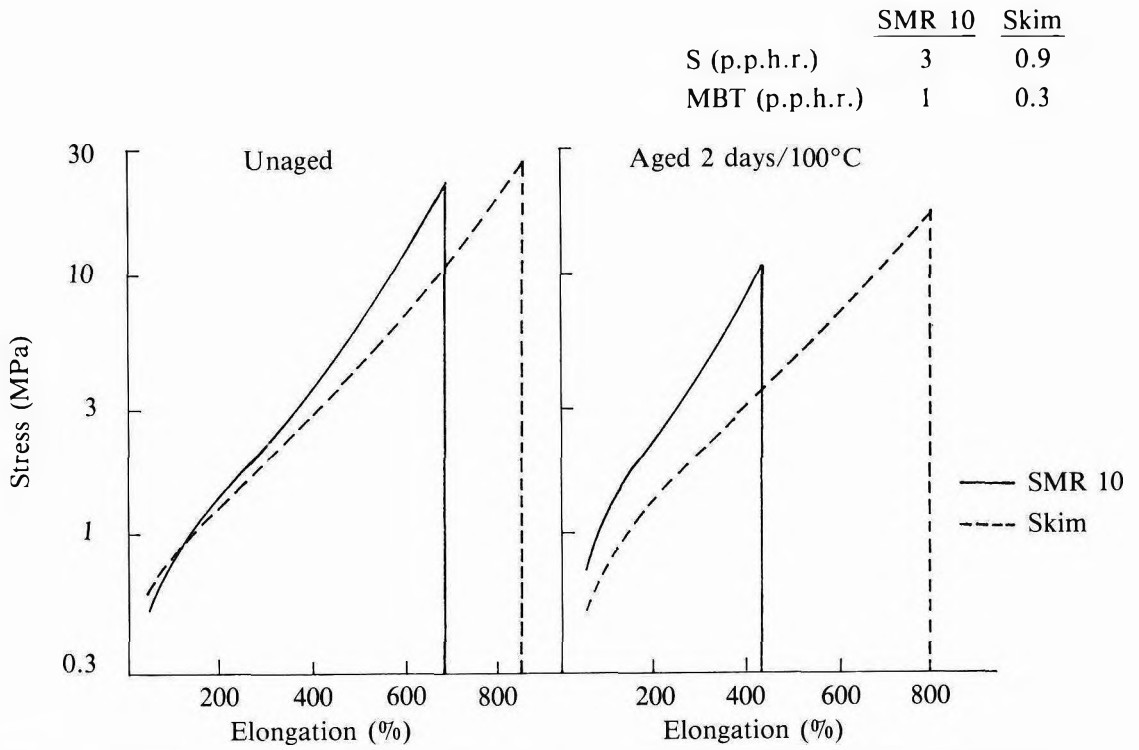


Figure 17. Stress-strain curves for low modulus vulcanisates of skim rubber and SMR 10 before and after ageing.

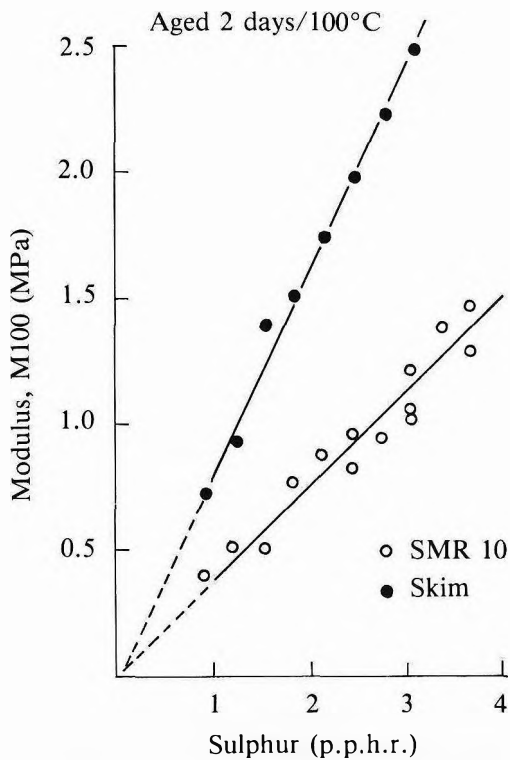


Figure 18. Modulus after ageing as a function of curative level for skim rubber and SMR 10.

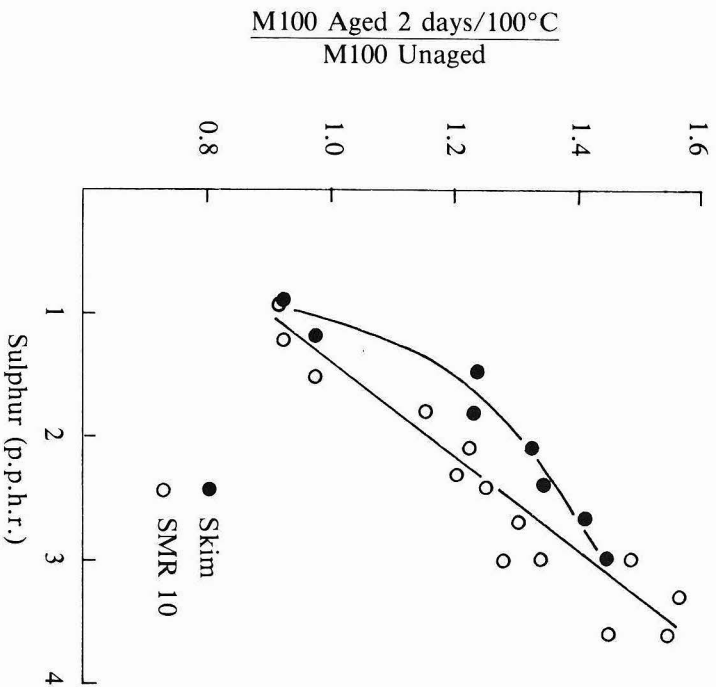


Figure 19. Ratio of aged to unaged modulus as a function of curative level for skim rubber and SMR 10.

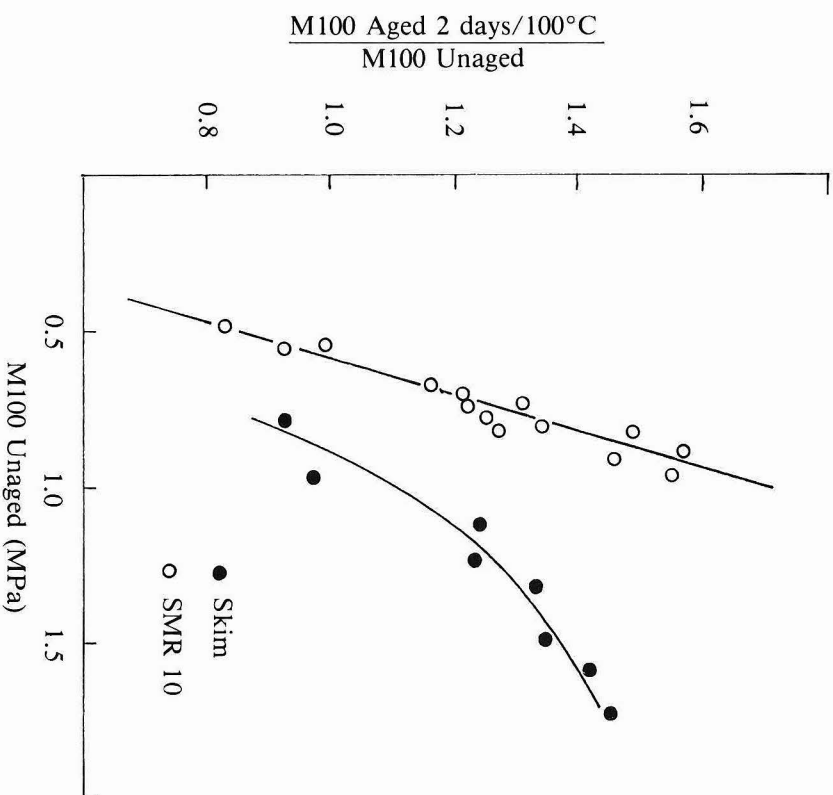


Figure 20. Ratio of aged to unaged modulus as a function of unaged modulus for skim rubber and SMR 10.

TABLE 4. SKIM RUBBER AND SMR 10 VULCANISATES OF COMPARABLE MODULUS

Item	SMR 10		Skim	
SMR 10	100			
Skim rubber			100	
Zinc oxide	5		5	
Stearic acid	2		2	
IPPD	2		2	
MBT	1.0		0.4	
Sulphur	3.6		1.2	
Monsanto rheometer, 140°C				
$M_{HR} - M_L$	19.8		15.1	
t_{s1}	1.8		3.3	
$t'_c(90)$	12.3		23.6	
$t'_c(95)$	15.2		31.1	
Tensile properties, unaged				
Cure time at 140°C (min)	15	20	31	36
Modulus (MPa)				
50% elongation (M50)	0.58	0.58	0.74	0.70
100% elongation (M100)	0.91	0.90	0.99	0.95
200% elongation (M200)	1.55	1.55	1.60	1.58
300% elongation (M300)	2.40	2.42	2.40	2.38
Tensile strength, TS (MPa)	23.2	23.3	27.8	28.6
Elongation at break, EB (%)	685	670	790	800
Tensile properties after ageing 2 days at 100°C				
M50 (MPa)	0.75	0.74	0.65	0.63
M100 (MPa)	1.33	1.31	0.97	0.92
M200 (MPa)	2.43	2.41	1.82	1.80
M300 (MPa)	—	—	2.92	2.88
TS (MPa)	4-7 ^a	4-7 ^a	20.2	20.9
EB (%)	200-250	200-250	735	755

^aTest data very scattered

Variability is the complaint most frequently levelled against skim rubber and the data of *Table 1* for the samples studied here substantiate this to some extent. The influence of this variability on both cure behaviour and vulcanisate properties of 100:20 natural:skim rubber blends for the eight samples studied here is given in *Tables 7* and *8*. Considering first the mean values for the 100:20 blends,

these data substantiate the conclusions drawn from the more limited data of *Tables 5* and *6*, that is the effects of adding 20 p.p.h.r. of skim are small, normally $\pm 10\%$ or less. The exceptions are $t'_c(95)$ at 160°C, compression set at 23°C, compression set at 70°C and modulus after ageing, though for the first two of these changes observed are little greater than the likely experimental error. For

TABLE 5. EFFECT OF ADDITION OF SKIM RUBBER ON CURE BEHAVIOUR

Item	MBT/S			CBS/S		
SMR 10	100	100	100	100	100	100
Skim A	-	20	-	-	20	-
Skim D	-	-	20	-	-	20
Sulphur	3	3	3	2.5	2.5	2.5
CBS	-	-	-	0.5	0.5	0.5
MBT	1	1	1	-	-	-
Mooney scorch time, 120°C						
t_{s1} (min)	5.1	3.8	5.5	18.8	23.2	20.4
Monsanto rheometer, 140°C,						
$M_{HR}-M_L$	17.7	15.9	18.0	18.4	17.1	17.3
t_{s1}	2.2	2.1	2.2	8.7	9.0	8.4
$t'_c(50)$	5.6	5.3	5.7	15.8	14.1	13.7
$t'_c(75)$	10.0	9.2	10.2	21.2	19.1	19.5
$t'_c(90)$	15.5	14.2	15.9	25.5	25.0	26.5
$t'_c(95)$	18.8	17.1	19.7	29.4	28.6	30.7
$t'_c(\max)$	~30	~27	~30	~44	~41	~45

All mixes contain: zinc oxide, 5; stearic acid, 3; IPPD 2 p.p.h.r.

