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CONTENTS

EPOXIDIZED NATURAL RUBBER

By

M. C. S. PERERA* AND J. H. BRADBURY
(Chemistry Department, Australian National University, Canberra, A.C.T. 2600, Australia)

Epoxidized natural rubber has certain very important properties. These include an increase in the glass transition temperature T_G as compared to natural rubber, increased tensile strength and abrasion resistance and improved solvent resistance to petrol and engine oil as well as to oxidation by ozone. These desirable properties make this modified natural rubber of potential industrial importance and there are papers at this conference which discuss these aspects.

It is also important to study the chemistry of the epoxidation process and the chemistry of epoxidized natural rubber and this is the thrust of this paper. Mr. Senake Perera from the Rubber Research Institute of Sri Lanka is completing a Ph.D. course at the Australian National University. He has used ^1H and ^{13}C NMR spectroscopy to identify the products of the epoxidation reaction and also to study the chemistry of epoxidation of natural rubber. Epoxidation of natural rubber and of other unsaturated elastomers has been known for many years and there have been several NMR studies (Gemmer and Golub, 1978, Hayashi *et al* 1980 and 1981), which have lead to various assignments of NMR resonances. In this paper we particularly focus attention on the question of whether or not epoxidation of natural rubber in solution or in latex is a random process.

MATERIALS AND METHODS

Epoxidation of natural rubber was carried out (Gemmer and Golub, 1978) in homogeneous solution in chloroform or benzene using the stoichiometric amount of m-chloroperoxybenzoic acid to give the required amount of epoxidation and (Hayashi *et al.*, 1980) in latex using formic acid and a slight excess of H_2O_2 for 18 h at 20°C (Bradbury and Perera not published). By careful control of the amount of acid used in the second method, the ring opening reaction, which produces a formyl ester and an alcohol, was prevented. Partly epoxidized rubber produced by method 1 was entirely soluble, but that produced by method 2 gave some gel, due to cross linking. The extent of epoxidation was determined by the ratio of the peak areas at δ 2·68 and the sum of the peak areas at δ 5·08 and δ 2·68 (Fig 1).

RESULTS AND DISCUSSION

The ^{13}C NMR spectrum of natural rubber in $CDCl_3$ shown in Figure 2 with assignments is a simple five line spectrum (5), whereas the spectrum of 40% epoxidized natural rubber is far more complex.

* Permanent address : Rubber Research Institute of Sri Lanka, Dartonfield, Agalawatta, Sri Lanka.

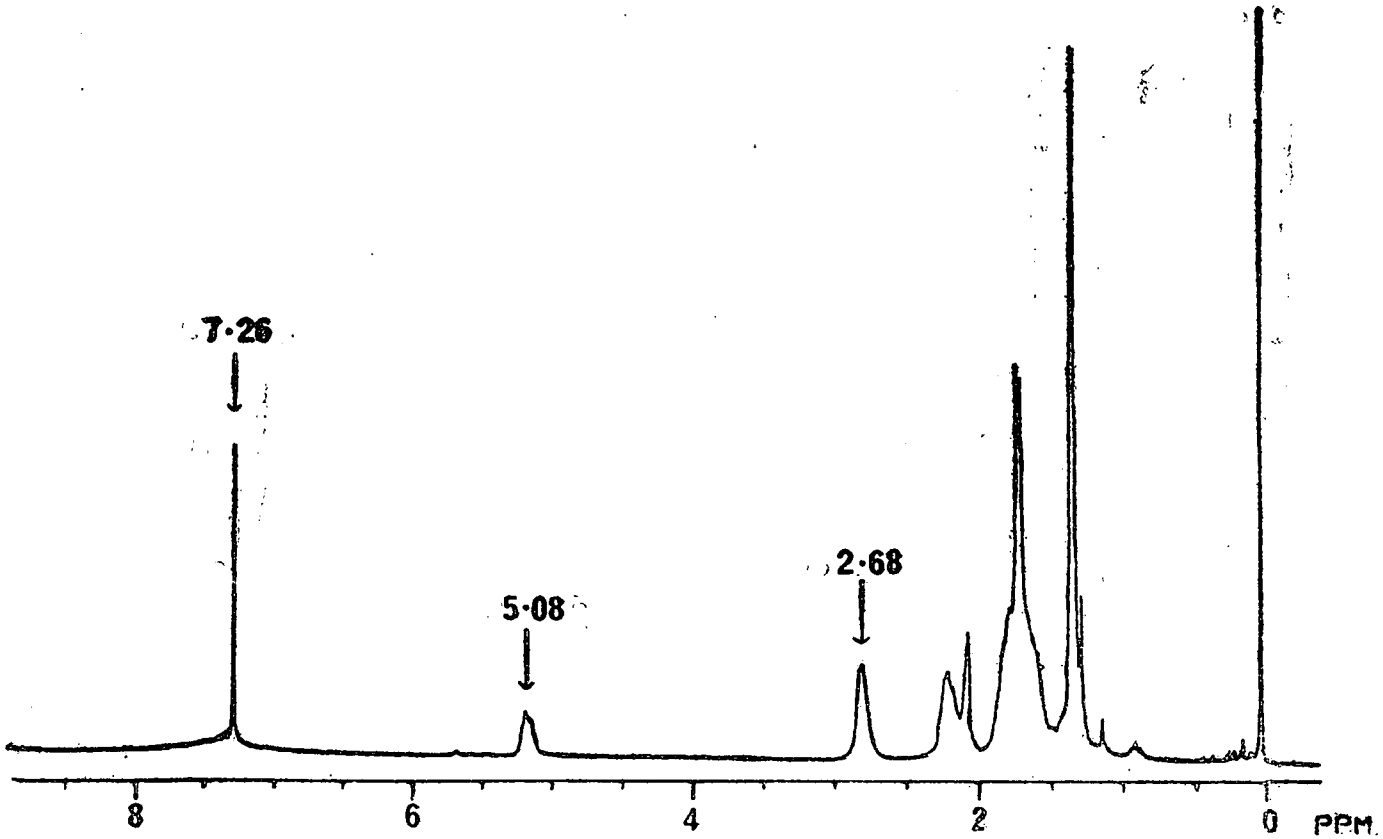
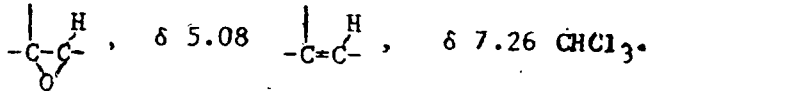


Fig. 1. ^{1}H NMR spectrum at 270 MHz in $CDCl_3$ of 65% epoxidized natural rubber. Peak assignments are δ 1-2·5 $-CH_2$ and $-CH_3$, δ 2·68



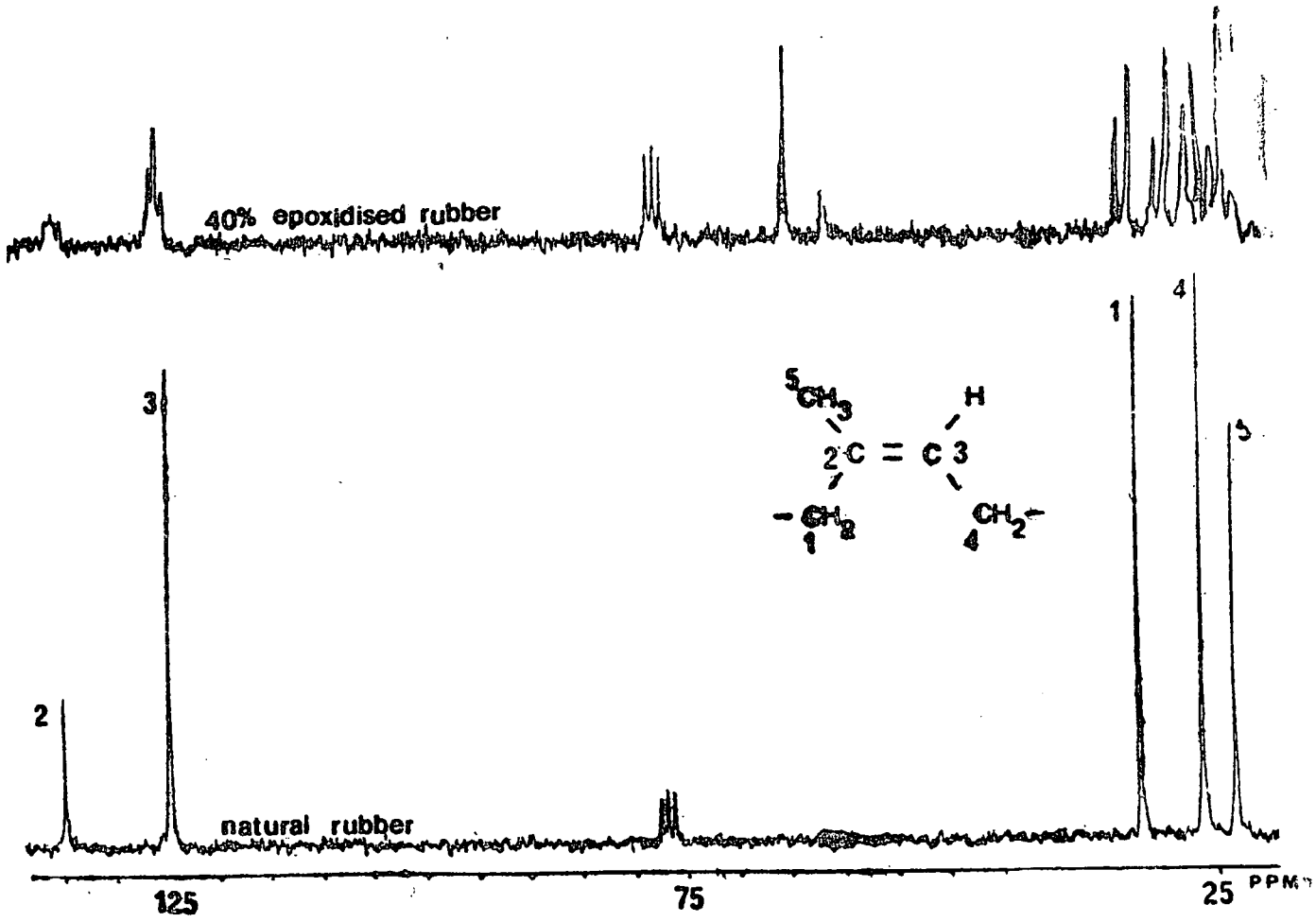


Fig. 2. ^{13}C NMR spectra (67·89 MHz) in $CDCl_3$ of natural rubber and of 40% epoxidized rubber. Triplet due to solvent at δ 77.

We note (a) the downfield position of the resonances of the olefin carbon atoms of natural rubber and of the corresponding resonances in 40% epoxidized rubber, (b) the occurrence of new peaks at 60 — 65 δ in the 40% epoxidized rubber spectrum due to the -C-C- carbon atoms and (c) the resonances at high field in both spectra due to
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the methyl carbon atom (resonance 5) and to the methylene carbon atoms (resonances 1 and 4). In order to interpret the complex spectrum observed with 40% epoxidized natural rubber, it is necessary to study the spectrum of 100% epoxidized natural rubber shown in Fig. 3.

The assignment of resonances 2 and 3 given in Fig. 3 was confirmed by the use of a special pulse sequence INEPT (insensitive nuclei enhancement by polarization transfer) (Morris and Freeman, 1979) which caused resonances from methyl and methine carbon atoms to remain in phase, methylene resonances to be inverted and quarternary resonances to disappear. The splitting of the resonances was at first surprising, because we had expected to obtain a simple five line spectrum as was observed for natural rubber in Fig. 2 However there are two possible modes of attachment of the epoxy group to the double bond which gives rise to form possible stereoisomers if one considers two adjacent epoxide groups as shown in Fig. 4. Structures a and b are optical isomers (enantiomers) and so are structures c and d, hence a and b would give the same NMR spectrum and c and d would also give the same spectrum. But each pair are diasterecisomers, hence each pair will give rise to a separate resonance, *i.e.* the pair a + b will have a different resonances from c + d. This accounts for the splitting of resonances 3, 2 and 1 in Fig. 3.

Assignment of NMR Spectrum of Partially Epoxidized Rubber

The expansion of the high field region of the ^{13}C NMR spectrum of partially epoxidized rubber given in Fig. 2 is shown in Fig. 5. The two resonances labelled C_5 - 1 and C_5 - 2 are assigned to methyl carbon atoms attached to olefinic and oxirane groups respectively. The detailed interpretation of the resonances C_1 - 1 to C_1 - 6 and of C_4 - 1 to C_4 - 6 is made in terms of the triad structures shown in Fig. 6. The triad sequence is a sequence of three monomer (isoprene) units using C to represent an unmodified isoprene unit and E to represent an epoxidized unit, e.g. CCC represents three isoprene units in sequence. The eight possible structures are given in Figure 6 and we will consider the environment of the five carbon atoms of the *central* unit only of the triad structure. The five carbon atoms are designated 1 to 5 as shown in Figure 2 and a shorthand notation is used in which the carbon atoms on the left of the double bond 'or (oxirane unit) are put on the left and those on the right of the double bond on the right. For example E^1EE refers to the C_1 atom of the middle monomer (oxirane) unit and EE^3E means the C_3 atom of the middle unit.

Rather than describe all the details of the assignment which are given elsewhere (Bradbury and Perera, not published), we will focus attention on the various methods that have been used. Resonances that increase in intensity from zero as the level of epoxidation increases must arise from EEE and these which decrease in intensity to zero at 100% epoxidation arise from CCC. Some resonances increase in intensity from zero to a maximum and then decrease again to zero at 100% epoxidation and these arise from

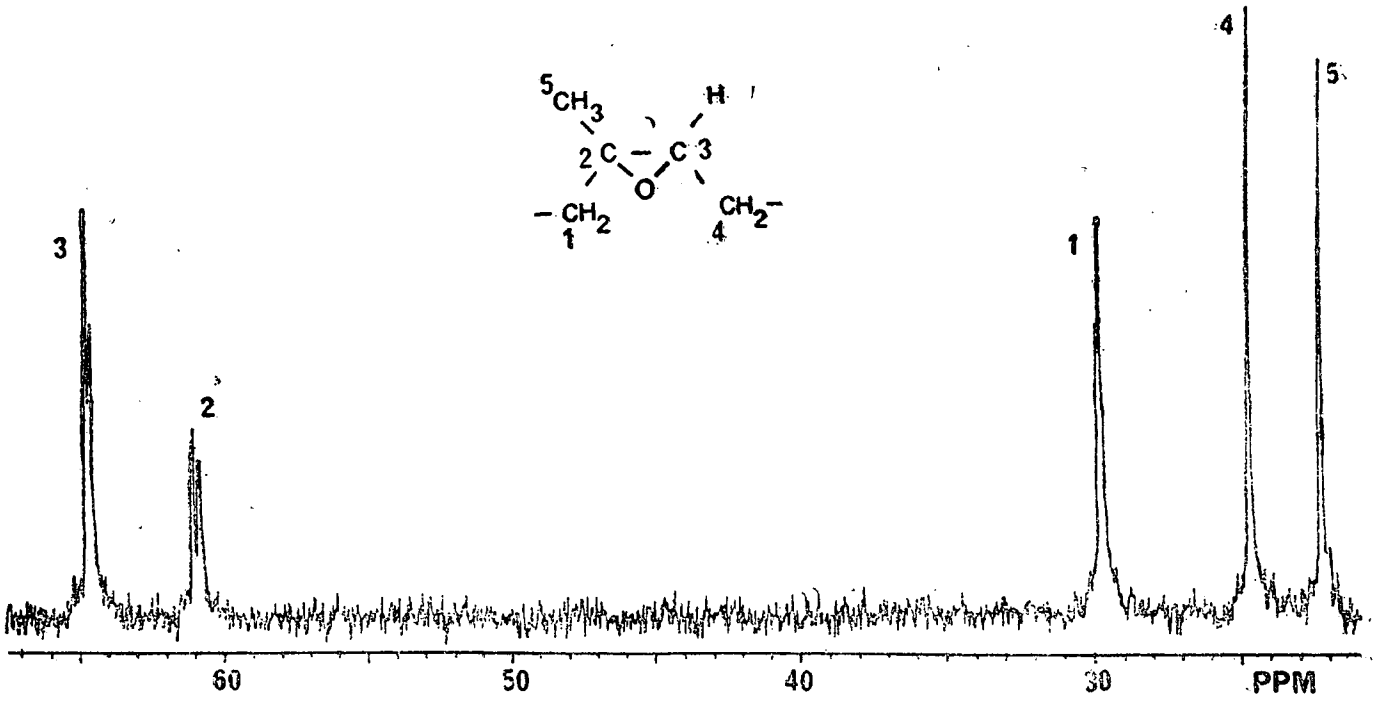


Fig. 3. ^{13}C NMR spectrum (67·89 MHz) of fully epoxidized natural rubber swollen in $CDCl_3$.

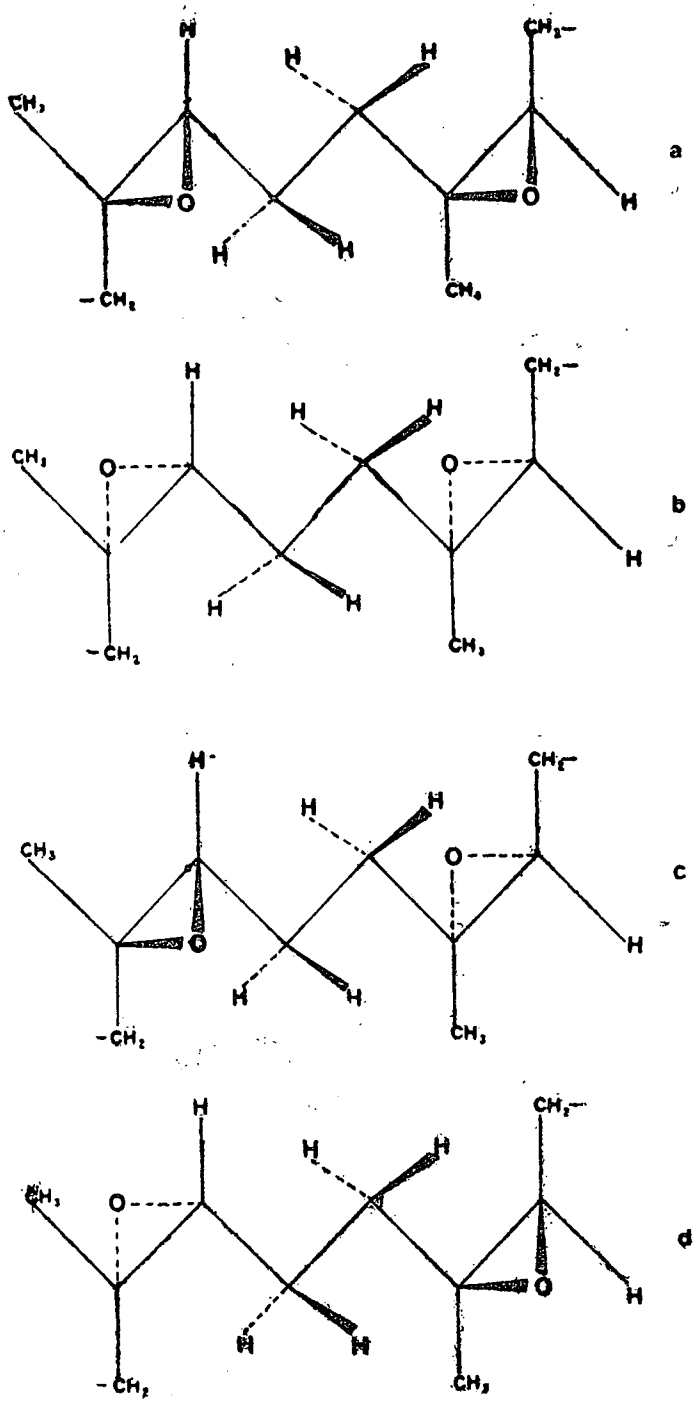


Fig. 4. Four possible isomers of two adjacent epoxide units.

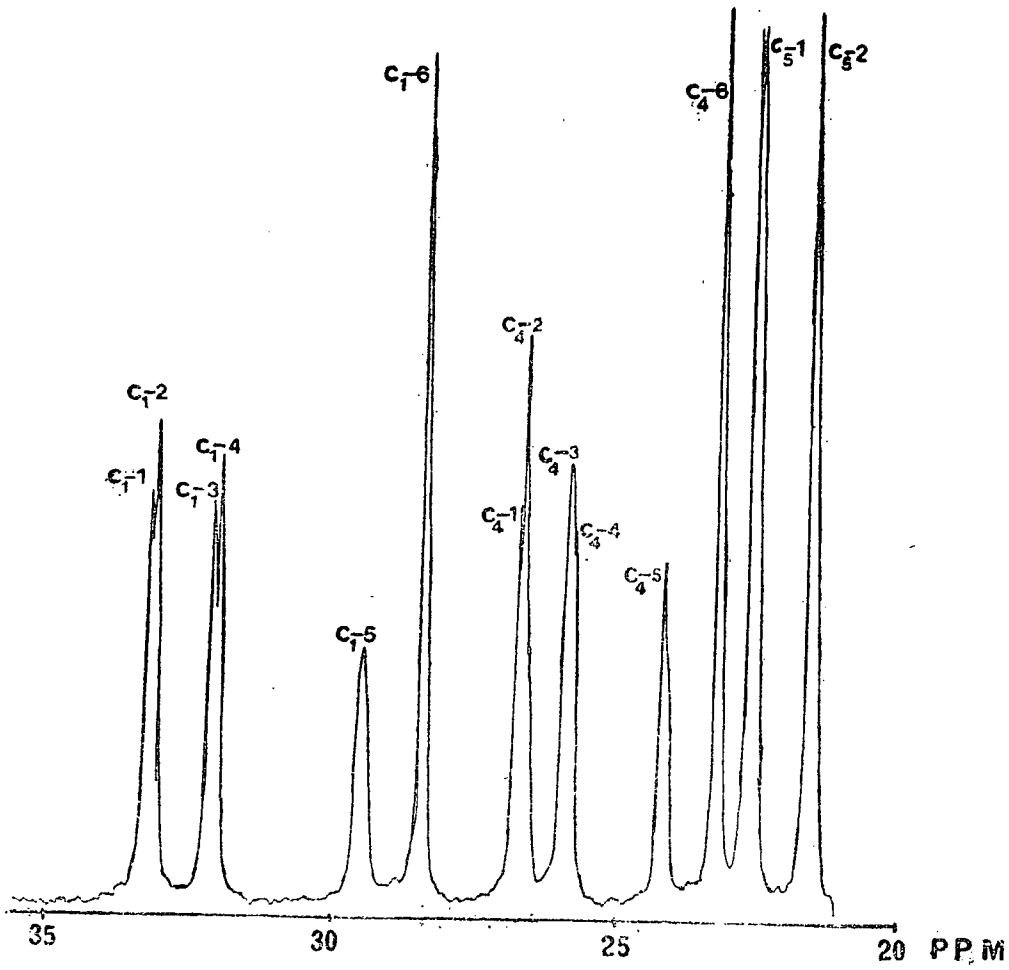


Fig. 5. Expansion of the high field region of the ^{13}C NMR spectrum of 40% epoxidized natural rubber shown in Figure 2.

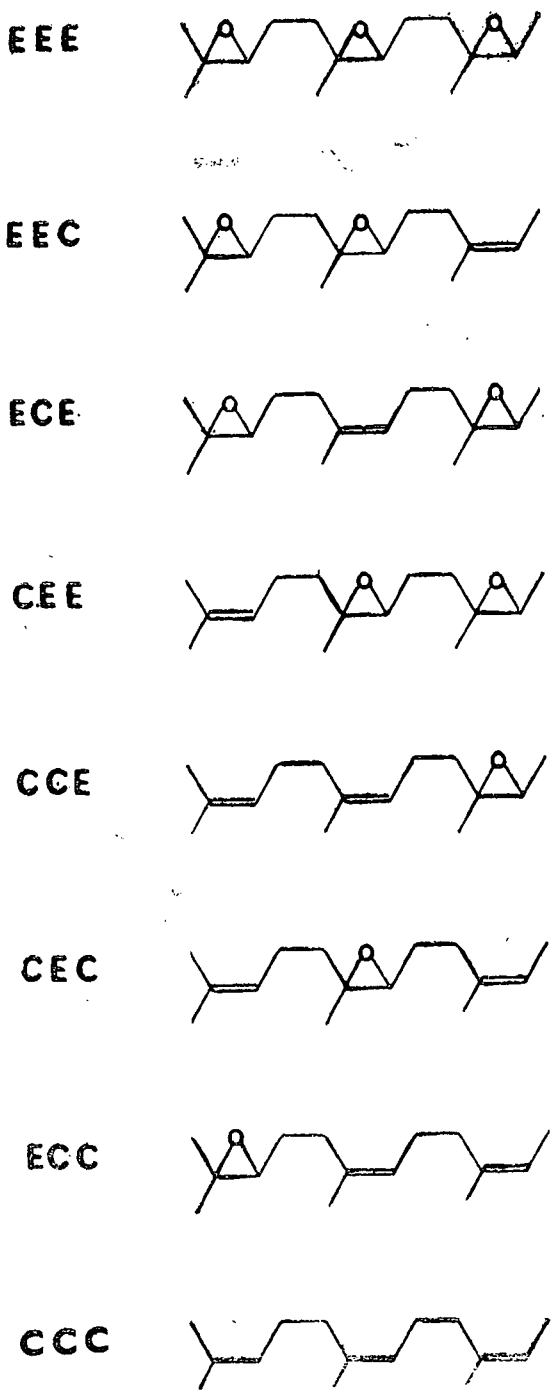


Fig. 6. Triad sequences of epoxy isoprene units (E) and of unepoxidized isoprene units (C) in partly epoxidized natural rubber.

C_1 and C_4 atoms that are not present at 0% or 100% epoxidation. Also a lanthanide shift reagent ($Eu(fod)_3$) was used (Bradbury and Perera, not published). The metal binds to epoxide groups and the paramagnetic species causes a progressive shift of the resonances, which increases with the concentration of the lanthanide reagent added. The shifts for various C_1 resonances are shown in Fig. 7. Resonance C_1 - 3 undergoes no shift on addition of Eu $(fod)_3$ which would be consistent with no binding of $Eu(fod)_3$, hence the triad is assigned to CCC (Table 1). Resonance C_1-6 shifts more strongly on addition of the lanthanide shift reagent than C_1-4 and this is consistent with the assignments given in Table 1. By the use of these methods we have obtained assignments shown in Table 1 and the earlier assignments due to Gemmer and Golub (1) have been confirmed. By the use of similar techniques it has been possible to make assignments of the ^{13}C NMR resonances of the olefinic and oxirane regions of the spectrum shown in Fig. 2 (4).

Table 1. *Resonance assignments for methyl and methylenecarbone* (see Fig. 5)

Resonance (see Figure 5)	Chemical Shift ppm	Assignments
C_1 - 1	33·31	C_1EC*
C^1 - 2	33·21	C_1EE
C^1 - 3	32·24	C_1CC*
C_1 - 4	32·11	C_1CE
C_1 - 5	29·73	E_1EC, E_1EE
C_1 - 6	28 78	E_1CC, E_1CE
C_4 - 1	27·15	CE_4C*
C_4 - 2	27 07	EE_4C
C_4 - 3	26 43	CC_4C*
C_4 - 4	26·36	EC_4C
C_4 - 5	24·76	EE_4E, CE_4E
C_4 - 6	23 89	EC_4E, CC_4E
C_5 - 1	23·43	^5C *
C_5 - 2	22·34	^5E *

*Assignments by Gemmer and Golub (1).

Monomer Sequence Distribution

It is possible to determine the amount of each of the eight possible triads (Fig. 6) by measuring the intensities (areas) of the ^{13}C NMR resonances. These are proportional to the amounts of carbon atoms providing that (Gemmer and Golub, 1978) pulse repetition times on the spectrometer are $> 5\ T_1$ (where T_1 is the spin lattice relaxation time) and (Hayashi *et al*, 1980) that the nuclear Overhauser enhancements are constant. The latter were assumed to be constant for all methylene groups and the former proviso was met. It is therefore possible to compare the experimentally determined amounts of the various triad structures with those expected based on a random distribution (Table 2).

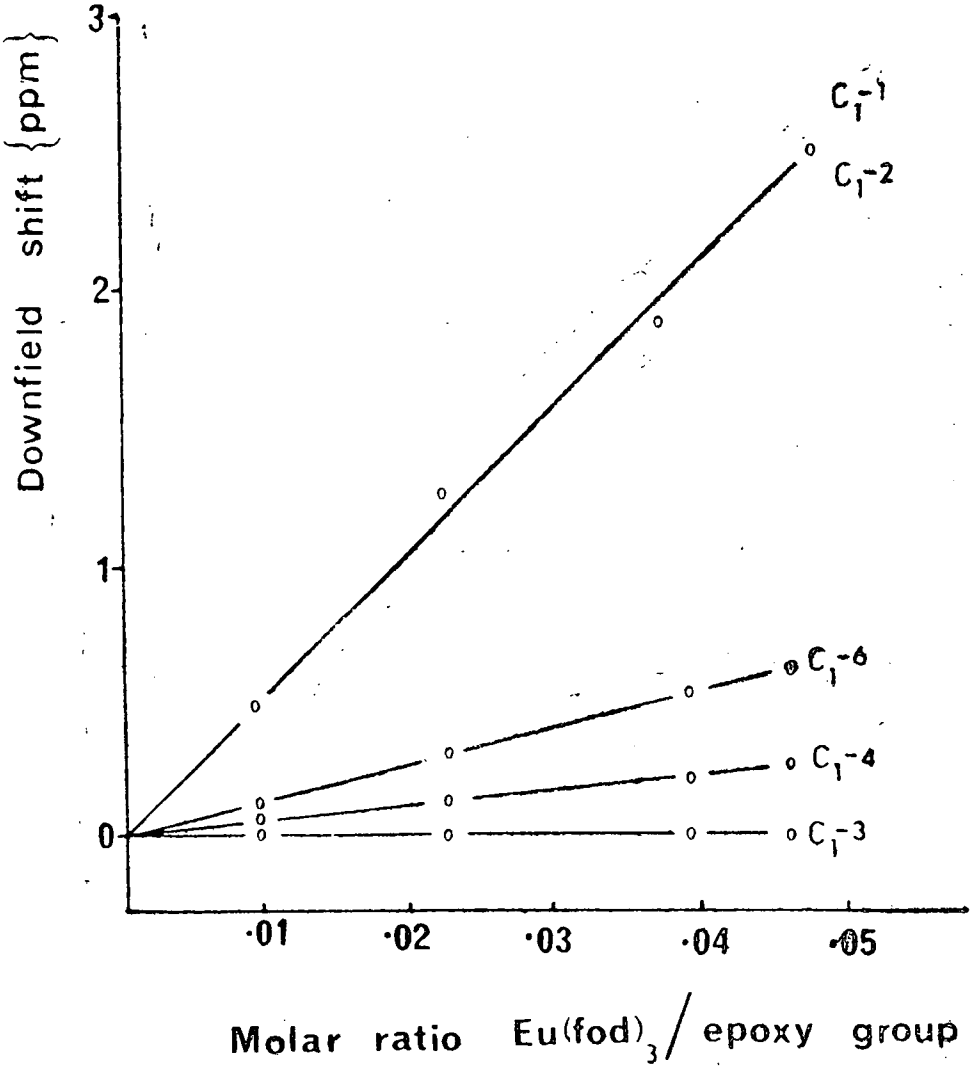


Fig. 7. Shifts of resonances from C_1 atoms (Figure 7) on addition of the lanthanide shift reagent $Eu(fod)_3$.

It is noted that, considering the likely errors in the experimental procedure, there is reasonable agreement between the values obtained by either the solution method or the latex method of epoxidation with the theoretical value calculated on the basis of random epoxidation. The agreement, obtained at three different levels of epoxidation shows that random epoxidation occurs in both homogeneous solution (solution method) and in the colloidal system (latex). The latter result shows that performic acid readily penetrates the latex particle and effects epoxidation evenly throughout the droplet. This agrees with a related study by Burfield *et al* (Burfield, Lim and Lan 1984) who found random epoxidation using peracetic acid and an independent study by Davey and Loadman (Davey and Loadman, in press) who also reached the same conclusion as we have, using other physico-chemical methods.

Table 2. *Experimental and theoretical* percentages of occurrence of triad sequences in natural rubber epoxidized to different levels*

Method of Epoxidation	Level of Epoxidation %							
	40			54		64		
	Solution	Latex	Theor.	Latex	Theor.	Solution	Latex	Theor.
Triad Sequence								
CEC, CEE	23	23	24	21	25	22	24	23
CCC	20	19	22	8	9	4	6	4
CCE	16	15	14	10	11	7	8	8
EEC, EEE	18	15	16	28	31	44	39	42
ECC	16	17	14	10	11	7	7	8
ECE	11	11	10	17	14	16	17	15

* The theoretical percentage occurrence of a particular triad is calculated assuming random placement of epoxide groups along the chain.

Finally, epoxidized natural rubber may be used as an intermediate in further chemical reactions to produce desired products. For example, we have been able to produce furanised natural rubber which consists of a five membered furan ring structure repeating along the polymer chain. The chemistry of the modification of natural rubber is a rich field of study and we are currently studying further reactions with a view to the preparation of possibly useful polymeric material.

ACKNOWLEDGEMENTS

Dr. J. A. Elix is thanked for useful discussions and Dr. A. J. Jones for obtaining some of the NMR spectra. Mr. M. C. S. Perera is the recipient of a Colombo Plan Ph.D. Award.

REFERENCES

BRADBURY, J. H. AND PERERA, M. C. S. *J. Appl. Polym. Sci.*, accepted for publication.

BURFIELD, D. R., LIM, K. L. AND LAN, K. S. (1984). *J. Appl. Polym. Sci.* **29**, 1661.

DAVEY, J. E. AND LOADMAN, M. J. R. *Brit. Polym. J.*, in press.

DUCH, M. W. AND GRANT, D. M. (1970). *Macromolecules* **3**, 165.

GEMMER, R. U. AND GOLUB, M. A. (1978). *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2985.

HAYASHI, O., TAKAHASHI, T. KURIHARA, H. AND UENO, H. (1980). *Kobunshi Ronbunshi* **37**, 195.

HAYASHI, O., TAKAHASHI, U., KURIHARA, H. AND UENO, H. (1981). *Polym. J.* (Japan) **13**.

MORRIS, G. A. AND FREEMAN, R. (1979). *J. Am. Chem. Soc.*, **101**, 760.

DISCUSSION

Q — L. M. K. TILLAKERATNE, (RRISL) : Formic acid & hydrogen peroxide system in the presence of H_2SO_4 is a very strong oxidising system.

Are there possibilities of chain cleavage of rubber due to oxidation during the reaction ? If so how do you control it ?

A — M. C. S. PERERA, (RRISL) : We get no evidence of chain cleavage either by NMR studies or by viscosity studies (Bradbury, Elix & Perera, J. App. Poly. Sci., submitted for publication) on our product, epoxidised by use of formic acid and hydrogen peroxide in controlled amounts at 20°C for 18 h. However use of excess acid (particularly H_2SO_4) causes chain cleavage as obtained by earlier workers.

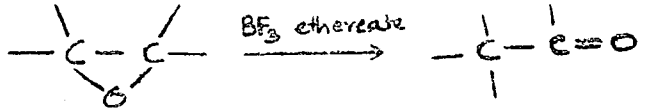
Q — W. S. E. FERNANDO, (RRISL) : How do you explain acidity (low pH) in epoxy rubbers — Malaysian version ? Is it residual acid or main chain modifications ?

A — M. C. S. PERERA, (RRISL) : It is unlikely to be due to main chain modifications because we do not see any evidence of new groups in our NMR spectra, even at 100% epoxidation. It is therefore probably due to residual formic acid which remains in the rubber and would be difficult to remove.

Q — S. W. KARUNARATNE, (RRISL) : Epoxidation in solution is advocated by you because of the gel formation using latex ?

A — M. C. S. PERERA, (RRISL) : Epoxidation of latex causes some gel formations whereas epoxidation of rubber dissolved in solution (benzene or chloroform) gives no gel formation. From the practical point of view the only reaction that can be done cheaply enough is epoxidation of latex with formic acid and hydrogen peroxide and so we must be willing to accept a small amount of cross-linking.

Q — D. K. WEERASINGHE, (TRI) :



Should be very good leading to a lot of derivatives

A — M. C. S. PERERA, (RRISL) : I agree that this reaction may be potentially very useful new modified rubber products.

Q — J. LOADMAN, (MRPRA) : You suggested some crosslinking in latex epoxidation. Have you any NMR data to support this ?

A — M. C. S. PERERA, (RRISL) : The amount of crosslinking is too small to be obeserved by NMR spectroscopy.

Q — ABU AMU, (RRIM) : During epoxidation, gellation occurs. Can you explain the reason for this gellation ?

A — M. C. S. PERERA, (RRISL) : This must be due to the formation of crosslinks in the case of epoxidation of latex but they do not occur on epoxidation in solution.

The crosslinks in the former case may be due to the presence of non rubber compounds such as proteins in the latex or to the closer contact between adjacent chains in latex droplets as compared with a dilute solution of rubber in benzene or chloroform.

GRAFT COPOLYMERISATION OF ACRYLONITRILE WITH NATURAL RUBBER

By

N. M. CLARAMMA, G. RAJAMMAL AND E. V. THOMAS
(Rubber Research Institute of India, Kottayam 686 009, India)

INTRODUCTION

Graft copolymers are particular kinds of polymers in which a second monomer is copolymerised with an existing polymer. When vinyl monomers are polymerised in presence of natural rubber (NR) under suitable conditions, some of the new polymeric chains formed, get attached to rubber molecules and a graft copolymer is obtained. These graft copolymers have a combination of properties of both natural rubber and the vinyl polymer. In this way the properties of natural rubber can be widely modified according to the nature and quantity of the graft copolymer.

Polymerisation reactions of various vinyl monomers dispersed in natural rubber latex have been reported (Bloomfield et al 1954. Burfield & Ng 1975, Rajammal et al 1980). The most promising graft copolymers based on natural rubber, so far obtained are those derived from methyl methacrylate and styrene. Acrylonitrile (ACN) when grafted with natural rubber, gives a reinforced material with improved resistance to oils and solvents (Naunton 1961). Graft copolymers of natural rubber containing acrylonitrile have been made from latex (Fernando et al 1978).

Polymerisation of acrylonitrile monomer to polyacrylonitrile using potassium persulphate/sodium bisulphite initiator system has been reported (Sorenson & Campbell 1961). This paper discusses the standardisation of a procedure for graft copolymerisation of acrylonitrile with natural rubber in latex stage, using potassium persulphate/sodium bisulphite initiator system. The technological properties of the resultant product have also been evaluated in comparison with, those of natural rubber and nitrile rubber.

MATERIALS AND METHODS

Field latex collected from RRII Experiment Station and acrylonitrile (Reagent Grade) were used as the Starting materials. Other chemicals like sodium lauryl sulphate, potassium persulphate and sodium bisulphite were of AR grade.

Acrylonitrile was graft copolymerised with natural rubber field latex using potassium persulphate/sodium bisulphite initiator system. For evolving the optimum conditions for the graft reaction, the following factors were studied.