TABLE 6. EFFECT ON CURE BEHAVIOUR AND VULCANISATE PROPERTIES OF ADDITION OF 5 - 20 P.P.H.R. SKIM RUBBER

Item	1	2	3	4
SMR 10	100	100	100	100
Skim A	-	5	10	20
ML(1+4) 100°C	20	21	21	21
Mooney scorch, 120°C				
t_{s5} (min)	19.7	20.7	20.8	20.0
Monsanto rheometer,				
40°C, t_{s1}	8.4	8.4	8.2	8.0
$t'_c(95)$	27.4	26.9	27.0	28.2
60°C, t_{s1}	3.1	3.1	3.2	3.0
$t'_c(95)$	8.4	8.2	8.3	8.5
Cure 27min/140°C				
Resilience (%)	91.7	91.6	90.8	89.3
M300 (MPa)	1.85	1.83	1.84	1.74
TS (MPa)	24.6	25.2	25.9	25.1
EB (%)	720	720	735	755

All mixes contain: zinc oxide, 5; stearic acid, 3; IPPD, 2; sulphur, 2.5; CBS, 0.5 p.p.h.r.

TABLE 7. EFFECT ON CURE BEHAVIOUR OF ADDITION OF 20 P.P.H.R. SKIM RUBBER FROM EIGHT DIFFERENT SOURCES

Item	Formulation										Compounds 2-9	
	1	2	3	4	5	6	7	8	9	Mean	CV (%)	% change ^a
SMR 10	100	100	100	100	100	100	100	100	100			
Skim rubber	-	20A	20B	20C	20D	20E	20F	20G	20H			
ML(1+4), 100°C	27	32	31	29.5	29.5	32	29.5	28.5	31.5	30.4	4.4	+13
Mooney score, 120°C, t ₅	23.6	24.9	27.6	(32.1)	23.1	25.4	27.3	24.9	24.4	26.2*	10.7*	+11*
Monsanto rheometer, 140°C, M _{HR} -M _L	18.6	16.5	16.0	16.6	17.4	16.6	16.6	16.3	16.2	16.5	2.5	-11
t ₅₁	7.9	8.9	9.8	8.1	8.6	8.7	9.2	8.8	8.3	8.8	0.5	+11
t' _c (90)	23.9	24.3	25.8	24.3	25.7	25.0	25.7	25.3	23.7	25.0	0.8	+4
t' _c (95)	27.3	27.7	29.5	27.7	29.7	28.8	29.5	29.0	27.0	28.6	1.0	+4
160°C, M _{HR} -M _L	17.3	15.5	15.2	15.6	15.8	15.6	15.5	15.3	15.3	15.5	1.3	-11
t ₅₁	3.3	3.5	3.5	3.2	3.2	3.3	3.5	3.3	3.0	3.3	5.5	0
t' _c (90)	8.8	9.0	9.4	8.8	8.8	9.0	9.3	9.1	8.6	9.0	3.0	+22
t _R (10) ^b	22	24	25	24	25	25	26	24	22	24	4.9	+11
* Values for means, etc, if data for Compound 4 are omitted										25.4	6.3	+8

All mixes contain: zinc oxide, 5; stearic acid, 3; IPPD, 2; Sulphur, 2.5; CBS, 0.5 p.p.h.r.

^a(Mean of Compounds 2-9 - Compound 1)%

^bTime to 10% reversion

TABLE 8. EFFECT ON VULCANISATE PROPERTIES OF ADDITION OF 20 P.P.H.R. SKIM RUBBER FROM EIGHT DIFFERENT SOURCES

Property	Formulation									Compounds 2-9		
	1	2	3	4	5	6	7	8	9	Mean	CV(%)	% change ^a
Unaged properties												
Cure 30 min/140°C												
Hardness (IRHD)	43.3	42.0	41.0	41.8	42.0	42.0	41.2	41.0	41.0	41.5	2.4	-4
M50 (MPa)	0.58	0.56	0.52	0.54	0.57	0.61	0.60	0.56	0.56	0.57	5.2	-3
M100 (MPa)	0.86	0.82	0.77	0.80	0.83	0.87	0.85	0.83	0.82	0.82	3.7	-4
M300 (MPa)	2.08	1.87	1.81	1.94	2.02	1.83	1.83	1.80	1.79	1.86	4.3	-11
TS (MPa)	27.5	28.3	26.9	25.3	28.4	27.2	27.4	27.3	27.1	27.2	3.5	-1
EB (%)	720	765	780	745	775	765	775	765	780	770	1.4	+6
Resilience (%)	92.7	90.3	90.0	89.8	89.7	90.4	90.6	90.5	90.3	90.2	0.4	-3
Properties after ageing												
2 days/100°C												
M50 (MPa)	0.55	0.54	0.45	0.45	0.49	0.51	0.46	0.44	0.48	0.48	7.2	-13
M100 (MPa)	0.85	0.81	0.71	0.69	0.75	0.79	0.71	0.68	0.72	0.73	6.4	-14
M300 (MPa)	2.44	2.31	2.04	1.99	2.20	2.23	2.06	1.92	2.01	2.10	6.5	-14
TS (MPa)	14.5	19.6	14.4	11.6	11.0	19.6	14.4	14.8	16.3	15.2	21.1	+5
EB (%)	585	650	630	635	570	645	610	625	630	625	4.0	+7
Percent retention after ageing												
M100	99	99	92	86	90	91	84	82	88	89	6.0	-10
TS	53	69	54	46	39	72	53	54	60	56	19.7	+5
EB	81	85	81	85	73	84	79	82	81	81	4.9	0
Compression set (%)												
1 day/70°C	29	33	35	34	32	36	41	38	34	35	8.3	+22
1 day/100°C	61	63	63	63	61	63	66	64	62	63	2.3	+3
3 days/23°C	3	5	7	3	6	4	0	3	3	4	(56)	+29

^a(Mean of Compounds 2-9 - Compound 1)%

compression set at 70°C, the +22% change noted refers to a control natural rubber mix with a set value of 29%. A set of 34% is, however, recorded in *Table 6* for a mix of the same formulation, and this appreciably higher value is more comparable with the set values for the blends. In addition, the cure time 30 min is almost certainly too short to achieve the best compression set resistance. (*cf Table 9*). Mean aged modulus values are also over 10% less than those for the control, but here, as noted above, the lesser degree of stiffening is probably beneficial.

Variability within the eight 100:20 blends, as expressed by the coefficients of variation, is

also small, normally less than 5%. As might be expected, this is less than that found for 100% skim, insofar as comparisons can be made (*cf Table 1*). Compression set at 23°C and aged tensile strength are again exceptions. For aged tensile strength, the high variability observed probably stems mainly from the well known difficulty in obtaining reliable tensile strength data for gum vulcanisates after ageing.

Natural rubber vulcanisates are subject to loss of properties, or reversion on overcure, especially at high curing temperature. It is important that the addition of skim rubber should not augment such reversion. Data for optimum and *ca* 4× overcure for the 100:20

TABLE 9. EFFECTS OF ADDITION OF SKIM RUBBER ON OVERCURE

Item	27 min/140°C		9 min/160°C		40 min/160°C	
	Nil	20	Nil	20	Nil	20
Skim A (p.p.h.r)	Nil	20	Nil	20	Nil	20
Hardness (IRHD)	40	39	38	37	30	31
Resilience (%)	91.7	89.3	90.4	88.1	77.0	76.7
M100 (MPa)	0.76	0.72	0.69	0.66	0.47	0.49
M300 (MPa)	1.85	1.74	1.61	1.55	0.98	1.01
TS (MPa)	24.6	25.1	22.6	21.2	8.9	8.5
EB (%)	720	755	750	760	765	750
Properties after ageing						
2 days at 100°C						
M100 (MPa)	0.91	0.77	0.86	0.74	0.56	0.50
M300 (MPa)	2.42	1.93	2.23	1.91	1.21	1.19
TS (MPa)	20.6	18.2	16.9	15.4	10.1	8.8
EB (%)	625	670	595	645	680	680
Percent retention after ageing						
M100	120	107	125	112	119	102
M300	131	111	139	123	123	118
TS	84	73	75	73	113	104
EB	86	89	79	85	89	91
Compression set (%)						
3 days/23°C						
	6	7	8	6	13	15
1 day/70°C						
	34	36	30	34	23	23
1 day/100°C						
	64	66	63	63	42	40

natural:skim rubber blend of *Table 6* are given in *Table 9*. The performance of the 100% natural rubber control is as expected and this behaviour is closely paralleled by that of the blend. There is no indication of any adverse influence of skim on reversion resistance.

CONCLUSIONS

The eight samples of skim block rubber studied show considerable variation in composition, in oxidisability as evinced by PRI and in cure behaviour. Copper content is about twenty times greater than that found with typical latex grades of natural rubber such as RSS and SMR L but this does not result in a very low PRI, indeed there is no correlation between copper content and PRI. Rate and state of cure are much higher than for normal natural rubber and this can be used to advantage in blends of normal and skim rubber. Up to 20 p.p.h.r. of skim can be added to normal rubber without any increase in curative level and a high level of vulcanisate properties retained. Variability in such 100:20

blends is far less than in the 100% skim rubbers. For vulcanisates of comparable modulus, the ageing resistance of skim rubber is found to be superior to that of normal rubber grades despite the presence in the former of up to 30 p.p.m. of copper.

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Graft Copolymers of cis-1, 4-Polyisoprenes with Poly(methyl methacrylate)

D.S. CAMPBELL* AND P.K. SEOW**

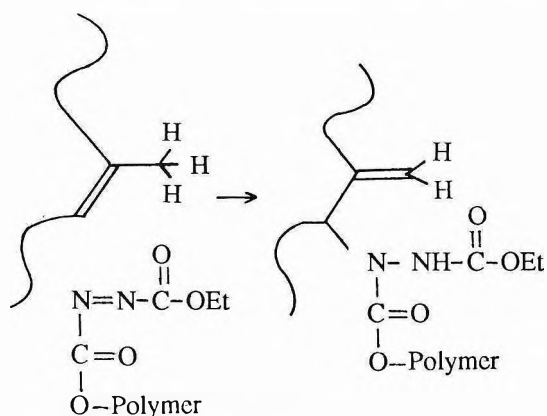
Graft copolymers of natural and synthetic cis-1, 4-polyisoprene with poly(methyl methacrylate) have been prepared by reaction of the polyisoprenes with azodicarboxylate-functional poly(methyl methacrylate). The reactivity of the functional polymer is compared with that previously observed for reactions of similarly functional polystyrene. Within an appropriate composition range, the unvulcanised graft copolymers have elastomeric properties. The dependance of these properties on material and sample preparation conditions is discussed.

Both graft and block copolymers of natural rubber (NR) with poly(methyl methacrylate) (PMMA) have been known for many years. Block copolymers can be prepared by mechanical breakdown of NR in the presence of methyl methacrylate monomer¹ but although the technique has considerable versatility in some respects², control of the block structure and the block molecular weight is poor. Graft copolymers have been prepared by free radical polymerisation of methacrylate monomer in NR solution³ or in NR latex^{4, 5}. The technological product prepared from NR latex (Heveaplus-MG) is discussed by Pendle⁵. Heveaplus-MG contains little PMMA homopolymer when prepared by the method of Sekhar⁶ but it does contain ungrafted NR. The latter material can be removed by extraction⁷.

NR-g-PMMA obtained by these free-radical processes characteristically has PMMA chains of high molecular weight⁸, and consequently has a small average number of graft sites per backbone chain. Such a structure is believed to be inappropriate for the evolution of a strong elastic network by micro-phase separation in the unvulcanised copolymer⁹ and it is the case that Heveaplus-MG does not behave as a thermoplastic elastomer.

Graft copolymers of NR or synthetic polyisoprene (IR) can be prepared in which the

length of the graft chains and the average number of graft chains per backbone are controlled¹⁰⁻¹³. The process uses molecular cyclo-addition reactions ('ene' reactions) of azodicarboxylate functional groups in which one of the ester alkyl groups of the azodicarboxylate is a polymeric species (*Scheme 1*). The reaction as represented in *Scheme 1* is one of three regiochemical alternatives, of which the other two give rise to double-bond migration within the polymer chain. The process has been applied to the preparation of graft copolymers of polyisoprenes with methacrylates having higher ester alkyl groups¹³. We now use the same



Scheme 1

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

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

procedure to prepare NR-g-PMMA and IR-g-PMMA copolymers with relatively short graft chains and higher grafting frequencies than are obtainable from the free-radical grafting techniques. Features of the preparation of these materials and of their properties relative to other graft copolymers of similar molecular architecture will be discussed.

EXPERIMENTAL

Infra-red spectra were recorded on a Perkin-Elmer 157 spectrometer, ^1H NMR spectra were recorded on a Perkin-Elmer R32 spectrometer. Vapour-phase osmometry (VPO) was performed on a Coran Wescan 232A molecular weight apparatus at 50°C using toluene as solvent and benzil as calibration standard. Gel permeation chromatography (GPC) used Laboratory Data Control equipment. Five Micrel columns of nominal pore size 10 , 1×10^2 , 1×10^3 , 1×10^4 and 1×10^5 nm were run in series with an ultra-violet (UV) detector. The chromatograms were run at 25°C using tetrahydrofuran as solvent and molecular weights were calculated from a calibration prepared using PMMA standards supplied by Polymer Laboratories.

Polyisoprenes were Cariflex IR305 (Shell Chemical Co.; 92% *cis*-1, 4-, 4.5% *trans*-1, 4- and 3.5% 3, 4- and 1,2-) and NR (commercial SMR 5L). Hydroxyl-terminated PMMA was prepared by free-radical polymerisation of methyl methacrylate in the presence of 2-mercaptoethanol as chain transfer agent. The procedure was described earlier¹³ for the preparation of hydroxyl functional poly(alkyl methacrylates) with higher alkyl ester chain lengths. Values of 0.62 for the transfer constant¹⁴ and 3.6×10^5 for the PMMA molecular weight in the absence of transfer were used in the Mayo equation¹⁵ as a basis for trial runs carried out to $>50\%$ conversion. Reaction was carried out at 60°C with equal weights of benzene and monomer and with azobis(2-methyl-propionitrile) (AIBN) as initiator (0.01% weight/weight on monomer). Molecular weights of the products indicated that under these conditions, the effective

transfer constant varied with the ratio of transfer agent to monomer and with the monomer conversion. The preparative conditions for the main batch of polymer were: monomer 611 g, benzene 611 g, 2-mercaptoethanol 15.2 g, AIBN 0.61 g, 22 h at 60°C . Polymer was recovered by precipitation into a five-fold excess of a mixture of methanol and petroleum spirit (boiling point $40^\circ\text{C} - 60^\circ\text{C}$) (4:1) and dried in vacuo. Monomer conversion was 68%.

Hydroxyl polymer (200 g, nominally 0.03 mole hydroxyl group) was further dried by azeotropic distillation of toluene¹¹ before esterification with a four-fold molar excess of 2-carbethoxyazo-carbonyl chloride (CEAC). CEAC reagent solution was prepared immediately before use by drop-wise addition of bromine (20.7 g, 0.130 mole) to a solution of 2-carbethoxyhydrazinecarbonyl chloride¹⁶ (20.8 g, 0.151 mole) and pyridine (60 g, 0.74 mole) in dried dichloromethane (300 ml), the reaction being maintained below 5°C with an ice bath. The reagent solution was added to the dried solution of the polymer in toluene and the mixture heated under gentle reflux overnight. Azodicarboxylate functional polymer was recovered by precipitation into aqueous methanol (1:3) and dried in vacuo. The azodicarboxylate functionality of the polymer was confirmed by the presence of a UV absorption maximum at 409 nm (10% weight/volume solution in dichloromethane) and by an infra-red shoulder at 1780 cm^{-1} which was clearly visible on the side of the ester carbonyl of the polymer backbone. An extinction coefficient of 34 was used to calculate the azodicarboxylate concentration from the UV absorbance.

Graft copolymers with polyisoprenes were prepared either by reaction in toluene solution (3% weight/volume) for seven days at 60°C or by direct mixing of the polyisoprene and the functional polymer in a Hamden-Shawbury Torque Rheometer¹². Grafting efficiency (GE) was determined by GPC analysis in tetrahydrofuran solution using a separately determined response factor for PMMA to estimate the amount of material present in the elution peak for ungrafted polymer,

which immediately followed the main peak of the chromatogram¹⁷. GE was expressed as the percentage by weight of the total prepolymer that became bound to the backbone in the course of the reaction. The values are therefore influenced by the presence of any non-functional material in the polymer sample.

RESULTS AND DISCUSSION

Earlier work with poly(isoprene-*g*-styrene) copolymers prepared by the azodicarboxylate coupling process has identified a graft chain molecular weight range of 5×10^3 to 10×10^3 as being appropriate for conferring elastomeric strength to the copolymers. This range can be seen⁹ as representing a compromise between a sufficiently high average number of graft sites per backbone chain and a sufficiently high molecular weight to ensure that the glass transition temperature for the graft chains does not drop too far towards ambient temperature. Reactive prepolymer preparation for the present work concentrated on obtaining material with \bar{M}_n in the region of 6×10^3 , on the assumption that similar criteria would apply to PMMA graft copolymers. Use of free-radical polymerisation with chain transfer necessarily introduced a substantial broadening of the molecular weight distribution of the PMMA prepolymers relative to the narrow distribution materials used in the work with poly(styrene) (PS).

Characterisation of the hydroxyl and azodicarboxylate functional PMMA prepolymers is summarised in *Table 1*. There is some discrepancy between the \bar{M}_n values

from VPO and GPC analyses which results in an ambiguity in the calculated values for the effective transfer constant in the polymerisation reaction and the percentage azo functionality of the azo polymer. The source of the discrepancy was not identified but the results for extent of grafting to IR (see below) suggest that the functionality based on GPC molecular weight is the more reliable figure and that the prepolymer contained some 10% to 15% of non-functional material.

The azo functional PMMA reacts with IR in the presence of a common solvent. Analytical demonstration that the reaction occurs is less straight-forward than for previous work with functional PS, where the UV absorption characteristics of the aromatic ring were used to selectively identify PS in the GPC peaks of the reaction product¹¹. In the absence of a selective absorption for PMMA, it was necessary to identify the decrease in absolute area of the longer retention peak corresponding to PMMA prepolymer and to isolate material from the shorter retention peak (graft product) for identification of methacrylate and isoprene components by ¹H NMR.

Work with azo functional PS¹¹ established rate constants for reaction with IR in cyclohexane and toluene solutions at 60°C. Cyclohexane gives the higher reaction rate but was not suitable for the present work because it is a non-solvent for PMMA. The rate constant for reaction in toluene (pseudo-first-order kinetics) gives an expectation of >97% reaction of the azo functionality in seven days (168 h). When the same experimental conditions were applied to reaction of the azo functional PMMA, the GE at seven days was 76% and 71% in duplicate experiments. However, the reactions were incomplete. Evaporation of the solvent and heating the total polymer residue at 150°C for 10 min increased GE to 88% and 87% respectively. The reaction of the PMMA in solution was therefore slower than the corresponding PS reaction. Using the single-point values for GE at seven days and assuming pseudo-first-order reaction conditions, the second-order rate constant for the PMMA-IR reaction is estimated to be

TABLE 1. CHARACTERISATION OF HYDROXYL AND AZODICARBOXYLATE FUNCTIONAL POLYMERS

Item	Analyses	
	VPO	GPC
\bar{M}_n (Hydroxyl polymer)	6 400	5 300
\bar{M}_w/\bar{M}_n	—	1.47
Effective transfer constant	0.48	0.58
Azo end groups (%)	103	85

0.7×10^{-5} litre $\text{mol}^{-1} \text{s}^{-1}$ (c.f. 2.47 litre $\text{mol}^{-1} \text{s}^{-1}$ for azo functional PS under the same conditions).