Concentration of latex stabiliser

Ammonia is the most suitable preservative for natural rubber latex. But polymerisation of acrylonitrile is inhibited by ammonia (Mark et al 1964) and hence ammonia was

not used as the preservative for natural rubber latex in the present study. The suitability of other stabilizers like ethylene oxide condensate (Vulcastab LW) and sodium lauryl sulphate at different concentrations (2·5 to 7·5 phr) was studied. The recipe used for the study was as follows :

Ingredients	*Parts by Weight*	
	Dry	*Wet*
Field latex (35% DRC)	100	286
Acrylonitrile	66·7	66·7
Stabiliser	varying	varying
Potassium persulphate (20%)	5	25
Sodium bisulphite (10%)	2·5	25

Temperature — Room temperature (30°C)

Period of reaction — 24 hrs.

Field Latex was suitably stabilised and acrylonitrile, after removing inhibitor, was added to the latex with stirring. When complete dispersion was effected potassium persulphate as a 20% solution was stirred in. Stirring was continued for 30 minutes. Sodium bisulphite as a 10% solution was then added with stirring. The reaction vessel was closed and kept undisturbed for 24 hrs. The reacted latex was then coagulated using 10% calcium chloride solution. The coagulum was filtered, washed, dried and weighed.

Concentration of initiator

The above reaction condition was used for fixing up the concentration of initiator. Stabiliser used for the study was sodium lauryl sulphate at a concentration of 7·5 phr. The concentration of initiator was varied from 1 to 6 phr of potassium persulphate/0·5 to 3 phr of sodium bisulphite. The yield of the product obtained in each case was noted. Results obtained are given in Table I.

Table 1. *Effect of concentration of initiator on yield*

Concentration of initiator (phr) $K_2S_2O_8/NaHSO_3$	Yield (%)
1·23/0·62	61·0
2·46/1·23	61·5
3·69/1·84	88·6
4·92/2.46	96.0
6·15/3·07	96·5

Period of reaction

The reaction was allowed to continue for various periods of time keeping all other conditions constant, as stated earlier. The concentration of initiator used was 5 phr of potassium persulphate/2·5 phr of sodium bisulphite. The products obtained were extracted with petroleum ether to remove free natural rubber and then with Dimethyl formamide to remove free polyacrylonitrile and the amount of graft product obtained was calculated. Total yield in each case was also noted. The data obtained are given in Table 2.

Table 2. *Effect of time of reaction on yield and amount of graft product*

Time of reaction (hr)	Yield (%)	Free NR (%)	Free poly ACN (%)	Graft product (%)
1	78·0	65·8	22·2	12·0
1½	82·4	62·7	24·0	13·3
2	89·5	57·7	27·3	15·0
2½	90·0	55·8	28·4	15·8
3	92·0	52·8	30·7	16·5
5	92·8	52·9	31·2	15·9
7	91·9	52·7	31·2	16·1
9	95·5	52·3	31·3	16·4
24	96·0	51·5	32·0	16·5

Effect of varying acrylonitrile content

The reaction was carried out by varying the amount of acrylonitrile (NR : ACN = 90 : 10, 80 : 20, 70 : 30, 60 : 40) and the yield of the reaction product was determined in each case. Results are given in Table 3.

Table 3. *Effect of concentration of acrylonitrile on yield*

NR : ACN	Yield (%)
50 : 50	96·2
60 : 40	96·5
70 : 30	96·9
80 : 20	97·5
90 : 10	98·5

Graft reaction was conducted by mixing natural rubber latex and acrylonitrile in the ratio, NR : ACN = 60 : 40, at the selected conditions and the technological properties of the product were compared with those of natural rubber and nitrile rubber (chemaprene N — 3309). Compound recipe is given in Table 4. The tensile Strength, elongation at break, modulus at 100 % elongation, ageing resistance, tear Strength, hardness, resilience and compression set were determined as per IS 3400. Percentage swell in petrol and hydraulic oil were determined as per ASTM No : D 471 - 79.

Table 4. *Compound formulation*

Ingredients	Parts by weight		
	I	II	III
Natural rubber	100	—	—
Nitrile rubber	—	100	—
Graft rubber	—	—	100
Zinc Oxide	5	5	5
Stearic acid	1	1	1
SRF black	50	50	50
DBP	—	5	5
Aromatic Oil	5	—	—
CBS	3·5	3·5	3·5
Sulphur	0·5	0·5	0·5
Optimum cure time			
Optimum cure time at 150°C (minutes)	13	20·5	9·5

RESULTS AND DISCUSSION

It was observed that the reaction mixture was stable when sodium lauryl sulphate at a concentration of 7·5 phr was used. The results of the study for fixing up the optimum concentration of initiator, as given in Table 1, Show that upto a concentration of 5 phr. of potassium persulphate/2·5 phr of sodium bisulphite, yield is increasing and after that the increase in yield is not much appreciable. So optimum concentration of initiator was fixed as 5 phr of potassium persulphate/2·5 phr of sodium bisulphite. From Table 2 it is seen that as the time of reaction is increased, the yield of the product is also increased and yield is maximum at about 9 hrs. The maximum amount of graft product obtained is 16·5% and for this a minimum time of 3 hrs is required. In the present study the reaction mixture was kept overnight. The results of the yield obtained by varying Acrylonitrile Content, as given in Table 3, show that under the selected conditions more than 96% yield is obtained for all the concentrations studied.

The physical properties of the vulcanisates prepared from Natural Rubber, nitrile Rubber (ACN Content 33%) and graft rubber (obtained by mixing NR and ACN in the ratio 60 : 40) are given in Table 5. It is seen that hardness and modulus at 100% elongation of the graft rubber are superior to those of natural rubber and nitrile rubber. The resistance to swelling in oils and solvents of the graft rubber is much higher than natural rubber but lower than that of nitrile rubber. There is reduction in prope ties like tensile strength, elongation at break, ageing resistance, tear strength and resilience for the graft rubber.

Although a high percentage recovery of 96% is obtained as a result of the reaction only 16·5% of the reacted product is existing as graft acrylonitrile. The rest of it may be present as free polyacrylonitrile. The variation in some of the physical properties for the product developed may be due to this.

Table 5. *Physical properties of the vulcanisates*

ST. No.	Physical properties	I	II	III
1.	Modulus at 100% Elongation (kg/cm²)	15·5	13	50
2.	Elongation at break (%)	610	675	200
3.	Tensile strength (kg/Cm²)	210	120	75
4.	After ageing at 70°C for 96 hrs.			
	(a) Retention of Modulus at 100% elongation (%)	100	95·2	100
	(b) Retention of elongation at break (%)	90	95	77
	(c) Retention of Tensile strength (%)	98·5	100	85
5.	Hardness (shore A)	52	57	88
6.	Resilience (%)	57	38·5	32
7.	Compression set (%)	21	30	46
8.	Tear strength (kg/cm)	60	53	37
9.	Swelling in petrol after 70 hrs. (%)	195	21	90
10.	Swelling in hydraulic oil after 70 hrs (%)	40	0·5	12·6

CONCLUSION

A method for the preparation of acrylonitrile graft natural rubber was standardised using potassium persulphate/sodium bisulphite initiator system. Oil and solvent resistance of natural rubber is substantially improved by grafting with acrylonitrile. The physical properties like hardness and modulus are enhanced. Properties like tensile strength, elongation at break, ageing resistance, tear strength and resilience are slightly lowered. The procedure gives around 17 percent of graft rubber.

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REFERENCES

BLOOMFIELD, G. F., MERRETT, F. M., POPHAM, F. J. AND SWIFT, P. McL (1954). Graft polymers derived from Natural Rubber. *Proc. Rubb. Tech. Conf. London*, 185 — 195.

BURFIELD, D. R. AND NG. S. C. (1975). Graft Copolymerisation of Methacry lamide in Natural Rubber Latex. *Proc. Int. Rubb. Conf. Kuala Lumpur*, 235 — 248.

FERNANDO, W. S. E., COOMARASAMY, A. AND TILLEKERATNA, L. M. K. (1978). Some aspects of Chemical modification of Natural Rubber. *IRRDB Symposium, Kuala Lumpur* (preprint).

MARK HERMAN, F., GAYLORD, NORMAN G. AND BIKALES NORBERT, M. (1964). Encyclopedia of Polymer Science and Technology. New York. *Interscience Publishers.* Vol. 1, P. 383.

NAUNTON, W. J. S. (1961). The Applied Science of Rubber. London : Edward Arnold Publishers, P. 144.

RAJAMMAL, G., CLARAMMA, N. M. AND THOMAS, E. V. (1980). Preparation of styrene graft natural rubber and its evaluation in footwear items. *Paper presented at the Int. Rubb. Conf. India.*

SORENSON WAYNE, R. AND CAMPBELL, TOD W. (1961). *Preparative Methods of Polymer Chemistry.* New York. Interscience Publishers, P. 169.

DISCUSSION

Q — LAL DE ALWIS, (Chemanex Ltd.) : (1) Have the studies of graft copolymerisation of acrylonitrile with NR been scaled up for commercial production ?

(2) What are its applications and advantages over NR ?

A — N. M. CLARAMMA, (RRII) : (1) Percentage of copolymerisation is only 16·5%. Hence this product is not a substitute for nitrile rubbers where resistance to solvents is concerned.

(2) Further work is in progress to increase the degree of coplymerisation.

AN OVERVIEW OF THE CHEMICAL MODIFICATION OF NATURAL RUBBER

By

D. BARNARD

(Tun Abdul Razak Laboratory, MRPRA, Brickendonbury, Hertford, England.)

INTRODUCTION

The producers of general purpose synthetic rubbers have put a great deal of effort into the equipping of such rubbers with chemically-functional groups along the backbone chains. The purpose has been manifold, ranging from the improvement of tack and green strength to the provision of sites for novel forms of crosslinking, grafting, antioxidant activity and even pharmacological properties. Usually the most efficient route to such functionalisation is to incorporate small amounts of a monomer carrying the desired group in the polymerisation process.

As we cannot as yet interfere with the polymerisation in the tree which leads to NR then any modification of the latter must be achieved by direct chemical reactions on the rubber itself.

NR already possesses excellent physical properties — why then should we wish to modify it ? Chemical modification offers a route to more dramatic improvements in areas such as bonding, frictional characteristics, ageing protection etc than can be obtained via conventional compounding as well as routes to novel vulcanisation and grafting. There is also the possibility of NR as a renewable resource replacing special purpose synthetic rubbers if properties such as oil resistance can be markedly improved.

Type and extent of modification

The types of chemical modification possible are as follows :

(1) Changes induced in the NR molecule such as cyclisation, cis-trans isomerisation or depolymerisation without the introduction of new chemical material

(2) Attachment to the NR molecule of pendent functional groups

(3) Grafting of a different polymer at one or more points along the NR molecule.

Neglecting category 1 as outside the theme of the review it is self-evident that the other modifications must be carried out with high efficiency either in latex or during conventional mixing or curing of dry rubber to stand any chance of economic viability. Solution chemistry must be completely avoided.

Even so the level of modification possible can be further defined on economic grounds

(a) Reagents which can insert pendent functional groups will be expensive and therefore must be used at the lowest level adequate for the purpose of providing sites for crosslinking etc, *i.e.* about 1 mole% giving a spacing of 6800 molecular weight units between groups. At this level a reagent costing ten times as much as NR and having a molecular weight of 200 will add 30% to the price of NR.

(b) Only cheap reagents can be used for macro modification at the 20 — 100 mole % level to endow NR with quite new physical properties.

Functional Group Modification

Functional groups of biochemical origin

From the known mechanism of biosynthesis each NR molecule should terminate in an allylic pyrophosphate group or, more likely, the allylic alcohol hydrolysis product of this. No firm analytical data exists and no-one appears to have utilised the group for chain doubling via a bifunctional reagent or for grafting with, say, an isocyanate terminated polymer.

The evidence for pendent aldehyde groups to the extent of 1—10 per million molecular weight is quite definite and they no doubt arise from the biochemical oxidation of side chain methyl groups — a common occurrence with terpenoids in both plant and animal systems. Apart from their implication in the storage hardening of NR and their ability to give low levels of crosslinks when reacted with difunctional reagents such as hydrazine or borane they again have not been utilised.

Naturally occurring epoxide groups are reputed to be present in freshly tapped rubber to the high level of 50 — 100 groups per million molecular weight. Epoxidase enzymes are known to be present in latex and are presumably responsible.

Both these modifications show a strong clonal dependence and it might be that their levels could be increased through breeding if desired.

Although a more profound alteration in the structure of NR seems unlikely, it may not be impossible. The enzymes involved in the biosynthesis of NR have been found to be not completely specific and they will accept modest deviations from the isopentenyl pyrophosphate building block. It is not entirely fanciful to imagine that via genetic engineering such deviants could be introduced to give NR carrying modifications such as hydroxyl, carboxyl, halogen or other groups. For the present, however, direct chemical manipulation of NR has to be used.

Chemical modification

In theory NR can be treated as a simple olefin and it should therefore be subject to the myriad reactions known for such species. In practice it is far from being as simple

as this. NR contains significant proportions of non-rubbers which can compete or interfere with many reactions. It does not normally dissolve completely in solvents because of its gel content and when solutions are obtained they are difficult to handle being of high viscosity at low concentrations. Reactions carried out in latex or in dry rubber are affected by the heterogeneity of the first and by the effect of a viscous polymeric environment in the second.

Fig. 1 gives a fairly complete list of reagents that have been used with NR subdivided into reactions in solution, in latex and in dry rubber. As already indicated, only the latter two environments need be considered.

The 'ene' reaction

Most of the promising reagents listed have been investigatetd and the conclusion reached that for low levels of modification the thermal 'ene' reaction is possibly unique. The general reaction is illustrated in Fig. 2.

It has the following advantages :—

(1) It is a non-catalytic reaction and does not therefore rely on catalysts which can be poisoned by non-rubbers in NR (although non-rubbers may compete for the reagent in a stoicheometric manner)

(2) It is usually of high efficiency and does not induce side reactions such as cross-linking, degradation, cyclisation or isomerisation

(3) It is particularly suited to NR as it requires an electronrich alkyl substituted double bond — an advantage over other elastomers

(4) It is versatile — can carry a varied selection of functional groups.

Of the 'ene' reactions available the activated azo addition (Fig. 3) seems to be superior to the others in terms of efficiency and versatility of spread of rates and synthesis of differently functionalised examples (Fig. 4).

Typical uses for functional groups introduced into NR by this route are shown in Fig. 5. The exploitation of these and the development of new uses is a continuing exercise but I wish to review the future direction of modification chemistry in a more general sense.

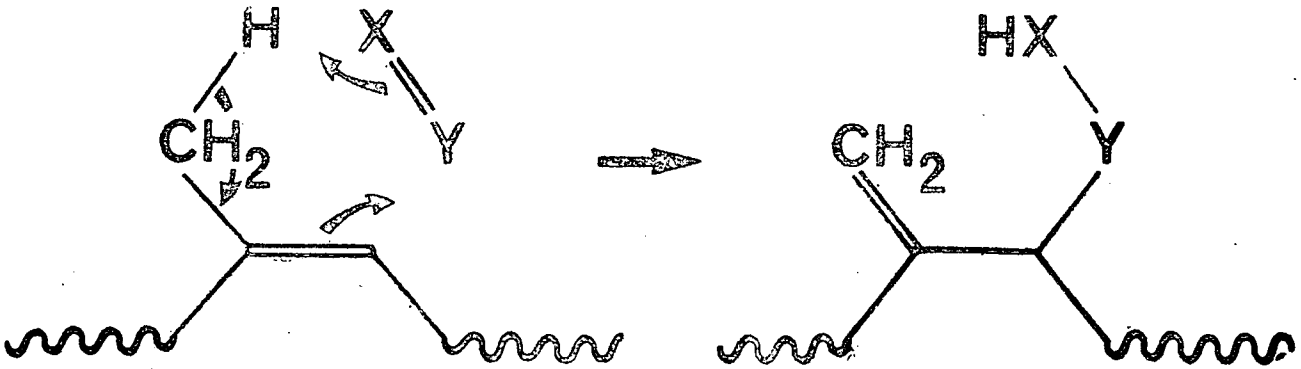
Modification methods

The azo reaction is so efficient that new ways of using it will be sought but it has limitations. The azo group can be reactive in other ways than the 'ene' addition; for example it is a mild dehydrogenating agent, and it can be incompatible with the functional group it is used to introduce. Thiol, certain amine and alcohol groups can be oxidised, for instance. It is necessary, therefore, to keep in mind alternative methods of functionalisation.

MODIFYING AGENT	SOLUTION	LATEX	DRY RUBBER
H_2	+		
HCl	+		
Cl_2	+		
RSCl	+		
$SiCl_3H$	+		
I·NCO	+		
SO_2	+		
CO	+		
$PhNO_2$	+		
$SO_2Cl·NCO$	+		
RCN→O	+		
BuLi	+		
Metathesis	+		
Quinonediimines	+		+
Resin resols	+	+	+
Epoxidation	+	+	
BH_3	+		+
RSH	+	+	+
Maleic anhydride	+		+
Maleimides	+		+
Carbenes	+	+	+
Nitrenes	+		+
Nitrones	+		+
Sydnones	+		+
Singlet oxygen	+		+
Aldehydes	+	+	+
C-Nitroso cpds.	+	+	+
Azo compounds	+	+	+
CCl_3Br	+	+	
Grafting	+	+	+

Fig. 1. Reagents which React with NR

THE GENERAL 'ENE' REACTION



X=Y can be O=N–, –N=N–, >C=S

>C=O, or >C=C<

Fig. 2.

'Ene' Reaction of Azodicarboxylates with cis-1,4-Polyisoprene.

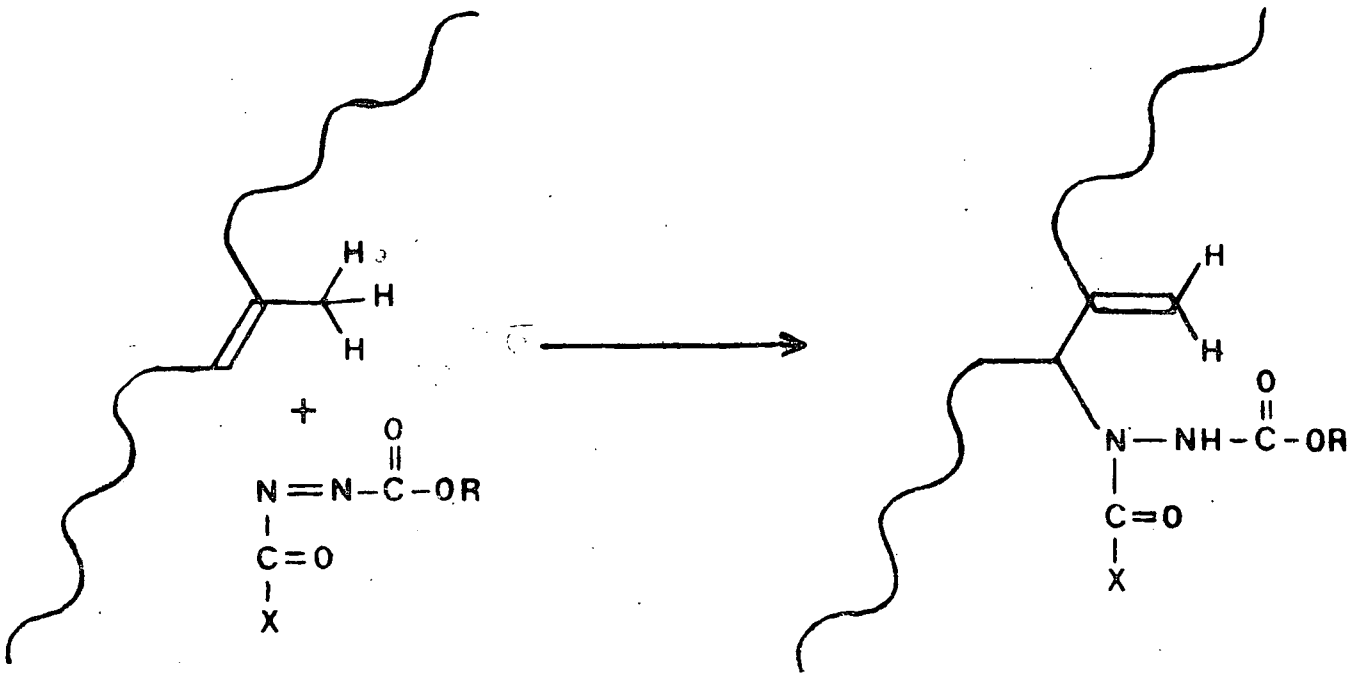


Fig. 3.

Rates of addition of Azo Compounds to the NR double bond

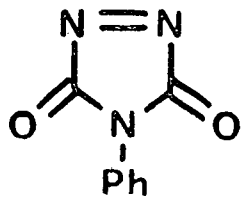
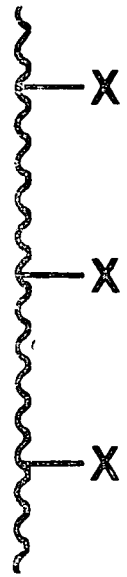
Azo Compound	k_2 (litre mole^{-1} s^{-1}) x 10^4
PhCO·N=NCO·Ph	2·20
EtOCO·N=NCO·OEt	2 84
PhNHCO·N=NCO·NHPh	3 95
PhCO·N=NCO·OEt	5 53
Bu^{t}NHCO·N=NCO·OEt	19 5
PhNHCO·N=NCO OEt	109·6
	ca 10^5

Fig. 4.

APPLICATIONS OF CHEMICAL MODIFICATION



X = Polymer chain - graft copolymers

X = Aminophenol group - crosslinking by diisocyanates

X = Cinnamate group - photo crosslinking

X = Carboxyl group - crosslinking by metal oxides

X = Alkoxysilane group - bonding to glass and silica

X = p-Phenylenediamine group - bound antioxidant

Fig. 5.

C-nitrosoarenes undergo the 'ene' addition with NR to give a variety of products depending on the nature of the arene ring substituents (Fig. 6). Where the substituent is electron releasing as with NH_2, NHR, OR or OH the major product is the secondary amine pendent group. This has already been utilised for the production of rubber bound antioxidants and the urethane vulcanization system. It is possible that this reaction could be made a more general functionalisation method but suffers from the restrictions on the substituent group carried, from a tendency to form coloured by-products and from a slight concurrent crosslinking reaction.

Maleic anhydride and N-substituted maleimides react with NR via two mechanisms — a free radical addition at modest temperature and an 'ene' addition at high temperature (Fig. 7). It is doubtful whether the latter can ever proceed alone. NR modified with maleic anhydride in a dry mixing process exhibits a degree of self-reinforcement and be crosslinked with metal oxides or diamines. It is claimed that the adventitious crosslinking can be eliminated by the addition of simple amines. N-aryl-maleimides have been used to functionalise NR through COOH, NO_2 or Cl substituents on the aromatic ring but the method is made less useful because of crosslinking and the fact that substituents which possess radical scavenging ability reduces the efficiency of addition very severely.

Carbenes and nitrenes will attack most polymers by either double bond addition or C-H insertion reactions (Fig. 8).

Carbenes are difficult to generate in situ in other than solution reactions. However nitrenes can be generated by the thermolysis of azido compounds at temperatures of 120° — 160° and are applicable to dry rubber reactions. Aryl sulphonyl azides are easily prepared and safe to handle and have been used to functionalise polymers with a variety of groups including isocyanates and hydroxyl (Fig. 9). We have examined the potential of this reaction in NR and found surprisingly that a 1, 3-cycloaddition of the azide to NR occurs at modest temperatures (100° — 120°) before the nitrene is liberated. The resulting triazoline breaks down to give the aryl sulphonyl group bound to NR via a hydrolysis resistant imine bond (Fig. 10).

This still provides the desired functionalisation and merits further attention as an alternative to the azo modification route.

General effects of pendent groups

The physical effects of pendent groups are now well understood. Most pendent groups are polar with respect to NR, especially those derived from azo chemistry. Because of this and the restrictive effect of large groups on segmental motion T_g will be progressively raised and oil resistance and air permeability will be improved. Such effects are well documented and can be induced to any desired level by extant modifications such as ENPCAF or epoxidation. Resistance to low temperature crystallisation is a possible applicational area. Preliminary work suggests, however, that pendent groups are less effective than other chain irregularities such as crosslinks and are unlikely to be cost-effective.

The Reaction of Nitrosoarenes with 2-Methylpent-2-ene.

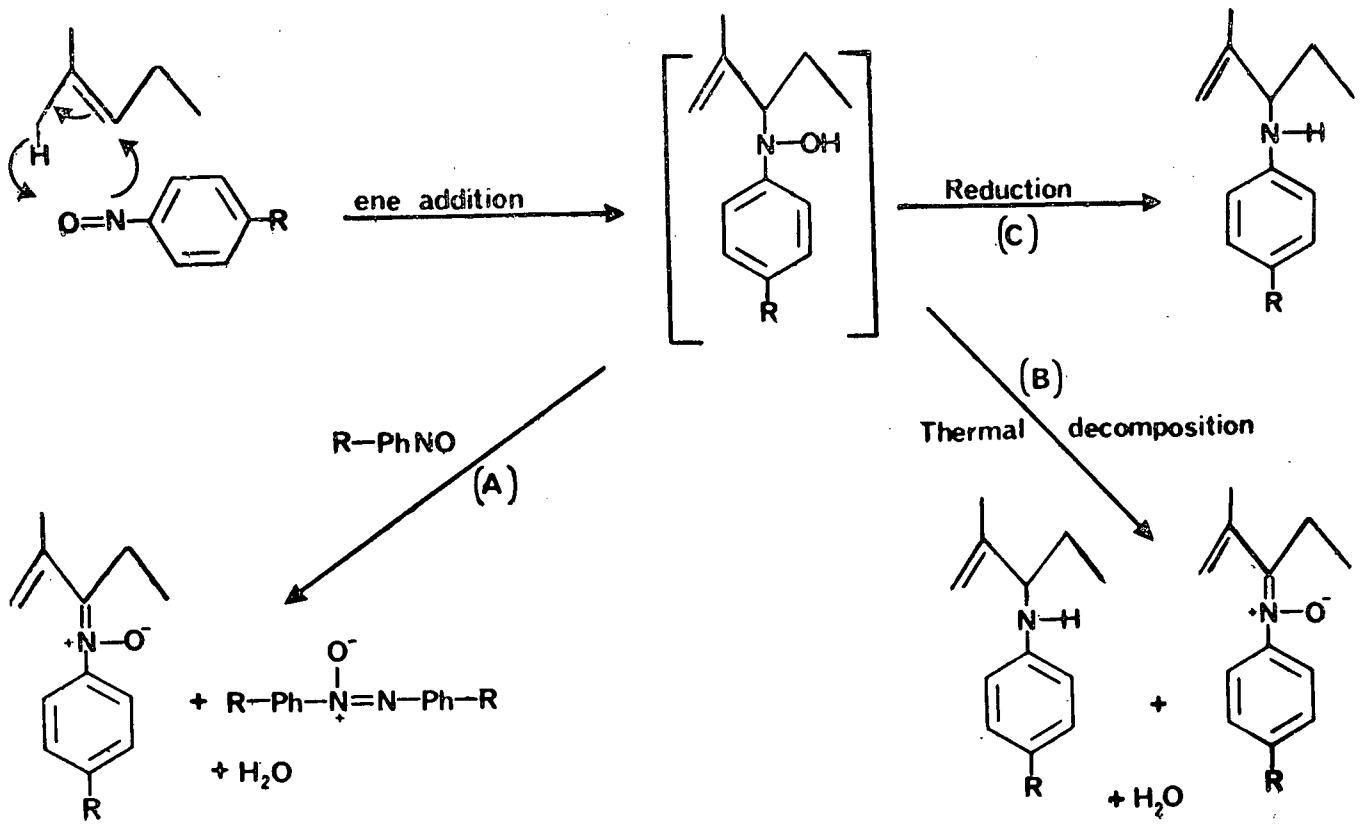


Fig. 6.

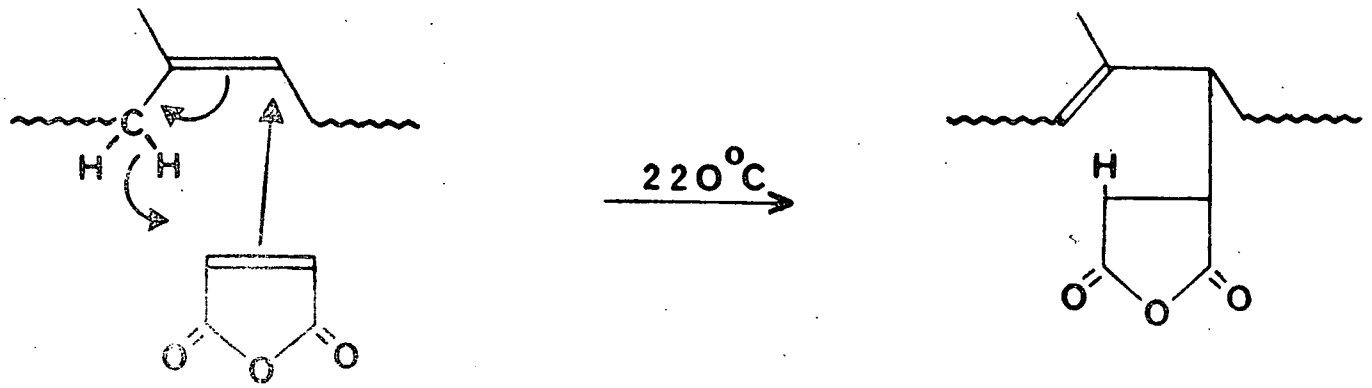


Fig. 7. Ene addition of maleic anhydride

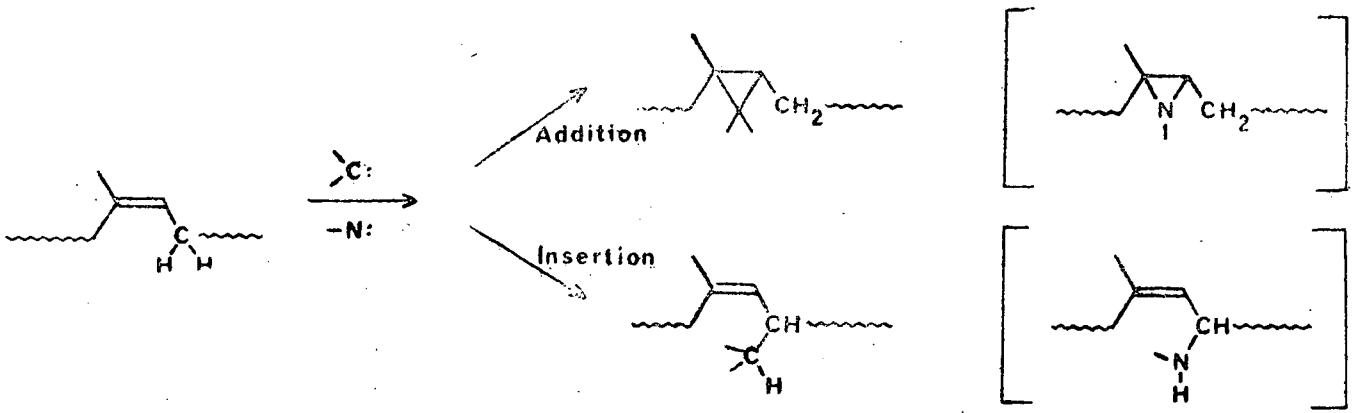
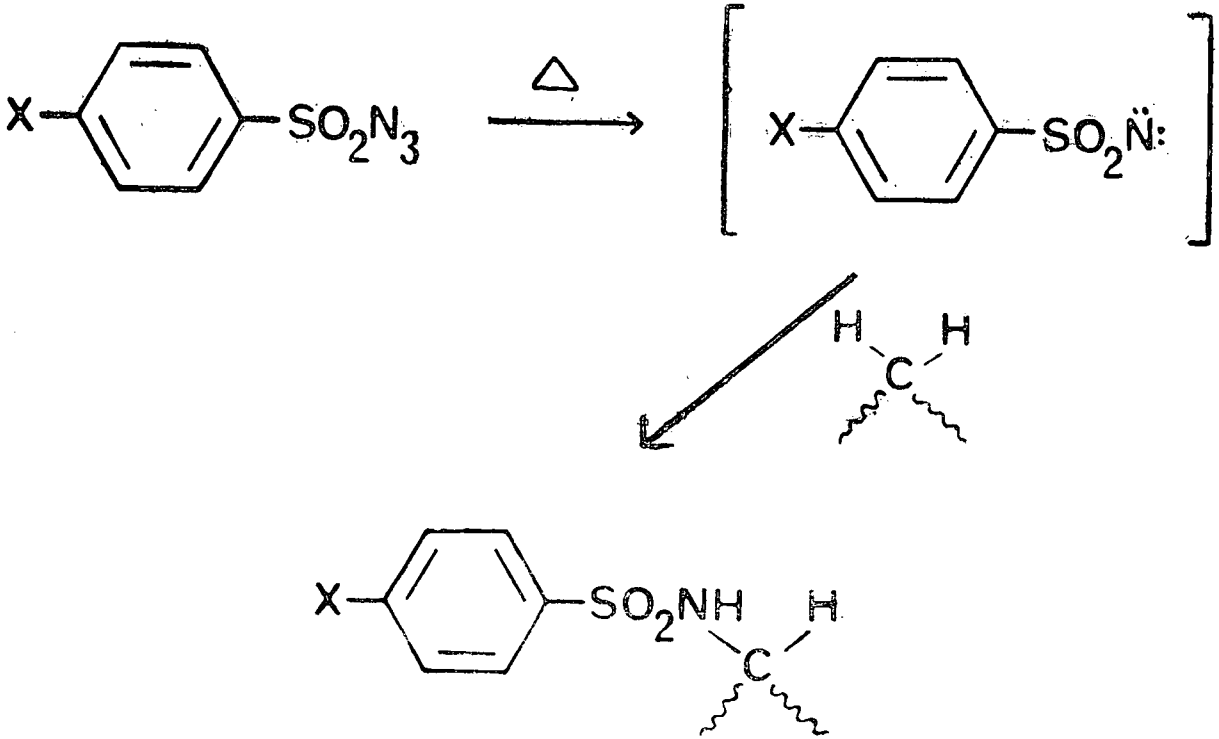


Fig. 8. Reaction of carbenes and nitrenes with NR.



$$X \equiv -NH\overset{\overset{O}{\|}}{C}OCH_2CH_2OH$$

Fig. 9. Reaction of sulphonyl azides with polymers

Sulphonyl azide addition to polyisoprene

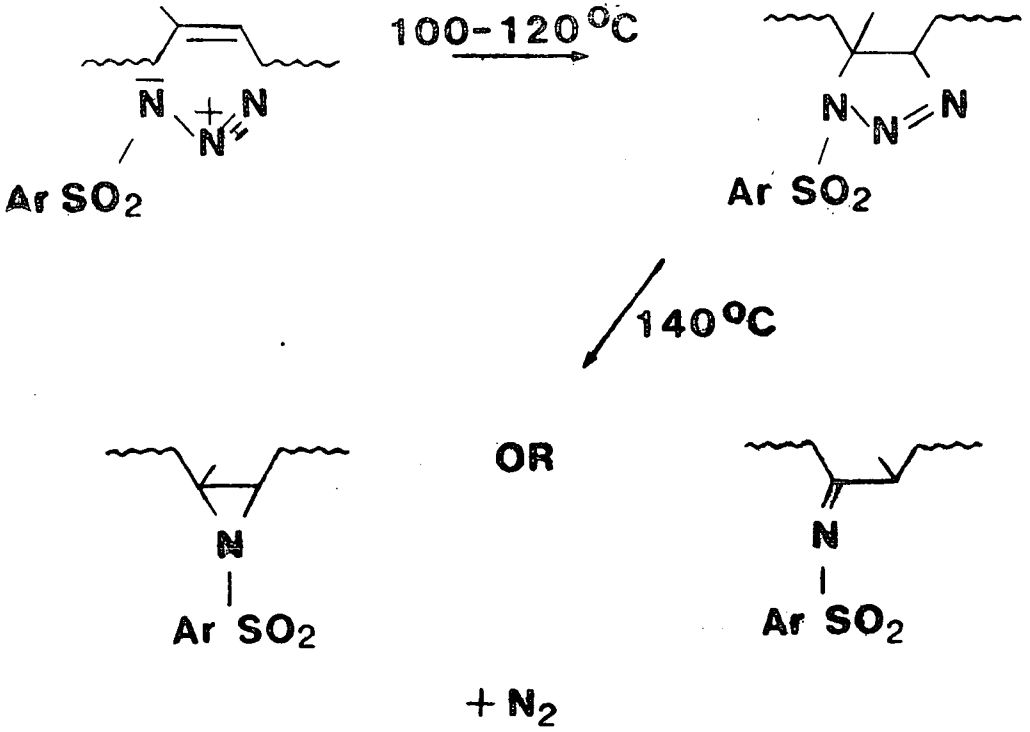


Fig. 10.

Chemical effects have also been well explored. Reactive sites for crosslinking and grafting have been introduced. Pendent p-phenylenediamine residues are produced by the reaction of p-nitrosophenylaniline or quinonediimines with NR and impart powerful, non-egtractable antiogidant activity. The benefits of rubber bound antiogidants were initially ignored by rubber manufacturers but there are now signs that they are beginning to be appreciated and there is scope for further investigations into improved protective systems, particularly non-staining antiogidants, introduced via chemical modification.

The same can be said for pendent groups tailored to give powerful bonding to specific substrates. The introduction of siloaxne groups via the azo reaction enables NR to be bonded extremely well to glass and it is almost certain that other pendent groups could be designed to improve bonding to steel, fibres, fillers etc.

Curing ingredients such as accelerators could be usefully bound to NR as pendent groups to prevent migration in blends of rubbers and, possibly, to reduce the release of hazardous residues.

Future applications of pendent group modification

Crosslinking. One obvious application is the crosslinking of NR through low levels of reactive pendent groups.

This has already been exploited in the NOVOR or urethane system in which pendent aminophenol groups introduced on NR by a nitrosophenol ene reaction are crosslinked by a diisocyanate (Fig. 11). It may be that the practical limit has now been reached in cross-link stability and reversion resistance and that the cost-effectiveness of alternative new vulcanizing systems would not merit their development.

Modification directed towards specialist crosslinking applications could be more fruitful. Thus, in latex products there is a question mark over sulphur systems using dithiocarbamates on toxic grounds. SILCAF, a compound carrying a reactive azo group at one end and an alkoxy-silyl group at the other can be used to pre-vulcanize latex. The azo group adds to NR and the silyl group hydrolyses in the presence of water to form siloxane crosslinks (Fig. 12).

Another application for latex is the addition of an azo-cinnamate. When thin, transparent articles such as surgeons gloves or condoms are made from the modified latex by dipping then they can be crosslinked by exposure to light (Fig. 13). This would make possible a continuous production line and both applications have the advantage that the vulcanizing agent becomes firmly bound to the rubber with no extractable residues. Both work but need more development of the concepts to become suitable for industrial take-up.

Molecular weight reduction. It is often useful to reduce the molecular weight of NR to give a lower plasticity raw rubber and indeed essential during mixing to get good processability. Both operations commonly use peptising agents added to latex or to the internal mixer which work by catalysing oxidative scission of the rubber. Such materials, often thiols, are difficult to control and may leave undesirable residues in the rubber to affect ageing or vulcanization.