Figure 1 and Table 2 summarise information on the formation of graft copolymer from azo

functional PMMA and IR by direct mixing in the Hamden-Shawbury Torque Rheometer. Data for a similar reaction with functional PS is included for comparison. The maximum in the curve for the PS reaction between 4 min and 8 min is associated with the major part of the

Mixing speed 150 r.p.m.

Functional polymer loading, 40% w/w

Polymer	\bar{M}_n	Starting temp.
— PMMA	6400	90°C
- · - PMMA	6400	130°C
- - - PS	8200	90°C

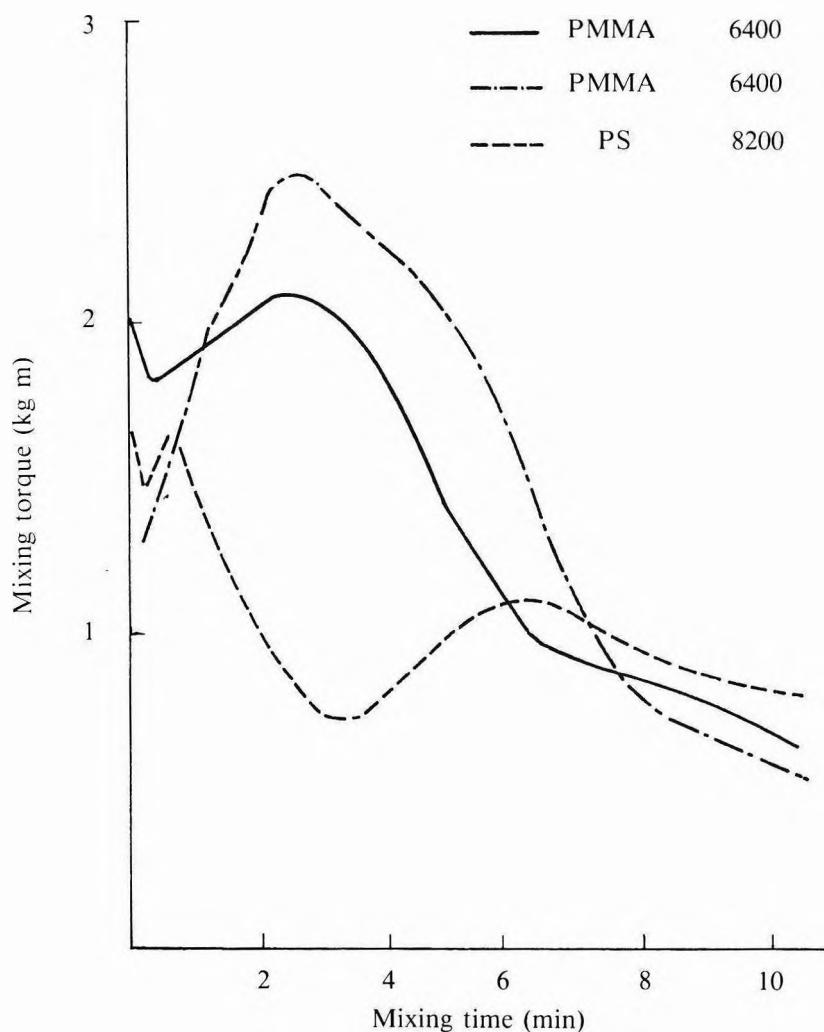


Figure 1. Mixing torque versus time for azodicarboxylate functional polymers with Cariflex IR305 polyisoprene.

TABLE 2. GRAFTING OF FUNCTIONAL POLYMER TO CARIFLEX IR305 POLYISOPRENE BY DIRECT MIXING

Polymer	\bar{M}_n^a	Initial temp. (°C)	Final temp. (°C)	GE (%)	
				Mix	Solution
PS	8 200	90	143	75	76
PMMA	5 300	90	128	64	86
PMMA	5 300	130	174	82	86

^aGPC estimate of molecular weight

grafting process¹² and the GE at 10 min mixing time is essentially the same as the estimated polymer functionality. Under the same mixing conditions, azo functional PMMA gives a torque maximum at an earlier mixing time but the GE at 10 min mixing is substantially less than the highest values obtained in the solution experiments. The final mix temperature is also lower than for the PS reaction. Increasing the initial mix temperature to 130°C for the PMMA reaction results in an expected decrease in the initial mixing torque but gives a sharper rise in torque and a higher maximum torque. The GE after 10 min is now within a few percent of the maximum value for the solution reactions and the mix temperature is higher than for the other reactions.

Although the torque traces give the impression that the PMMA reaction is faster than the PS reaction at the same initial mix temperature, the grafting efficiencies suggest that this is not the case. The results are more consistent with the viscosity of the PMMA reaction mixture being more sensitive to the number of graft chains that have become attached to the backbone compared with the PS system. Such behaviour is consistent with the greater thermodynamic incompatibility of the polyisoprene-PMMA polymer pair compared with that of the polyisoprene-PS pair as expressed in the difference in solubility parameter for each of the pairs (Table 3). The mixing process is not isothermal. There is an autocatalytic effect of a rise in temperature causing increasingly rapid reaction of the functional polymer. This thermal imbalance is likely to be strongly sensitive to the mix viscosity and thus to the magnitude of the

TABLE 3. SOLUBILITY PARAMETERS^a

Polymer	Solubility parameter, σ
<i>cis</i> -polyisoprene	8.10
PS	9.05
PMMA	9.24

^aCalculated from group molar attraction constants of Hoy by the procedure documented by Krause¹⁸.

solubility parameter difference of the reacting polymer pair. Further evidence that the increased incompatibility between the graft and backbone chains is important in the polyisoprene-PMMA system comes from the sharp decrease in viscosity after the torque maximum. The decrease is not accompanied by a decrease in the amount of grafted PMMA (Table 4). It is the result of mechanical

TABLE 4. VARIATION OF GRAFTING EFFICIENCY WITH MIXING TIME FOR THE REACTION OF FUNCTIONAL PMMA WITH IR BY DIRECT MIXING^a

Mixing time (min)	GE (%)
5	77
7	84
10	82
12	83
15	84

^aInitial cavity temperature 130°C

breakdown of the backbone chains, the severity of which is enhanced relative to the PS system because of the higher energy required to move PMMA chains through the IR matrix.

The pattern of behaviour shown in *Figure 1* is repeated in mixes having different levels of PMMA prepolymer and, with minor variations, in mixes where NR is the polyisoprene. Grafting efficiencies decrease slightly with increasing PMMA levels for the IR reactions (*Table 5*). This is thought to be a

TABLE 5. VARIATION OF GE WITH PMMA LOADING FOR DIRECT MIXING REACTIONS OF FUNCTIONAL PMMA WITH IR AND NR

PMMA loading (% w/w)	GE(%) ^a	
	IR	NR
25	78	—
30	76	36
35	72	38
40	71	42
45	67	—
50	65	48

^aInitial cavity temperature 130°C, mixing time 10 min

consequence of a side-reaction between the azodicarboxylate functional groups and the thioether link that is present as a consequence of incorporation of the radical transfer agent¹³. The situation is different for reaction with NR. Grafting efficiency is lower at all PMMA levels relative to the IR reactions, because of reaction of azodicarboxylate functional groups with non-rubber constituents¹¹, but the grafting efficiency increases with increasing PMMA level, *i.e.* as the ratio of functional groups to non-rubbers increases.

The tensile properties of IR-g-PMMA and NR-g-PMMA copolymers vary with PMMA content in a way similar to that previously reported¹² for analogous polyisoprene-g-PS copolymers. Low PMMA content gives low modulus materials with relatively high

elongations at break. Increasing PMMA content increases modulus, decreases elongation at break and eventually introduces plastic yield at low elongations. The tensile strength measured at any given composition is affected by the conditions of preparation of the test sample (*Figure 2*), compression moulding at 180°C resulting in significantly stronger samples compared with compression moulding at 140°C, with a further improvement occurring if the test samples are obtained as cast films from toluene solution.

The inferior strengths of the compression moulded samples are indicative of residual moulding stresses or flaws. Visual imperfections from poor mould flow were evident at 140°C and even at 180°C, the quality of the moulded sheets was not as good as that obtained for corresponding PS copolymers moulded at 150°C. The effects are another manifestation of the increased viscosity of polyisoprene-g-PMMA relative to polyisoprene-g-PS, arising from the difference in the solubility parameters.

Tensile strengths of the PMMA graft copolymers are at a maximum in the composition range 40% to 50% weight/weight PMMA (*Figure 3*, solution cast films). For NR-g-PMMA, the maximum strength is comparable to that obtained for the NR-g-PS copolymers, and is probably associated with extensive strain-induced crystallisation of the highly stereo-regular NR backbone. The strengths at lower PMMA contents are lower than for corresponding PS copolymers and the strengths for the IR-g-PMMA copolymers are appreciably lower than for IR-g-PS copolymers at all compositions. We believe that these differences are related to differences in relaxation behaviour under the testing and failure conditions but a more extensive study of physical properties would be required to be able to construct a full explanation of the behaviour.

CONCLUSION

NR-g-PMMA copolymers can display rubbery strength in the unvulcanised state provided

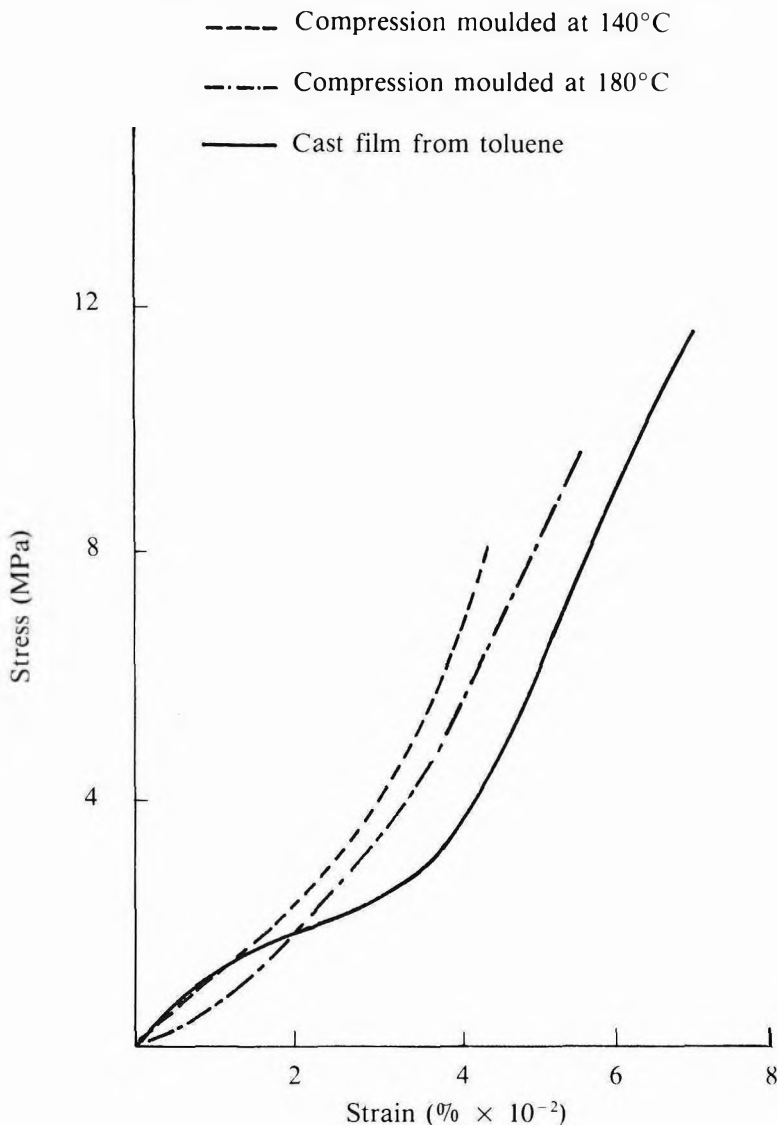


Figure 2. Stress-strain curves for NR-g-PMMA copolymer samples (30% w/w PMMA) from different sample preparation techniques.

sufficient attention is paid to the details of the molecular architecture. The greater thermodynamic incompatibility of the polyisoprene-PMMA polymer pair relative to the polyisoprene-PS polymer pair has a

pronounced effect on the ease of reaction of the functional polymer with the backbone, and is also apparent in the higher temperatures required to prepare compression moulded sheets of the PMMA graft copolymer.

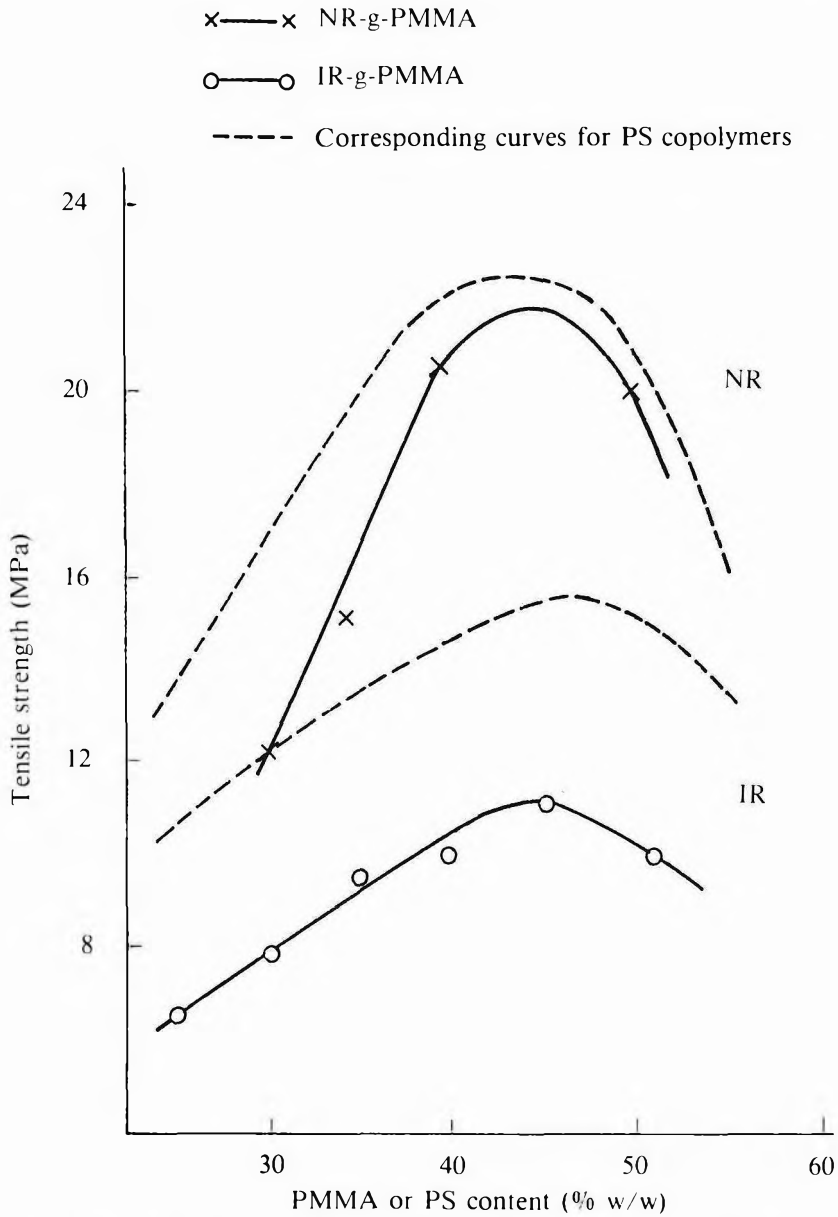


Figure 3. Tensile strength versus composition for polyisoprene-g-PMMA copolymers (cast films).

The behaviour of Heveaplus-MG in the unvulcanised state, where heavy mastication is necessary to achieve processability and the masticated material does not show useful strength, can be readily interpreted on the basis

of these new results and the known architecture of Heveaplus-MG.

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A Stress-Strain Relationship for Filled Rubber

ALIAS BIN OTHMAN* AND M.J. GREGORY**

A semi-empirical relationship relating stress to strain has been developed based on a model which expresses nominal stress as a function of strain invariant I_1 . The relationship has been observed to be applicable to various types of black-filled rubber subjected to three different modes of deformation, namely uniaxial extension, compression and simple shear. At equal I_1 , the moduli in tension, compression and simple shear were observed to be the same and prediction of the stress-strain values for one mode of deformation could be made using parameter constants for the relationship developed from another mode of deformation.

The stress-strain relationship is a fundamental property of a rubber-like material, and the ability to predict the response of an elastomer under a known load or deformation facilitates the design of engineering rubber products.

There are two main approaches in defining the constitutive equation to describe the elastic nature of rubber-like materials. The molecular approach considers the response of the molecular network to deformation. Typically, this is the statistical or Gaussian theory where the parameters are calculated from such quantities as finite molecular length and molecular weight between crosslinks¹. There is also the phenomenological approach where the elasticity theory was derived from entirely mathematical consideration. The models of Mooney², Rivlin^{3,4} and Valanis-Landel⁵ are among those which are derived from or based on the phenomenological approach.

Neither the statistical nor the phenomenological theory can satisfactorily describe the stress-strain behaviour of filled rubber because these theories are based on the assumption that the stresses are uniquely determined by the strain imposed. The assumption is valid provided there is a complete reversibility in the stress-strain

behaviour of rubber-like materials, and no hysteresis occurs. With rubber-like materials, in particular filled rubbers, the assumption is not valid. Thus, the existing statistical and phenomenological theories can not describe the stress-strain behaviour of filled rubber. This paper describes an alternative form of a stress-strain relationship which is applicable to filled rubber subjected to moderate deformation.

EXPERIMENTAL

Rubbers

All samples were based on natural rubber, using the formulation given in *Table 1*. The rubbers were vulcanised at 150°C for the time required to develop maximum torque on the Monsanto rheometer. Fillers used ranged from N110 (SAF) to N762 (SRF) with the mean particle diameter of about 10–20 μm for N110 and 60–100 μm for N762.

Stress-Strain Measurements

Tension. Measurements were made on an Instron 1122 tensile testing machine using parallel-sided dumbbells (or bongo shape) 100 mm long, 2.0 mm thick held in spring-loaded grips. The strain rate was 20%/min,

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

**Deceased. Formerly with Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford, SG13 8NL, United Kingdom

TABLE 1. FORMULATION

Compound	Sulphur system	Peroxide system
Natural rubber (SMR L)	100	100
Carbon black	5 - 60	5 - 60
Zinc oxide	5	-
Stearic acid	1.5	-
Flectol H ^a	1.0	-
Process oil ^b	0.5 - 6.0	
Sulphur	0.17 - 3.75	
CBS ^c	0.3 - 7.5	
DCP ^d	-	1 - 4.5

^aPoly - 2, 2, 4 - trimethyl - 1, 2 - dihydroquinoline

^bDutrex

^cN - cyclohexyl benzothiazole - 2 - sulphenamide

^dDicumyl peroxide

and samples were extended to a maximum extension of 150% (where possible).

Compression (lubricated). Compression measurements were carried out on cylinders having 25.4 mm diameter, 9.0 mm thickness using the Instron testing machines. The samples were compressed to a maximum of 50% strain at a strain rate of about 20%/min. The loaded surfaces of the rubber cylinders were lubricated using silicone oil.

Simple shear. Shear measurements were carried out on two rubber disks (6 mm thick and 25.4 mm diameter) bonded between three metal pieces. The stress-strain values were obtained by shearing the sample to 100% shear at a rate of 20%/min and all measurements were for 'static' condition.

RESULTS AND DISCUSSION

A Form of Stress-Strain Relationship

The theory of Mooney^{3,4} expresses the stored energy function, *W*, as a function of

strain invariants *I*₁ and *I*₂ where

$$\begin{aligned}
 I_1 &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\
 I_2 &= \lambda_1^2 \lambda_2^2 \lambda_3^2
 \end{aligned}
 \dots 1$$

and λ_1, λ_2 and λ_3 are the extension ratios in the three principal directions. If *W* is strongly dependent on both strain invariants, *I*₁ and *I*₂, then a simple mathematical equation relating the modulus in tension, compression, *H* ($H = \sigma/\lambda - \lambda^{-2}$, σ is the nominal stress) and simple shear, *G* ($G = \sigma/\gamma$, γ is the shear strain) cannot be obtained because the contributions due to *I*₁ and *I*₂ will be different for different types of strain. Only if *W* is independent of either *I*₁ or *I*₂ are these moduli likely to be related.