MECHANISM OF NOVOR CROSSLINKING

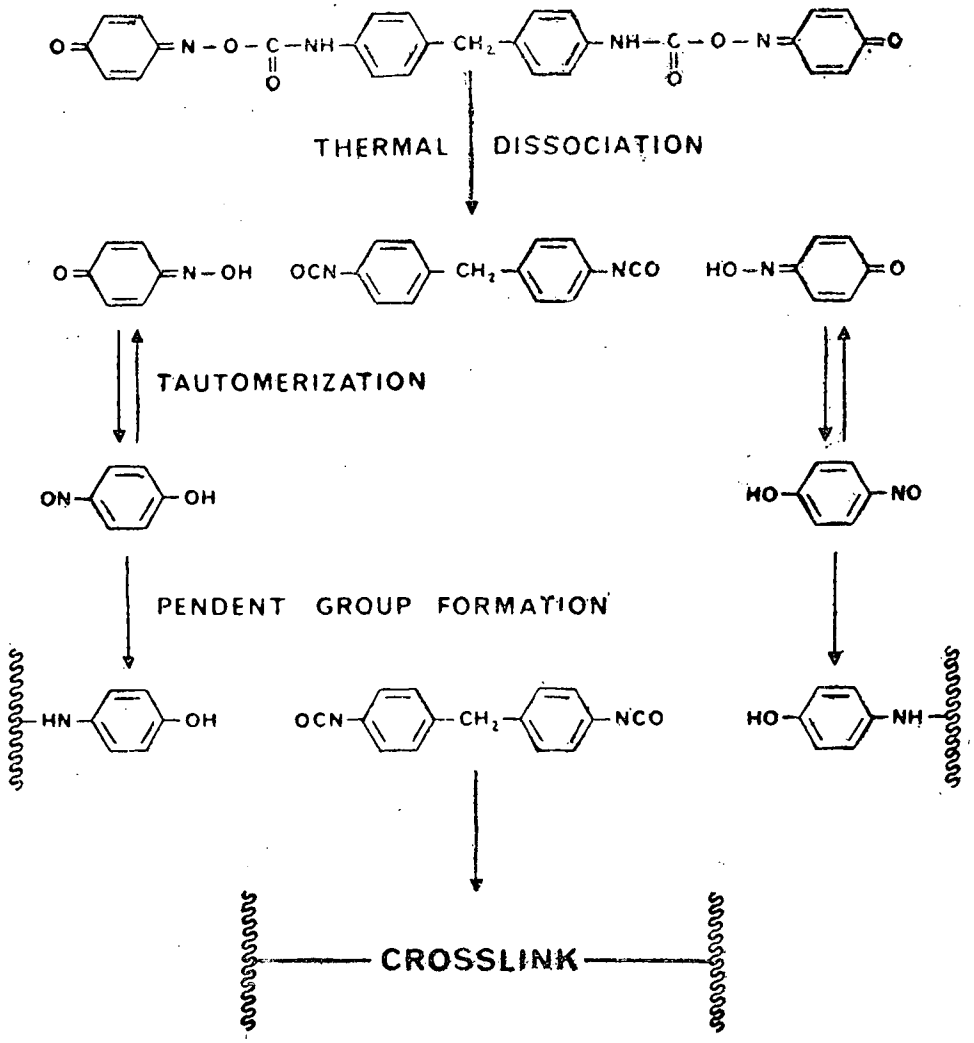


Fig. 11.

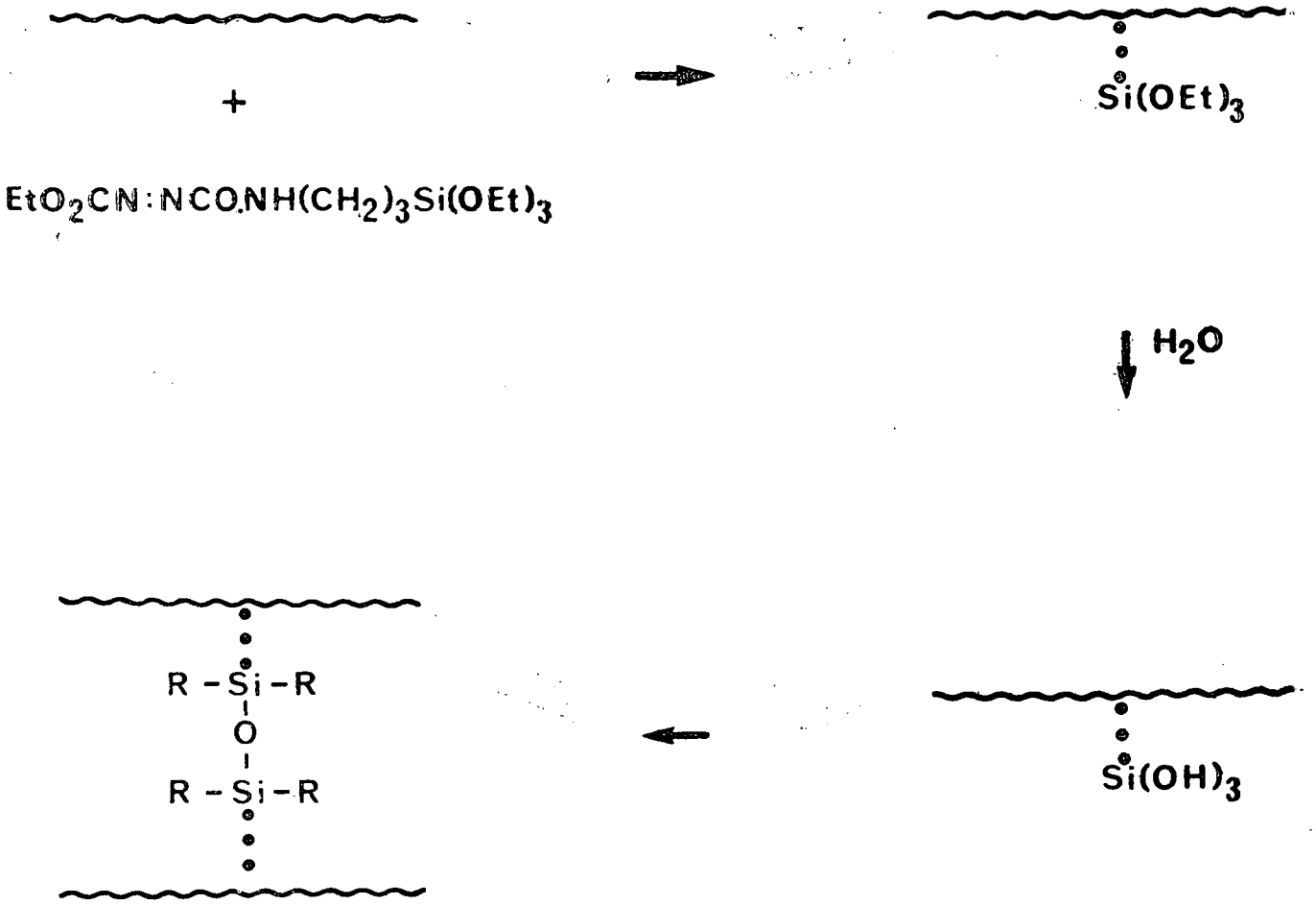


Fig. 12. Principle of crosslinking with SILCAF.

PRINCIPLE OF PHOTOCHEMICAL CROSSLINKING OF NR

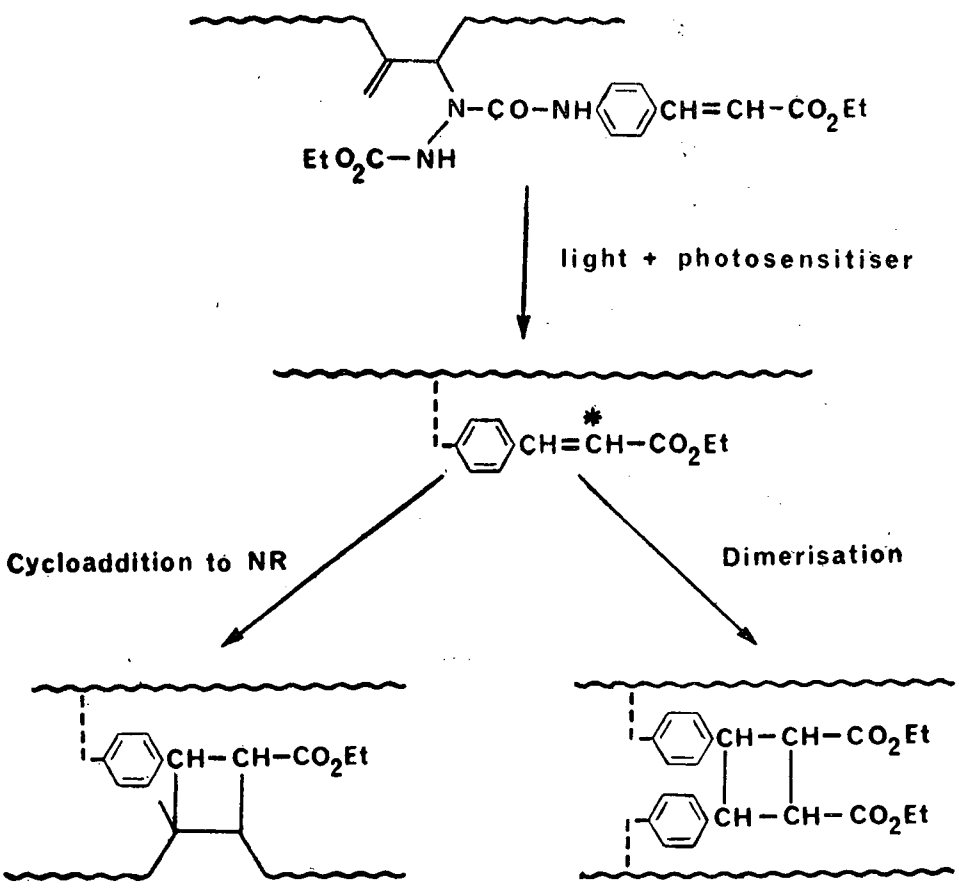


Fig. 13.

It would be a useful development to have reagents available which brought about scission of the NR chain in a clean and controlled manner, and an added advantage if the cut chains were terminated with reactive groups (telechelic polymer) so that chain recombination and crosslinking could be performed if desired at a later stage.

One modification reaction that leads to a profound fall of molecular weight of latex rubber is the addition of nitrobenzene in the presence of uv light (Fig. 14).

For rubber in solution this works admirably leading eventually to a liquid rubber of MW ca 10,000 which is effectively terminated by carbonyl groups and chain extendable by a bis-hydrazide. In latex the system needs further development as efficiency is reduced by factors such as coagulation on the uv lamp.

The reaction of sydnones with NR occurs by a 1, 3 dipolar addition, the product rearranging to give chain scission (Fig. 15). The sydnone is dispersed in NR in an internal mixer and the rubber heated at 170°C. As seen in the Table, peptisation is efficient but sydnones are required which operate at lower temperatures before the process can be viable.

Table 1. *Reaction of p-chlorophenylsydnone with NR*

Sydnone % w/w	Heating °C/hr	MW of NR
0	—	440 000
10	—	440 000
0	170/1	gel
1	170/1	114 000
3	170/1	77 000
5	170/1	18 000

Surface modification. If a reagent is very reactive, of the triazolinedione in Fig. 4, then the surface of NR can be modified by spraying or dipping using a solution of the reagent. This will modify surface properties in respect of hardness, friction, bonding etc. The surface of latex particles can in theory be modified using a water-soluble reagent dissolved in the serum phase. For example, the carboxylation of latex to give enhanced stability and processability could be achieved using a reagent carrying a carboxyl substituent.

For both dry rubber and latex the cost of modification will be low since only a fraction of the reagent needed for bulk modification is consumed and this could be an area worthy of more intensive exploration.

Thermoplastic NR. The usual route to a thermoplastic elastomer is to use the ' physical ' crosslinks resulting from the aggregation of segments of polymer chains into hard domains. This applies to the SBS block copolymers, comb grafts, polyurethanes etc. An attractive alternative is a heat-labile, reversible chemical crosslink. This would be expected to give physical properties as good as a conventional vulcanizate at temperatures up to the point where the crosslinks break open.

Scission Of NR By Nitrobenzene

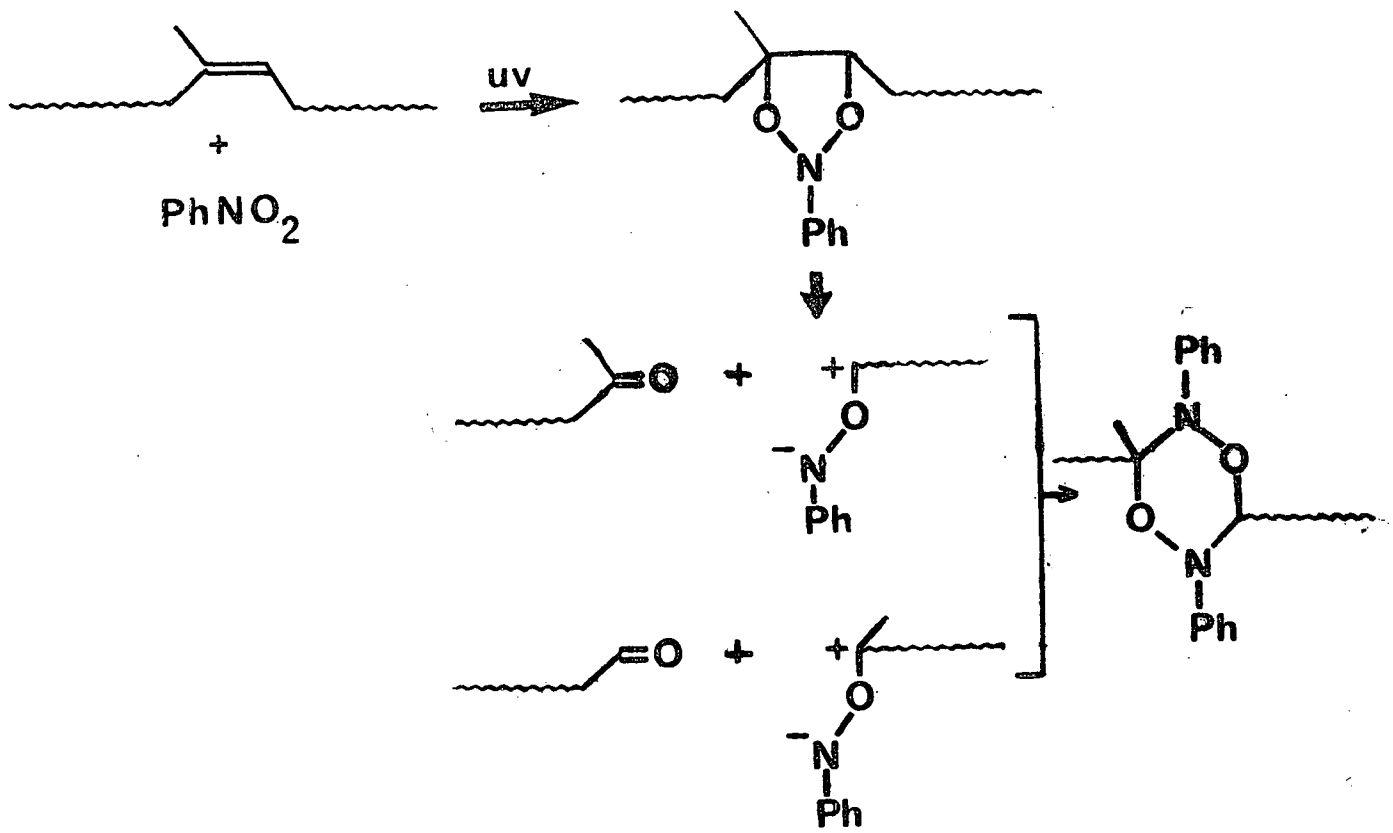


Fig. 14.

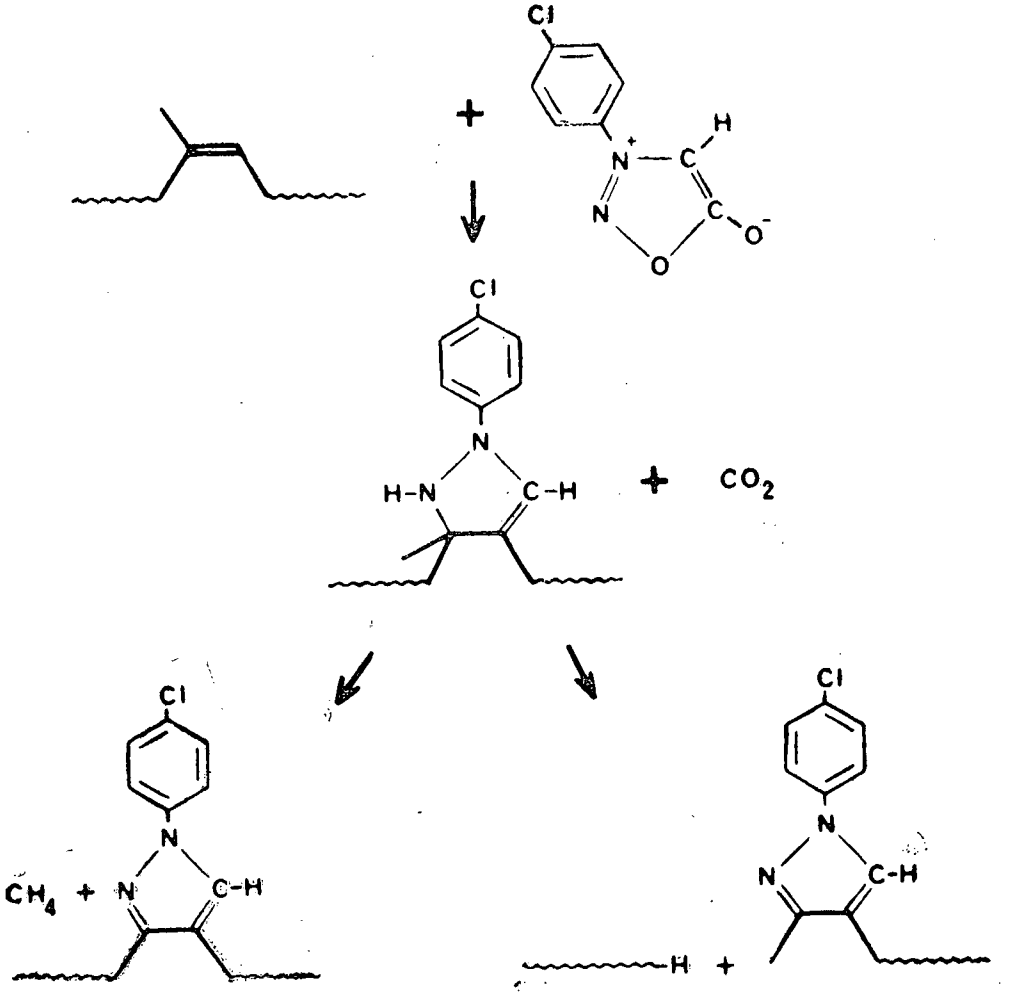


Fig. 15. Reaction of sydnones with NR.

Several attempts have been made to achieve this goal. The most successful have aimed at low crosslink levels only to improve the green strength of polybutadiene. Pendent amino groups were introduced along the polybutadiene chain by copolymerisation techniques and crosslinked by quaternisation with a bis alkyl halide (Fig. 16). This gave significant improvements in green strength without interfering with processability because, it was claimed, the crosslinks were shear and/or temperature labile. Our attempts to get higher levels of crosslinking in NR by an analogous method were not successful because pendent bromo-alkane groups introduced via the azo compound RO-OC-N=N·CO·$OCH_2 \cdot CH_2Br$ proved very slow to quaternise with a diamine in the rubber environment.

Much higher degrees of crosslinking were obtained by a route in which NR was first equipped with pendent hydroxyl groups some of which were transformed into crosslinks by reaction with a difunctional B-keto ester. The ester crosslinks underwent a rapid ester exchange reaction with the remaining hydroxyl groups at temperatures of 180°C or so give a degree of thermoplasticity. Unfortunately side reactions intervened at these temperatures leading to permanent crosslink formation.

A possibility which merits more attention is the introduction of metal chelating pendent groups on to NR by azo or azide chemistry and to form crosslinks with metal ions.

By variation of the chelating group, metals to be chelated and ligands already attached to the metal it should be possible to vary the strength of the complex formed, ie the crosslink, so that adequate temperature reversibility might be obtained along with good physical properties and the resistance to creep at ambient temperatures that simple ionomers lack (Fig. 17).

A patent by Monsanto claims some progress in this direction. Diene rubbers were prepared with pendent pyridine groups by copolymerisation with vinyl pyridine. Complexes of nickel crosslinked the rubber, the crosslinks disappearing reversibly at 180°C. The physical properties claimed were reasonable.

With NR we cannot add pendent groups by copolymerisation but our experience in modification chemistry should enable us to improve and extend this system.

Graft Copolymers

One of the most useful outcomes of the azo modification work has been the ability to bring about the controlled grafting of many polymers to NR.

For this purpose the polymer of desired molecular weight needs to be synthesised with a terminal hydroxy group. Anionic polymerisation is convenient as the molecular weight can be accurately controlled and the termination of the living chains with ethylene oxide provides the hydroxyl group. The reaction of this functionalised polymer with an azo acid chloride leads to azo tipping in high yield (Fig. 18).

Simple dry mixing of the azo polymer with NR in an internal mixer leads to highly efficient grafting by the principle shown in Fig. 19. The mixing torque and dependence of grafting efficiency with time is given in Fig. 20.

Labile Quaternary Salt Crosslink

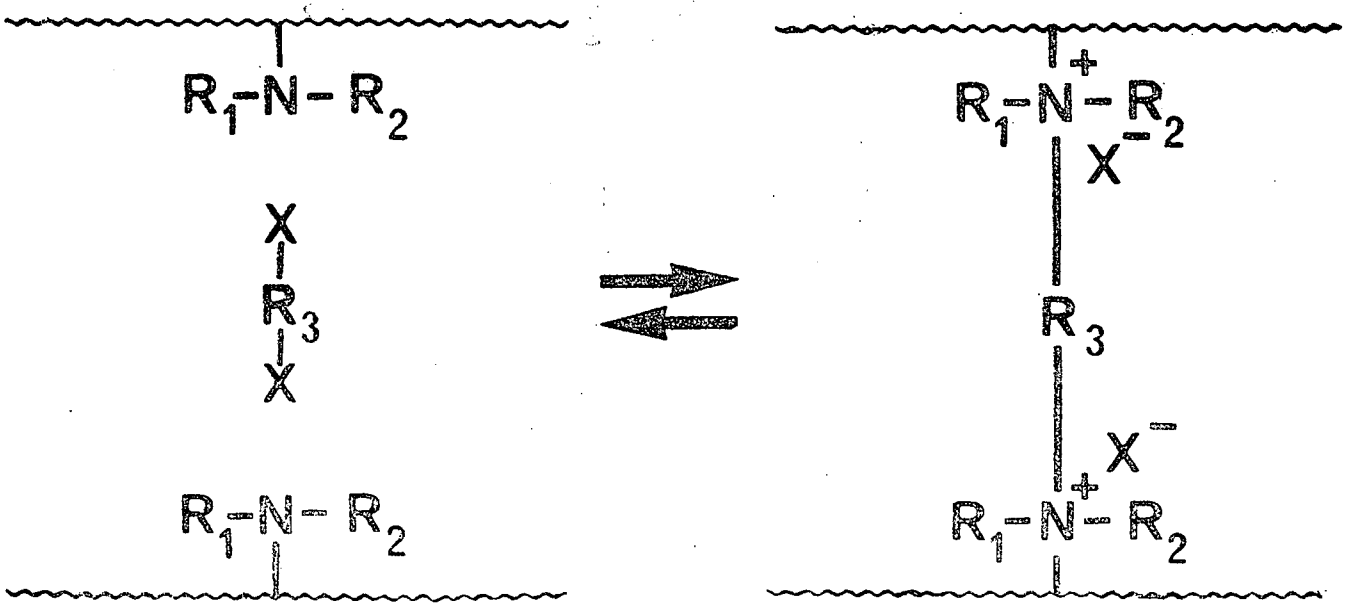
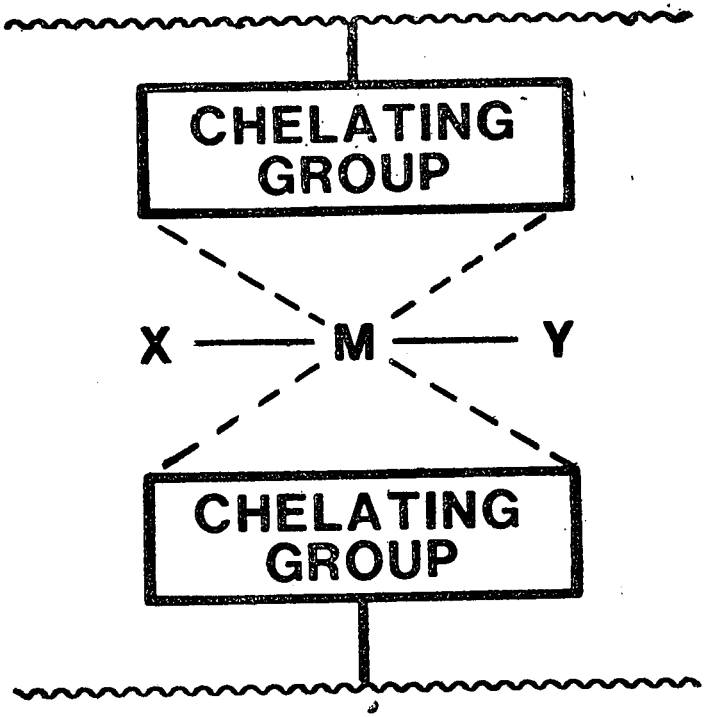


Fig. 16.



Variation of chelating group, metal M and ligands X, Y will give wide control of crosslink strength

Fig. 17.

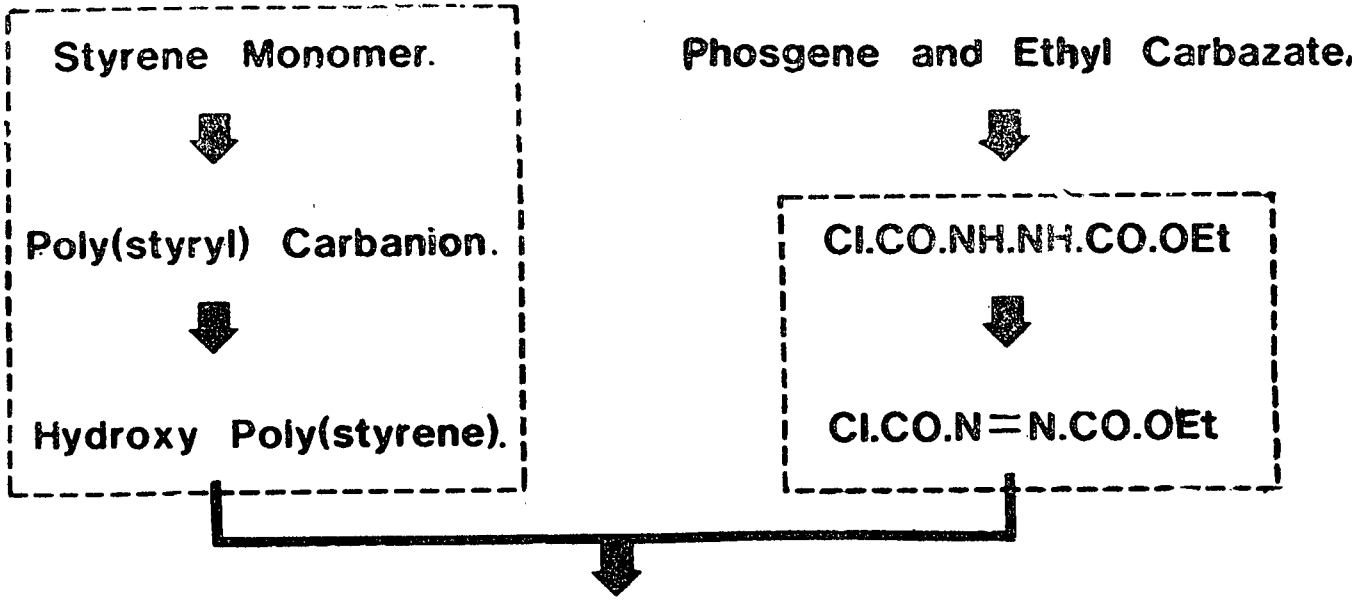


Fig. 18. Azo functionalisation of a polymer.

GRAFTING VIA REACTIVE POLYMER

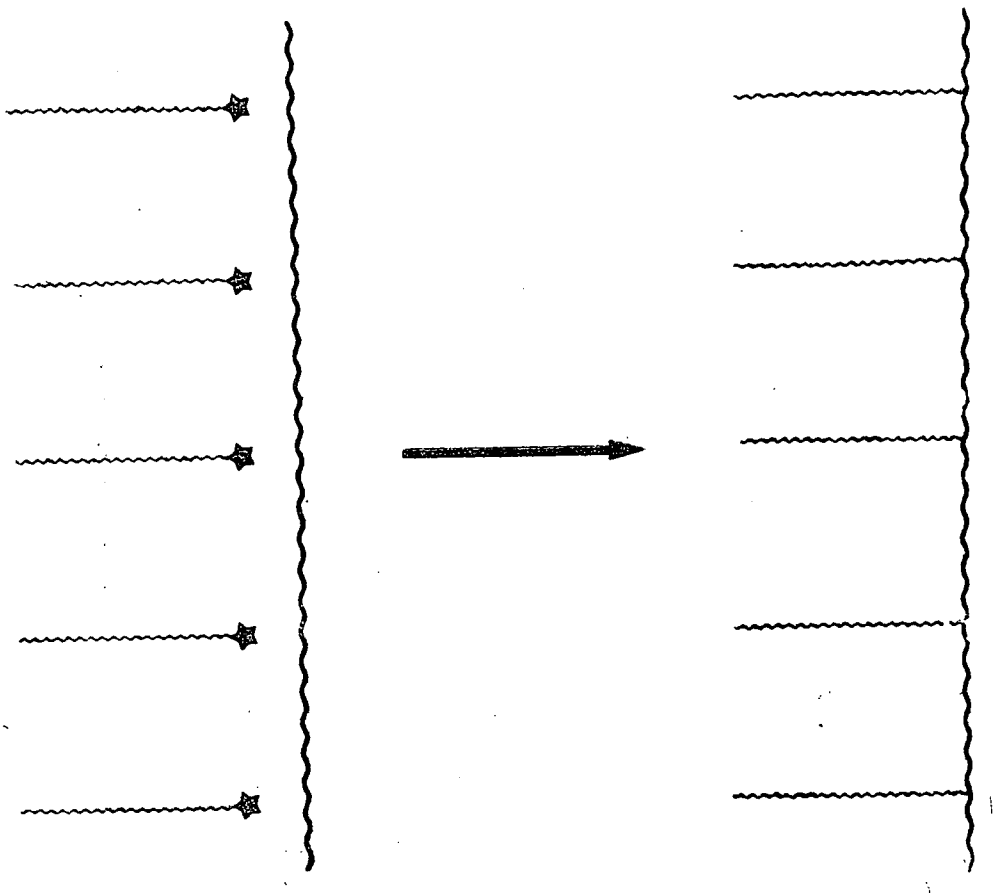


Fig. 19.

Grafting Efficiency During Mixing.

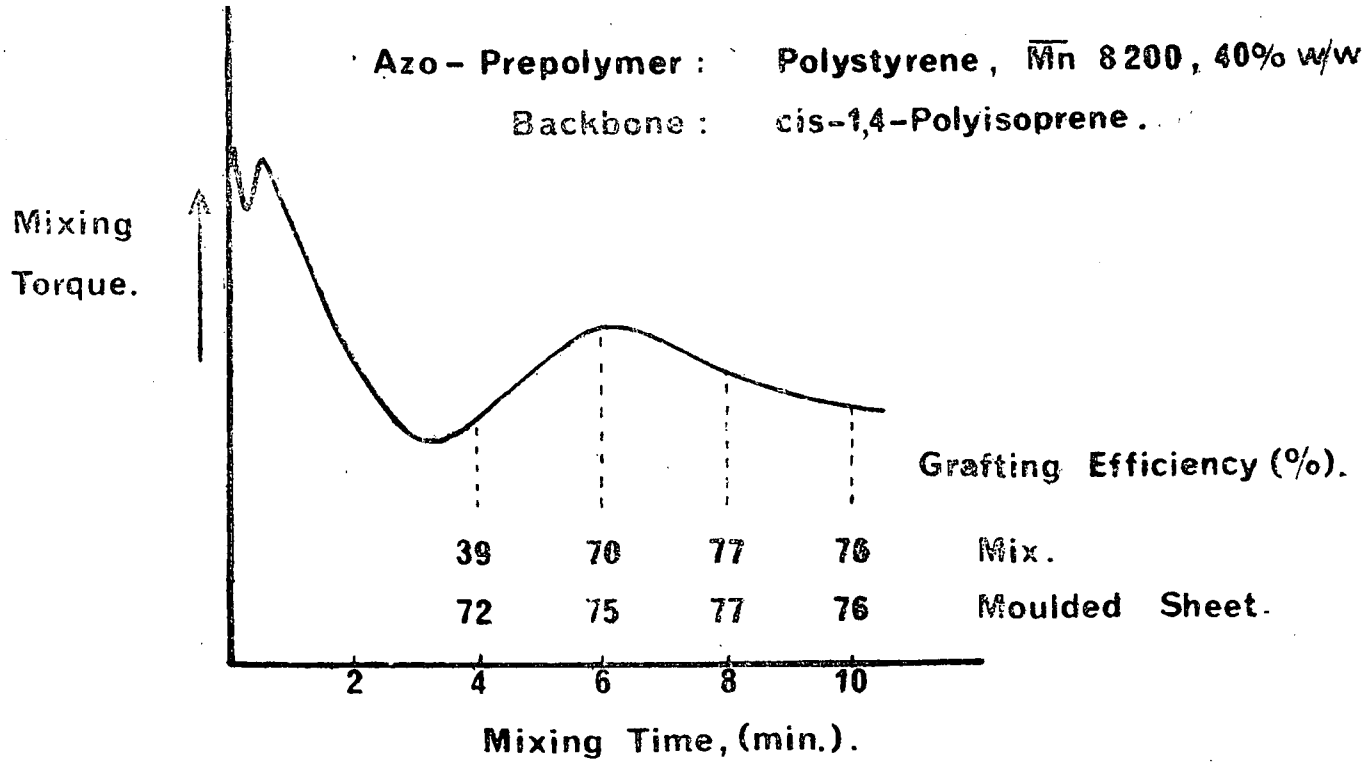


Fig. 20.

This method of grafting has several advantages

(i) The MW of the polymer to be grafted can be accurately determined

(ii) The number and therefore spacing of the grafted chains can be controlled

(iii) The reactivity of the azo tipping group allows efficient grafting not only in solution but in dry mixing

(iv) The method is theoretically applicable to all other polymers that can be reactively tipped, and indeed to mixtures of two or more polymers so that a very wide range of grafts, perhaps with unique properties, might be possible

Using poly (styrene) as an example, it was found that at optimum poly (styrene) content (40% w/w) and molecular weight ($\bar{M}_N$ 8200) the graft had the properties of a thermoplastic elastomer with a high tensile strength without vulcanization (Fig. 21) and the ability to be injection moulded. Unfortunately, taking into account the cost and the level of properties achievable the poly (styrene) grafts are not quite as good as the commercial synthetic block copolymers.

Feasibility guidelines for other graft systems

While it is true that any azo-tipped polymer will graft to NR if a common solvent can be found, this is not so for dry-mix-grafting. Here a certain degree of compatibility of the polymer with NR at the mix temperature is required for the azo group to react with NR. The solubility parameter (SP) of a polymer is a concept based on cohesive energy calculated from group molar attraction data. The difference in SP's between two polymers is a measure of their compatibility. Experimental results suggest that dry-mix grafting will only occur if the SP difference is not more than 1·3 units.

T_g (or T_m for a crystalline polymer) is equally important. If T_g is too low the graft will not show thermoplastic rubber behaviour, if it is too high the graft will not be processable. Taking into account that the usual low molecular weight of the polymer will depress the normal value of T_g or T_m it is possible to specify that these normal values should lie between 70° and 230°C for T_g and 40° and 200°C for T_m, the latter being lower because of the relative sharpness of melting and a lower sensitivity to depressive effects.

Figure 22 predicts those polymers which, if functionalised, would graft to NR to give a thermoplastic rubber. The preferred polymers would occupy the bottom right hand corner of the 'feasibility rectangle', ie they have a reasonably high T_g/T_m for retention of physical properties at high service temperature and a low solubility parameter difference for easy grafting. Most of the polymers within the rectangle have been grafted on to NR but possibly the most interesting, poly (propylene), has proved difficult to functionalise.

Although it now seems unlikely that a graft copolymer of NR will have outstanding properties as a thermoplastic rubber, other uses are possible. Thus some grafts have excellent adhesive properties while their ability to act as blending aids when NR is mixed with materials such as EPDM, which are difficult to disperse, is an unexplored area.

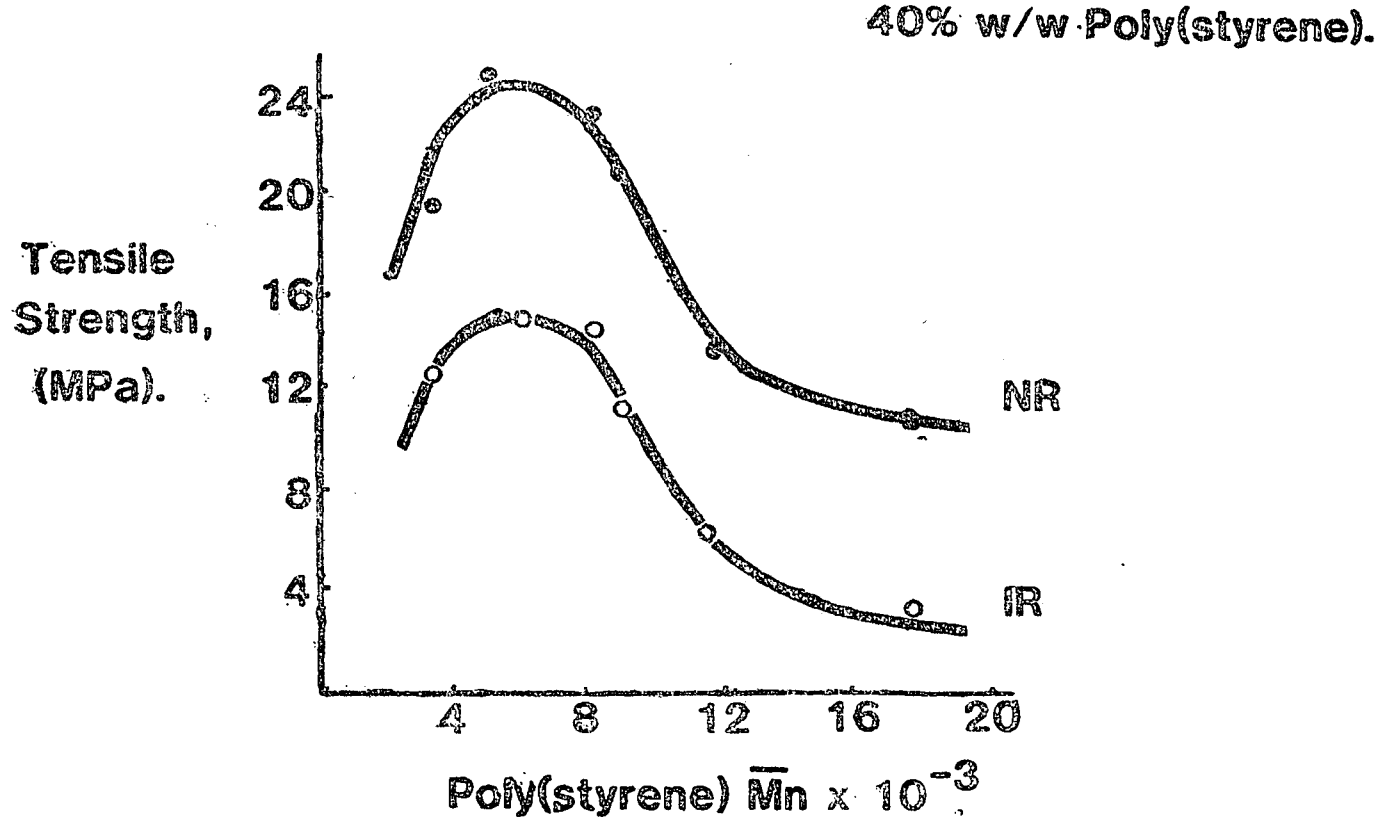


Fig. 21. Plot of tensile strength versus composition of NR/polystyrene graft.