Previous work by Gregory⁶ which has been restricted to filled rubber, suggested that the stored energy function for the three simple modes of deformation, viz. tension, compression and simple shear, was dependent only on *I*₁ and the contribution due to *I*₂ was small. This has been shown by comparing the modulus at equal value of *I*₁ (Figure 1). If

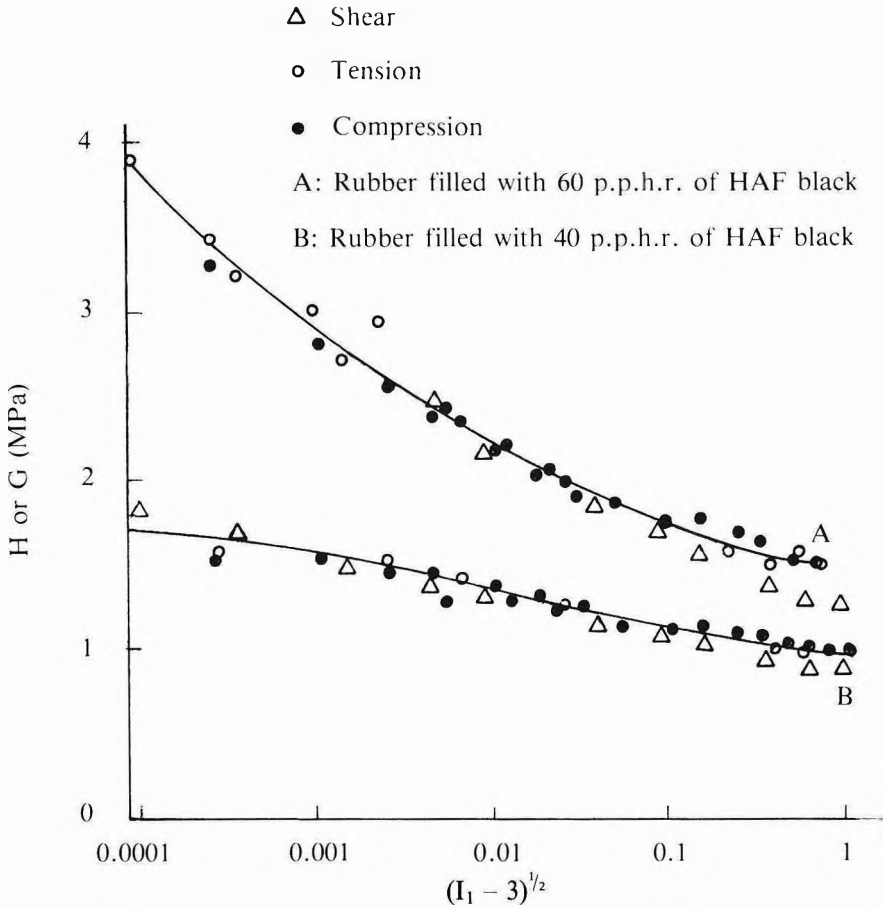


Figure 1. Variation of H and G with strain invariant I_1 for rubber filled with 60 p.p.h.r. and 40 p.p.h.r. of HAF (N330) black⁶.

the partial derivative $\frac{\delta W}{\delta I_1}$ is dependent on I_2 and the contribution due to $\frac{\delta W}{\delta I_2}$ is not small, differences in the values of tensile/compression and shear modulus at equal I_1 will be observed. However, the agreement observed in practice between H and G at moderate strain suggests that serious errors are not introduced if one assumes that the moduli in tension, compression and shear are only a function of I_1 .

Thus assuming that, at low to moderate strains, the moduli in tension, compression and simple shear are a function of I_1 only,

then we may write, for simple extension or compression

$$\sigma_T = F(I_1) (\lambda - \lambda^{-2}) \quad \dots 2$$

and for simple shear

$$\sigma_s = F(I_1) \gamma \quad \dots 3$$

where σ_T and σ_s are the nominal tensile and shear stresses respectively, γ is the shear strain and $F(I_1)$ is a term which is a function of the strain invariant I_1 . It follows that, if $F(I_1)$ is known, the stress-strain behaviour in tension, compression and simple shear can be predicted.

Let us consider a simple shear deformation. When the shear stresses are plotted against shear strain, the relationship is linear at moderate strains (*Figure 2*). The linear region may be expressed as,

$$\sigma_s = A\gamma + k \quad \dots 4$$

where A is the modulus at moderate strain and k the intercept. However, at low strain, *Equation 4* cannot be applicable since the predicted shear stress does not approach zero at limiting shear strain. To accommodate the behaviour at low strains, the value of k may take the form,

$$k = f(\gamma) \cdot \gamma \quad \dots 5$$

where $f(\gamma)$ is a function which decreases with shear strain. The simplest possible form of $f(\gamma)$ which gives the required decrease in $f(\gamma)$

with increasing γ , but which provides a finite value of $f(\gamma)$ at zero strain is:

$$f(\gamma) = \frac{1}{B\gamma + C} \quad \dots 6$$

where B and C are constants.

Shear strain is related to the strain invariant¹ I_1 , by

$$\gamma = (I_1 - 3)^{1/2} \quad \dots 7$$

Substitution of *Equation 7* into *Equation 6* gives,

$$f(\gamma) = \frac{1}{B(I_1 - 3)^{1/2} + C} \quad \dots 8$$

From *Equations 4, 5* and *8*, it follows that the shear stress may be expressed as:

$$\sigma_s = \left[A + \frac{1}{B(I_1 - 3)^{1/2} + C} \right] \gamma \quad \dots 9$$

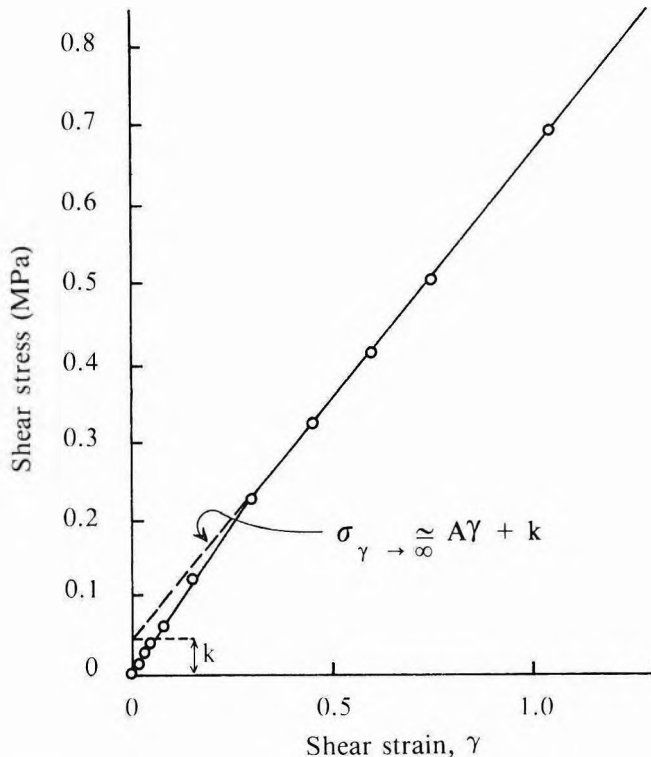


Figure 2. Shear stress as a function of shear strain for rubbers filled with 25 p.p.h.r. N330 black.

The plots of $\frac{\sigma_T}{\lambda - \lambda^{-2}}$ versus $(I_1 - 3)^{1/2}$ were to be approximately the same as the corresponding plots of $\frac{\sigma_s}{\gamma}$ versus $(I_1 - 3)^{1/2}$ for low to moderate strains, suggesting that the function $F(I_1)$ for simple extension and compression is the same as that for simple shear⁶. It follows that a more appropriate form of Equation 9, which is applicable to the three modes of deformation considered will be

$$\sigma = \left[A + \frac{1}{B(I_1 - 3)^{1/2} + C} \right] f(e) \dots 10$$

where $f(e) = \lambda - \lambda^{-2}$ for tension or compression and $f(e) = \gamma$ for simple shear.

Verification of the Stress-Strain Relationship

Correlation between stress and strain. The relationship given by Equation 10 is applicable to tension, compression and simple shear, but verification of the expression is carried out on rubbers subjected to tension deformation because, experimentally, tensile tests are much easier to perform than shear or compression. Furthermore, repeat tests can be carried out for rubbers originating from the same source (*i.e.* same moulded sheet), thus reducing variability.

In tension, Equation 10 may be written as,

$$H = A + \frac{1}{B(I_1 - 3)^{1/2} + C} \dots 11$$

where $H (= \sigma/\lambda - \lambda^{-2})$ is an elastic modulus which depends on the three unknown constants, A , B , and C . Rearranging Equation 11 gives,

$$(H - A)^{-1} = B(I_1 - 3)^{1/2} + C \dots 12$$

If Equation 12 is valid, then plots of $(H - A)^{-1}$ versus $(I_1 - 3)^{1/2}$ should be linear with a slope B and an intercept C .

In principle, A can be estimated from the limiting value of $\frac{d\sigma}{d(\lambda - \lambda^{-2})}$ at high strain. For lightly filled (<20 p.h.r. black) rubbers, a fairly good estimation of A can be obtained

graphically, but for unfilled rubbers estimation of A becomes difficult and inaccurate because the slope of σ versus $\lambda - \lambda^{-2}$ plots at high strains does not reach a limiting value. For heavily filled rubbers on the other hand, the on-set of non-affine deformation at relatively lower strain makes determination of A difficult.

Taking $\frac{d\sigma}{d(\lambda - \lambda^{-2})}$ from the linear portion of σ versus $\lambda - \lambda^{-2}$, curves as the value of A , plots of $(H - A)^{-1}$ versus $(I_1 - 3)^{1/2}$ were made. Typical results are shown in Figures 3 and 4 and the good straight line obtained suggests that Equation 11 gives a good description of the stress-strain behaviour for the low to moderate strain region.

It may be noted that straight lines were only obtained from the plots of $(H - A)^{-1}$ versus $(I_1 - 3)^{1/2}$ in the region before the upturn in the stress-strain curve, or in the region of affine deformation because the proposed relationship (Equation 11) was derived based on the stress-strain behaviour in this region.

The linearity of the plots of $(H - A)^{-1}$ versus $(I_1 - 3)^{1/2}$ is sensitive to changes in A , particularly at high strains where H approaches A . An accurate determination of A is therefore required in order to get accurate values of B and C . Since graphical determination of A was inaccurate, a statistical technique using the method of least squares was subsequently used to obtain parameters A , B and C . In the analyses, variables H and $(I_1 - 3)^{1/2}$ were known, but parameter A was unknown. In order to obtain parameters A , B and C by this method, values of A were fed into Equation 12 at an incremental step of 0.01 MPa. As a first approximation, a limiting value of $\frac{d\sigma}{d(\lambda - \lambda^{-2})}$ was taken as the value A . The values of A , B and C which correspond to the maximum correlation coefficients were taken to be the best fit to the experimental data.

Typical values of parameters A , B and C and the corresponding maximum correlation coefficients obtained are shown in Tables 2-5.