Solubility Parameter Difference Versus T_g/T_m

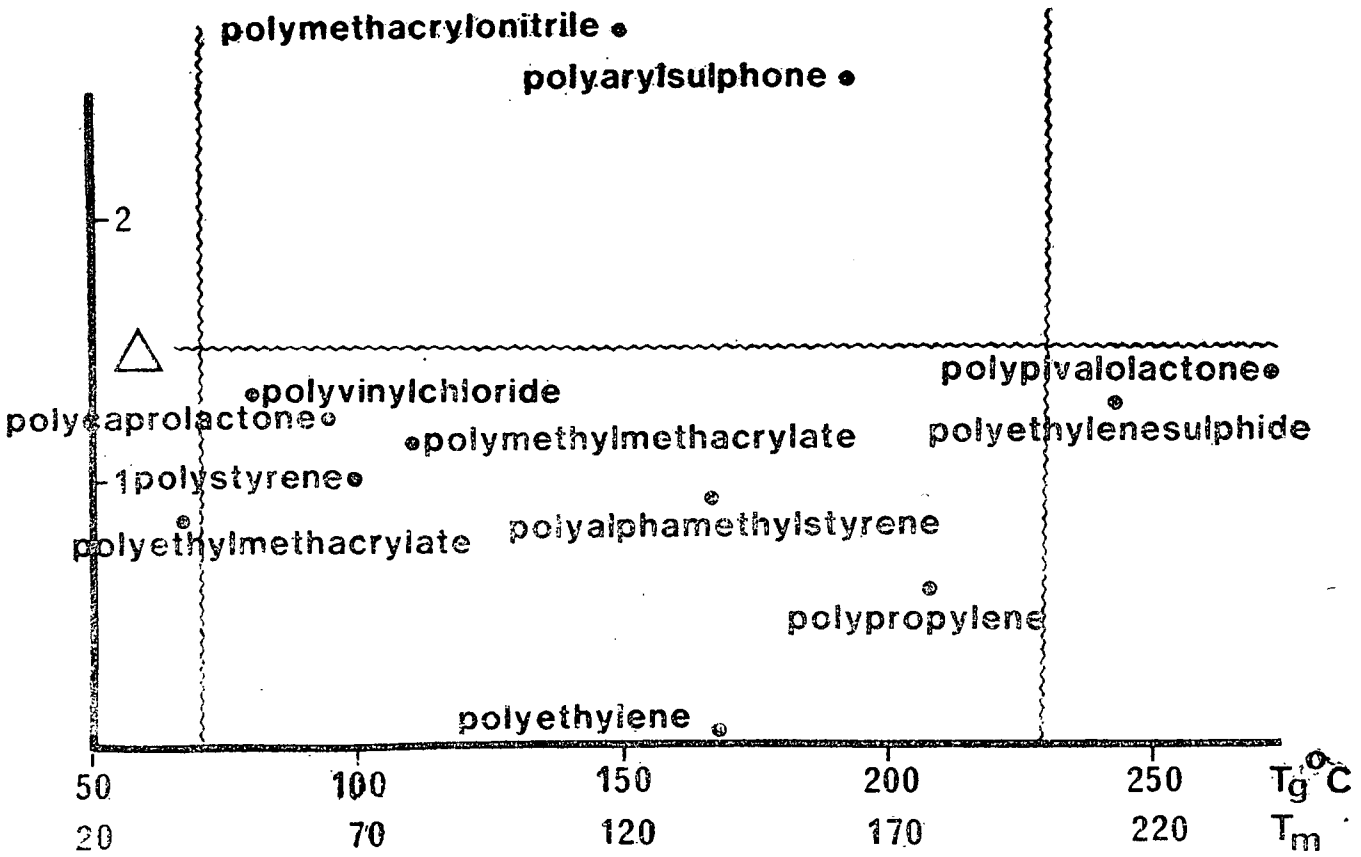


Fig. 22.

Q — S. W. KARUNARATNE, (RRISL) : Solution processes are discouraged due to economic reasons. Can you comment please ?

A — D, BARNARD, (MRPRA) U.K. : NR usually has a high gel content which will not dissolve. The solvents required are either toxic or inflammable or both and are costly and difficult to recover.

The solutions become viscous at quite low NR concentrations and the product is not easily isolated free from solvent.

Q1 — H. NARANGODA, IDB : Dr. Barnard, you mention that prevulcanising of NR latex could be carried out with siloxane crosslinks. Does it take place without an activator system (eg. Zno). What is the prevulcanising temperature and heat resistance performance in relation to conventional sulphur crosslinking system ?

A — D. BARNARD, (MRPRA) UK : Yes. No accelerator or activator is needed. The heat resistance of the Siloxane crosslink will be very high.

Q2 — Is the chemical you indicated in prevulcanising latex with siloxane crosslinks, available as a commercial raw material ? How is the price when compared to dithiocarbamates ?

A2 — No. The chemical is not commercially available although reasonably easily synthesised.

It would be more expensive than dithiocarbamates. A' guesstimate ' would be a factor of 2.

Q — D. K. Weerasinghe, (TRI) : Has there been any work done on the addition of sulphenium ions ?

A — D. BARNARD, (MRPRA) UK : We have done nothing on this but the addition of $RS^{+}CL^{-}$ to olefins is well known (Karash *et al*) and has been carried out with NR in solution. I would think that stable examples of such compounds could be added during dry mixing procedures.

Q — W. S. E. FERNANDO, (RRISL) : How safe is latex crosslinking process by azo compounds ? Is there a possibility of formation of nitroso-amines ?

A — D. BARNARD, (MRPRA) UK : We think the azo compounds would be safe because they become bound to the rubber and non leachable. Neither the hydrazo products of addition nor the silane/ Siloxane groups are known to be toxic. Nitrosamines would not be formed but can arise when dithiocarbamates are used via the release of secondary amines.

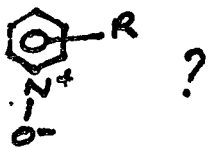
Q — G. SCOTT. (University of Aston in Birmingham): In the mechanochemical grafting process using the azo adduct why do you not get grafting in the initial period when the viscosity of the polymer is the highest ?

A — D. BARNARD, (MRPRA) UK : This not a free radical mechanochemical reaction. As mixing proceeds the temperature rises and the NR/polymer become more compatible allowing the ene-azo addition to proceed and grafting to occur.

Q — L. M. K. TILLEKERATNE, (RRISL) : Fractioned bleached crepe rubber is the easiest grade of NR to dissolve without a gel. Have you tried this grade and if so what are your observations ?

A — D. BARNARD, (MRPRA) UK : Pale crepe, especially when milled has a low gel content. Solution is still slow and the objections to solution chemistry on a large scale still apply - toxicity, inflammability and cost of solvent, viscous solutions for low NR concentrations etc.

Q — D. K. WEERASINGHE, (TRI) : Could one expect NR to add onto



?

A — D. BARNARD, (MRPRA) UK : I am not sure that pyridine N-oxide would add. Nitrile N-oxides and nitrones do add to NR at elevated temperatures.

THE EFFICIENCY OF A HOT WATER HEATING SYSTEM IN A CREPE DRYING TOWER

By

N. C. C. WALPITA*, T. L. GUNARUWAN FERNANDO* AND RISHANI NANDADEWA**
*(*Rubber Research Institute, Sri Lanka.**)*

INTRODUCTION

It has been observed on visits to estates with crepe drying towers that the efficiency of traditional boiler/radiator type heating systems was rather low from a modern point of view. Efficiency for our purposes is defined as the ratio,

$$\frac{\text{Total heat output from radiators.}}{\text{Total heat value of fire wood burnt in boiler.}}$$

(The term in the denominator is taken as equal to the nett calorific value at constant pressure, in accordance with most modern day practice, See App. 1 Section B)

The effect of the low efficiency is that very much more firewood is being used for crepe drying purposes than would be the case if the system had been optimised. These boilers had been designed many years ago, when fuel prices were a small fraction of the present day price and when conservation of firewood resources was not an issue. Since conservation is an important issue today, it was therefore decided to carry out a fairly precise investigation of the efficiency of the system fitted in the drying tower at RRI, Dartonfield.

MATERIALS AND METHODS

At Dartonfield, the system consists of a small (neoclassic type) vertical, water jacketed, firewood burning boiler connected to seven radiators at the ground floor level of the drying tower. The circuit diagram is given in Fig. 1. Hot water circulates in pipes by thermo-siphon action from the top of the boiler to the top of the radiators and cooler water is returned to the boiler by means of another set of pipes at a lower level.

The test method was as follows :

A quantity of firewood estimated as being sufficient for 12 hours operation was weighed. The boiler and radiators were allowed to cool down to ambient temperature.

The boiler was then fed with firewood and fired up at about 4-00 p.m. on the particular day. Firewood was fed at regular intervals and finally terminated at 12-00 midnight. Temperature measurement were taken every half an hour from the time of commencement until 3-00 a.m. the next day (in order to obtain the temperature drop curve after firewood feeding was terminated).

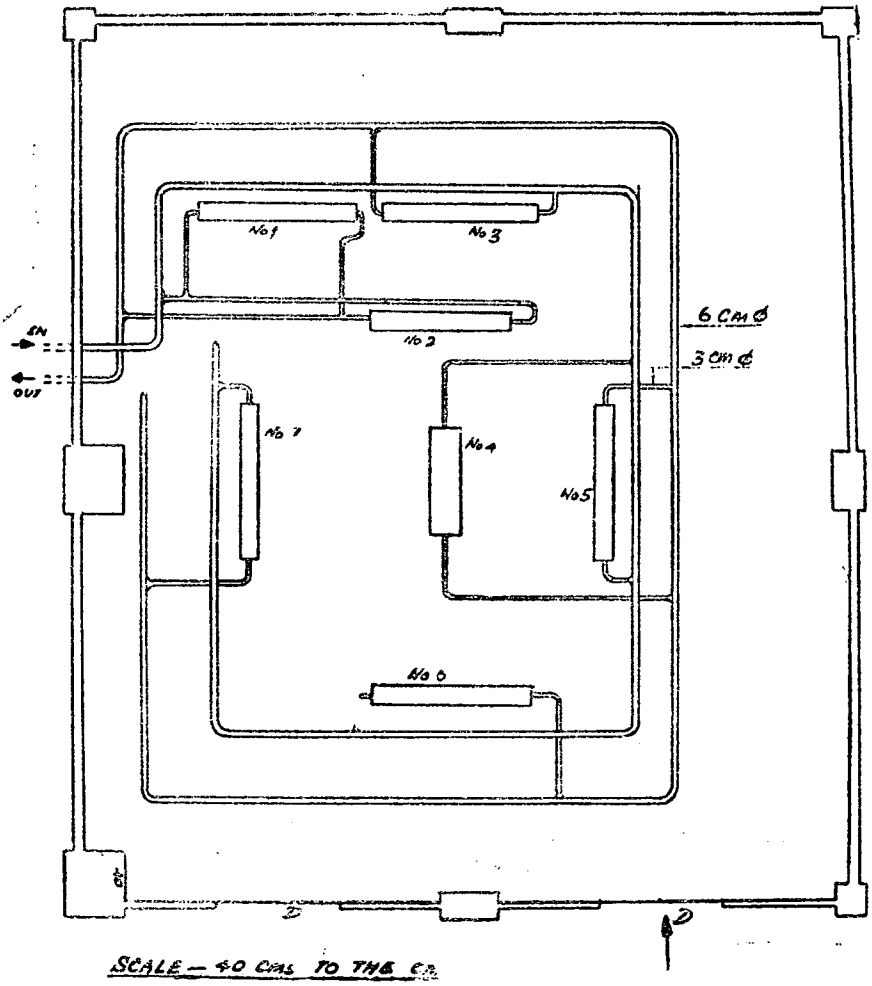

No 1
No 3
No 2
6 CM Ø
3 CM Ø
IN
OUT
No 7
No 4
No 5
No 6
D
D
SCALE — 40 CMS TO THE CM

Fig. 1

Temperatures were measured at the top and bottom of each of the 1st and last radiator, the boiler inlet and outlet pipes, the ground, first and second floors in the drying tower (ambient values) and external to the tower. All these temperatures are shown plotted in Figs. 2 and 3.

RESULTS

The total heat transfer coefficient with respect to the surface of each radiator is taken to be the sum of the convective and radiative coefficient *i.e.*

$$H_{rad} = \sigma\delta\left(T_{rad}^{2} + T_{amb}^{2}\right)\left(T_{rad} + T_{amb}\right)$$

$$H_{conv} = 1{\cdot}42\left(T_{rad} - T_{amb}\right)^{0\,25}/h^{0\cdot25}$$

$$H_{ToT} = H_{rad} + H_{conv}$$

H_{rad} = Radiative heat transfer coefficient

H_{conv} = Convective heat transfer coefficient

H_{ToT} = Total heat transfer coefficient

T_{rad} = Temperature of the radiator surface

T_{amb} = Ambient temperature within the ground floor level of the drying tower

h = Vertical height of radiator

σ = Stefan - Roltzmann constant

δ = Emmissivity of radiator surface

The equation for the convective term is a standard result for vertical flat plates, undergoing natural convection. Because the surface of the radiator is ridged and curved, the actual natural convection coefficient is likely to be somewhat higher than that for a vertical flat plate. This is counteracted by the fact that surfaces within the body of the rediator are effectively " covered " resulting in a lower actual coefficient in these areas.

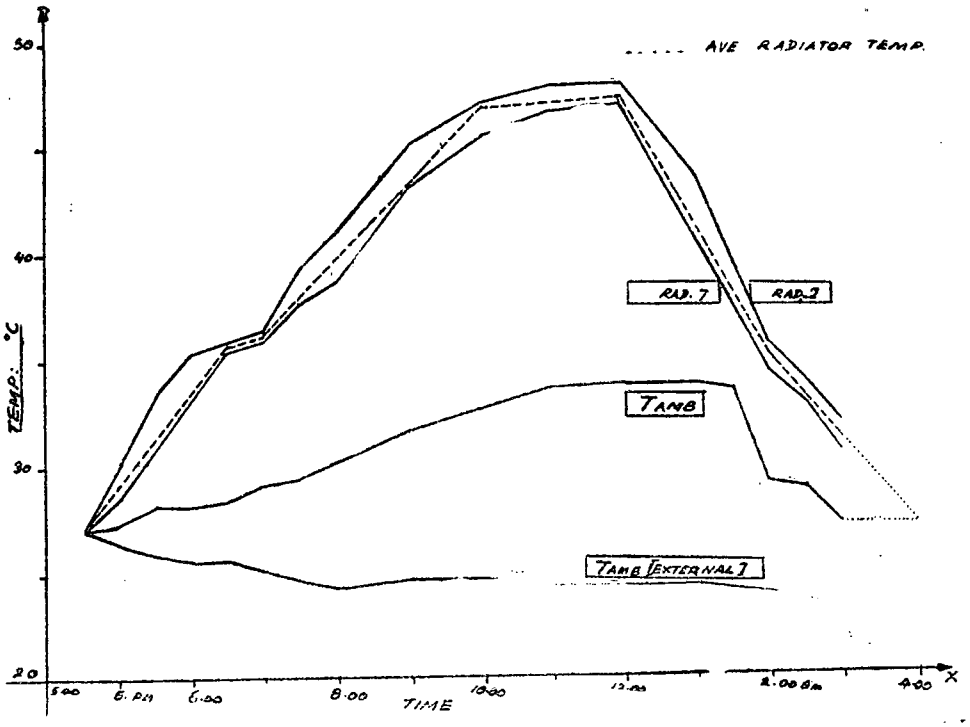

AVE RADIATOR TEMP.
RAD. 7
RAD. 3
TAMB
TAMB (EXTERNAL)
TEMP: °C
50
40
30
20
5.00
6. PM
6.00
8.00
TIME
10.00
12.00
2.00 Pm
4.00
X

Fig. 2

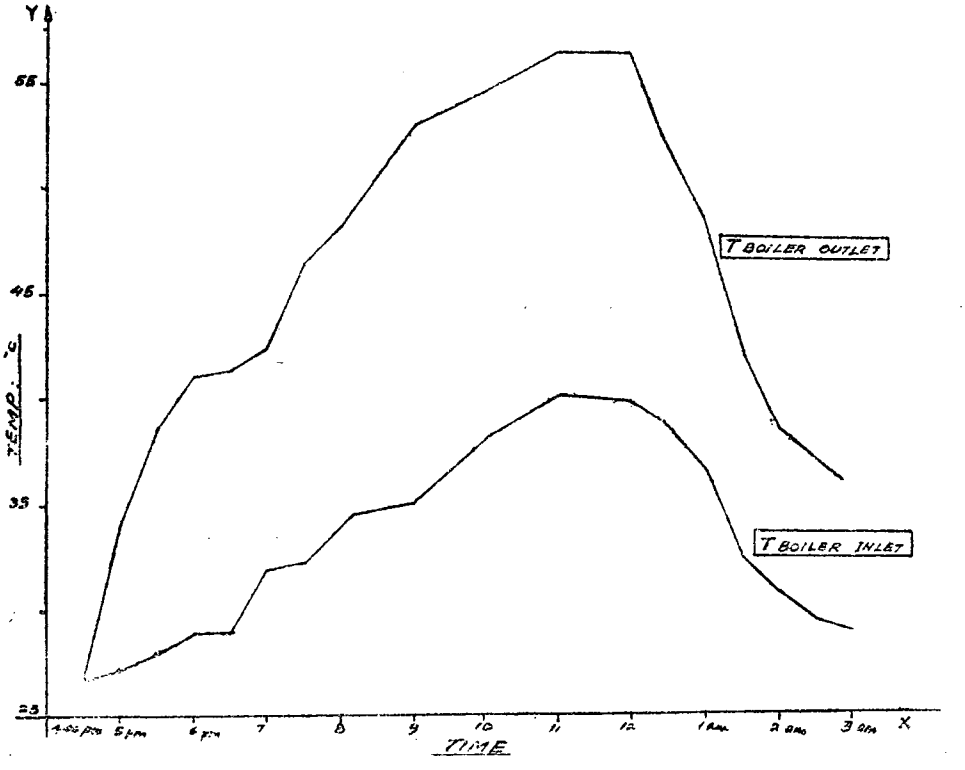

Y
55
45
35
25
TEMP. °C
T BOILER OUTLET
T BOILER INLET
4.30 pm
5 pm
6 pm
7
8
9
10
11
12
1 am
2 am
3 am
X
TIME

Fig. 3

In calculating the radiative heat transfer coefficient, the emmissivity has been taken equal to 1. Since the actual emmissivity is likely to be around 0·8 — 0·9, this assumption results in an over estimate of efficiency.

The average temperature curve for a radiator is assumed to be the dotted line between the curves for the 1st and last radiators, as shown in Fig. 2. In order to estimate heat output, the curve was divided into eight sections along the time axis.

The total heat output is calculated from,

$$Q_{ToT} = A \sum_{n=1}^{8} (T_{rad} - T_{amb})\, \delta t\, H_{To}$$

Where, A = Total surface area of all radiators plus inlet and outlet pipes

δt = Time interval

For each section (See Fig. 4, Appendix III B)

$$(T_{rad} - T_{amb})\, \delta t = \tfrac{1}{2} \delta t \left[T_{rad_1} + T_{rad_2} - T_{amb_1} - T_{amb_2} \right]$$

The numerical results are shown summarised in Table 1. In the final section of the curves, heat output is estimated from an extrapolation since there were no readings in this range. However even a 50% under estimation here will cause only a 0·3 percentage point error in the final efficiency result.

Total heat output from radiators	—	17·9 × 10^7 Joules
Total heat input to boiler, (assuming 10% moisture content by weight)	—	135·328 × 10^7 Joules.
Overall thermal efficiency	—	13·23% (See Appendix I)

DISCUSSION AND CONCLUSION

It is apparent that most of the heat value of the fuel is being lost up the chimney and as losses from the sides of the boiler and the furnace box.

Present day gas and liquid fuel fired boilers and radiator systems can be up to 80—85% efficient overall. It would be difficult to reach these levels with solid fuels such as firewood because of poor combustion control and burning characteristics. However, 50—60% should be achievable.

TABLE I

T_{rad} (°K)	T_{amb} (°K)	$T_{rad}+T_{amb}$	$T_{rad}-T_{amb}$	$T_{rad}^2+T_{amb}^2$	$\sigma\delta$	$\left(\frac{T_{rad}-T_{amb}}{h}\right)^{1/4}$	H_{rad}	H_{conv}	H_{TOT}	$\sum(T_{rad}-T_{amb})\delta t$	$H_{TOT}\cdot A$	Q_{TOT} (J)
304.075	300.5	604.575	3.575	182761.86	56.7×10^{-9}	1.432	6.265	2.033	8.298	19440	466.348	0.9066×10^{7}
308.5	301.33	609.83	7.17	185972.02	56.7×10^{-9}	1.704	6.430	2.420	8.850	25920	497.370	1.2892×10^{7}
314.414	304.3	618.714	10.114	191454.65	56.7×10^{-9}	1.857	6.716	2.637	9.353	113940	525.639	5.9891×10^{7}
319.8	306.27	626.07	13.53	196073.35	56.7×10^{-9}	1.997	6.960	2.836	9.796	100080	550.535	5.5096×10^{7}
315.68	306.38	622.06	9.3	193522.57	56.7×10^{-9}	1.819	6.826	2.583	9.409	48330	528.786	2.5556×10^{7}
309.5	304.2	613.7	5.3	188327.89	56.7×10^{-9}	1.580	6.553	2.244	8.797	9450	494.391	0.4672×10^{7}
306.167	301.4	607.567	4.767	184580.19	56.7×10^{-9}	1.539	6.359	2.185	8.544	18000	480.173	0.8643×10^{7}
302	300	602	2.0	181204.0	56.7×10^{-9}	1.239	6.185	1.759	7.944	7200	446.453	0.3214×10^{7}

Area of Radiators (A) = 56.2m (see App.II Sec.A)

17.903×10^{7}

Total Heat energy comes out by Radiators = 17.903×10^{7} Joules

In order to improve efficiency, a simple air heater arrangement which extracts heat from the flue gases prior to discharge up the chimney will be designed and tested in the first instance. This type of device could be easily retrofitted into drying tower installations without disturbing existing boiler/radiator systems.

REFERENCES

Encyclopedia of polymer chemistry & technology V. 15, Page 15.

APPENDIX 1

SECTION A

EFFICIENCY CALCULATION

Total firewood used = 118·00 kg

Total input energy = (Calorific value) × (Weight of wood)

Average calorific value of firewood = 2730·5 kcal/kg

(see App. II sec. B)

Total energy input = 2730·5 × 118 Cal

= 4·2 × 2730·5 g × 118 KJ

= $135 \cdot 328 \times 10^7$ Joules

Total energy used in heating system = $17 \cdot 903 \times 10^7$ Joules

Efficiency (%) = $\dfrac{17 \cdot 903 \times 10^7 \times 100}{135 \cdot 328 \times 10^7}$

= 13·229%

SECTION B : CALORIFIC VALUE OF RUBBER FIREWOOD AS A FUEL

Actual burning of wood takes place in three stages.

(i) Moisture removal before ignition takes place. (Temperature remains constant around 100°C).

(ii) Polymeric complex compounds brake down or destructively distill around 150°C — 500°C.

(iii) Oxidation of the carbon left after the volatiles have been driven off.

GROSS HEATING VALUE (GHV)

Total heating potential of a unit of wood as derived (effect of moisture displacing).

HIGH HEATING VALUE (HHV)

Total thermal energy released by a unit of oven dry fuel.
(Ave. HHV for wood bark = 4,726 kcal/kg).

NET HEATING VALUE (NHV)

Energy available for doing work. This value takes into account the negative heating value of water in wood.

$$GHV = HHV(1 - Mc/100)$$
$$NHV = HHV(1 - Mc/100) - Mc/100 \times L.H_2O$$

$L.H_2O$ = Heat to vaporize and superheat 1 kg of water. (Approx. 667 kg)

MC = Moisture content of wood (%) (See Appx. I sec. C).

As per our measurements the water content of our wood is about 36·85% (App. I Sec. C)

GHV = HHV (1 - Mc/100)
4726 (1 — 0·37) = 2977·38 Kcal/kg.

$L.H_2O$ = 667 Kcal/kg
(net energy added to 1 kg of super heated stream at 1 at & 200°C).

$$NHV = GHV - \frac{MC}{100}(L.H_2O)$$

= 2977·38 — 0·37 (667)

= 2790·59 kcal/kg.

CALORIFIC VALUE OF RUBBER WOOD = 2730·50 kcal/kg

SPECIFIC HEAT OF WOOD :

It is particularly independent of species and specific gravity.

Normally 0·317 — 0·337 Cal (g^{-1}) deg^{-1}
between 106° — 0°C.

Equation governing SPECIFIC HEAT with Tem. T(°C) is,

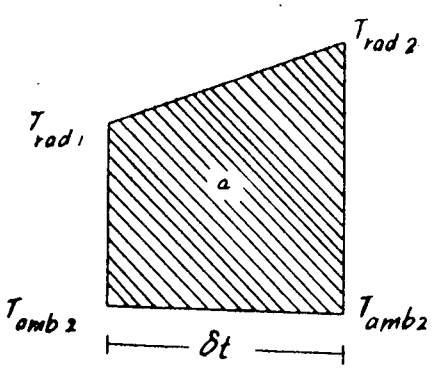
$$C - 0{\cdot}266 + 0{\cdot}00116\ T$$ (Ref. I)

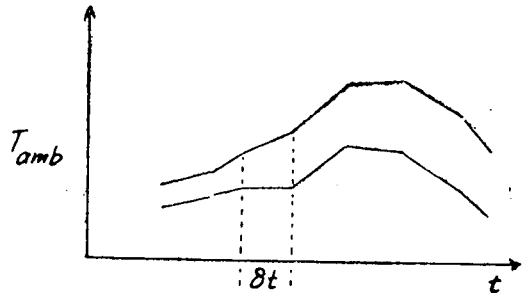
THERMAL CONDUCTIVITY :

$(2{\cdot}2 \times 10^{-4} - 4{\cdot}0 \times 10^{-4})$ Cal Sec^{-1} (cm^{-2}) $(°C/cm^{-1})$ (Ref. I)

SECTION B

CALCULATION OF A GAS BETWEEN THE CURVES





$$a = \frac{1}{2}\left[(T_{rad_1} + 273) + (T_{rad_2} + 273)\right] \delta t$$

$$\left[(T_{amb_1} + 273) + (T_{amb_2} + 273)\right] \delta t$$

$$a = \frac{1}{2}\,\delta t \left[T_{rad_1} + T_{rad_2} - T_{amb_2} - T_{amb_2}\right]$$

Using above general equation : and refering to Figure (4)

PART I Time period = 00 minutes = 5400 sec.
$= \frac{1}{2} \times 5400\ (17 + 35.2 - 27 - 28)$
$= 2700 \times 7.2$
$= \underline{19{,}410}$

By the same procedure :

PART II $a_2 = \underline{25{,}020}$

PART III $a_3 = \underline{113{,}940}$

PART IV $a_4 = \underline{100{,}080}$

PART V $a_5 = \underline{48{,}330}$

PART VI $a_6 = \underline{9{,}450}$

PART VII $a_7 = \underline{18{,}000}$

PART VIII (By extrapolation) $a_8 = \underline{7{,}200}$

SECTION C :

MOISTURE CONTENT OF RUBBER FIRE WOOD

DATE	07-09-83	12-09-83	22-09-83	24-09-83
SAMPLE NO.	WEIGHT (g)	WEIGHT (g)	WEIGHT (g)	WEIGHT (g)
1	12·2351	9·8553	9·5155	9·4237
2	8·4792	9·0959	6·8479	6·8172
3	12·6416	9·1995	8·8472	8·7970
4	9·9829	8·3094	8·0000	7·9332
5	18·3432	13·8616	13·3692	13·2513
6	18·8137	14·2199	13·6631	13·5424
7	13·0642	8·4665	8·1564	8·1071
8	14·6934	9·5139	9·1850	9·1119
9	11·3991	7·3991	7·1356	7·0900
10	12·9186	8·4585	8·1526	8·6971
11	11·5527	7·7142	7·4065	7·3700
12	7·1810	5·7789	5·4741	5·5635
13	9·8334	7·3344	7·0600	7·0182
14	14·4365	8·7266	8·3700	8·3000
15	8·6242	6·5514	6·3260	6·2988
16	12·5703	9·6339	9·2195	9·1815
TOTAL	193·769	142·119	136·734	122·361
Average	12·1106	8·8824	8·546	7·6476
Difference :	—	3·2282	3·5646	4·4630
Percentage Loss :	—	26·66%	29·43%	36·85%

APPENDIX - II

Section A: RADIATOR SURFACE AREAS

RADIATOR NO.	TYPE	AREA (m^2)
1	A	6.52295
2	B	5.67636
3	A	6.52295
4	C	9.46357
5	A	6.52295
6	A	6.52295
7	A	6.52295

Total surface area of Radiators = 47.8m^2

Section B: Surface Areas of Radiator Pipes

INPUT PIPES	- 6 cm Ø	= 3.20 m^2	
	- 3 cm Ø	= 0.66 m^2	
			3.86 m^2
OUTPUT PIPES	- 6 cm Ø	= 3.77 m^2	
	- 3 cm Ø	= 0.79 m^2	
			4.56 m^2
TOTAL SURFACE AREA OF RADIATOR PIPES			8.42 m^2

TOTAL SURFACE AREA OF RADIATORS	= 47.8 m^2
TOTAL SURFACE AREA OF RADIATOR PIPES	= 8.4 m^2
TOTAL SURFACE AREA (A)	= 56.2 m^2

APPENDIX III

SECTION A : CALCULATION OF AVERAGE TEMPERATURES

PART I :

$$T_{rad_1} = \frac{26{\cdot}86 + 29{\cdot}8 + 32{\cdot}5 + 35{\cdot}2}{4}$$

$$= 31{\cdot}075\ C°C = 304{\cdot}075\ K$$

$$T_{amb_1} = \frac{27 + 27{\cdot}1 + 27{\cdot}9 + 28}{4}$$

$$= 27{\cdot}5\ O°C = 300{\cdot}5\ K$$

$$T_{amb,\,Ex_1} = \frac{27 + 26{\cdot}3 + 25{\cdot}8 + 25{\cdot}5}{4}$$

$$= 26{\cdot}15\ °C = 299{\cdot}15\ K$$

Similarly the T_{rad}, T_{amb} & T_{amb}, E_x could be calculated per each part of the curves, and could be tabulated as follows.

	T_{rad} (K)	T_{amb} (K)	T_{amb},E_x (K)
PART I	304·075	300·5	299·15
PART II	308·5	301·33	298·5
PART III	314·414	304·3	297·56
PART IV	319·8	306·27	297·3
PART V	315·68	306·38	297·25
PART VI	309·5	304·2	297·0
PART VII	306·167	301·4	296·6
PART VIII (extrapolation)	301·0	300·0	

PROBLEMS INVOLVED IN THE MANUFACTURE OF QUALITY CREPE RUBBER IN SRI LANKA

By

M. D. R. J. GOONETILEKA AND S. WEERASINGHE
(*Rubber Research Institute, Sri Lanka*)

Sri Lanka produces around 35,000 m. tons of latex crepe annually. This represents 60% of the worlds total crepe rubber out put. Since the latex crepe rubber is a special purpose rubber used in specific applications, such as pharmaceutical and surgical purposes where its purity light colour, and toxicity-free additives, are of paramount importance.

Crepe rubber is graded visually, according to the Green Book specifications. On this basis crepe rubber is divided into four different groups viz 1X, 1, 2, 3. The main difference between the grades are colour and purity. Of the four grades 1X grade is known as the best quality crepe rubber produced. In order to obtain high percentage of No. 1X following factors are of great importance.

(1) Clones which produce light colour latex.
(2) Adequate supply of good quality water.
(3) Cleanliness and uniformity of process.
(4) Collection, transportation and bulking of latex under controlled hygienic conditions.
(5) Use of correct amounts of pure chemicals.
(6) Efficient use of proper machinery.
(7) Adequate and efficient hot air drying facilities.
(8) Prompt and timely attendance to maintenance work.
(9) Proper management and supervision of the manufacturing processes.

Since No. 1X grade of latex crepe is the best form of latex crepe it is interesting to find out Sri Lanka's performance in this sphere during the past few years. The table 1 shows the different grades of latex crepe rubber exported during the last 3 years.

Table 1. *Percentages of total exports of latex crepe rubber in Sri Lanka*

Year	% of No. 1X	% of No. 1	% of No. 2	% of No. 3
1981	33·09	46·81	9·17	10·83
1982	31·50	44·76	11·29	12·45
1983	31·07	45·35	8·29	14·83

The table 1 illustrates the fact that the production of quality crepe is only 30% which indeed amounts to a loss of a considerable sum of foreign exchange to the country Tables 2 and 3.

Table 2. *Average prices for all grades of latex crepe*

	1981	1982	1983
No. 1X	11·68	11·48	17·12
No. 1	11·11	11·14	16·87
No. 2	10·02	10·92	16·09
No. 3	8·53	8·98	13·70

Table 3. *Amount of rupees lost by not producing 1X latex crepe (80% maximum)*

Year	1981	1982	1983
Amount Rs. in Million	10.3	15·7	6·3

In Sri Lanka most of the rubber estates have PB - 86 clone (about 60% of the total) and RRIC — 100 series clones which are ideal for latex crepe production. Most of the estates have good, quality water in abundance.

However the common defects observed in the latex crepe rubbers are,

(1) Pale and dull appearance in latex crepe, slightly stained and mottled crepes (IX).

(2) Dullish, slightly yellowish, stained and mottled crepes (No. 1)

(3) Dullish, yellowish, highly mottled and stained crepes (Nos. 2 and 3).

The Janatha Estates Development Board (JEDB) and State Plantations Corporation (SPC) produce 90% of the total crepe rubber in Sri Lanka. Tables 4 shows the production figure of these two organisations during the past four years.

Table 4. *Production of latex and sole crepe*

Year	1980	1981	1982	1983
JEDB	18613 (44%)	17584 (46%)	17164 (44%)	18675 (46%)
SPC	20128 (47%)	18694 (49%)	18085 (46%)	15325 (37%)
% Total	91	95	90	83
Exports				

Table 5. *% of factories that produce No. 1X and 1 grades latex crepe (out of 60 factories)*

Grade %	% Factories			
	1980	1981	1982	1983
85%	3	6	3	11
70 — 84	57	53	53	65
50 — 69	30	29	20	19
50	10	22	24	5

The amount of 1X and 1 produced in these factories are given in Table 5. It is seen that there is a slight improvement in 1983. Nevertheless some factories still need basic facilities for crepe manufacture. A survey was conducted by the raw rubber development unit on forty factories coming under the purview of JEDB & SPC to evaluate & assess their capabilities & requirements. Table 6 shows some results of this survey.

Table 6. *Crepe rubber factory survey date (81MT/day)*

	At present	Required	% Required
Bulking tanks litres	677925	1040275	53·4
Coagulating tanks litres	7036625	1083656	54·0
Machinery (good condition)	215	305	41·9
Drying towers kg.	240000	397506	65·6

There is an acute shortage of necessary facilities for crepe manufacture. To improve the quality, these factories need at least one half times the facilities existing at present. In addition periodic maintenance work is necessary especially on machinery to achieve the smooth running of the factory. Moreover field and factory hygiene have been neglected in most factories and resulting in deterioration of quality.

The Factory Development Subsidy Scheme came into operation for the first time in 1975. This was designed to increase the manufacturing capacity of factories producing premium grades of rubbers such as pale crepe, sole crepe TSR, either by making authorised improvements to existing factories or by constructing new factories. In order to assist factory owners to embark on development programmes, the government authorised the payment of subsidy to cover one third of the cost of approved items and rubber machinery. The amount of subsidy payment since 1975 to the three major organizations and the private sector is given below.

Table 7. *Factory development subsidy payment up to 24-01-1984*

Organization	SPC	JEDB	SRMC	PVT
Amount paid in million	1·06	0·3	1·5	10·8
% paid	7·5	2·5	11·0	79·0

Table 7 shows that the private sector is more active in making use of the opportunities to put up new factories. Most of these subsidies obtained are for block rubber factories as seen in table 8.

Table 8. *Subsidy paid for crepe and block rubber factories*

Factory	Crepe	Block rubber
Amount paid in millions Rs.	5·3	8·5
% paid	39·0	61·0

Table 9. *Export figures of latex crepe and block rubber*

Year	1980	1981	1982	1983
Latex and sole crepe	42707	3814	39996	65034
Block rubber	8450	14644	10758	5427
% Crepe/block	84	73	79	92·56

These tables show that, though more subsidy was paid for block rubber, as an incentive, the two largest organizations such as JEDB and SPC had not entered the block rubber production, ignoring the opportunities given in the scheme. Furthermore, if we consider the subsidy scheme as a guide in monitoring the development programme the performance of the state-sector they appear to be far behind the private sector. On the other hand it can be observed that even though the private sector factories obtained subsidy for their factories for the manufacture of crepe rubber, most of them have changed over lately, to scrap crepe which is, more profitable, easier to handle and require less labour. Therefore it is clear that in such cases the aims of this scheme have not been fulfilled. Furthermore, some block rubber factories had closed down while some are almost defunct. Therefore, to prevent malpractices we propose that the subsidy should be given on the basis of production, over a period of 5 — 10 years. This would encourage and compel them to produce the kind of rubber that the subsidy has been paid for. The present scheme is beyond, the control of the RRI and the Rubber Controller and therefore in future a scheme similar to the one suggested should be implemented.

The following strategies may be suggested to improve the manufacture of quality latex crepe.

(1) Factory and field hygiene

It has been observed that most of the factories have neglected the hygiene in the field and the factory. Therefore, necessary that training and guidance have to be provided on these lines.

(2) Bulking facilities

Bulking tanks are used both in the factory and fields. Very often the bulking tanks situated in fields appear to be neglected and abandoned due to their distant location from the main factory. Not only should the bulking facilities be adequate but also that the bulking tanks should be paved with glazed tiles so that they can be kept clean.

(3) Transportation of latex

Unless circumstances are well beyond control of the producer, latex must be essentially, transported to the main factory. But, due to insufficient transportation facilities some estates coagulate the latex in divisions and bring the coagula on the following day. Due to the lack of knowledge of the divisional supervisor, such coagulum become sub-standard and also contaminated with foreign matter during transit leading to further deterioration of quality. Therefore, it is necessary to provide an adequate fleet of vehicles for efficient transportation of latex to the main factory with the minimum delay.

(4) Use of correct dosages and storing of chemicals

It has been a common practice through ignorance to use deteriorated chemicals in the manufacture such as sodium sulphite, bisulphite, bleaching agents. The storage conditions of the chemicals are quite unsatisfactory at times and therefore proper storage facilities should be provided. In this connection factory officers must be trained to identify the deteriorated chemicals and refrain from using those.

(5) Coagulating tanks

Coagulating tanks should be constructed so that the latex can flow from the bulking tanks under gravity. This prevents unwanted handling of latex and diminishes labour requirements. Arrangements have to be made to construct bulking and coagulating tanks where necessary.

(6) Machinery

This is the most neglected item of all. Unlike other items, heavy equipment tend to wear off rapidly and would break down unless the necessary maintenance work is carried out. There should be a programme of periodic and routine maintenance of each roller of mills, as milling affects the quality of the final product. The old mills have to be replaced with new mills as they are of lower output, and need more labour.

(7) Drying towers

Many factories lack hot-air drying facilities and in others the existing drying facilities are not adequate to meet the demands. Loft drying has to be avoided as much as possible as it leads to delay in drying and consequently mould growth could take place. The boiler radiator system should be checked periodically for the efficient operation of the drying tower.

DISCUSSION

Q — ANON : On factory subsidy scheme you commented that block rubber factories were committing malpractices by closing down factories after obtaining subsidies.

Can you please elaborate on this as I consider it as an unfair comment by all TSR manufacturers in Sri Lanka who have upgraded thousands of tons of low grade scrap and RSS 4 & 5 ?

A — M. D. R. J. GOONETILLEKE, (RRISL) : We have come across such cases.

Q — K. G. TILLEKERATNE, (JEDB) : What do you recommend to eliminate main defects like mould, stains etc. in crepe rubber manufactured under available facilities ?

A — M. D. R. J. GOONETILLEKE, (RRISL) : The causes of these problems should be carefully studied and the solution found. Mould growth occurs during drying. Use of artificial drying reduces mould growth. Fractionation can minimise mould growth.

Q — R. F. PONNAMPERUMA, (SLSPC) : When you say that bulking tanks are less than the requirement do you mean the square area or the cubic capacity ?

A — M. D. R. J. GOONETILLEKE, (RRISL) : Cubic capacity. Surface area is not important.

Q — D. D. JAYASINGHE, (Neuchatel S. P., Neboda) : What are your views about fractionated unbleached rubber (FUB) ?

A — M. D. R. J. GOONETILLEKE, (RRISL) : Present grading system does not include this grade. However 1 MT of this grade has been recently supplied to a buyer in West Germany. There might be a big demand for this type of rubber in the near future specially for food & pharmaceutical products.

Q — M. NADARAJAH, (Ceymac Rubber Co.) : In your table on grades of latex crepe, was fraction rubber included in No. 3 crepe ?

If so, do you agree with its inclusion ?

A — M. D. R. J. GOONETILLEKE, (RRISL) : No. Because (i) according to the green book latex crepe should be made under controlled and uniform conditions (ii) yellow fraction rubber is obtained not by deliberate coagulation but by autocoagulation. YF rubber has a set of completely different properties from normal crepe rubber. Therefore YF should not be included as latex crepe No. 3.

SEPARATION AND CHARACTERISATION OF PHENOLIC SUBSTANCES IN SMOKE DEPOSITS IN RSS

By

S. W. KARUNARATNE, L. B. K. SILVA AND H. N. K. K. CHANDRALAL
(Rubber Research Institute of Sri Lanka)

INTRODUCTION

Smoking is a traditional method of drying rubber. During the smoking operation wet rubber in sheet form (approximately 3 mm in thickness) is introduced into the smoke room after allowing the wet sheets to drip for about 1 to 2 hrs in the open air. The moisture content of the wet sheets when it is introduced into the smoke room is about 40%. The temperature of the smoke room is maintained around 50 to 75°C and the heat is provided by maintaining a smouldering fire with plenty of smoke getting into the smoke room from the burning of fuel wood. The common fuel wood that is used in the drying of rubber is rubberwood which is available in abundance in the rubber growing areas. Alternative fuel sources such as paddy husk, coconut husk and jungle wood are also used to reduce the cost of drying.

Ideal drying conditions can be achieved by using rubberwood and some jungle wood but the same cannot be said in the case of paddy husk and other fuel sources which result in less smoke generation than fire and the heat without an adequate supply of smoke tends to make the rubber sticky and also results in a light coloured sheet much less in intensity than the honey colour of the standard smoked sheet.

Smoking not only helps in the drying but it also results in the deposition of smoke constituents on the surface of the sheet. These constituents are believed to have an anti-septic and antioxidant effect and the superior keeping qualities of RSS can be attributed to the presence of these constituents on the surface of the sheet.

An attempt is made to separate and characterise the constituents of gaseous compounds, produced by the burning of various fuel sources which give a characteristic colour and odour to the RSS by :

(a) Direct analysis of the smoke produced by burning fuel sources.

(b) Extraction of surface deposits of RSS and comparison of these extracts with those obtained from air dried sheet.

Experimental

Fuel sources such as rubberwood, jungle wood, paddy husk, coconut husk and RSS prepared using these fuel sources were used in the experiments.

Collection of smoke from fuel sources

For the collection of smoke a glass apparatus (Fig. 1) consisting of a funnel (A) to burn the fuel source, a connecting tube (B) to collect the tar deposit and an attachment tube (C) containing a wet swab of cotton wool to trap the gaseous components was used. Suction was applied at the end of the attachment tube to pull the gases through it.

Extraction of surface deposits

Ribbed smoked sheets were extracted in a soxhlet extractor with acetone for 24 hrs. The extracts were concentrated in a rotary evaporator into a brown sticky mass which was examined by Thin Layer Chromatography (TLC) and Gas Liquid Chromatography (GLC) with and without further separation.

Thin layer chromatography (TLC)

Preparation of plates

The slurry (prepared by dissolving 30 g of silica gel — G, which is the stationary phase, in 75 cm^3 of distilled water) was spread over glass slides (7·5 cm × 2·5 cm) and thin glass plates (20 cm × 20 cm). They were dried at room temperature and activated for 30 min at 110°C, before using.

Solvent system

Solvent systems with varying degree of polarity were used as the mobile phase.

(a) benzene : methanol (95 : 5)
(b) benzene : methanol (95 : 10)
(c) benzene : acetone (90 : 10)
(d) ethyl acetate : hexane (1 : 4)
(e) n-butanol : acetic acid : water (6 : 1 : 2)
(f) benzene : 1, 4 dioxan : acetic acid
(g) ether : chloroform
(h) cyclohexane : cyclohexanone
(i) ether : cyclohexane
(j) methylene chloride : cyclohexane
(k) toluene : ethyl acetate
(l) chloroform
(m) di-isopropyl ether : petroleum ether.

Collection of Smoke of paddy husk and rubber wood

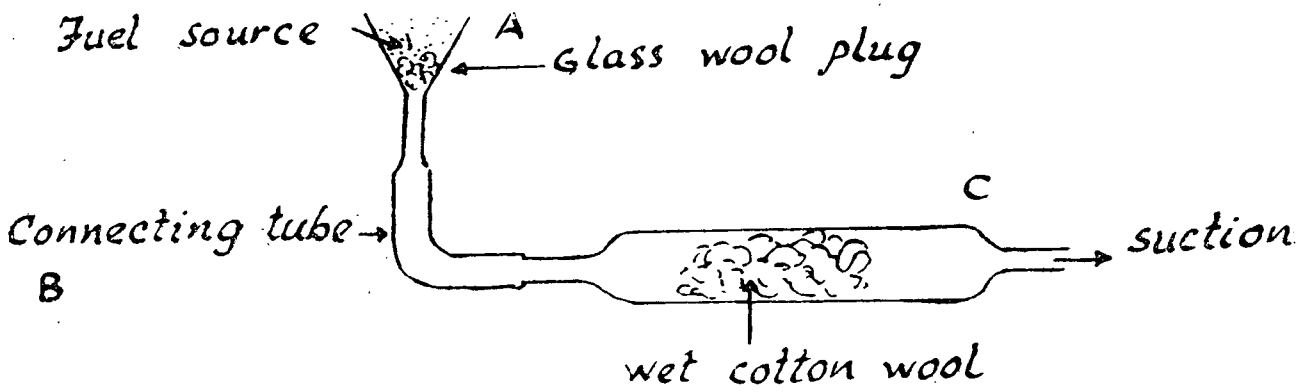


Figure 1

Visualization agents

The following visualization agents were used for the detection of phenolic compounds.

(a) Diazotised p-nitro aniline

10 cm^3 of 0·5 p- nitro aniline in 2N HCl was mixed under cooling (0-5°C) with 1 cm of 5% aqueous sodium nitrite solution and 30 cm^3 of 20% aqueous sodium acetate solution.

(b) Potassium ferricyanide/ferric chloride. Equal amounts of 1% aqueous potassium ferricyanide solution and 1% ferric chloride solution were mixed just before use.

The colours were intensified by subsequent spraying with 2N HCl.

(c) Folin — Denis reagent

Method of separation of the concentrated solvent extract into phenols, carboxylic acids and neutral compounds

The extract was treated with a saturated aqueous solution of sodium bicarbonate to obtain the sodium salt of carboxylic acids which on treatment with ether in a separating funnel separates out into the aqueous phase leaving the phenols and neutral substances in the ether phase. The phenols were separated from the neutral substances by treatment with a 5% aqueous solution of sodium hydroxide followed by extraction with ether. Sodium phenates would dissolve in the aqueous phase leaving the neutral substances in the ether phase. The sodium salts were acidified to obtain the respective carboxylic acids and phenols.

The separation is described in the following flow chart :

Gas liquid chromatography

A Perkin — Elmer F — 17 Gas Chromatograph fitted with a stainless steel column (L—2 m I.D—3 mm) packed with 5% di (3, 3, 5 trimethyl—cyclohexyl) O-phathalate on chromosorb G AW DMCS 80,—100 mesh was used for the analysis. The chromatograms were obtained under the following conditions.

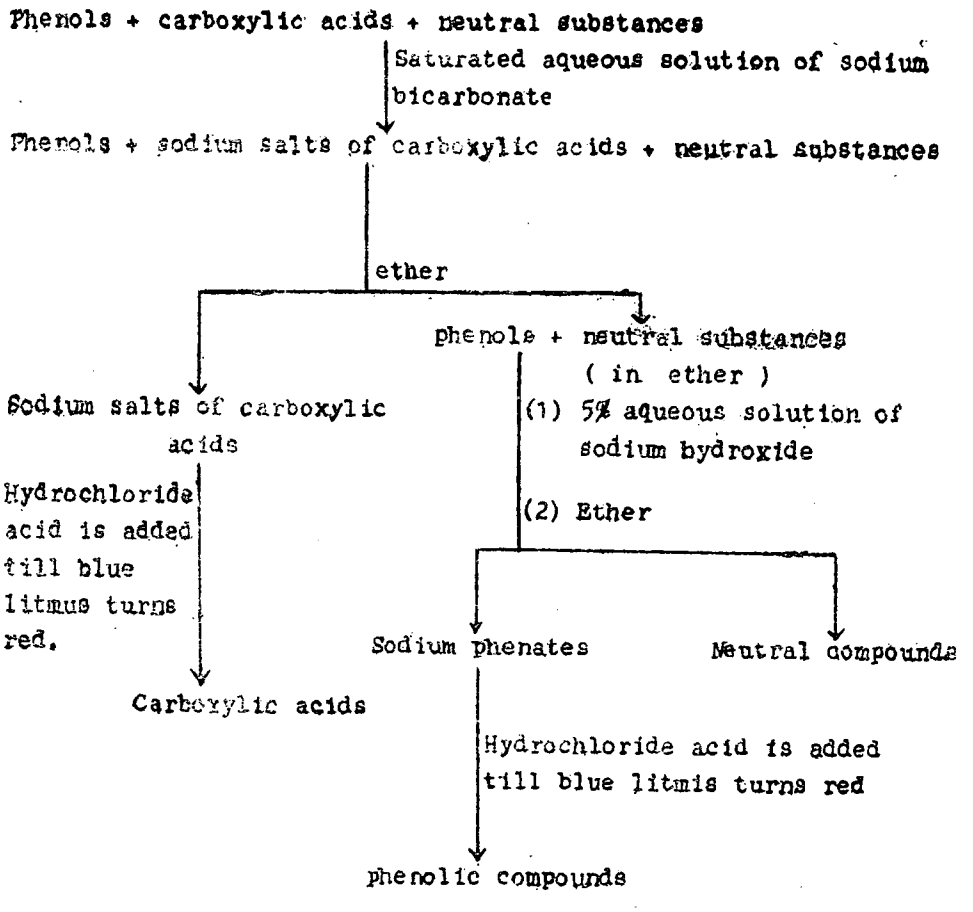
Column temperature	150°C
Injector temperature	200°C
Carrier gas	Helium at 15 ml/min
Detector	FID

RESULTS

The acetone extract was subjected to thin layer chromatography using a combination of solvent systems with decreasing polarity. A finer separation was observed (as detected

(5)

(product)



by the development of coloured spots when sprayed with visualization reagent) when the polarity of the solvent system was reduced by varying the benzene : methanol ratio. When a mixture of methylene chloride (80%) and cyclohexane (20%) was used the best results were obtained and two clear spots a brown spot and a pink spot could be identified when sprayed with diazotised p-nitroaniline. When potassium ferricyanide/ferric chloride and Folin-Denis reagent were used as the spray reagents on these plates, a dark blue colour was obtained indicating the presence of phenols. These spots had R_f values of 0·36 and 0·72.

Rubberwood smoke constituents and paddy husk smoke constituents trapped in cotton wool moistened with water were extracted and subjected to Gas Liquid Chromatography along with acetone extract of air dried sheets. While no peaks were observed in the chromatogram of the extract from air dried sheets several peaks were obtained in both extracts of RSS using paddy husk smoke and rubberwood smoke.

Fig 2: G L C of authentic phenols

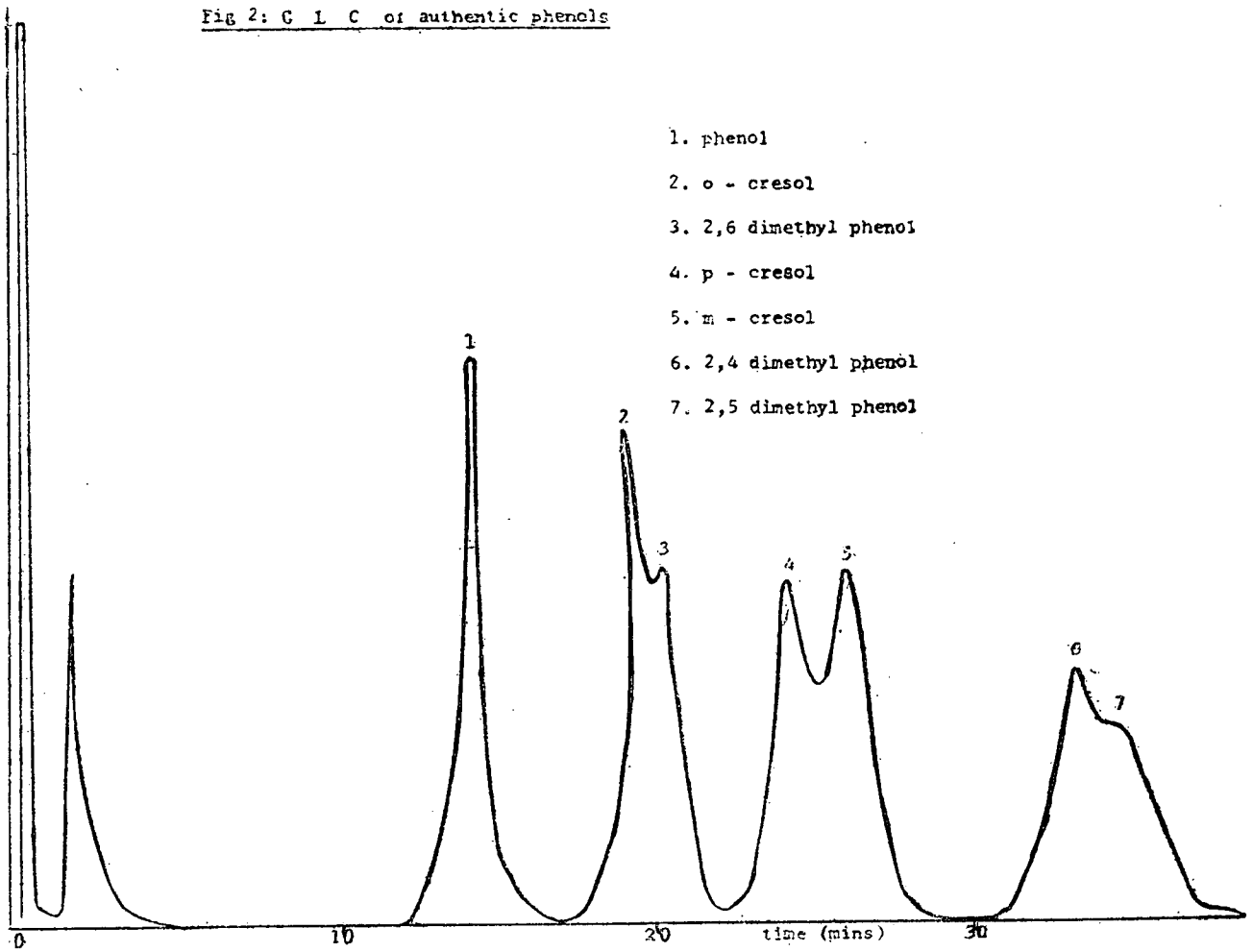
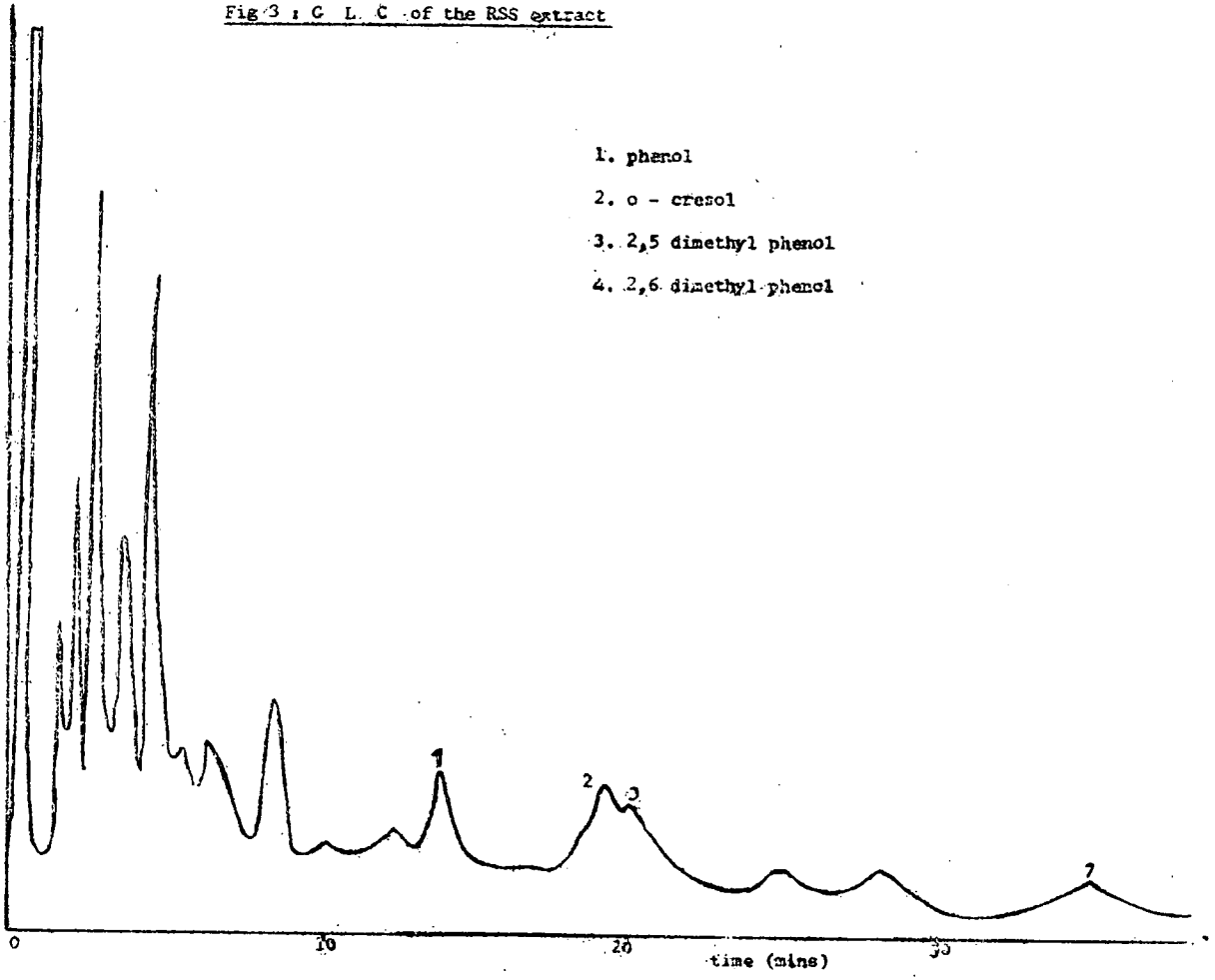


Fig 3 : G L C of the RSS extract



The phenolic constituents which were separated from neutral compounds and carboxylic acids were subjected to gas liquid chromatography and compared with the chromatograms (Fig. 2) of the following authentic substances obtained under identical conditions.

(a) Phenol
(b) O-cresol
(c) p-cresol
(d) 2, 4 dimethyl phenol
(e) 2, 5 dimethyl phenol
(f) 2, 6 dimethyl phenol

The chromatogram of the mixture of phenolic components from the RSS extract showed eleven peaks altogether (Fig. 3). Of these, four peaks corresponding to phenol, O-cresol, 2—6 dimethyl phenol and 2, 5 dimethyl phenol could be identified.

ACKNOWLEDGEMENTS

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DISCUSSION

Q — DHARMARATNAM, (Sherman Sons) : What are creosotic substances in sheet rubber due to and how do you eliminate them ?

A — S. W. KARUNARATNE, (RRISL) : They are phenolic substances deposited by smoke. They are responsible for the keeping qualities of sheet rubber.

Q — S. ILLANGATILEKA, (Dept. of Agricultural Engineering, University of Peradeniya) : Since rubber wood has other potentials (in furniture etc.) isn't there a possibility of using readily available paddy husk and coconut fibre dust by means of some process of removing undesirable phenolic substances ?

A — S. W. KARUNARATNE, (RRISL) : Phenolic substances are not undesirable in sheet rubber. However paddy husk and coconut fibre dust generate more heat and less smoke and the resulting sheets are sticky.

SMR SURVIVING IN THE MARKET WITH RELIABILITY

By

ABDUL AZIZ B. YOUP KAMARUDDIN
(*Rubber Research Institute of Malaysia*)

SUMMARY

This paper reviews the growth of Standard Malaysian Rubber (SMR) since its introduction to the Natural Rubber Industry in 1965. SMR's growth is principally attributed to its product reliability and quality. As a case-study of the progress of the Technically Specified Natural Rubber (TSNR) industry, it indicates that the survival of the NR industry in the elastomer market would be highly dependent on the growth of the TSNR industry.

INTRODUCTION

The Standard Malaysian Rubber (SMR) scheme was the forerunner of the now successful nationally run Technically Specified Natural Rubber (TSNR) schemes in various natural rubber (NR) producing countries.

This paper reviews the growth of SMR from its introduction in 1965 till 1983. The objective is to assess its development thus far, and consequently to determine its future prospects and potential.

The review will cover the following aspects of the development of the SMR scheme:

Marketing Orientation : The SMR Scheme
SMR Production Growth Trends
Consumers' Preference for SMR
Price Premium Earned by SMR
Consumers' Complaints

MARKETING ORIENTATION : THE SMR SCHEME

Historical perspective

Adam Smith in his *Wealth of Nations* said : "*Consumption is the sole end and purpose of all production ; and the interest of the producer ought to be attended to, only so far as it may be necessary for promoting that of the consumer. The maxim is so perfectly self-evident that it would be absurd to attempt to prove it. But in the mercantile system, the interest of the consumer is almost constantly sacrificed to that of the producer ; and it seems to consider production, and not consumption, as the ultimate end and object of all industry and commerce.*"

The practical marketing implications of *consumption being the purpose of production* was recognised by the NR industry through improvement of its quality with the intro-

duction of nineteen grades proposed by the Rubber Manufacturers Association, New York in 1929. Another event geared towards meeting the market requirements of consumers was the introduction of the Technical Classification (TC) Scheme in 1949. The TC Scheme classified NR quality according to three curing levels.

NR's decrease in its share of the total elastomer market — from practically 100% in 1940 to 48% in 1960 (*Table 1*), stimulated further efforts in meeting consumers' requirements. The Rubber Research Institute of Malaysia (RRIM) took the lead in the 1960s, and successfully introduced the Standard Malaysian Rubber (SMR) Scheme in 1965. To meet the consumers' requirements, the SMR Scheme introduced the following marketing innovations :

the use of comprehensive technical specification parameters for the specification of quality (hence the term *Technically Specified Natural Rubber*)

better product presentation (33 1/3 kg. bales in dispersible polyethylene)

palletised load for convenient mechanical handling and transport

introduction of comprehensive control systems administered by the Malaysian Rubber Export and Registration Board (MRERB) and the Rubber Research Institute of Malaysia (RRIM) (technical advisor to the MRERB).

Table 1. *Consumption and market share 1930 - 1960* (Allen, *et al* 1975)

Year	Total world rubber consumption ('000 tons)	NR consumption ('000 tons)	NR share of the market (%)
1930	722	722	100
1940	1 127	1 227	100
1950	2 339	1 750	75
1960	4 400*	2 095	48

*FAO estimates, including SR consumed in centrally planned countries.

SMR specifications

The original SMR technical specifications were improved as the Scheme grew the last major revision was in 1979 (RRIM, 1979). The 1979 Revisions (Table 2) took into account, the consumers' need for :

uniform viscosity and consistent processing behaviour within grades,

information on cure behaviour based on the rheometer test,

stricter specification limits in the SMR Scheme,

the need for large volume General Purpose (GP) rubber which is to be viscosity stabilised has also been identified. It was also felt that the number of grades and subgrades should be reduced wherever possible.

Table 2. *Standard Malaysian rubber specifications mandatory from 1 January, 1979*

Parameter[a]	SMR CV	SMR LV[b]	SMR L	SMR WF	SMR 5	SMR GP	SMR 10	SMR 20	SMR 50
	Latex			—	Sheet material	Blend	Field grade material		
	Viscosity stabilised					Viscosity stabilised			
Dirt retained on 44 μ aperture (max., % wt)	0·03	0·03	0·03	0·03	0·05	0·10	0·10	0·20	0·50
Ash content (max., % wt)	0.50	0·50	0·50	0·50	0·60	0·75	0·75	1·00	1·50
Nitrogen content (max., % wt)	0·60	0·60	0·60	0·60	0·60	0·60	0·60	0·60	0·60
Volatile matter (max., % wt)	0·80	0·80	0·80	0·80	0·80	0·80	0·80	0·80	0·80
Wallace Rapid Plasticity — minimum initial value (Po)	—	—	30	30	30	—	30	30	30
Plasticity Retention Index, PRI (min., %)	60	60	60	60	60	50	50	40	30
Colour limit (Lovibond Scale, max.)	—	—	6·0	—	—	—	—	—	—
Mooney viscosity ML 1 + 4, 100°C	-[c]	-[d]	—	—	—	—[e]	—	—	—
Cure	R[f]	R[f]	R[f]	R[f]	—	R[f]	—	—	—
Colour coding markers[g]	Black	Black	Light green	Light green	Light green	Blue	Brown	Red	
Plastic wrap colour	Trans-parent	Trans-parent	Trans-parent	Trans-parent	Trans-parent	Trans-parent	Trans-parent	Trans-parent	Trans-parent
Plastic strip colour	Orange	Magenta	Trans-parent	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white

[a]Testing for compliance shall follow ISO test methods.
[b]Contains 4 p.h.r. light, non-staining mineral oil. Additional producer control parameter : acetone extract 6% — 8% by weight.
[c]Three subgrades, viz. SMR CV 50, CV 60 and CV 70 with producer viscosity limits at 45 - 55, 55 - 65 and 65 - 75 units respectively.
[d]One grade designated SMR LV 50 with producer viscosity limits at 45 - 55 units.
[e]Producer viscosity limits are imposed at 58 - 72 units.
[f]Cure information is provided in the form of a rheograph (R)
[g]The colour of printing on the bale identification strip.

The success of the above innovations which improved the reliability and quality of Malaysian NR are described in the following sections.

SMR production growth trends

Introduction

This section describes the growth trends of SMR production. Such trends indicate the consumers' reaction to (and evaluation of) SMR as a product-offering in the NR market. The growth patterns would also indicate SMR's market potential and prospects.

Shipment data is used to represent SMR production trends because of its ready availability. It would also be a more accurate reflection of the SMR demand trend.

Singaporean SMR production (which was allowed during the period 1967 - 1974) is excluded in this study, so as to ensure a more consistent basis for analysis/comparison.

Annual SMR production and growth

SMR production has shown rapid and continuous annual increases (the year 1980 being the only exception) since its introduction (Table 3). Accepting the basic principle of economics that consumption is the sole end and purpose of all production, SMR's rapid growth (both in absolute tonnage as well as % of Malaysian NR production) is therefore also a reflection of its rapid acceptance by the consumers. This consumer acceptance is the ultimate measure of the reliability and quality of the SMR Scheme.

Table 3. *SMR shipments — 1965 to 1983 (Tonnes) (RRIM and Malaysia Dept. Statistics)*

Year	SMR shipments excluding Singaporean sources (tonnes)*	SMR as % Malaysian NR production
1965	707	0·1
1966	8 719	0·9
1967	23 471	2·4
1968	62 569	5·7
1969	101 562	8·0
1970	159 403	12·6
1971	224 686	17·1
1972	282 786	21·6
1973	376 097	24·4
1974	404 906	26·6
1975	433 005	29·7
1976	518 746	32·2
1977	541 866	34·1
1978	555 530	35·1
1979	576 367	36·7
1980	561 447	36·2
1981	629 120	41·2
1982	649 273	42·8
1983	710 822	45·5

* During 1967 — 1974 (before Singapore started her national TSNR Scheme known as Singapore Specified Rubber (SSR), Singapore's TSNR production was also classified as SMR

Market shares of the various SMR grades

The market share of each of the SMR grades provides an indication of its relative demand by the consumers. Table 4 gives the market shares for the SMR grades for the periods 1965 — 1978 (before the latest SMR revisions) and 1979 — 1983.

SMR 20, SMR 10, SMR CV and SMR L remained the most popular grades during both periods. From the figures, it appears that the majority of the consumers are going for the SMR 20 (about 55%) and SMR 10 (about 15%) grades. For the higher quality (latex-source) grades, SMR CV and SMR L appear to have a market share of about 10% each.

The figures also indicate that if any new rationalisation of the number of SMR grades is to be formulated, either four grades (evolving around the grades as indicated above) or five grades (the addition of SMR 5) should be the aim.

Table 4. *Market shares of the various SMR grades*

Grade	Tonnage		Percentage	
	1965 — 1978	1979 — 1983	1965 — 1978	1979 — 1983
SMR 20	2 032 265	1 701 661	49·2	54·4
SMR 10	522 845	527 280	12·7	16·9
SMR CV	463 358	360 765	11·2	11·5
SMR L	470 653	294 646	11·4	9·4
SMR 5	314 906	163 722	7·6	5·2
SMR 50	256 650	25 073	6·2	0·8
SMR GP	—	20 770	—	0·7
SMR LV	70 763	16 792	1·7	0·5
SMR WF	—	16 320	—	0·5

Consumers' preference for SMR

The consumers' satisfaction with the reliability and quality of SMR can be gauged from the feedback through the Technical Advisory Service officers of the various Malaysian Rubber Bureaux situated throughout the major consuming countries. Some of the feedback obtained is given below (the references within brackets being the Report Reference Nos.) :

> According to the president of a Korean Trading Agent, consumers prefer Malaysian grade (of TSNR) because of consistency (*K4/81*).
>
> A Korean rubber dealer is looking for a Malaysian supplier because the majority of his clients are insisting on rubber of Malaysian origin (*K 13/82*).
>
> According to this largest importer of NR in Australia, most of the customers prefer SMR (to other TSNRs) even at a slight premium (*AUS 88*).

A Taiwanese manufacturer of cellular rubber products has recently converted from RSS 3 to SMR 5 because of high dirt content and viscosity variability in RSS 3 (*J 82/83*).

An Italian general rubber goods manufacturer prefers SMR to RSS because of :

(i) easier storage, handling, and cutting

(ii) lesser problems encountered during winter months when rubber becomes half frozen (*IT 16/81*).

A US rubber dealer realised that small-sized companies are loyal to SMR despite being sold at a premium of 8 - 10 MC/lb to a competing TSNR (*A 67*).

A French, linings and roller covering manufacturer, intends to change from RSS 3 to SMR 10 because of its improved consistency, easier handling and storing, and at no extra cost (*R42/81*).

According to a German rubber dealer, NR of Malaysian origin is top in quality, and his clients do not mind paying slightly higher (*Zfl 6/82*).

The general conclusion from the above consumer feedback is that SMR is a more reliable and quality product, compared to either the conventional grades (RSS) or other TSNR schemes. This reliability and quality is the reason why consumers are often willing to pay a premium for SMR. It is also the reason for SMR's continued survival and growth in the almost stagnant NR market.

Price premium earned by SMR

Other things being equal, " price " is an important element of the marketing mix because a higher price would mean a higher profit. " Price " is also an important determinant (or measurement) of the *relative standing of the reliability and Quality* of one product or product-line vis-a-vis another within the product mix. It is within the latter context of the price element that this section addresses itself to — the price differentials between SMR and the conventional (RSS) grades.

The NR latex (tapped from the tree) can be processed into the dry form as either RSS 1 or SMR CV/SMR L. SMR CV is chemically treated with Hydroxylamine Neutral Sulphate so that it has a constant viscosity characteristic (which eliminates the pre-mastication step in rubber manufacturing operations). SMR L is a light coloured rubber, specially suited for use in light coloured NR products such as baby teats.

SMR CV generally commands a price premium to SMR L, although frequently it is quoted at the same price as SMR L. Because of its data availability, this study will compare the price of SMR L and RSS 1 as an indication of the price differentials between SMR and RSS.

Table 5 shows that the SMR L price has been at a premium of 4 - 26 Malaysian cents, compared to RSS 1, for 8 out of the 10-year period (1974 — 1983) considered. The rather abnormal RSS 1 premium over SMR L for the years 1981 and 1982 could perhaps be ascribed to speculative elements in the NR market (RSS 1 being a hedging grade), at a time of severe world economic recession. However, taking the overall picture for the 10-year period, it can be seen that the average price premium of SMR L over RSS 1 is about 7·5 Malaysian cents per kilogram.

Table 5. *Natural rubber prices (Malaysian cents per kilo)**

Year	Grade		
	SMR L**	RSS 1	SMR L premium
1974	189	179	+ 10
75	141	137	+ 4
76	213	199	+ 14
77	213	203	+ 10
78	234	230	+ 4
79	294	279	+ 5
80	319	312	+ 7
81	256	258	— 2
82	197	200	— 3
83	273	247	+ 26

* Buyers' midday prices, f.o.b., at Kuala Lumpur 81010 (Rubber Statistic Bulletin).

** Prior to Jan. 1979, SMR 5L

The price premium therefore attests to the better product reliability and quality of SMR vis-a-vis the conventional grades. It also attests to the successful achievement of the principal objective of the SMR Scheme — to offer a product that meets market requirements. Because the price premium also means a bigger profit margin, it also explains the structural changes in the NR production pattern (as discussed in an earlier section).

Consumer complaints

" *Quality should be primarily customer-driven, not technology-driven, production-driven, or competitor-driven.*

Customers, after all, serve as the ultimate judge of quality in the market place ".

H. Takeuchi
J. A. Quelch
Harvard Business Review, July /August 1983

To ensure the reliability and quality of all SMR that is produced, the RRIM closely monitors the various complaints that are received. These complaints come either direct from the consumers, or through the Malaysian Rubber Bureaux located in major NR consuming countries.

These consumer complaints act as an invaluable information feedback towards enabling corrective and preventive action to be taken in further enhancing the reliability and quality of SMR.

A detailed analysis of trends in consumer complaints on SMR for the period 1965—1978 concluded that SMR had most certainly improved over the years. (NG and Abd. Aziz, 1984)

Table 6 gives the nature and number of SMR complaints received for the period 1979 — 1983. The two main complaints are in regard to wet rubber and contamination.

Table 6. *Consumer complaints on SMR (RRIM, An. Rep. 1979 - 1983)*

Year	1979	1980	1981	1982	1983
Nature of complaint					
Wet rubber	20	15	12	15	10
Contamination	18	12	15	10	21
Incorrect identification	6	5	5	3	—
Pallet problems	5	3	1	2	—
Bale adhesion	5	1	—	1	3
Po/PRI	3	2	—	1	—
Miscellaneous	10	6	22	21	22
Total	67	44	55	53	56
Complaints per 100,000 tonnes shipped	11·6	7·8	8·7	8·2	7·9

Most of the wet rubber complaints are caused by external water ingression during transport/shipment. Although the frequency of wet rubber complaints has shown a downward trend, it still indicates that a better (or water-proof) packaging method may be needed for SMR pallets.

Most of the contamination complaints with regard to the higher latex grades relate to the presence of tiny black specks of carbon soot or oxidised rubber on the surface of the rubber bale. In the lower grades (principally SMR 20), the main contaminants relate to the presence of tiny isolated pieces of leaf twigs or of bark shavings (arising from the tapping of the rubber tree) on the surface of the rubber bale. SMR producers are taking preventive measures to eliminate these forms of complaints through better control of field practices in the estates, and through improvements in the processing-line in the factories.

However, taking an overall view of the complaints, it is significant that there is a decreasing trend in the number of complaints per 100,000 tonnes of SMR shipped. This is an indication of the successful consequence of the seriousness with which the RRIM considers consumers' dissatisfaction. It also indicates that SMR reliability and quality is constantly improving.

CONCLUSIONS

The SMR scheme was formulated with the clear objective of meeting market requirements through developing a product mix that conformed to product reliability and quality characteristics.

That the declared objective is being successfully met, and thereby contributing to the survival of the Malaysian NR industry in the elastomer market, has been demonstrated through the :

continuous and rapid growth of SMR production

increasing market share of SMR in the Malaysian NR market

positive feedback from consumers indicating their preference for SMR compared to the conventional grades

price premium obtained by SMR vis-a-vis the conventional grades

decreasing trend in the complaints received from consumers.

As a case-study of the TSNR industry, it also indicates that the NR industry should gear itself to produce TSNR if it intends to survive in the very competitive elastomer market.

REFERENCES

ALLEN, P. W., THOMAS, P. O. AND SEKHAR, B. C. (1975). The Techno-Economic Potential of NR in Major End Uses. *MRRDB Monograph No. 1, Malaysian Rubber Research and Development Board.*

INTERNATIONAL RUBBER STUDY GROUP. *Rubber Statistical Bulletin (Various issues).*

MALAYSIA, DEPARTMENT OF STATISTICS. *Rubber Statistics Handbook Malaysia (Various issues).*

NG, Y. T. AND ABD. AZIZ, B. Y. K. (1984). Patterns of Standard Malaysian Rubber Expansion 1965 — 1978. *Technology Series Report No. 12, Rubb. Res. Inst. Malaysia.*

RUBBER RESEARCH INSTITUTE OF MALAYSIA (1979). Revisions to Standard Malaysian Rubber Scheme, 1979. *SMR Bull. No. 9, Rubb. Res. Inst. Malaysia.*

RUBBER RESEARCH INSTITUTE OF MALAYSIA. *Standard Malaysian Rubber Monthly Statistical Bulletin (Various issues).*

RUBBER RESEARCH INSTITUTE OF MALAYSIA. *Specifications and Quality Control Division Annual Reports, 1979 — 1983.*

Q — H. NARANGODA, (IDB) : Is it true that Malaysia cannot produce a grade of SMR comparable to pale crepe due to lack of pure water ? How does SMR 5 EQ compare with pale crepe ?