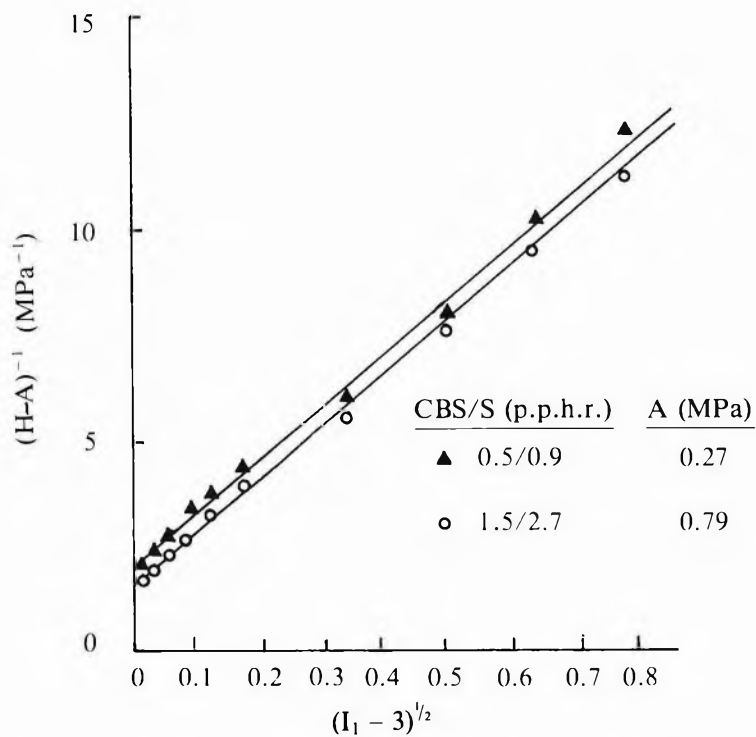


Figure 3. $(H - A)^{-1}$ as a function of $(I_1 - 3)^{1/2}$ for rubbers filled with 20 p.p.h.r. N347 black.

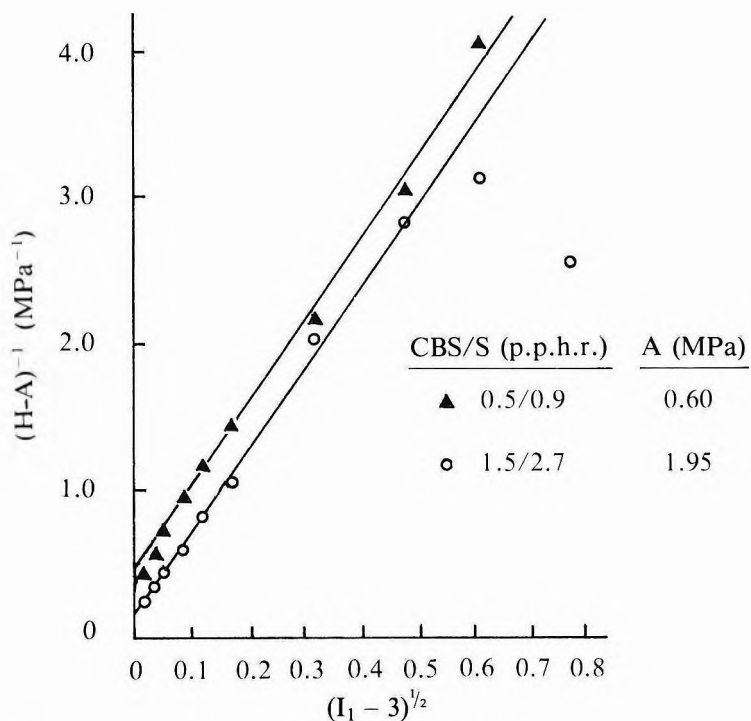


Figure 4. $(H - A)^{-1}$ as a function of $(I_1 - 3)^{1/2}$ for rubbers filled with 60 p.p.h.r. N347 black.

TABLE 2. VALUES OF A, B AND C FOR UNFILLED RUBBERS (SULPHUR AND PEROXIDE SYSTEMS)

Sulphur/Peroxide system	A (MPa)	B (MPa ⁻¹)	C (MPa ⁻¹)	Maximum correlation coefficient
CBS/S (p.p.h.r.)				
0.25/0.45	0.08	5.78	5.55	0.9990
0.5/0.9	0.15	4.73	5.37	0.9983
0.75/1.35	0.22	3.30	5.07	0.9983
1.0/1.8	0.27	2.86	5.06	0.9983
1.25/2.25	0.36	4.29	5.73	0.9976
1.5/2.7	0.450	6.83	5.74	0.9934
DCP (f.p.h.r.)				
1	0.21	7.31	6.41	0.9962
2	0.33	3.40	5.35	0.9973
3	0.50	6.67	7.23	0.9964
4	0.70	6.56	5.90	0.9965

TABLE 3. VALUES OF A, B AND C FOR SULPHUR-CURED N550 BLACK FILLED RUBBERS

Black loading (p.p.h.r.)	CBS/S (p.p.h.r.)	A (MPa)	B (MPa ⁻¹)	C (MPa ⁻¹)	Maximum correlation coefficient
20	0.25/0.45	0.08	7.17	2.89	0.9984
	0.5 /0.9	0.26	9.79	2.71	0.9988
	0.75/1.35	0.35	4.91	3.53	0.9944
	1.0 /1.8	0.56	11.40	3.90	0.9987
	1.25/2.25	0.63	11.22	3.56	0.9983
	1.5 /2.7	0.79	15.12	3.61	0.9981
40	0.25/0.45	0.15	8.47	1.97	0.9986
	0.5 /0.9	0.41	12.04	1.50	0.9975
	0.75/1.35	0.59	10.08	1.49	0.9976
	1.0 /1.8	0.79	11.82	1.51	0.9986
	1.25/2.25	0.97	11.18	1.52	0.9988
	1.5 /2.7	1.13	14.8	2.29	0.9975
60	0.25/0.45	0.21	8.74	1.25	0.9992
	0.5 /0.9	0.54	8.6	1.162	0.9992
	0.75/1.35	0.93	11.06	0.794	0.9991
	1.0 /1.8	1.10	7.45	0.918	0.9987
	1.25/2.25	1.48	8.73	0.688	0.9997
	1.5 /2.7	1.51	10.22	0.613	0.9990

TABLE 4. VALUES OF A, B AND C FOR SULPHUR-CURED N347 BLACK FILLED RUBBERS

Black loading (p.p.h.r.)	CBS/S (p.p.h.r.)	A (MPa)	B (MPa ⁻¹)	C (MPa ⁻¹)	Maximum correlation coefficient
20	0.25/0.45	0.10	10.46	2.99	0.9995
	0.5 /0.9	0.28	9.30	2.52	0.9994
	0.75/1.35	0.46	10.22	2.33	0.9991
	1.0 /1.8	0.52	9.33	2.26	0.9997
	1.25/2.25	0.68	13.93	2.34	0.9989
	1.5 /2.7	0.80	12.94	2.08	0.9993
40	0.25/0.45	0.09	8.63	1.61	0.9993
	0.5 /0.9	0.36	8.15	0.93	0.9989
	0.75/1.35	0.58	7.65	0.71	0.9996
	1.0 /1.8	0.76	8.07	0.77	0.9990
	1.25/2.25	0.93	8.09	0.57	0.9995
	1.5 /2.7	1.13	9.09	0.41	0.9982
60	0.25/0.45	0.32	7.63	0.53	0.9996
	0.5 /0.9	0.62	5.94	0.43	0.9985
	0.75/1.35	0.97	5.38	0.31	0.9995
	1.0 /1.8	1.35	7.13	0.17	0.9981
	1.25/2.25	1.57	5.00	0.19	0.9995
	1.5 /2.7	2.05	7.67	0.068	0.9940

For unfilled rubbers of different crosslink densities (Table 2), the maximum correlation coefficients of the range 0.9934 – 0.9990 were obtained. For sulphur-cured rubbers, the values of the maximum correlation coefficients improved with decreasing crosslink density (*i.e.* lower sulphur content) averaging about 0.9975. For peroxide-cured rubbers, the average maximum correlation coefficient was about 0.9966, which was comparable to that of the corresponding sulphur system.

Typical values of the correlation coefficients for filled rubbers are given in Tables 3–5. For rubbers filled with N550 black and crosslinked using the sulphur vulcanising system (semi-EV), maximum correlation coefficients from 0.9944 to 0.9992 were obtained. The correlation coefficients appeared to be generally better for those containing 60 p.h.r. black than those

containing 20 p.h.r. black. The maximum correlation coefficients of rubbers filled with N347 black and crosslinked using the sulphur vulcanising system (semi-EV) ranged from 0.9940 to 0.9998, with less heavily filled rubbers (*e.g.* 20 p.h.r. black) having higher correlation coefficients than the heavily filled rubbers. The peroxide-cured rubbers showed equally good maximum correlation coefficients, ranging from 0.9943 to 0.9999 (Table 5).

Generally, the lightly filled and unfilled rubbers gave relatively poorer maximum correlation coefficients compared to heavily filled rubbers. For over two hundred rubbers tested, the maximum correlation coefficients obtained varied from 0.9934 to 0.9999, which are fairly good and these results showed that the plots of $(H-A)^{-1}$ versus $(I_1 - 3)^{1/2}$ were linear and that Equation 11 is valid.

TABLE 5. VALUES OF A, B AND C FOR PEROXIDE-CURED N550 AND N347 BLACK FILLED RUBBERS

Black loading	Dicumyl peroxide (p.p.h.r.)	A (MPa)	B (MPa ⁻¹)	C (MPa ⁻¹)	Maximum correlation coefficient
20 p.p.h.r. FEF	1	0.25	14.75	4.39	0.9982
	2	0.47	23.43	4.53	0.9991
	3	0.62	15.30	4.93	0.9998
	4	0.82	25.75	3.67	0.9998
40 p.p.h.r. FEF	1	0.38	13.45	2.42	0.9991
	2	0.67	17.85	2.01	0.9995
	3	0.92	17.15	2.01	0.9997
	4	1.21	19.07	1.50	0.9995
60 p.p.h.r. FEF	1	0.51	10.45	1.23	0.9996
	2	0.91	12.06	0.80	0.9997
	3	1.29	15.25	0.70	0.9997
	4	1.64	16.36	0.57	0.9998
20 p.p.h.r. HAF-HS	1	0.26	10.60	3.09	0.9997
	2	0.46	12.93	3.30	0.9997
	3	0.60	17.39	2.63	0.9986
	4	0.87	27.92	2.40	0.9998
40 p.p.h.r. HAF-HS	1	0.37	10.13	1.20	0.9993
	2	0.64	12.54	0.87	0.9943
	3	0.95	12.80	0.72	0.9999
	4	1.18	14.15	0.69	0.9997
60 p.p.h.r. HAF-HS	1	0.58	8.25	0.63	0.9989
	2	1.01	8.23	0.43	0.9993
	3	1.37	8.61	0.43	0.9994
	4	1.74	10.21	0.30	0.9994

Comparison between experimental and predicted values. Equation 10 gives the value of H or G as a function of $(I_1 - 3)^{1/2}$, with parameters A , B and C as constants. For either tension, compression or simple shear, values of A , B and C for a particular rubber would be the same if H and G are identical at equal $(I_1 - 3)^{1/2}$. Hence, knowing the values of A , B and C for any one mode of deformation may allow prediction of stress-strain values in other modes of deformation to be made.