A — ABDUL AZIZ B. YOUP KAMARUDDIN, (RRIM): SMR EQ which is out of the SMR scheme now had colour specifications of 3·5 on the Lovibond scale. Since the rubber was not fractionated and bleached there could be some yellowish tint in it compared to almost water white pale crepe/sole crepe. It is not correct to say that Malaysia cannot produce SMR EQ to colour of the sole crepe due to water problem.

Q — M. NADARAJAH, (Ceymac Rubber Co., Ltd.) : Dr. B. C. Sekhar said today that SMR grading may be revised on the three P's — processability, purity, performance. One of the three P's is processing i.e. the rubber must be a CV grade. Only a very small percentage of SMR are CV grades. Do you see the possibility of a dramatic increase in the amount of SMR CV produced in the near future ?

A — ABDUL AZIZ B. YOUP KAMARUDDIN, (RRIM) : CV features are provided through SMR CV for the latex grades and SMR GP for the general purpose grades. However the amount produced will be determined by market demand. If CV sheet is taken into consideration as mentioned then the amount of CV rubber will be larger in the near future.

Q — S. W. KARUNARATNE, (RRISL) : What are the main problems you have encountered in inspectorate visits to TSR factories regarding quality ?

A — ABDUL AZIZ B. YOUP KAMARUDDIN, (RRIM) : The main problems normally encountered are white spots & PRI.

Q — A. COOMARASAMY, (RRISL) : What is the market share of SMR GP ? Is this share likely to go up in the near future ?

A — ABDUL AZIZ B. YOUP KAMARUDDIN, (RRIM) : 12,000 MT were shipped last year. We have a rapid growth.

Q — JOHN MORRIS, (Malaysia) : What is done with off specification rubber ?

A — L. M. K. TILLEKERATNE, (RRISL) : Rejected grades of SLR are consumed locally and never exported.

A STUDY OF THE MECHANISM OF ACTION OF ALKALINE METAL SALTS OF AROMATIC THIOLS ON CAROTENOID COMPOUNDS PRESENT IN NR LATEX

By

L. M. K. TILLEKERATNE, P. H. SARATHKUMARA, S. WEERAMAN, M. MAHANAMA, R. NANDADEWA

(Rubber Research Institute, Sri Lanka)

Sri Lanka is the worlds biggest producer of latex crepe rubber (pale crepe) which is the purest form of natural rubber available in the market. This grade of rubber is therefore used mainly in pharmaceutical and surgical applications, adhesive industry, manufacture of light and bright coloured goods like toys as well as in the manufacture of equipment used in contact with foods. Owing to its very high degree of purity and light colour this grade of rubber is always paid a premium price in the market. The Government of Sri Lanka encourages the producers of raw rubber to go into the production of latex crepe. Hence in 1983 the latex crepe produced in Sri Lanka was 62 000 MT compared to 36 000 MT produced in 1982 and 24 000 MT produced in 1981.

Natural rubber latex contains carotenoid pigments, which are yellow in colour and this yellow pigmentation is a clonal effect. Latex to be used in the preparation of pale crepe should be relatively free from yellow pigments ; should not have a marked tendency to undergo enzymatic discolouration. If yellow pigments are present in the latex used in the production of crepe rubber, fractionation is carried out first ; which is a process by which the non rubber constituents in the latex consisting mainly of proteins are removed from the latex along with most of the plant pigments. However in order to achieve grade No. IX crepe, the remaining carotenoids in the fractioned latex too should be decolourised by means of a bleaching agent. Also the yellow fraction that is removed from the latex during fractionation is later converted to scrap crepe which is a cheap grade of rubber. Therefore in order to minimise the loss of rubber during fractionation, fraction removed is reduced to a minimum and the excess pigments present in the latex are bleached by means of a bleaching agent. Hence the quality of the crepe rubber produced by this method and the profitability of the process depends to a great extent on the efficiency of the bleaching agent used.

Bleaching agents used in latex crepe industry are aromatic thiols. Until 1979 only xylyl mercaptan was used for this purpose. But due to health reasons the production of this chemical was stopped and hence instead of xylyl mercaptan, Tolyl mercaptan is now used in the crepe industry as the bleaching agent. However due to the non ionic nature both these thiols have the following short comings.

(1) They are insoluble in water and hence they are used as a 35% solution in low aromatic white spirit (LAWS) or kerosene oil.

(2) They are volatile and hence they have a characteristic foul odour which is injurious to human health.

(3) Solution in a petroleum solvent cannot be directly added to aqueous latex. An emulsifier is required to make an emulsion before adding to the latex. Also from this process little oil gets into the rubber and it makes the final product softer.

(4) Being oil based it causes fire hazards and hence shipping is difficult and expensive.

In order to overcome the above defects, the thiol was converted to an alkali metal salt (sodium salt) which has a high melting point and hence non volatile and does not emit poisonous vapours and does not need to employ an emulsifier to mix with latex. It is reported in the literature that the bleaching effect of thiols on carotenoids in the latex is due to a free radical process because this bleaching effect is not observed in complete darkness. It is believed that during the bleaching action, the carotene molecule is excited to a high energy state by absorbing visible light and then there is transfer of energy to a thiol molecule, thus exciting it. The excited thiol molecule then breaks up into $RS^{\bullet}$ and $H^{\bullet}$ free radicals and the $RS^{\bullet}$ free radical ultimately reacts with the unsaturated structure of the carotene molecule thereby disrupting the conjugation of the double bonds and hence making it colourless.

This paper discusses the results of the experiments carried out to understand the reaction of the alkaline metal salts of thiols in the latex ; and thereby to explain the probable mechanism of the bleaching action of thiol salt on carotenoid pigments in natural rubber latex.

Experiment

(a) In order to study the behaviour of sodium salt of p. toluene thio phenol solutions of the salt in water were prepared at the following strengths. 60% w/w, 50% w/w, 40% w/w, 38% w/w, 35% w/w, 30% w/w, 25 % w/w, 20 % w/w, 10% w/w and 2% w/w.

The solutions were kept exposed to air at room temperature and the crystal formation was studied at different time intervals. pH of the solutions were also measured at each of the above cases using the pH meter.

Solution of strength 2% w/w which is the strength of the bleaching agent used in NR latex was allowed to stand at room temperature for a few days and the rate of crystal formation was studied at intervals of time.

(b) The rate of discolouration of a fresh aqueous extract of raw carrots in day light was studied using.

(i) a 2% solution of the sodium salt of the thiol.

(ii) a 2% emulsion of the non ionic thiol dissolved in LAWS and emulsified.

(iii) A mixture of Benzophenone and a 2% solution of the sodium p. toluene thiol.

(iv) A mixture of Benzophenone and a 2% emulsion of the p. toluene thiol.

(c) Reactions of pure carotene free of any oxygenated carotenoids (xanthophylls) with the thiol emulsion and with the thiol sodium salt solution were also studied, in benzene solution both in the presence and absence of benzophenone.

(d) Structural changes of carotene molecule in benzene before and after aeration were studied by IR spectroscopy.

(e) In order to show that the discolouration caused to carotene by the organic thiol is a free radical process where RS• radical is involved ; a well known RS• type free radical generating system 22' azobis. Iso butyre nitrile (AZBN) and mercaptobenzothiosole (MBT) dissolved in acetone was heated to 60°C and the mixture was added to the carotene solution.

RESULTS AND DISCUSSION

Results of the experiment (a) indicate that the sodium salt of p. toluene thiol is highly unstable at a pH below 13. Hence when the solid is dissolved in water the salt gets hydrolysed to the pure thiol and the crystals separate at concentrations below 38%. The pH of the solution at 38% concentration is around 13. Melting point of the crystals separating out is 41°C hence confirming that they are pure thiol crystals. This could be explained by means of the following equilibrium reaction which is pH dependent. At pH values below 13, the forward reaction is prominent.

$$RS\text{–}Na + H_2O \rightleftharpoons RS\text{–}H + Na\ OH$$

When the concentration of the salt solution is 2% w/w which is the concentration recommended to be added into latex the thiol formed is in colloidal form for at least 40 hours. When they are allowed to stand for longer periods tiny colloidal thiol particles aggregate to give crystals. Colloidal thiol particles are ideal for the bleaching reaction on carotenoids and hence freshly prepared solutions should be recommended for usage in crepe rubber industry.

Results of the experiment (b) are as follows.

When carrot juice is mixed with the pure thiol added as a 2% emulsion and kept in the dark there was no discolouration observed.

But when the same system is exposed to UV light the orange yellow colour of the carrot solution disappeared in 10 min.

When the same experiment was repeated using sodium salt of the tolyl mercaptan instead of the mercaptan added as an emulsion ; in the presence of light the discolouration was quicker and complete in 7 min.

In both these cases where either the thiol or the sodium salt of the thiol is added as the bleaching agent, in the presence of little benzophenone the bleaching reaction was faster than in the absence of it.

When pure carotene free of oxygenated carotene such as Xanthophylls is subjected to UV irradiation in benzene solution in the presence of the thiol or sodium salt of the thiol there was no discolouration observed even after 45 min. But when these solutions were exposed to light in air for 3 to 4 hours, the yellow colour disappeared in both cases.

Also when benzophenone is present in the above two systems, the bleaching action was quick under UV radiation.

From the results of this 2nd sequence of reactions where the discolouration of carotenoids and pure carotene was studied under UV light it is clear that both the thiol and the sodium salt of the thiol are capable of bleaching carotenoids in the presence of light. But pure carotene not containing oxygenated groups such as keto and OH groups in the molecule does not undergo bleaching reaction.

Hence the molecule which is responsible for the energy transfer in the bleaching reaction discussed above is xanthophylls and other oxygenated forms of carotene and not carotene itself. This is clear from the reactions where benzo phenone which contains a Carbonyl group was used as an external photo activator too. Further the IR spectra of the pure carotene and aerated carotene confirm this, where there is a clear growth of a carbonyl band at 1730 cm - 1 and a OH band at 3540 cm - 1 only in which case the colour of carotene disappeared under UV light.

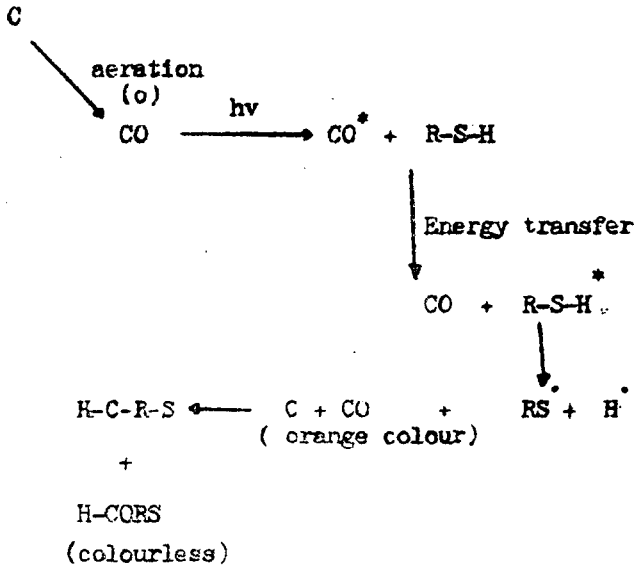
This was not observed when pure carotene is used along with the thiol or the thiol sodium salt in the absence of carbonyl compounds in the system. Quick discolouration seen in reaction (e) where a source of RS* type free radicals are added to carotene solution confirm that a free radical of the type RS* can discolour carotene. This confirm the assumption that RS* type radical is formed in the reaction between the thiol and the carotene which ultimately attack the latter and discolour it.

CONCLUSION

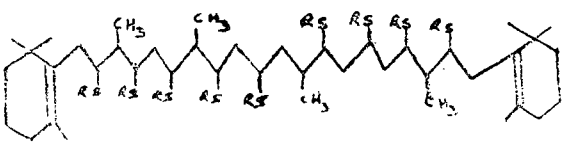
Bleaching action of the sodium salt of p. toluene thiol in natural rubber latex is caused by the fine colloidal particles of the hydrolysed p. toluene thiol crystals. Bleaching reaction of thiols and thiols salts with carotene is a free radical process and the mechanism of the bleaching reaction could be explained by the following sequence of steps.

If R-SH — Aromatic thiol.
C — Pure carotene.
CO — Oxidised carotene of xanthophyll type.

* represents an excited state of a mol.

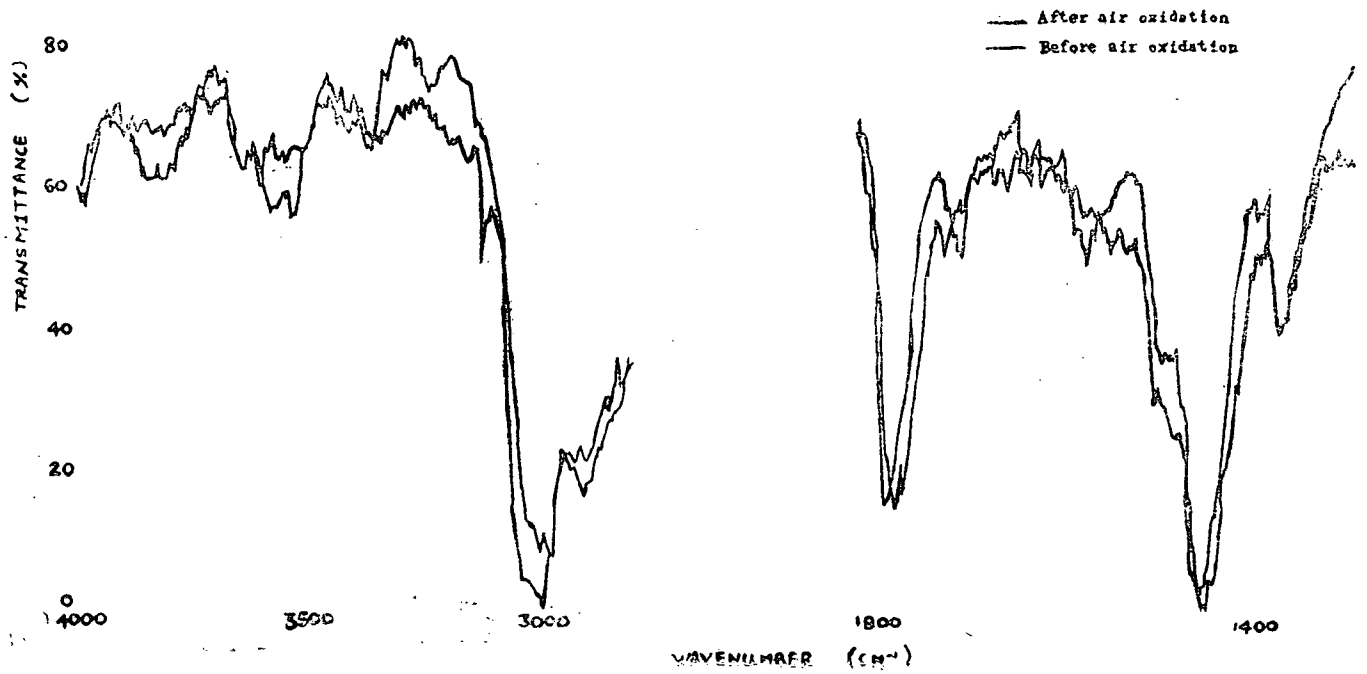


When C is carotene HC-RS will be of the following structure. Site of addition of the RS° free radical could be anywhere on the chain of double bonds.



Structure of HCORS will be similar to the structure given above with an oxygenated function at some position in the molecule.

IR spectra of carotene before and after air oxidation



REFERENCES

Annual Review 1979. of the R.R.I.S.L. P. 96,

COHEN SAUL C. ORMAN STANLEY & LAUFER D. 1962. *A.J.A.C.S.* **84.** P. 3905.

FINAR, I. L. **2**, *Organic Chemistry.*

PERIES O. S. (cd) 1970, *Pale Crepe* in Hand Book of rubber culture and processing R.R.I.S.L. P. 142.

DISCUSSION

Q — K. G. TILLAKERATNE, (JEDB) : How many grams of water soluble Nexobleech (per 100 kg of dry rubber) do you recommend for fractioned and non-fractioned rubber ?

A — L. M. K. TILLEKERATNE, (RRISL) : Same amount of bleaching agent should be added irrespective of whether it is water soluble or not and whether the rubber is fractioned or not.

Q — D. BARNARD, (MRPRA) : Thiols in alkaline solution are readily oxidised by air to disulphides. Is much tolyl thiol lost in this way in your preparation of the sodium salt ?

A — L. M. K. TILLEKERATNE, (RRISL) : Only lab preparation was carried out in Sri Lanka and all measures were taken to prevent aerial oxidation. Commercial manufacture is being done in the UK at present. It is carried out under nitrogen and the product is packed under nitrogen.

Q — N. HASSAN, (Chemanex Ltd.) : The RRI has proved that water soluble bleaching agent has advantages over oil based bleaching agents. Why is it necessary to have two types in the market ?

A — L. M. K. TILLEKERATNE, (RRISL) : We cannot withdraw from the market, a bleaching agent that is currently popular unless a proven alternative is made available to the consumer.

Due to health hazards the oil based bleaching agent may have to be withdrawn in the near future.

Q — PARANAVITHANA, (SRMC) : Are there any water soluble bleaching agents available in the market ?

A — L. M. K. TILLEKERATNE, (RRISL) : Yes. Nexobleech New Formula.

EFFECT OF STORAGE HARDENING OF THE PROCESSABILITY OF NR

By

E. L. ONG, C. L. LIM AND A. SUBRAMANIAM
(Rubber Research Institute of Malaysia)

ABSTRACT

It is a well-known fact that natural rubber, except for the viscosity-stabilised grades such as SMR CV, hardens on storage. This paper examines the increase in the gel content of RSS 1 and SMR L, brought about by accelerated storage-hardening the rubbers. The efficiency of gel formation is greater for the unmasticated rubber than for the rubbers which had been masticated. This increase in gel content generally leads to a corresponding increase in difficulty of extruding the rubbers. Extrusion of black-filled unvulcanized natural rubber also shows a similar trend of increase in shear viscosity with age-hardening.

INTRODUCTION

The increase in viscosity of natural rubber on storage (after preparation) is a well-recognized phenomenon, and is commonly known as storage-hardening. The increase in viscosity is brought about by a slow crosslinking process which continues over a period of several years (Bristow, 1974). The chemistry of this crosslinking process has been the subject of discussion in several publications (Sekhar, 1960 & 1962; Greggs and Macey 1973 ; Burfield, 1974 ; Gregory, and Tan 1975).

It is well-established that ordinary unmasticated natural rubber is not completely soluble in a rubber solvent ; the insoluble fraction is usually referred to as the gel phase or gel. The true structure of this gel phase is still not clear, but is believed to be formed by a random crosslinking reaction ; yet it is not a simple crosslinked network, for if it were the gel content would be independent of solvent power (Allen and Bristow, 1963). Being of a crosslinked nature, if would therefore be reasonable to suspect that the presence of gel may have some effect on the rheological and processing behaviour of natural rubber.

This paper examines whether storage hardening of natural rubber brings about any changes in the gel content, and if so, the effect of this change on the rheological characteristics of the rubber as determined by laboratory capillary extrusion. The effect of shelf-storage of black-filled unvulcanized natural rubber on its extrusion characteristics was also investigated.

EXPERIMENTAL

Freshly prepared SMR L and RSS 1 of Mooney viscosity (V_R) 68 and 80 respectively were masticated on a two-roll mill to Mooney viscosity 50. The unmasticated rubbers were stored at ambient temperature for up to eight weeks, while the masticated rubbers were subjected to accelerated storage-hardening, by heating over phosphorous pentoxide at 60°C, for up to forty-eight hours. The gel content of the rubbers in toluene was determined using the ' Harris cage ' method (Medalia and Kolthoff, 1951). Laboratory extrusion of the rubbers was carried out on an Instron capillary rheometer at shear rates from

3·5 to 1181S-^{1} at temperatures of 90, 100 and 120°C, with a capillary of L/D (length-to-diameter) ratio 20, the diameter being 1·27 mm.

SMR L and RSS 1 were also individually mixed with 50 phr of HAF black and masticated to a Mooney viscosity (V_B) of about 60. The black-filled masterbatches were stored in the laboratory at ambient temperature for up to fourteen days. Extrusion of these masterbatches at various stages of storage was carried out on a Monsanto Processability Tester (MPT) at temperatures of 90 and 120°C, using a L/D ratio of 20 and a capillary of diameter 1·50 mm.

RESULTS AND DISCUSSION

Unfilled rubbers

Table 1 shows the change in gel content of the unfilled rubbers on storage. The increase in gel is more pronounced for the unmasticated RSS 1, even though the Mooney viscosity shows substantial increases relative to the unhardened values, in both the unmasticated and masticated rubbers. The unmasticated SMR L does not show the same significant increase in gel content as the RSS 1. It is however known that sheet rubbers usually have higher gel content than crumb rubbers on storage, Mastication of the rubbers seems to inhibit the gel-forming capability of RSS 1. Why the unmasticated RSS 1 should exhibit a higher gel content and larger increase on storage compared to SMR L is not clear, but may in part be due to the difference in temperature, 60°C for the former and 100°C for the latter, at which the rubbers are dried. This has been known to lead to differences in extrusion of these two rubbers (Ong and Lim, 1982), and is also illustrated here by Fig, 1. At any one temperature, RSS 1 has a higher apparent viscosity of ($= \tau_w/\dot{\gamma}_w$ where τ_w, $\dot{\gamma}_w$ are the shear stress and shear rate at the wall of the capillary respectively) than SMR L. It is tempting to attribute the observed difference in this case as due to the difference in gel content.

Table 1

Rubber sample	NR grade	Treatment	VR (ML, 1'—4', 100°C)	% gel[a]
A	RSS 1	Unhardened	80	4·4
B	RSS 1	rth[b]— 8 weeks	86	15·9
D	masticated RSS 1	unhardened	50	0·4
E	masticated RSS 1	ash[c] — 16 hrs.	68	1·0
F	masticated RSS 1	ash — 48 hrs.	75	3·3
A'	SMR L	unhardened	68	1·5
B'	SMR L	rth — 8 weeks	73	2·7
D'	masticated SMR L	unhardened	52	0·1
E'	masticated SMR L	ash — 16 hrs.	65	1·5
F'	masticated SMR L	ash — 48 hrs.	78	3·7

a average of three measurements
b room-temperature-hardened
c accelerated-storage-hardened

The flow curve for SMR L at 90°C shows an inflextion at a shear stress value of about 0·3 MPa. This inflexion has been attributed to stress-induced crystallization of natural rubber, which occurs at and above a certain critical shear stress, the value of which is dependent on the temperature of extrusion and the capillary geometry but independent of the grade of natural rubber (Ong and Lim unpublished data). Hence at 90°C, it is reasonable to assume that this critical shear stress is of the order of about 0·3 MPa for natural rubber. Since the extrusion stress for the unmasticated RSS 1 exceeds this value even at the lowest shear rate of $3 \cdot 5S^{-1}$, it is susceptible to crystallization and is difficult to extrude. Increasing the temperature of extrusion shifts this critical shear stress for crystallization to higher values for example at 100°C, the value is about 0·4 MPa (Fig. 1).

The extrusion data (Table 2, Fig. 2) show that when masticated to similar Mooney viscosities, RSS 1 is easier to extrude than SMR L. This is as a result of the additional mechanical work expended on the RSS rubber to achieve the same level of Mooney viscosity as the SMR rubber (33 passes on the mill for the former compared to 13 passes for the latter), a fact consistently observed (Ong and Lim, unpublished data). In this particular case, the gel content of both rubbers are similar and negligible and would not account for the difference in extrusion behaviour ; rather molecular differences seem to be the cause, as it is known that progressive mastication leads to a reduction in the average molecular weight of natural rubber (Subramaniam, unpublished data).

The effect of storage hardening on the flow properties of the rubbers is best illustrated by Figs. 3a — d. Compared at the same shear rate, the apparent viscosity generally increases with increasing storage-hardening. It has already been mentioned that the increase in gel as a result of storage-hardening may account for the increased difficulty in extrusion of the unmasticated RSS 1. As for the unmasticated SMR L and masticated RSS 1 and SMR L, the increase in gel content as a result of storage-hardening is not significant (although on the average there is an trend of increase). Therefore, while storage-hardening of these rubbers leads to a progressive increase in apparent viscosity or difficulty in extrusion, it is inconclusive whether this is solely due to the increase in gel content. At 90 and 100°C stress-induced crystallization of the rubbers takes place readily, even for the masticated rubbers. Storage-hardening lowers the critical shear rate at which this becomes noticeable while essentially maintaining the stress level (see arrowed indicators in Figs. 3a and c, for example). An increase in gel content or crosslinking may explain the observation in the following manner. With a higher gel content (which acts as ' crosslinks ') the rubber is able to support a higher stress and allows it to rise to the critical level. With a lower gel content this load-bearing capacity is lowered and the rubber flows rather than deforms and hence the critical shear stress is only attained at a higher shear rate. Above where crystallization occurs, the influence of gel on extrusion is difficult to assess.

When the extrusion temperature is raised to 120°C, any sign of incipient crystallization is only evident at the highest shear rates, Figs. 3c and d. At this temperature and at shear rates below $354S^{-1}$, the apparent viscosity or extrusion stress seems to be a function of the gel content, and independent of the grade and mechanical work history of the rubber, Fig. 4.

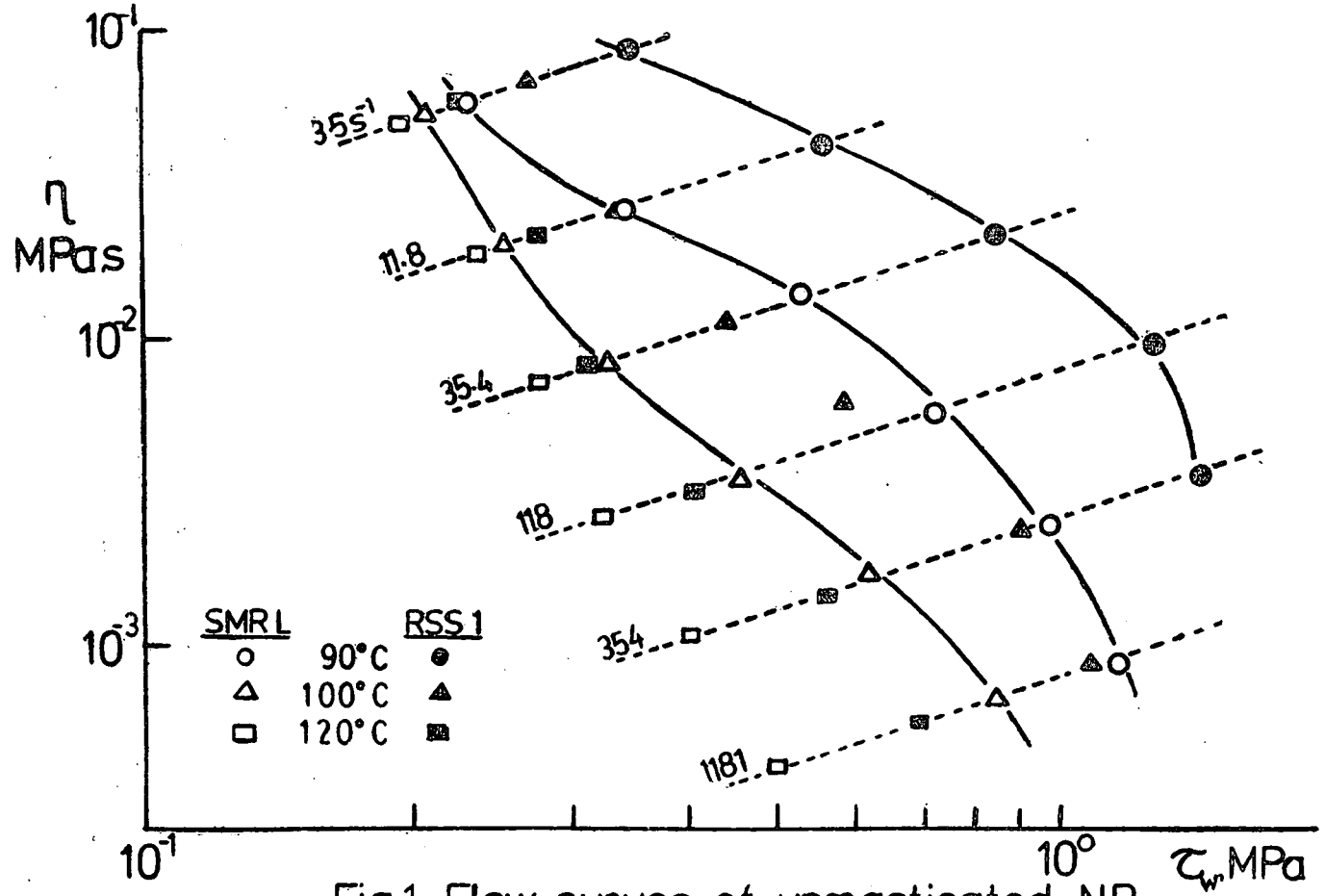


Fig.1 Flow curves of unmasticated NR

Table 2. *Extrusion data of Natural rubber samples*

Rubber sample	Mooney viscosity	Gel content %	Extrusion stress, MPa*								
			90°C			100°C			120°C		
			3·5s^{-1}	118s^{-1}	1181s^{-1}	3·5s-1	118s^{-1}	1181s^{-1}	3·5s^{-1}	118s^{-1}	1181s^{-1}
RSS	80	4·4	0·335	1·289	—	0·258	0·688	1·100	0·217	0·399	0·722
SMR L	68	1·5	0·223	0·739	1·169	0·199	0·447	0·877	0·186	0·316	0·509
Masticated RSS	50	0·4	0·168	0·316	0·670	0·144	0·272	0·502	0·124	0·268	0·371
Masticated SMR L	52	0·1	0·172	0·440	0·774	0·158	0·309	0·591	0·124	0·275	0·461

*Values at high shear rates and low temperatures are average values as the stress fluctuates considerably.

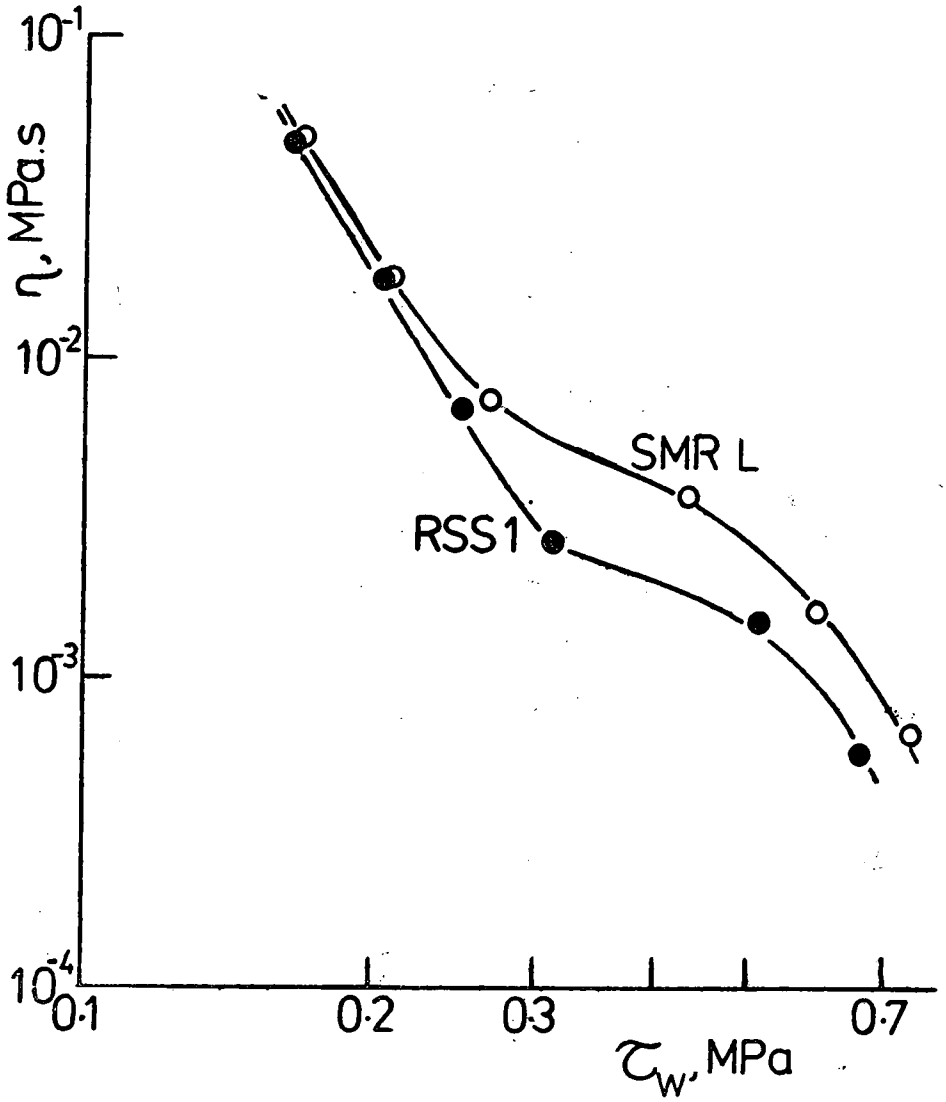


Fig. 2 Flow curves for masticated rubbers at 90°C

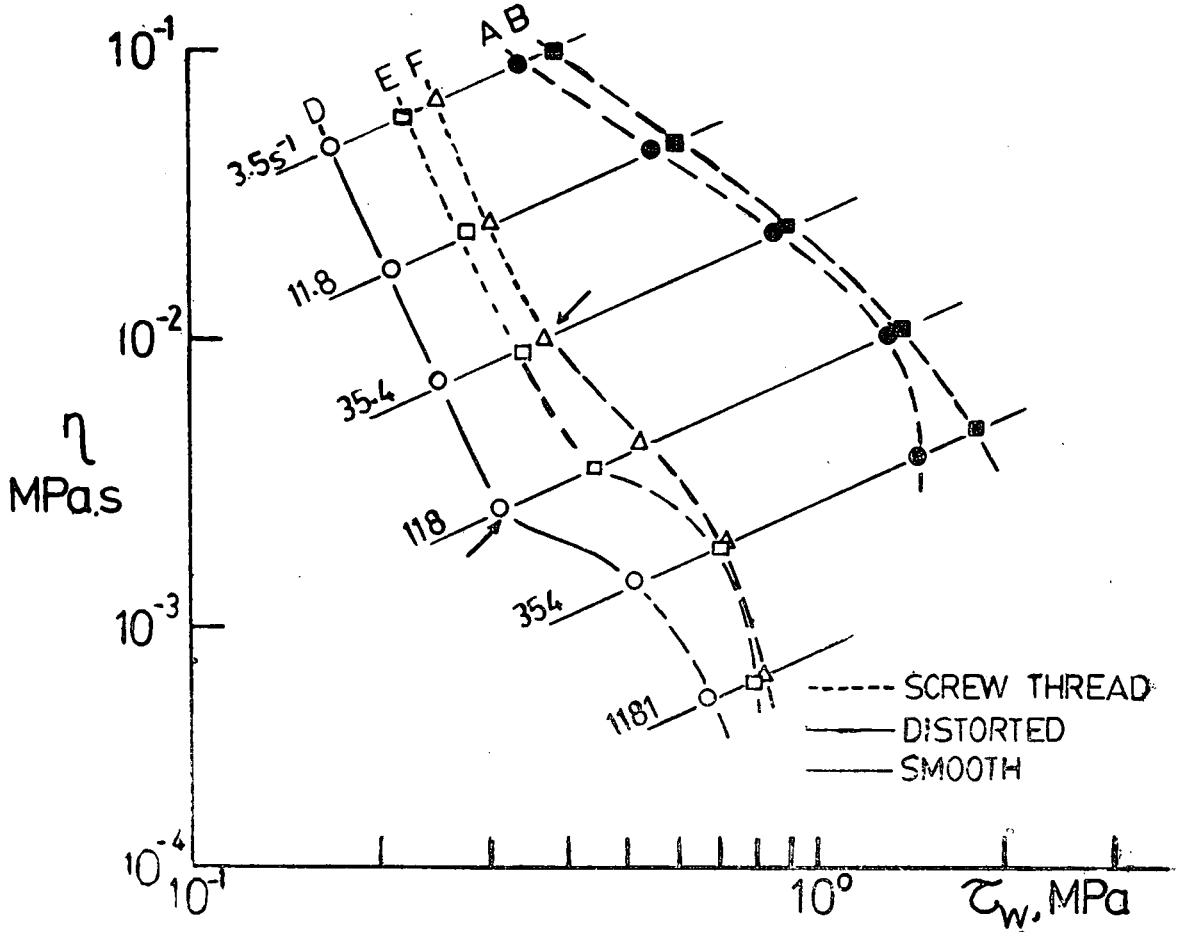


Fig 3a Flow curves for RSS1 at 90°C

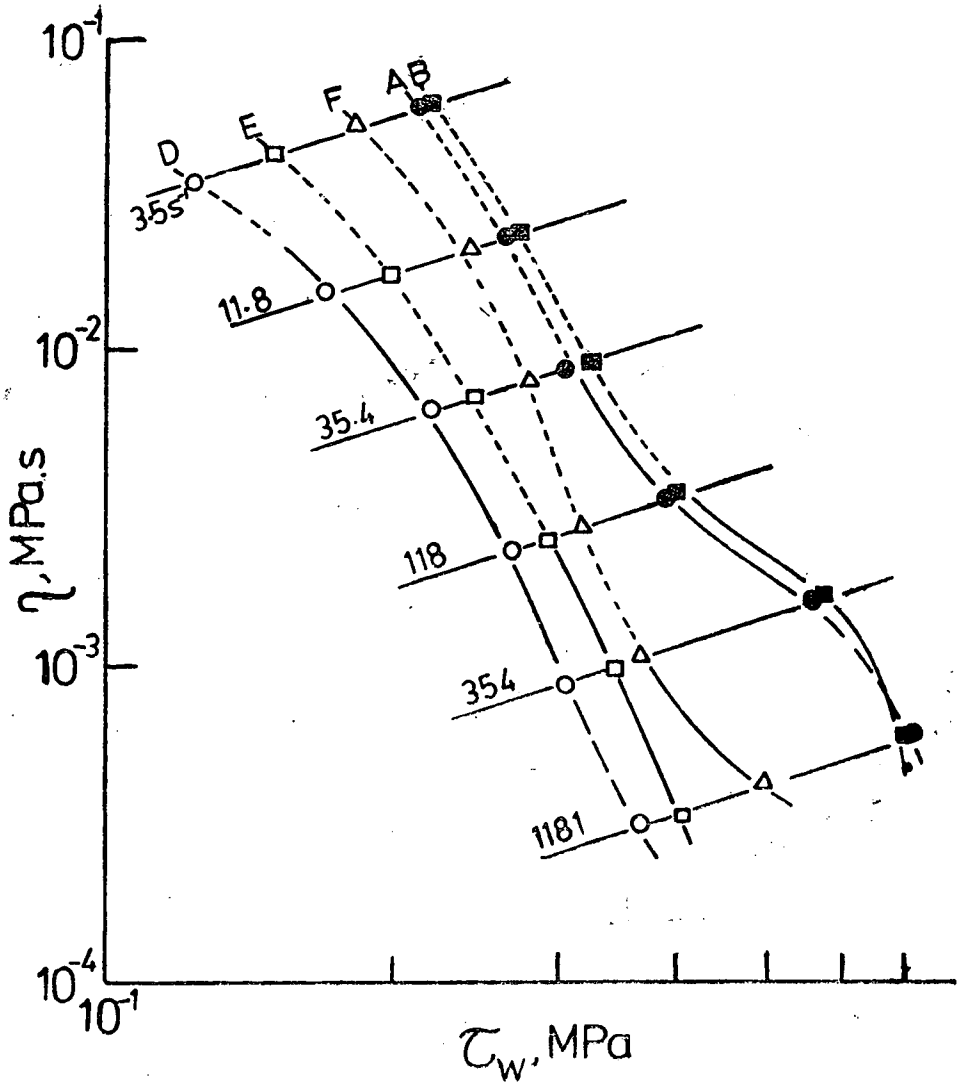


Fig. 3b Flow curves for RSS1 at 120°C

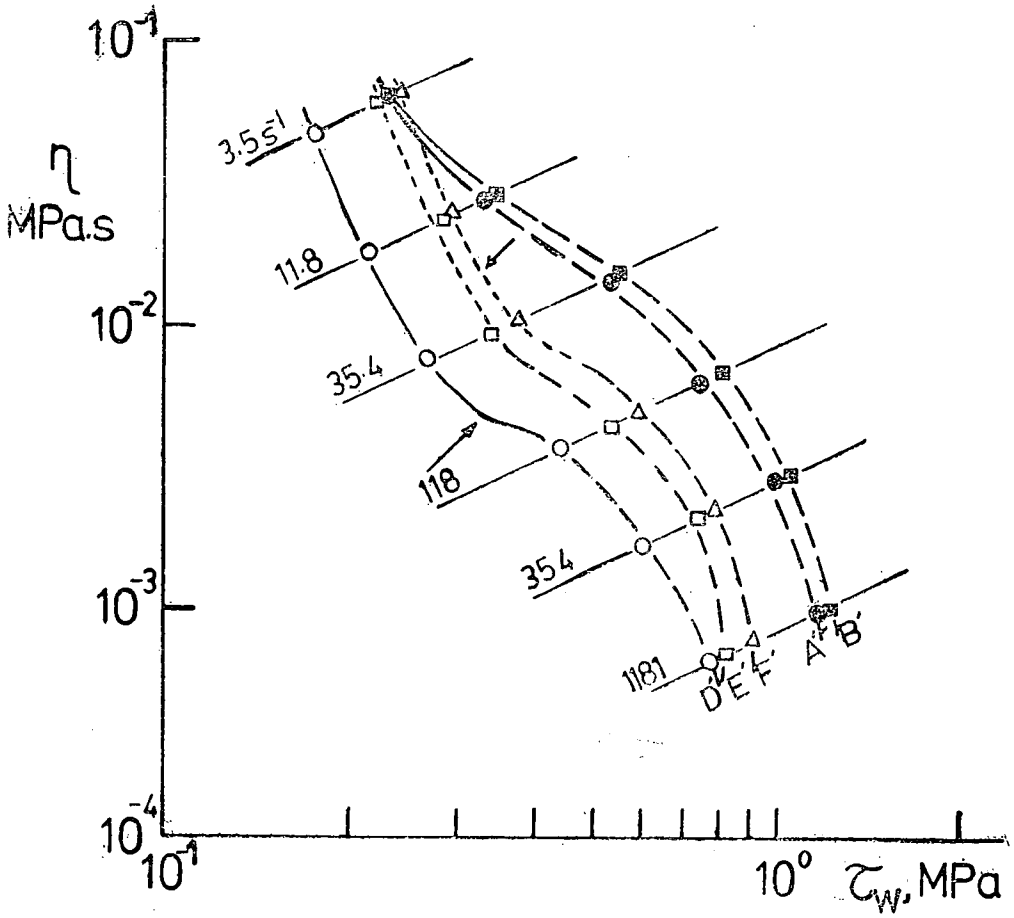


Fig. 3c Flow curves for SMR L at 90°C

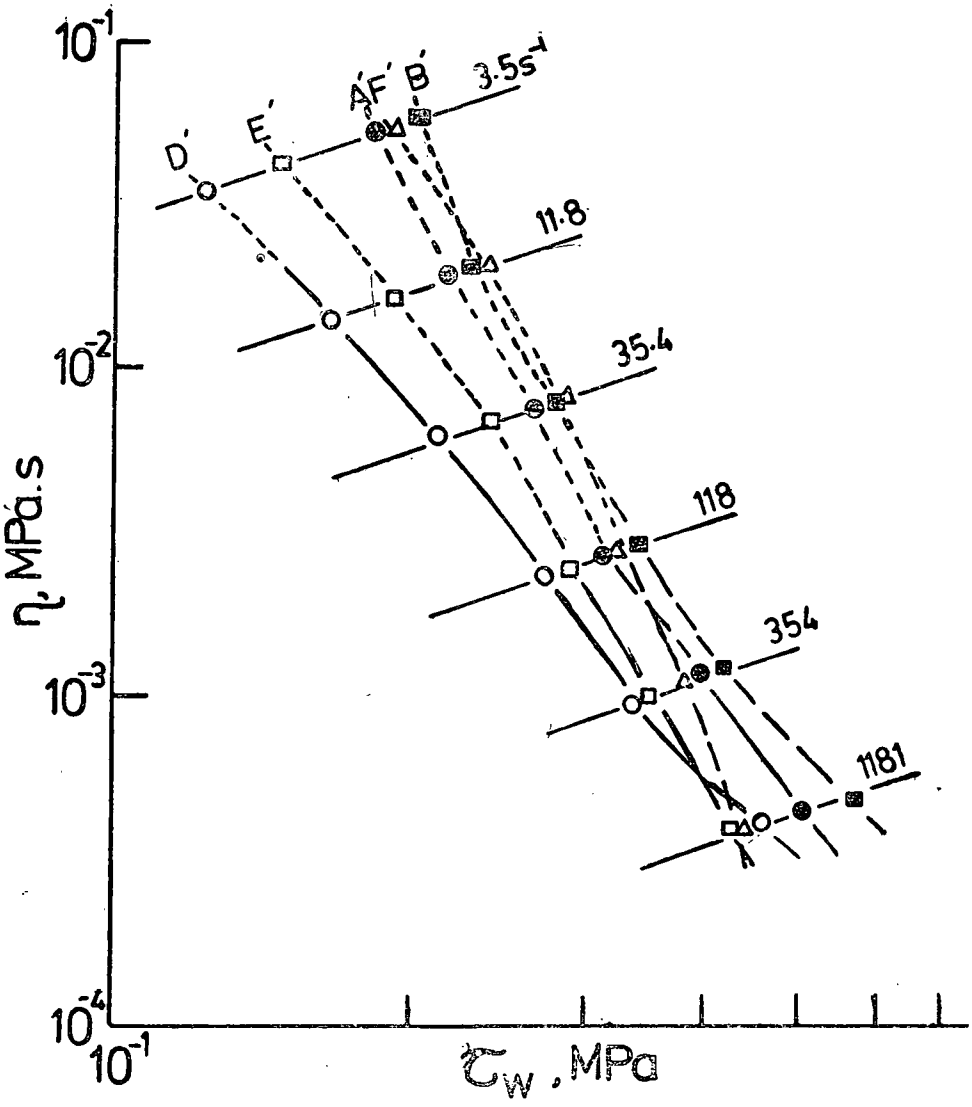
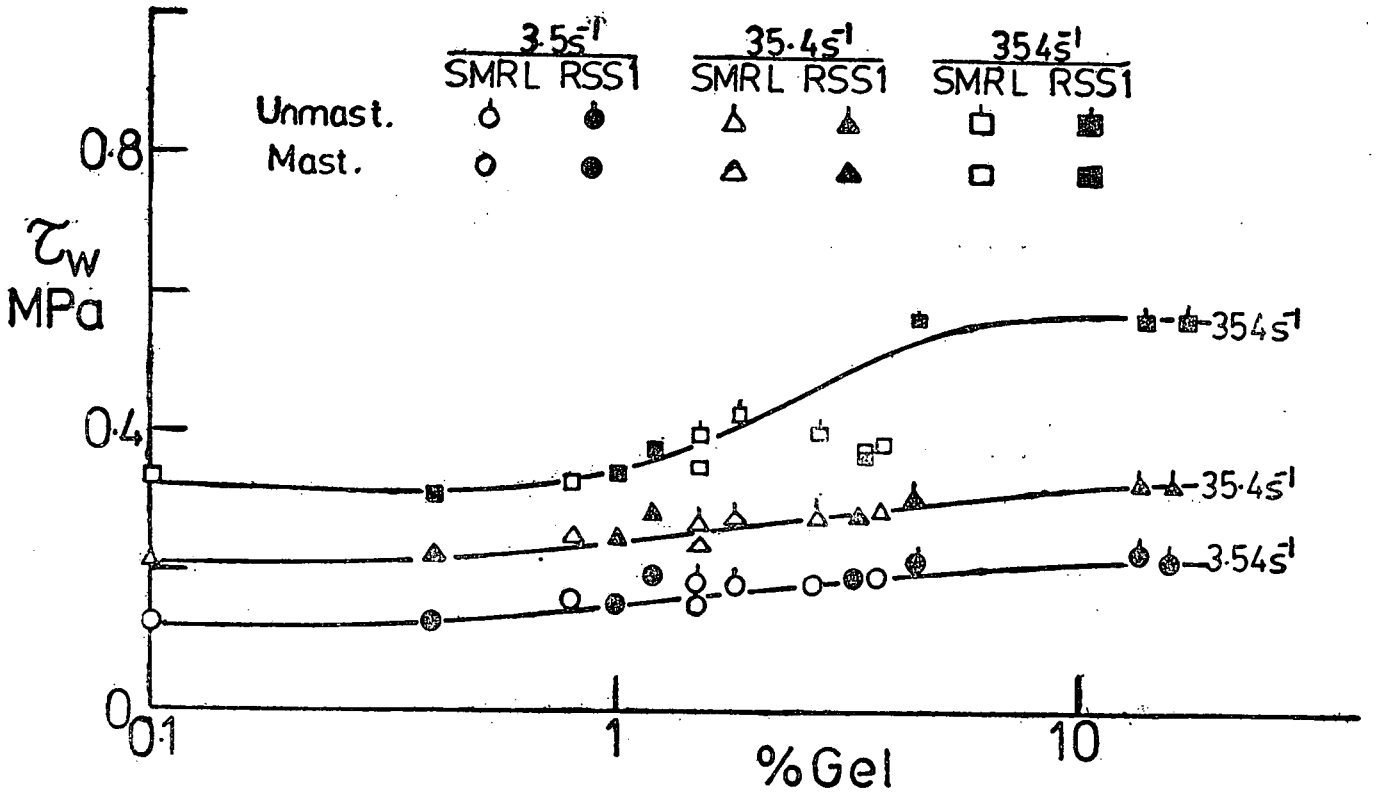


Fig. 3d Flow curves for SMR L at 120°C



Fig·4 Extrusion stress vs. gel content at 120°C

Black-filled rubbers

Observation of the short-term storage of black-filled RSS 1 and SMR L reveals the following :

(i) there is a gradual increase in the stock viscosity of 4 — 5 units after two weeks of storage (Table 3). The increase is similar for both RSS 1 and SMR L.

Table 3. *Change of Mooney viscosity V_B on Storage*

Day No.	V_B (ML (1' + 4', 100°C))	
	SMR L	RSS 1
1*	61·5	61·0
2	61·0	60·5
3	61·5	61·0
5	63·0	62·0
6	63·5	62·5
7	63·5	62·5
8	63·5	63·0
9	64·0	64·0
10	64·0	64·0
12	64·0	65·0
13	64·0	64·0
14	64·0	64·5

* Day 1 is the day stocks were prepared

(ii) storage-hardening leads to a progressive increase in the extrusion stress (Figs. 5a and b).

(iii) There is a significant increase in the die swell even within two weeks' storage (Fig. 6), which is similar for both the rubbers. Besides the increase in die swell, the extrudate appearance becomes progressively distorted on storage. This is shown in Fig. 7 where the extrudate undergoes a transition from a smooth appearance to that of to distorted nature.

Extrusion at 120°C shows a similar trend of behaviour as above except that the effects are reduced in magnitude. It is thus evident that shelf-storage of black-filled natural rubber leads to a progressive difficulty of extrusion, most probably as a result of the increase in bound rubber content (Blow, 1973). How this is so is not clear ; it has been suggested that the rubber shells around each filler particle contributes an additional number of effective crosslinks in the polymer network, and the number of such being proportional to the bound rubber content (Cotten and Boonstra, 1967). Hence the increase in bound rubber content on storage results in an increase of effective crosslinks, somewhat analogous to the increase in gel content in the unfilled rubber. If necessary, the resultant problem

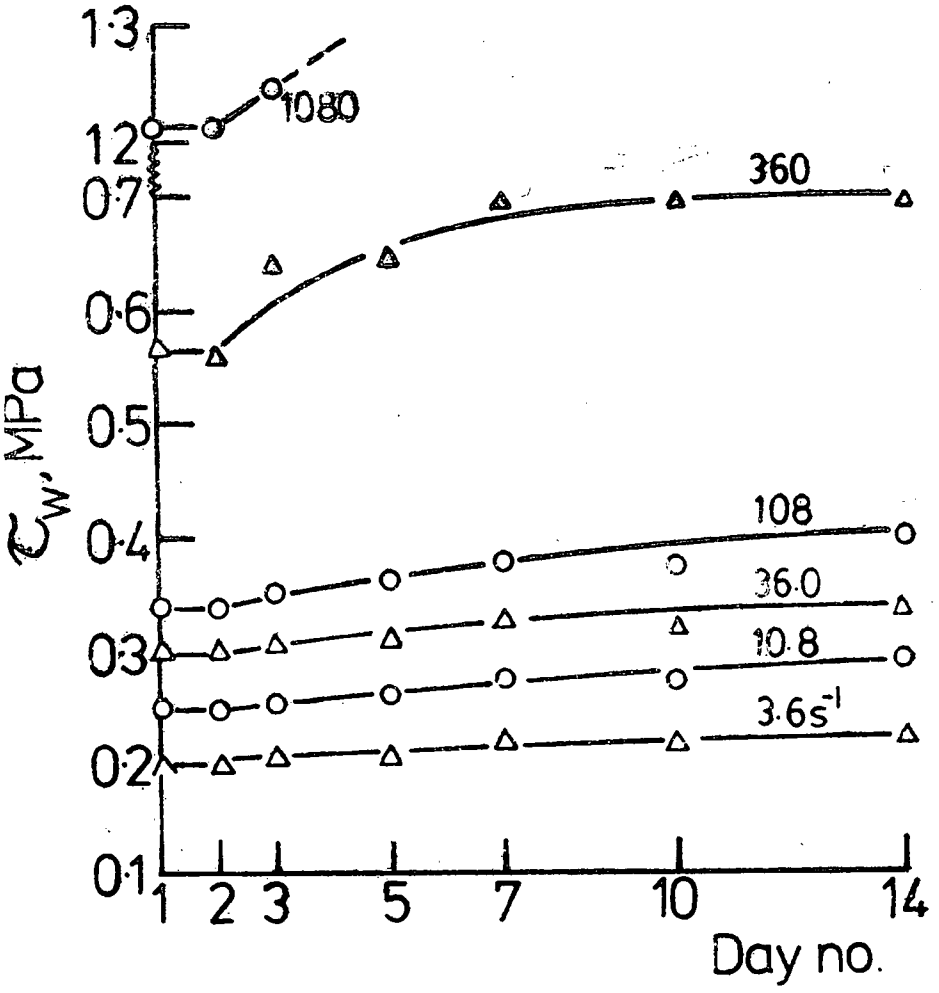


Fig.5a Effect of storage on extrusion stress for SMR L at 90°C

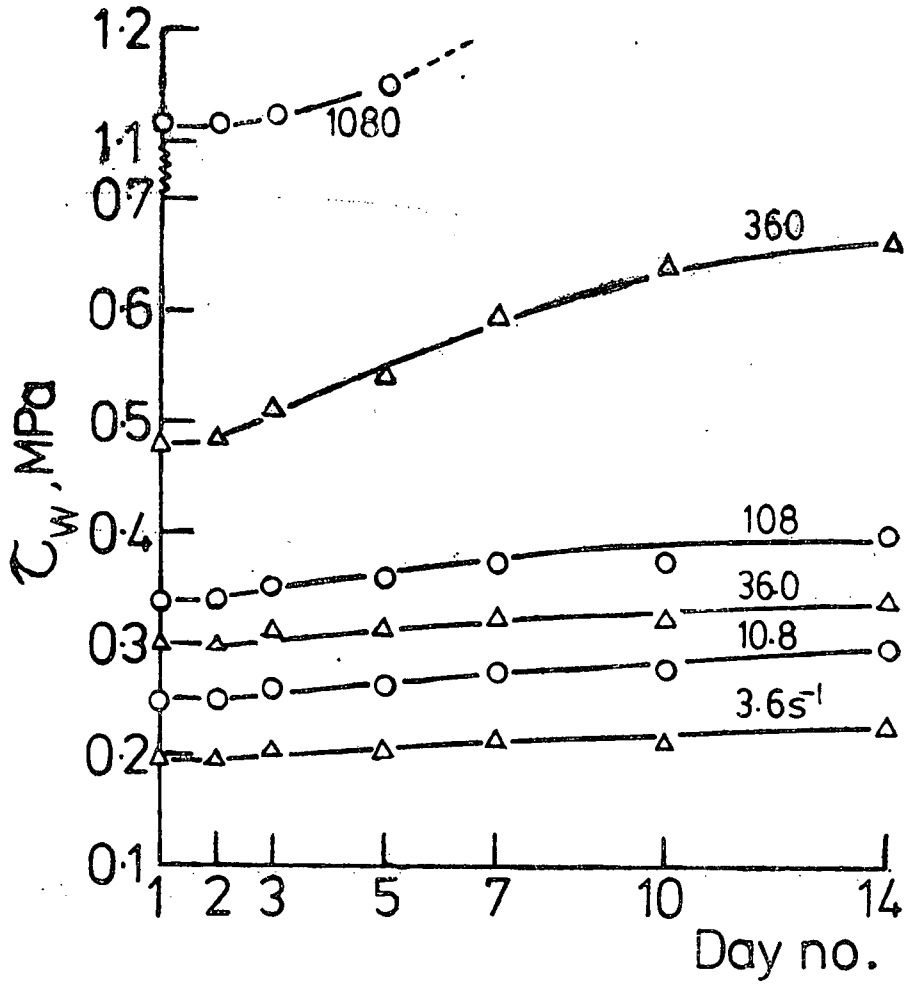


Fig. 5b Effect of storage on extrusion stress for RSS 1 at 90°C

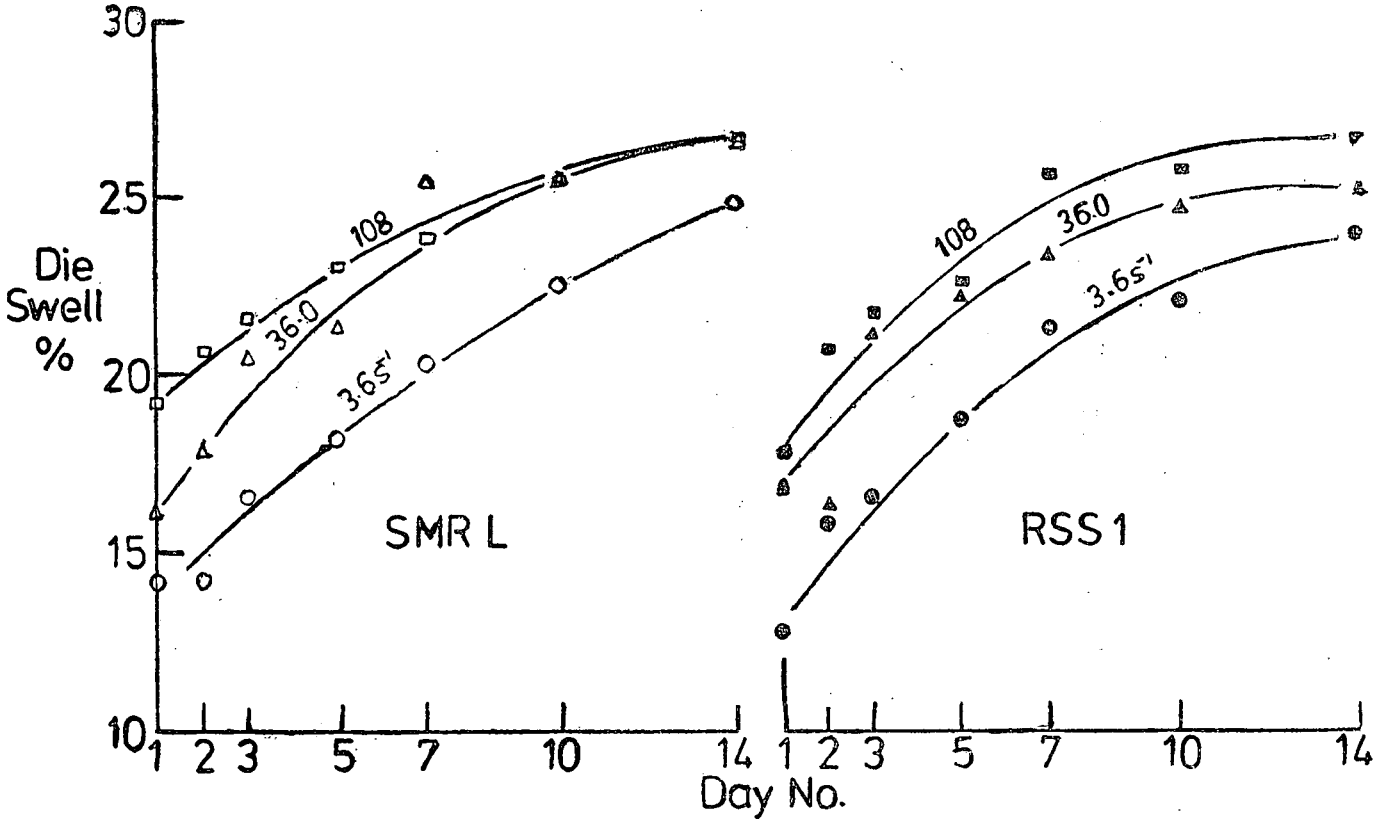


Fig 6 Effect of storage on die swell (90°C)

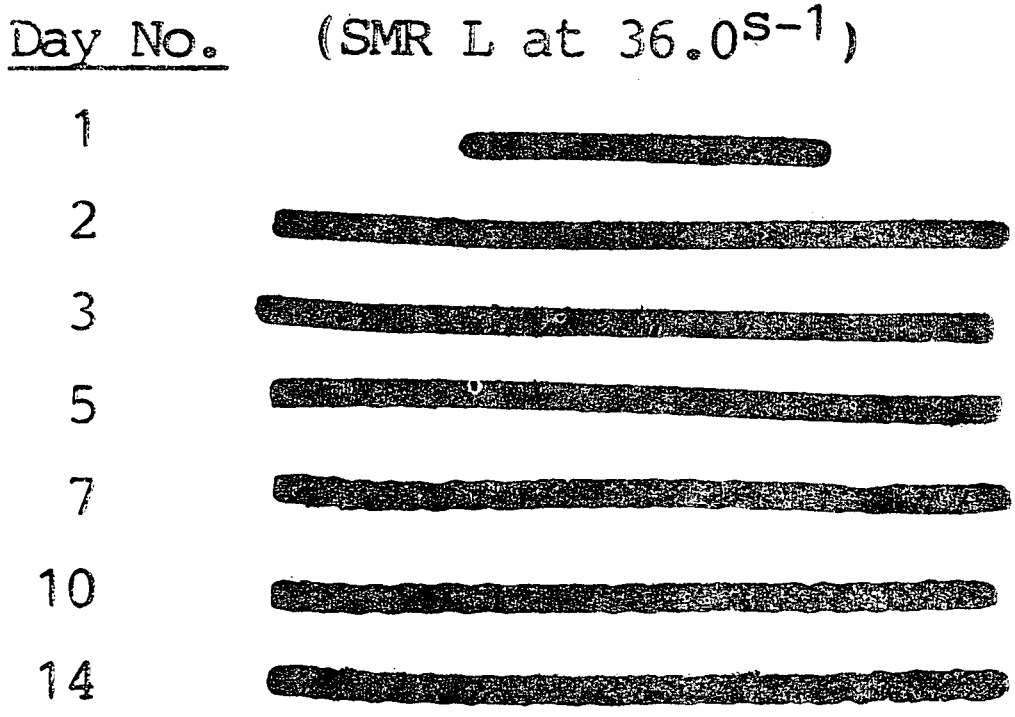


Fig. 7 Effect of storage on extrudate appearance

may be quite simply remedied by reworking the stored stocks. Fig. 8a shows the extrudate appearance after two weeks' storage. The improvement in the extrudate quality is evident if the stocks are reworked, Fig. 8b (where the stocks were treated to six passes on a 2-roll mill), besides a considerable drop in the extrusion stress and die swell, Table 4.

Table. 4. *Extrusion of SMR L at 90°C*

Shear rate S-1	Extrusion stress, MPa		Die swell, %	
	14 days' storage	6 passes after 14 days' storage	14 days' storage	6 passes after 14 days' storage
3·6	0·216	0·191	24·9	16·9
10·8	0·284	0·241	24·9	19·8
36·0	0·329	0·300	26·5	21·5
108	0·397	0·347	26·6	23·4
360	0·690	0·672	26·2	25·2
1080	>1·30	1·21	38·4	40·9

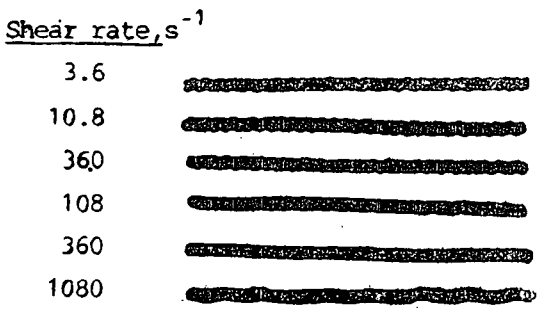


Fig. 8a RSS 1 extrudates (after 2 weeks storage of stock)

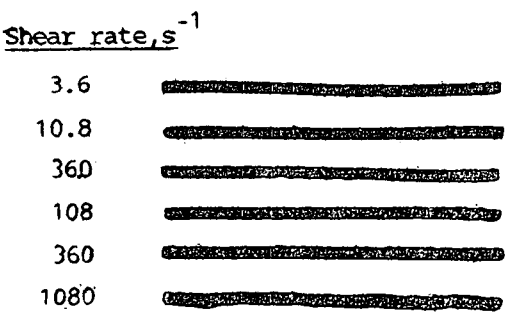


Fig. 8b RSS 1 extrudates (stock passed through mill after 2 weeks storage)

CONCLUSION

Storage-hardening of raw natural rubber leads to a deterioration of its processing characteristics. In unmasticated RSS 1 there is a significant increase in gel content on storage. The higher inherent gel content and larger increase on storage may partly account for the more difficult extrusion characteristics of this rubber as compared with unmasticated SMR L. Mastication of RSS 1 inhibits its gel-forming capability. The resultant crosslinking due to storage is not always necessarily reflected as a significant increase in gel content, as for example in unmasticated SMR L and the masticated rubbers. At low shear rates and higher extrusion temperatures, the progressive difficulty in extrusion would be consistent with an increase in gel content or crosslinking in the rubbers. At high shear rates and lower extrusion temperatures, other factors may be important, but as a result of stress-induced crystallization, it is difficult to be specific.

Shelf-storage of black-filled natural rubber on a short-term basis leads to a progressive deterioration in extrusion qualities, but can, however, be remedied by reworking the stocks.

ACKNOWLEDGEMENT

Thanks are due to the Directorate of the Rubber Research Institute of Malaysia for permission to publish this paper, and to the Officer-in-Charge of the Physics and Engineering Division, Dr A. Kadir, for his constant encouragement and valuable comments. The able technical assistance of Messrs S. Kanappan, Chan Woon Long and A. Majid Osman, Ms. Chua Soo Boon, and puan Hanimon is acknowledged.

REFERENCES

ALLEN, P. W. AND BRISTOW, G. M. (1963). *J. Appl. Polym. Sci*, 7, 63.

BLOW, C. M. (1973). *Polymer*, **14**, 309.

BRISTOW, G. M. (1974). *NR Technology*, **5** (1), 1.

BURFIELD, D. R. (1974). *Nature*, London, **249** (5452), 29.

COTTEN, G. R. AND BOONSTRA, B. B. (1967). *Rubb. Chem.* Tech. **40**, 829.

GREGGS, JR. E. C. AND MACEY, J. H. (1973). *Rubb. Chem.* Tech. **46** (1), 47.

GREGORY, M. J. AND TAN, A. S. (1975). *Proc. IRC, Kuala Lumpur*, **4**, 28

MEDALIA, A. Z. AND KOLTHOFF, I. M. (1951). *J. Polym. Sci.* **6**. 433.

ONG, E. L. AND LIM, C. L. (1982). *Proc. Polym. Seminar and IKM Conf., Kuala Lumpur.* **2**, 237.

ONG, E. L. AND LIM, C. L. Unpublished data.

SEKHAR, B. C. (1960). *Proc. NR Conf., Kuala Lumpur*, 512.

SEKHAR, B. C. (1962). *Revue gen. Caouth*, **39** (9), 1375.

SUBRAMANIAM, A. Unpublished data.

DISCUSSION

Q — W. S. E. FERNANDO, (RRISL) : (i) Do you envisage similar behaviour with CV rubbers too ? eg. extrudate distortion on storage. (ii) Can this be eliminated in RSS/SMR by the incorporation of HNS as a compounding ingredient ?

A — E. L. ONG, (RRIM) : (i) The Mooney viscosity increase of CV on storage is considerably less when compared with other grades of non-viscosity stabilised NR. Any deterioration of the processing properties will be considerably less than the other grades over the same period of storage. (ii) I have no experience in the use of HNS in the treatment of RSS/SMR in this manner and unable to comment on this.

Q — M. NADARAJAH, (Ceymac Rubber Co., Ltd.) : When masticated rubber or compounded rubber is stored, the Mooney viscosity rises. Wouldn't it be correct to say that the only way of using this rubber to get good processing properties is by remilling it ?

A — E. L. ONG, (RRIM) : It is correct to state that remilling stored masticated or compounded rubber will improve the processing properties ; as to whether it is the only method we would not say categorically that it is.

ASSUMPTIONS ABOUT THE CV RUBBER MOLECULAR STATE AND ITS SEASONAL VARIATIONS

By

G. MOUTON
(IRCA Côte d' Ivoire)

Researches undertaken at IRCA in Ivory Coast about latex collection and processing to prepare CV rubbers have enabled to check and develop some assumptions made at RRIM in the sixties. CV rubber appeared to be a natural polymer similar to the very one immediately collected after tapping. On the contrary, latex rubber processed under ordinary conditions appears to be the same polymer, the Mooney viscosity of which increases during drying because of chemical condensations. The chemical reactions involved in those condensations might be similar to the ones occurring during storage hardening.

The seasonal variations of latex DRC in relation to climatic factors seem to indicate a carbonyl and aminated groups contents evolution responsible for the stabilized viscosity modifications observed throughout the year.

SUMMARY

Patented in the sixties by B. C. Sekhar (British Patent, 1961), the stabilized viscosity, or CV, rubber has been largely studied by other well known researchers as Mrs Chin Peng Sung (1969), Subramaniam (1977), Ong (Burfield and Gan, 1975 and 1977) Burfield and Gan (Ong, 1973 and 1976), Sunny Sebastian and Thomas (Sebastian, 1980).

If clonal origin and age of trees have appeared to be the main factors affecting the Mooney viscosity level, very few results have been reported about its seasonal variations.

Some works have been undertaken at IRCA in Ivory Coast, especially to examine those seasonal variations. Many informations have been obtained and have allowed an attempt to explain how that stabilized Mooney viscosity changes throughout the year.

Preliminary works about latex processing

The following factors have been investigated :

— drying temperature ;
— hydroxylammonium neutral sulfate quantities ;
— factors affecting the non rubbers retention in the dry rubber.

Drying temperature

As a reference, we have taken the usual quantity of hydroxylammonium neutral sulfate, *i.e.* 0·15% W/W/dry rubber added to latex taken at *initial DRC* and then coagulated at a pH of 5·2.

Coagulums have been crumbled in a rotary cutter, avoiding the use of *any water*, then crumbs have been dried either at 60°C (7 hours) or between 90°C (starting) and 125°C (finishing).

Datas reported in Table 1 show that the drying temperature does not really affect the Mooney viscosity level, nor the increase of Wallace plasticity after Accelerated Storage Hardening Test when CV rubber is concerned.

Table 1

MV - ΔP ASHT versus latex treatement drying T°C

GT1	CONTROL		SHA	
DRYING T °C / RUBBER CHARACTERISTICS	60	90 ↓ 125	60	90 ↓ 125
ML 1+4 at 100°C	69	89	60	61
ΔP ASHT	38	10	5	4

On the contrary, rubber processed without any hydroxylammonium sulfate is largely affected by drying temperature :

— its Mooney viscosity is 20 points lower when it is dried at 60°C ;

— its Wallace plasticity increase after Accelerated Storage Hardening Test is 28 points higher when it is dried at 60°C.

Those results clearly show that some condensations happen during drying of crumbs, those condensations looking similar to the ones involved during storage and being promoted by a high drying temperature.

Hydroxylammonium neutral sulfate quantities

Two different quantities have been added to the latex taken at initial DRC : 0·15 and 0·075 % W/W. After coagulation at a pH of 5·2, coagulums have been crumbled in the rotary cutter, avoiding any water. Crumbs have been dried between 90 and 120°C.

Looking at Table 2 results, it appears that 0·075% of hydroxylammonium sulfate increase the stabilized viscosity of 3 Mooney points, compared to the one obtained with the usual quantity of 0·15%.

Table 2.

Mv - ΔP ASHST versus SHA content,

CLONE	LATEX TREATEMENT CHARACTERISTICS	REFERENCE		SHA 0,075 % w/w		0,15 % w/w	
		MV	ΔP ASHT	MV	ΔP ASHT	MV	ΔP ASHT
GT 1		81	8.0	57	4.0	55	4.0
PR107		79	7.0	56	4.2	54	4.0

Sekhar's assumptions (Sekhar, 1960, 1962), checked by Subramaniam (1977), have been taken into account, *i.e.* the storage hardening is the result of condensations between aldehydes fixed on the polymer chains and some aldehyde condensing groups fixed on the polymer or on non-rubbers contained in the latex. The hydroxylammonium sulfate added in latex reacts with the aldehydes thus avoiding further condensations during storage. Looking at the datas in Tables 1 and 2, hydroxylammonium sulfate seems to be competing with aldehyde condensing groups when reacting with aldehydes of the polymer chains. In fact, Subramaniam's works (Subramaniam, 1975) show that 0·15% W/W of hydroxylammonium neutral sulfate added in latex are equivalent to 3 to 11 times the molecular quantities of aldehydes fixed on rubber chains. Moreover, works carried out by Sekhar (Sekhar, 1962) show that the aldehyde condensing groups should be 5 to 23 times more numerous than the molecular quantities of hydroxylammonium sulfate we added in the latex. In such conditions *the hydroxylammonium sulfate condensing reactions with aldehydes might be hindered by the much more numerous aldehyde condensing groups to be found in the rubber.* Such a possibility has been checked successfully, as shown in Table 3. It appears that the stabilized viscosity value decreases when increasing quantities of hydroxylammonium sulfate are added in the latex.

Table 3.

MV versus SHA content

SHA %W/W	0	0.15	0.5	1	2	4	6
MV	69	55,5	51	50	48	42.5	39.5

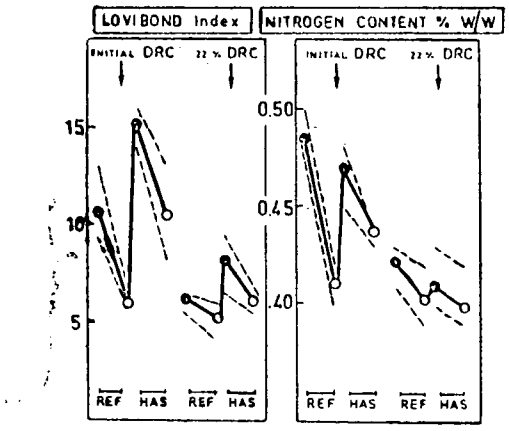
Non rubber retention during process

Works have been carried out with latex taken at initial DRC and with the same latex diluted with water to 22% DRC.

Two different samples issued from the same latex have been prepared : the former without any chemical, the latter receiving 0·15% W/W of hydroxylammonium sulfate, each latex being coagulated at a pH of 5·2.

Each coagulum has been processed in two different ways : crumbling in the rotary cutter without any water and crumbling under water in the rotary cutter, before drying between 90 and 120°C.

Fig. 1 shows that watering enables an easier removal of non rubbers (about 20% decrease in the animated products) the consequence being a decrease of 7 Mooney points for the untreated latex, the increase of Wallace plasticity after storage not being especially affected.



Fig·1 ● no washing —— ○ washing

Lovibon and nitrogen content versus latex treatments and processing conditions.

Nothing particular can be noticed for the hydroxylammonium treated latex.

Thus, it is clear that *the chemicals able to react with the aldehyde of the polymer chains do it mainly during drying*, as suggested in Table 1.

This fact is confirmed by the possibilities of preparing CV rubber having nearly the same Mooney value by taking either latex or cup lumps collected from the same tapping, as shown in Table 4.

It has to be noticed that for cup lumps hardening after accelerated storage is much lower (sometimes 0) than the one observed with acid coagulated latex. Referring to the fact that nitrogen contained in cup lumps is nearly half the one contained in latex rubber, results reported in Table 4 and Figures 1 and 2 suggest, first that the aldehydes fixed on polymer chains are the most important factor affecting the hardening during storage, and secondly that those aldehydes are responsible for some condensations during drying, as shown in Table 1. It seems likely that such condensations do not exist, or at least are much

Table. 4.

MV and ASHT versus clonal origine of CV rubber.

CLONE	GT 1		AVROS.2037		PB 235		PB 217	
PROPERTY / ORIGINE	MV	ΔP ASHT	MV	ΔP ASHT	MV	ΔP ASHT	MV	ΔP ASHT
latex	42.5	3.6	75.0	4.3	66.0	4.1	68.8	4.6
cup lump	39.1	0.8	73.0	0.5	63.0	0.8	68.0	0.6

reduced when the rubber is in the state of latex on coagulum at normal temperature. That assumption is in good agreement with Ong's results (Ong, 1976) who has considered different maturation times for both coagulums and crumbs : in every case, the stabilized Mooney viscosity is nearly the same when adding semicarbazide chloride to the latex before acid coagulation.

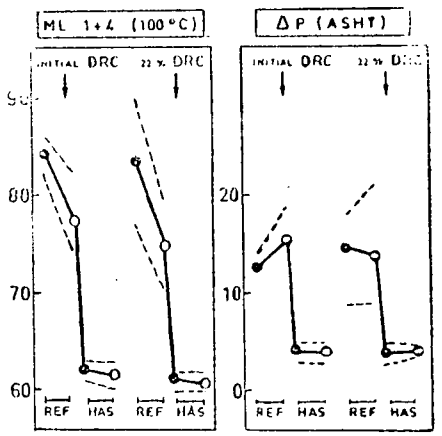


Fig. 2 ● no washing —— ○ washing

Mooney viscosity and ΔP (ASHT) versus latex treatments and processing conditions.