Values of A , B and C were obtained using the method of least squares from data obtained in simple extension. With these values of A , B and C , prediction of tensile,

compressive and shear moduli were made using Equation 11. Typical results are shown in Figures 5-7, where the continuous lines represent the predicted values and the points are the experimental values.

In tension (Figure 5), good agreement was obtained between the experimental and predicted values, with deviation differing with the former by not more than 3% for both unfilled and filled rubbers at low to moderate strains.

Comparisons between the experimental and predicted compressive moduli are shown in Figure 6. The agreement observed was also

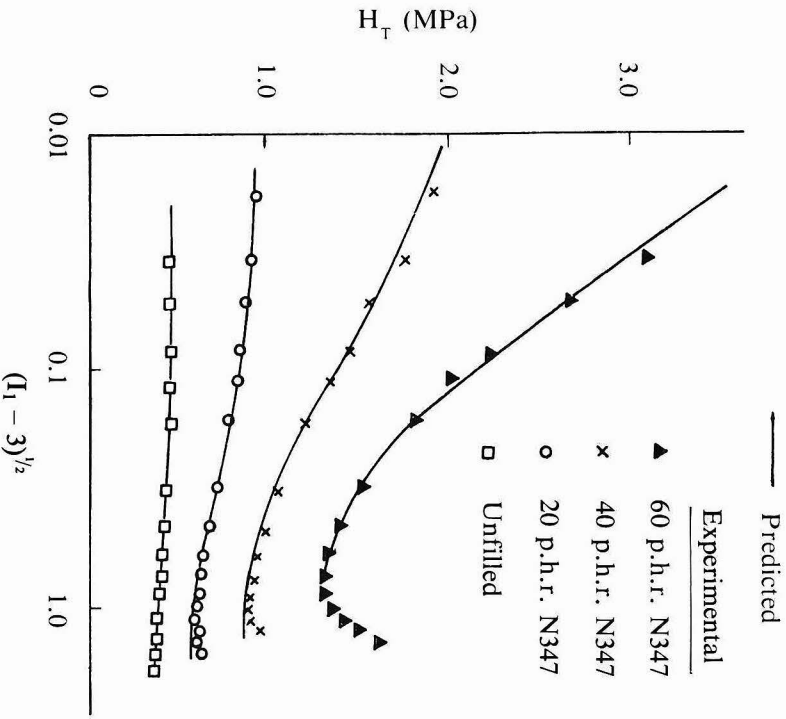


Figure 5. Comparison between experimental and predicted tensile moduli.

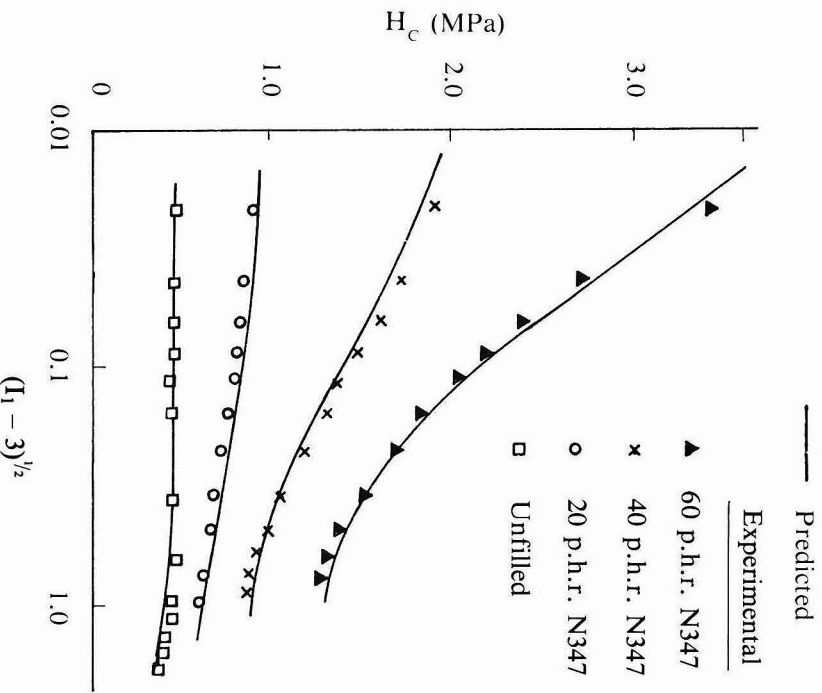


Figure 6. Comparison between experimental and predicted compressive moduli.

reasonably good, with the predicted values differing by not more than 5% from the experimental values for all rubbers tested.

For simple shear deformations (*Figure 7*), the agreement observed between the experimental and predicted moduli was similar to those observed with compression, with not more than 5% deviation. The agreement appears to be better with heavily filled rubbers (60 p.h.r. N347) than with lightly filled rubbers.

Thus, at low to moderate strains (*i.e.* before the upturn in stress-strain curve) *Equation 10* has been shown to give a good description of the stress-strain behaviour of both filled and unfilled rubbers crosslinked with different vulcanising systems. The shear and compressive moduli were able to be predicted to

within 5%, using the data from simple extension, and this will enable tests in different modes of deformation to be rationalised and simplified. The proposed equation is also more useful than the available stress-strain relationship because it is applicable to filled rubbers and it correctly predicts the non-linear stress-strain behaviour in simple shear.

Physical significance of parameters A, B and C. The proposed relationship between stress and strain takes the form

$$H \text{ or } G = A + \frac{1}{B(I_1 - 3)^{1/2} + C} \quad \dots 13$$

where $H = \sigma / \lambda - \lambda^{-2}$, $G = \sigma / \gamma$ and A, B and C are constants. The limiting conditions for the proposed relationship are:

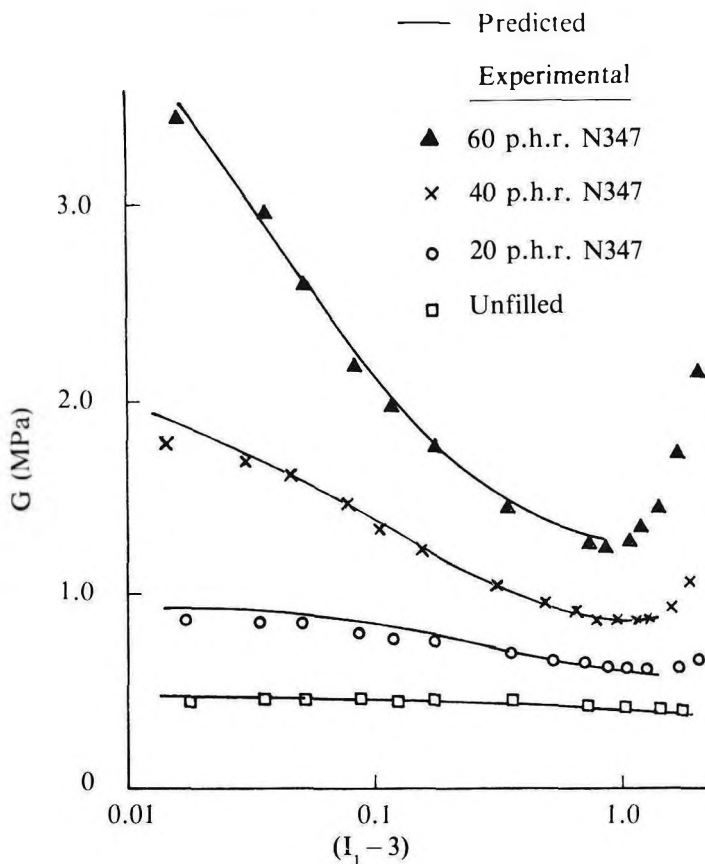


Figure 7. Comparison between experimental and predicted shear moduli.

as $(I_1 - 3)^{1/2} \rightarrow 0, H_c = A + \frac{1}{C} \dots 14$
 and as $(I_1 - 3)^{1/2} \rightarrow \infty, H_\infty = A$

The parameter A is equivalent to H_∞ or G_∞ , the modulus at high strain. According to Payne^{7,8}, G_∞ is the value of shear modulus which is independent of strain at sufficiently high strains *i.e.* at strains greater than those needed to breakdown any structure of carbon black.

The difference in modulus, $H_0 - H_\infty = \frac{1}{C}$ gives the value of the change in modulus with strains^{7,8}, which is normally expressed as $G_0 - G_\infty$. This term has been attributed to the structural effect of carbon black agglomeration *i.e.* $G_0 - G_\infty$ arises from the breakdown of the carbon black agglomerate structures. Since $\frac{1}{C}$ is equal to $G_0 - G_\infty$, the former describes the extent of breakdown of carbon black structure due to the effects of strains.

From Equations 13 and 14, it is clear that the parameter B is non-contributing at the limiting strains. However, in between the two strain limits, parameter B gives a significant effect since it is associated with the strain invariant, I_1 . The modulus contribution from the $B(I_1 - 3)^{1/2}$ term decreases with strain while that of A and $\frac{1}{C}$ are constant. Thus, parameter B may be associated with the manner in which H_0 changes to H_∞ .

CONCLUSION

A semi-empirical relationship which describes the stress-strain behaviour of filled rubber has been developed. The relationship, which expresses nominal stress as a function of strain invariant I_1 , is developed based on the assumption that the shear modulus is independent of strain at high strain.

The relationship is applicable to various types of filled rubbers subjected to low to moderate strains. It relates a modulus H in tension/compression or G in simple shear to a strain invariant I_1 and three parameters A, B, C , viz.

$$H \text{ or } G = A + \frac{1}{B(I_1 - 3)^{1/2} + C}$$

where $H = \sigma / \lambda - \lambda^{-2}, G = \sigma / \gamma, I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ and σ, λ, γ are the nominal stress, extension ratio and shear strain, respectively. At equal I_1 , the modulus H is observed to be identical to G .

The relationship enables the prediction of stress-strain behaviour of filled rubber in different modes of deformation to be made using known values of parameters A, B and C obtained from a simple mode of deformation. This enables the testing of rubber to be simplified and rationalised.

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