In other words, the CV rubber is very close to the natural polymer flowing out of the tree, compared to the untreated rubber the Mooney viscosity of which increases during drying because of chemical condensations similar to those involved during storage.

Stabilized viscosity seasonal variations

GT 1 and PR 107 latices have been studied more particularly, obtained from trees tapped in 1/2 S d/3 d/7 either unstimulated or stimulated 4 times per year with Ethrel

at 2·5%. Those latices have been treated at initial DRC with 0·15% W/W of hydroxylammonium sulfate and coagulated at a pH of 5·2. As before, coagulums have been crumbed in the rotary cutter without any water and the crumbs dried between 90 and 120°C. Fig 3 shows a very significant correlation between stabilized viscosity and DRC of latex collected from unstimulated trees.

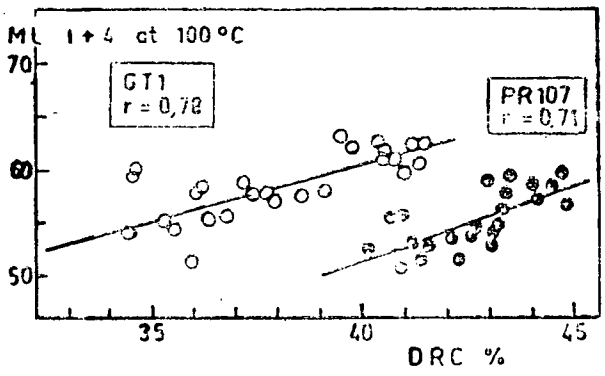


Fig - 3 STABILIZED VISCOSITY VERSUS DRC OF LATEX

Such a phenomenon appears also when a full spiral panel is changed from 30 cm to 180 cm high or when reopening the trees. Examples are given in Table 5 and Figs. 4 and 5.

A full spiral raised from 30 cm to 180 cm leads to an increase of both latex DRC and stabilized viscosity. Such results can be compared to Sekhar's works made with newly opened and reopened trees (Sekhar, 1962) Sekhar demonstrated that aldehyde

Table 5

DRC and stabilized viscosity versus tapping conditions

CLONES		GT1				AVROS 2037			
TAPPING SYSTEM		CONTROL		STIMULATION		CONTROL		STIMULATION	
PERIOD		DRC %	MV	DRC %	MV	DRC %	MV	DRC %	MV
CUT REMOUNTING	BEFORE	30.2	49	30.5	47	36.7	81	34.2	82
	AFTER	37.1	55	30.1	46	41.7	92	34.1	75

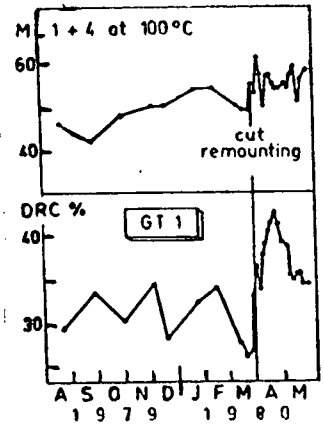


Fig - 4 REMOUNTING CUT EFFECT ON DRC AND MV

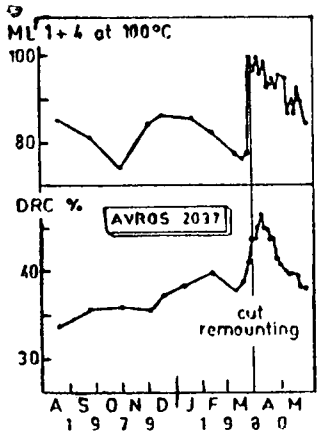


Fig - 5 REMOUNTING CUT EFFECT ON DRC AND MV

amounts are low in the early tappings whereas gel amounts and Wallace plasticity are high. After a few days tapping those trends change in the opposite way.

The origins of the seasonal variations of both latex DRC and stabilized viscosity have been searched out. Results reported in Tables 6 and 7 are highly significant.

Table - 6

Clone GT 1 - Correlation coefficients between air characteristics, latex DRC and stabilized viscosity -

VARIABLES		HYGROMETRY	SATURATION DEFICIT OF AIR	DRC
NO STIMULATION	DRC	- 0.611	+ 0.615	1
	MV	- 0.502	+ 0.509	+ 0.703
STIMULATION	DRC	- 0.544	+ 0.562	-
	MV	- 0.364	+ 0.350	+ 0.513

Table - 7

Clone PR 107 - Correlation coefficients between air characteristics, latex DRC and stabilized viscosity -

VARIABLES		HYGROMETRY	SATURATION DEFICIT OF AIR	DRC
NO STIMULATION	DRC	- 0.612	+ 0.617	1
	MV	- 0.516	+ 0.541	+ 0.436
STIMULATION	DRC	- 0.228	+ 0.269	-
	MV	- 0.282	+ 0.282	- 0.095

A high saturation deficit of air, *i.e.* a low hygrometry, is associated to both high stabilized viscosity and DRC when trees are not stimulated as shown in Figs. 6 and 7. If trees are stimulated, the correlation between saturation deficit of air and stabilized viscosity is less significant, but no change appears in the annual average value of that characteristic as shown in Table 8.

Looking at Compagnon and Cretin's works (Compagnon and Cretin, 1951) concerning the negative correlation between DRC and dry rubber nitrogen content, it seems difficult to assume that aminated groups might be responsible for stabilized viscosity seasonal variations. If this was right, a high DRC should be associated to a low nitrogen content and therefore to a low stabilized viscosity. It might be assumed that a high DRC is associated to a high stabilized viscosity. It might be assumed that a high DRC enables condensation between aldehydes and aldehydes condensing groups of the polymer chains. Datas reported in Table 8 and Figs. 1 and 2 would prove the contrary.

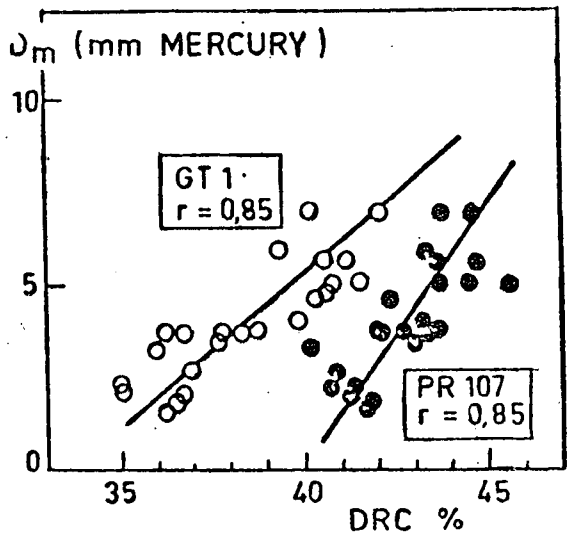


Fig - 6 DRC VERSUS DEFICIT OF AIR SATURATION

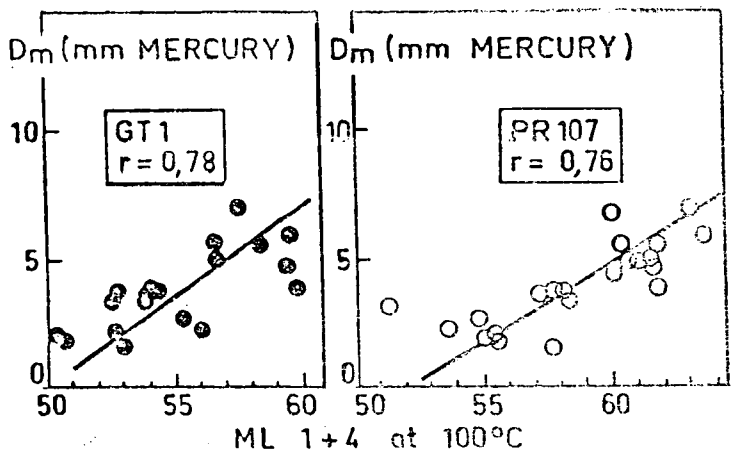


Fig - 7 STABILIZED VISCOSITY VERSUS DEFICIT OF AIR SATURATION

Table 8

Effect of Ethrel stimulation on latex DRC and stabilized viscosity -

CLONES	PR 107				GT 1			
STIMULATION	CONTROL		STIMULATED		CONTROL		STIMULATED	
VARIABLES	DRC %	MV	DRC %	MV	DRC %	MV	DRC %	MV
MEAN VALUE	42.8	55	37.6	55	38.2	58	36.7	59

In the same way, Gregory and Tan's works show that the dilution of latex with water to 20% DRC does not lead to any modification of Wallace plasticity before and after accelerated storage hardening test (Gregory and Tan, 1975). On the other hand, those same works show the influence of aminated non rubber latex components : on the Wallace plasticity increase after accelerated storage hardening test.

Considering Sekhar and Subramaniam's results (1962, 1975), it appears the aldehyde condensing groups fixed on non rubbers are 16 to 250 times more numerous than the aldehyde groups fixed on the polymer chain. So, it seems very unlikely that seasonal changes in aminated groups (aldehyde condensing groups) concentration could enable important changes of Wallace plasticity or Mooney viscosity. In fact, results obtained by Gregory and Tran (1975) lead us to the same conclusion. In those conditions, only modifications of the amount of aldehydes, or of their reactivity, allow an explanation seems all the more logical as it has been shown that decreases of 20% and even nearly 50% of the nitrogen content do not affect the stabilized viscosity level significantly.

CONCLUSION

It has been demonstrated that the CV rubber is a polymer very similar to the one flowing out of the tree, as Chin has already suggested (Sung, 1969). In fact, during drying the untreated rubber undergoes some condensations similar to those occurring during storage. Those condensations are not completely inhibited by the addition of hydroxylammonium sulfate to the latex. That chemical competing with particular aminated groups contained in the latex, therefore allows some changes of the stabilized viscosity during the year. The origin of those seasonal variations could be found in modifications of the aldehyde groups content in the rubber. We may suppose from the results reported in this paper that such modifications are in relation to the latex DRC *in situ* and the climatic factors affecting that DRC. A more detailed study of aminated and aldehyde groups of both latex and dry rubber could be undertaken to check such an assumption, assumption which agrees with Sekhar, Gregory and Tan's results.

REFERENCES

BRITISH PATENT (1961), 965 757.

BURFIELD, D. R., GAN, S. N. (1975), *J. Polym. Sci. : Polym. Chem.* **13**, 2725.

BURFIELD, D. R., GAN, S. N. (1977). *J. Polym. Sci. : Polym. Chem.* **15**, 2721.

CHIN PENG SUNG. (1969). *J. Rubb. Res. Inst. Malaysia,* **22**, (1) 56.

COMPAGNON, P., CRETIN, C. (1951). *J. Rubb. Res. Inst. Malaysia* **13**, 211.

GREGORY, M. J., TRAN, A. S. (1975). *Proc. Int. Rubb. Conf. IV, 3 — Kuala Lumpur.*

ONG, C. O. (1973). *Proc. of the RRIM Plant. Conf.* 419.

ONG, C. O. (1976). *J. Rubb. Res. Inst. Malaysia* **24**, (3), 160.

SEKHAR, B. C. (1960). *J. Polym. Sci.* **48**, 133.

SEKHAR, B. C. (1962). *Proc. 4th Rubb. Techn. Conf. London,* 460.

SEKHAR, B. C. (1960). *Proc. of the Natural Rubb. Res. Conf. III* 512 — *Kuala Lampur.*

SUBRAMANIAM, A. (1977). *J. Rubb. Res. Inst. Malaysia,* **25**, 61.

SUBRAMANIAM, A. (1975). *Proc. of Int. Rubb. Conf. IV,* 3 — *Kuala Lampur.*

SUNNY SEBASTIAN, M., THOMAS, E. V. (1980). *Int. Rubb. Conf. Kottahyam.*

DISCUSSION

Q — A. COOMARASAMY, (RRISL) : (i) What is the recommended DRC of latex for preparation of CV rubber at the IRCA ?

(ii) What is the dosage of Hydroxylamine neutral sulphate used ?

A — G. MOUTON, Ivory Coast : (i) In Ivory Coast CV rubber is produced from field latex.

(ii) 0·15% w/w.

SCORCH AND AGEING PROPERTIES OF EPOXIDISED NATURAL RUBBER

By

ABU AMU AND SIDEK DULNGALI
(The Rubber Research Institute of Malaysia Kuala Lumpur, Malaysia.)

ABSTRACT

This paper describes the importance of using bases for the compounding of epoxidised natural rubber. The relative merits of the bases in terms of scorch delay, ageing performance and compression set were discussed. The type and concentration of base were shown to be the determining factors in obtaining the optimal properties.

SUMMARY

Epoxidation of natural rubber (NR) changes its physical and chemical properties (Gelling and Smith, 1979 ; Baker *et al* 1984, MRRDB, 1984 and Abu Amu & Loh, 1984). The change in these properties was found to be dependent very much on the extent of epoxidation. For example, the sulphur vulcanisation chemistry and ageing of epoxidised natural rubbers (ENR), particularly those with higher epoxidation level, were reported (Gelling and Smith, 1979 ; Gelling and Morrison, to be published) to be different from that of NR. Such differences necessitate the use of bases for improving scorch delay and ageing performance of ENR vulcanisates. The choice and concentration of the investigated bases will become apparent as the relative merits of the bases are described.

Experimental

Mixing was conducted in a two-litre 00C Banbury at 80 rev/min starting at 50°C. Cooling of the mixer was done by running cold water immediately after the start of a given mixing cycle shown below :

0 min :	add rubber + base
1 min :	add zinc oxide, stearic acid and antioxidant
1½ min :	add ½ black + process oil
2½ min :	add remainder of black
3½ min :	sweep down feeding chute
4 min :	dump

Sulphur and accelerator were added later on a two-roll mill, and the formulation used in this study is as shown below :

ENR - 50* or ENR - 25*	100
Base	Variable
N - 330 black	40
Aromatic oil	4

Zinc oxide	5
Stearic acid	2
N - (1, 3-Dimethylbutyl) - N' - phenylparaphenylene diamine	2
Sulphur	1·5
4-(benzothiazole-2-sulphenyl) morpholine	1·5
Santogard PVI	0·3

*ENR-50 and ENR-25 contain 50 and 25 mole percent epoxidation respectively.

Physical testing procedures were adopted in accordance to the British Standards shown below :

Scorch time to BS 1673 Part 3, 1969.
Vulcanisation characteristics to BS 1673 Part 10, 1977.
Tensile strength to BS 903 Part A2, 1971.
Ageing to BS 903 Part A19, 1975.
Compression set to BS 903 Part A6, 1969.

RESULTS AND DISCUSSION

The vulcanisation characteristics of ENR, particularly ENR-50, has been observed to be different from those of NR. The rheometer traces, shown in Fig. 1, illustrate the differences in cure characteristics of NR, ENR-25 and ENR-50 compounded with 2·5 p.h.r. sulphur alone. A much more rapid and efficient reaction of sulphur occurs with ENR-50. This may partly account for the reduction in scorch delay of ENR-50 compounded with high dosage of sulphur. For this reason a sulphur system with low sulphur-to-accelerator ratio such as semi-EV was chosen in this study.

The pH of ENR is another determining factor in scorch delay of ENR compounds as illustrated by Fig. 2. The optimum scorch time obtainable from ENR-50 gum mixes based on semi-EV- formulation occurs at pH of 6·5. Acid catalysed ring-opening can occur with the rubber if the pH of the rubber is low and thus causing crosslinking via ether groups Gelling and Morrison. On the other extreme, *i.e.* higher pH, the vulcanisation process is accelerated by the base resulting in short scorch time. Even at pH of 6·5, it has been found that it is necessary to incorporate a base, such as sodium carbonate, when mixing ENR-50 with carbon black. As shown in Fig. 3 the presence of carbon black alone in ENR can promote crosslinking. A more pronounced extent of crosslinking was observed for ENR-50 as compared to that of ENR-25 ; presumably due to the presence of more epoxidised groups in the case of ENR-50. As shown in the figure, the extent of crosslinking at given cure temperature and time depends on the type of carbon black used. The more active is the carbon black the higher is the extent of crosslinking. By incorporating sodium carbonate at the start of mixing cycle, the premature vulcanisation of the rubber promoted by the black can be inhibited.

The effect of some bases on the scorch time of both ENR-50 and ENR-25 black-filled mixes are shown in Fig. 4. The optimum scorch time obtained by using these bases depends very much on their concentrations. The strongest base, *i.e.* sodium carbonate, is the most effective in adjusting the pH of the rubber and thus resulting in a narrow band

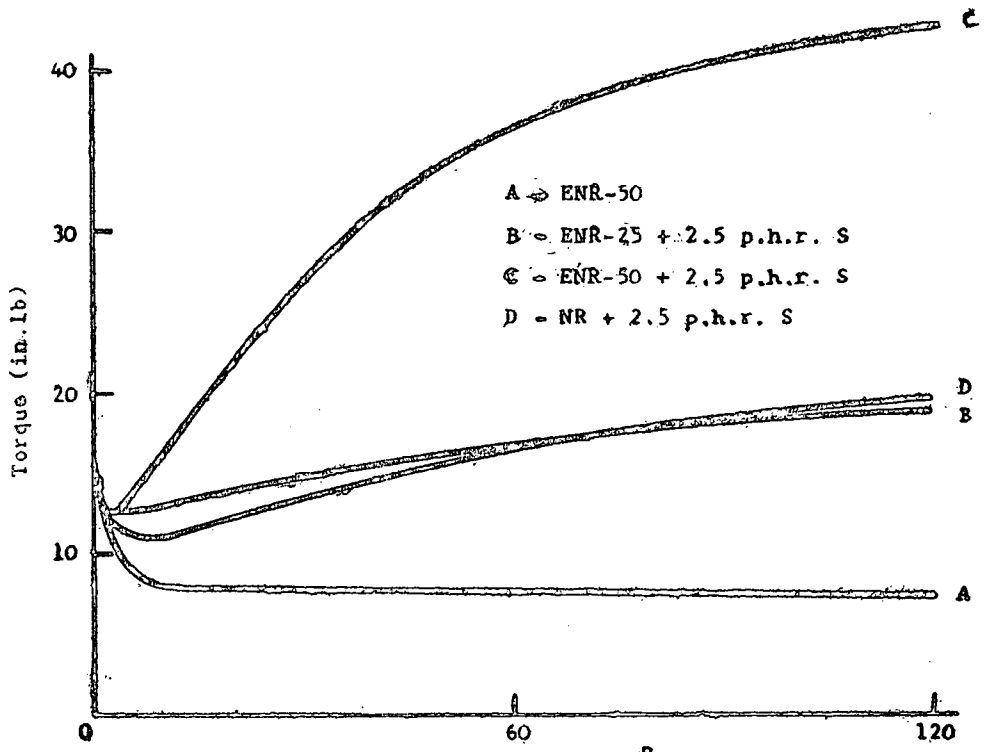


Fig 3. Monsanto Rheographs of ENR compounded with sulphur alone

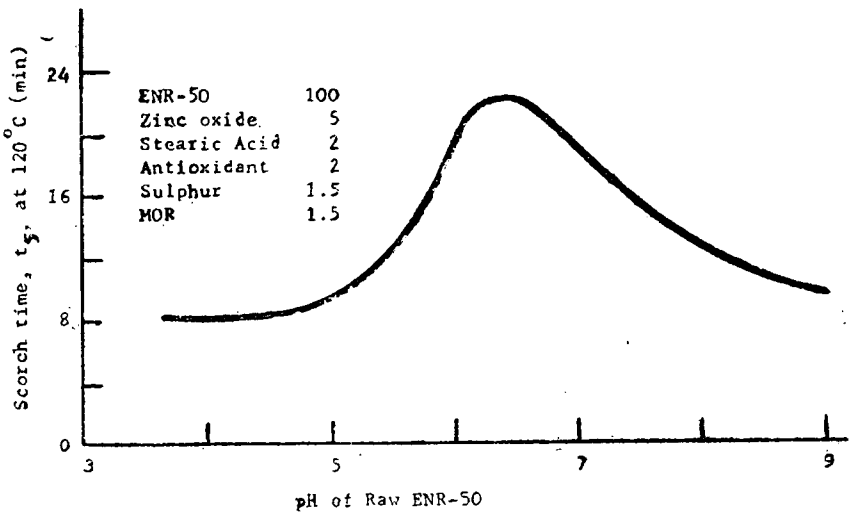


Fig 2. Effect of pH of ENR-50 on Scorch Time

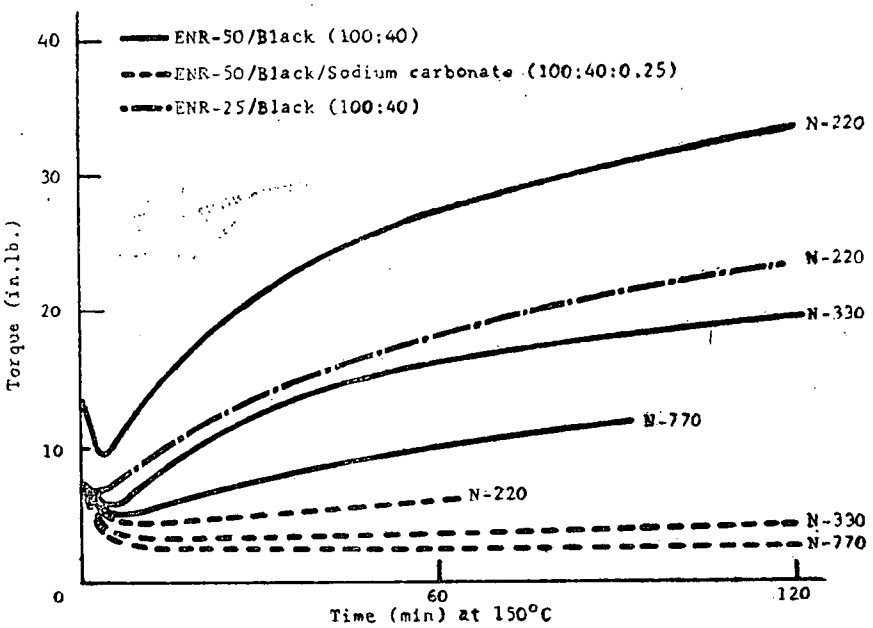


Fig 3. Monsanto Rheographs of ENR Carbon Black Masterbatches

of scorch delay response in the case of ENR-50 and a reduction in scorch time for ENR-25, On the other hand, calcium stearate was shown to give a rather broad scorch delay response for both ENR-25 and ENR-50. Hence for the purpose of improving the scorch time of both ENR-25 and ENR-50, the preferred base would be calcium stearate.

The poor ageing of ENR vulcanisates cured with sulphur vulcanisation systems is believed to be due to the formation of sulphur acid giving rise to crosslinks (Gelling and Morrison, to be published). The increase in crosslinks during ageing results in a substantial increase in modulus and consequent reduction in tensile strength.

The cure system with high sulphur level was shown to give poor ageing performance presumably due to the presence of high proportions of polysulphidic linkages which consequently can result in high concentrations of sulphur acid formed during the ageing of ENR vulcanisates. In order to counteract the acid formed, a high level of base is required but this will be at the expense of short scorch time. For this reason, coupled with the objective of obtaining ENR compounds with satisfactory scorch time, semi-EV or EV systems should be chosen for ENR.

The effect of some bases on the ageing performances of both ENR-50 and ENR-25 vulcanisates based on semi-EV formulation are shown in Figs. 5 — 7. Of all the bases studied, sodium carbonate was shown to perform well in resisting ageing. Significant improvement in the ageing performances of ENR-50 and ENR-25 vulcanisates can be obtained by using a high level of the base (1 — 2 p.h.r.) but this was shown to be at the expense of short scorch time. Unexpectedly high percentage retention in tensile strength was observed for ENR-25 incorporated with 5 p.h.r. magnesium oxide and this can be accounted by the low unaged tensile strength. Similar trends on the effect of bases on the percentage retentions in tensile strength and elongation at break were shown for both ENR-50 and ENR-25 vulcanisates. Based on these two properties as the criteria for ranking the ageing performances of ENR vulcanisates, the order of effectiveness of these bases for resisting ageing can be ranked as follows : Sodium carbonate > Calcium oxide or Calcium hydroxide > Calcium stearate or Magnesium oxide.

The gradual reduction in the formation of crosslinks during ageing by increasing the concentration of the bases is demonstrated by Fig. 7. The percentage retention in modulus at 100% strain also depends very much on the base used. Sodium carbonate is the most effective in preventing the hardening effect on ageing of both ENR-50 and ENR-25 vulcanisates.

The effect of concentration and the type of base on compression sets of ENR vulcanisates is shown in Fig. 8. Both sodium carbonate and calcium stearate gave relatively lower compression set as compared to that of the other three bases. It is to be noted that for ENR vulcanisates which require low compression set, a formulation based on EV system is recommended.

CONCLUSIONS

Both the processing safety and ageing resistance of ENR-25 and ENR-50 vulcanisates depend very much on the concentration and type of base to be used. Sodium carbonate

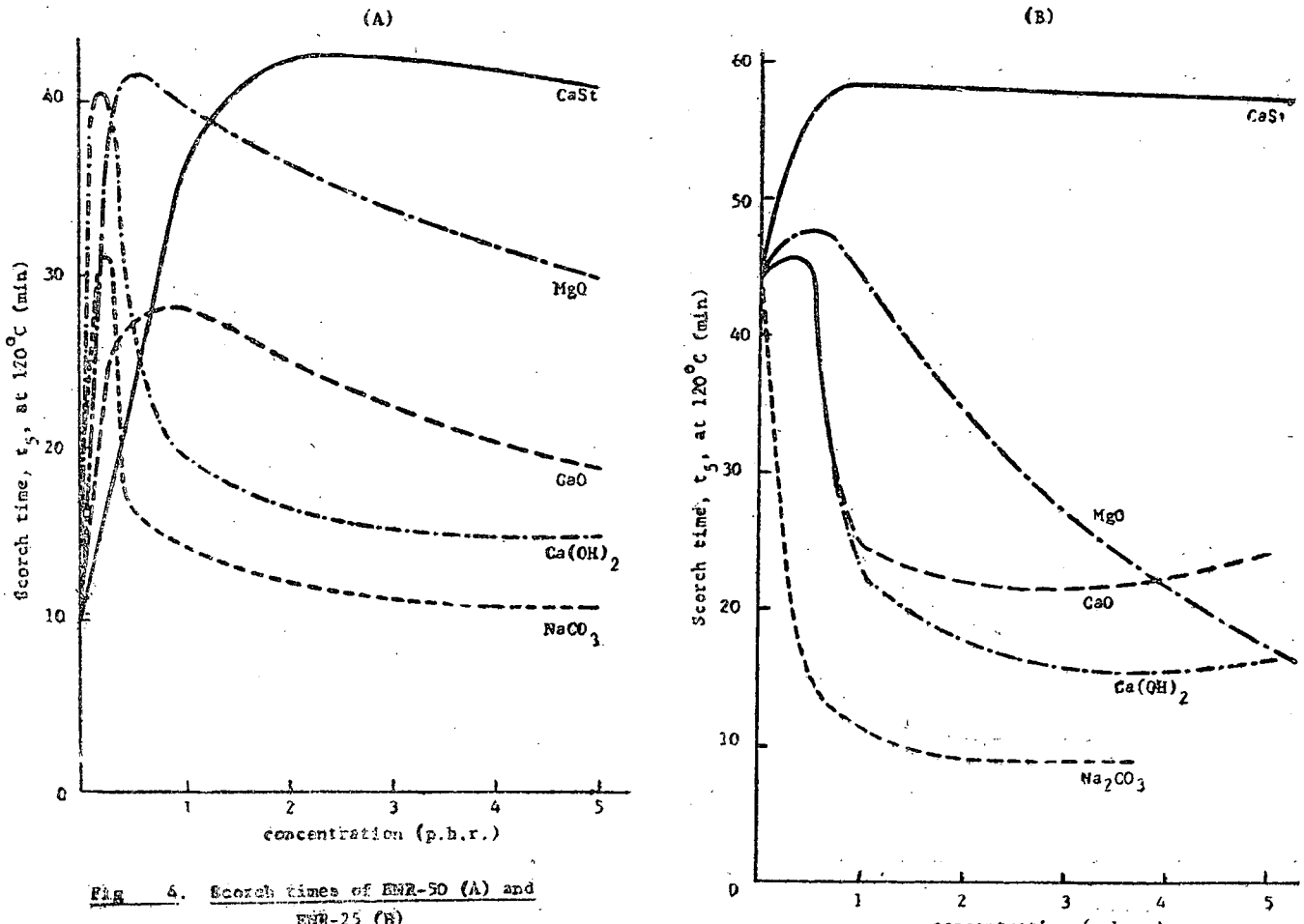
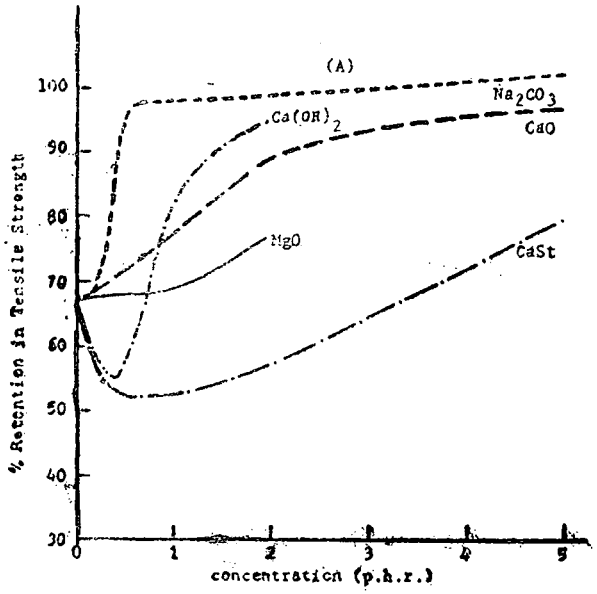


Fig 6. Scorch times of ENR-50 (A) and ENR-25 (B)



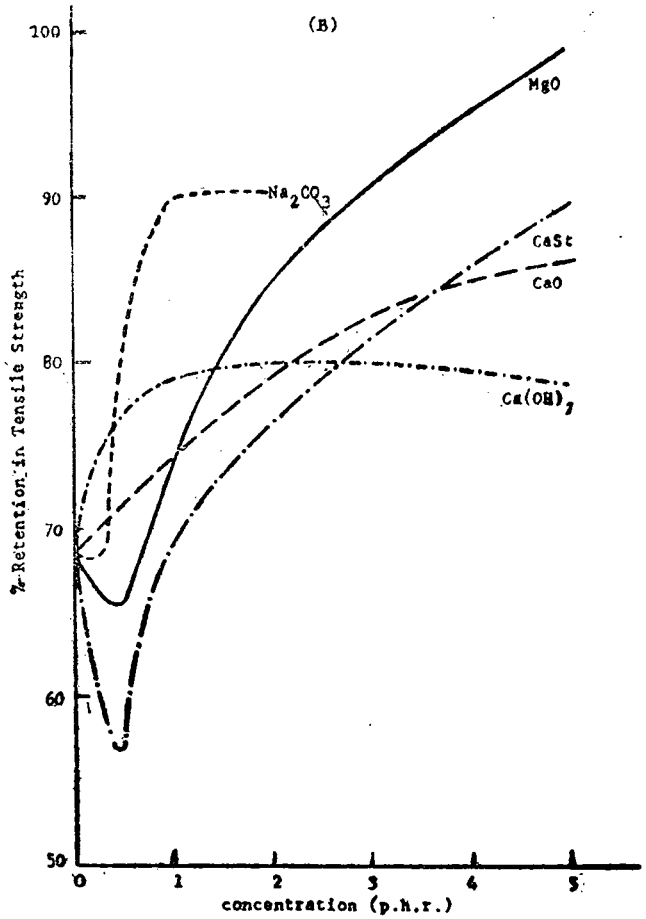
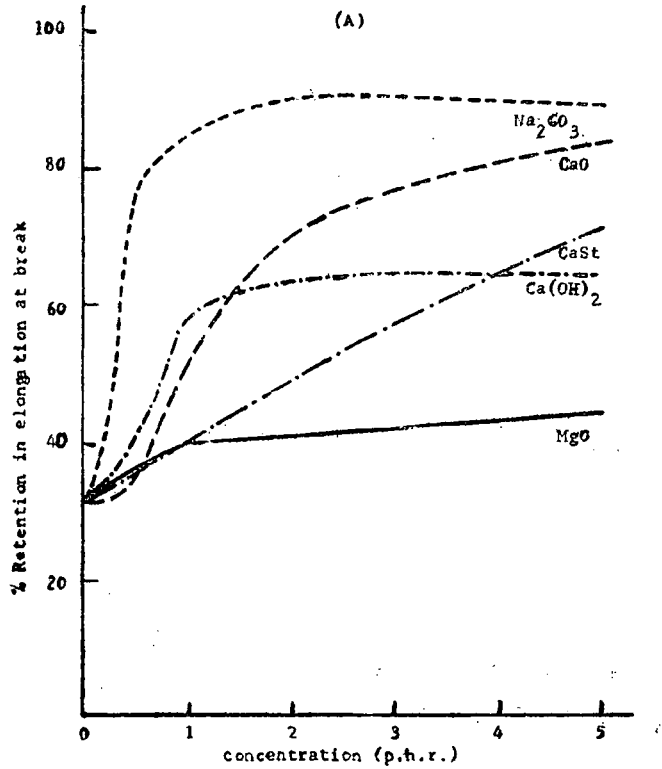


Fig 5. Retention in Tensile Strength (3 days/ 100°C) of ENR-50 (A) and ENR-25 (B)



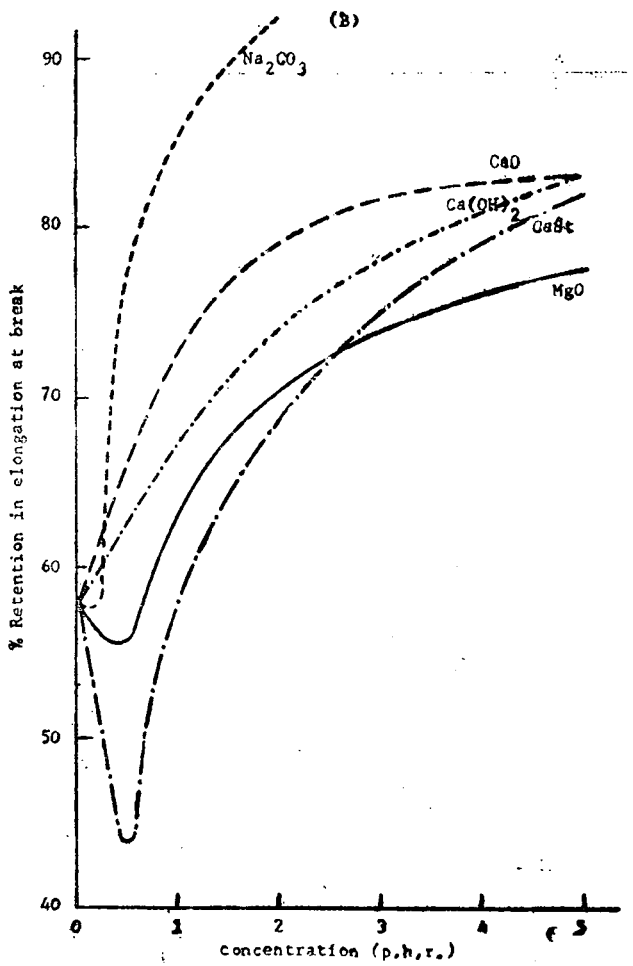
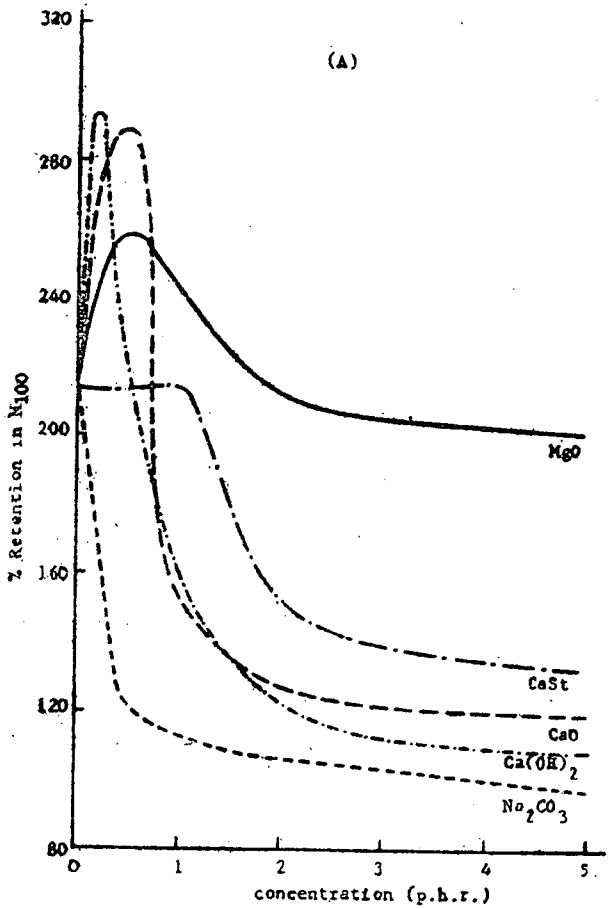


Fig 6. Retention in elongation at break (3 days/ 100°C) of ENR-50 (A) and ENR-25 (B)



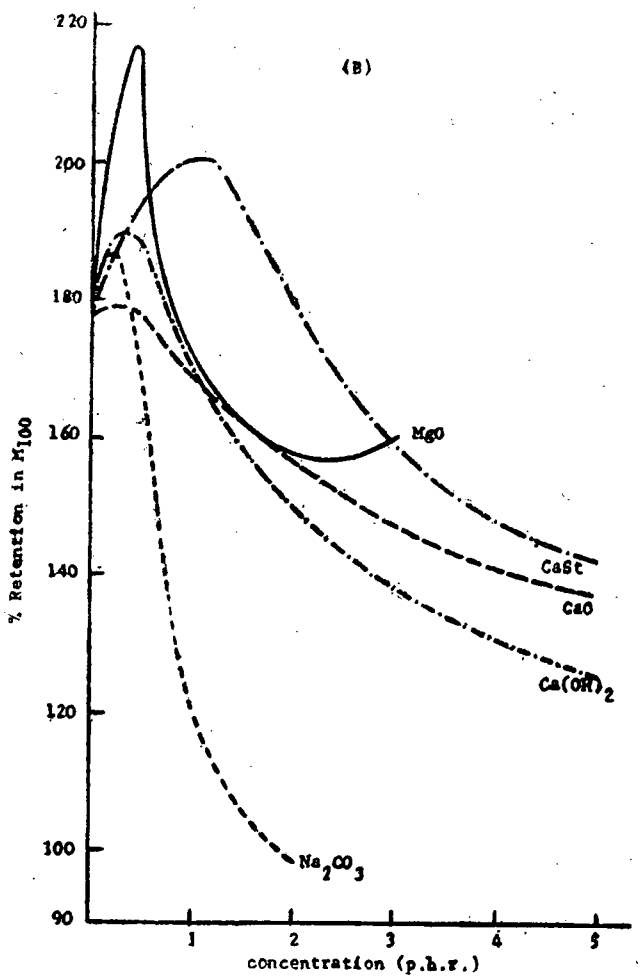


Fig 7. Retention in Modulus at 100% (3 days/100°C) of ENR-50 (A) and ENR-25 (B)

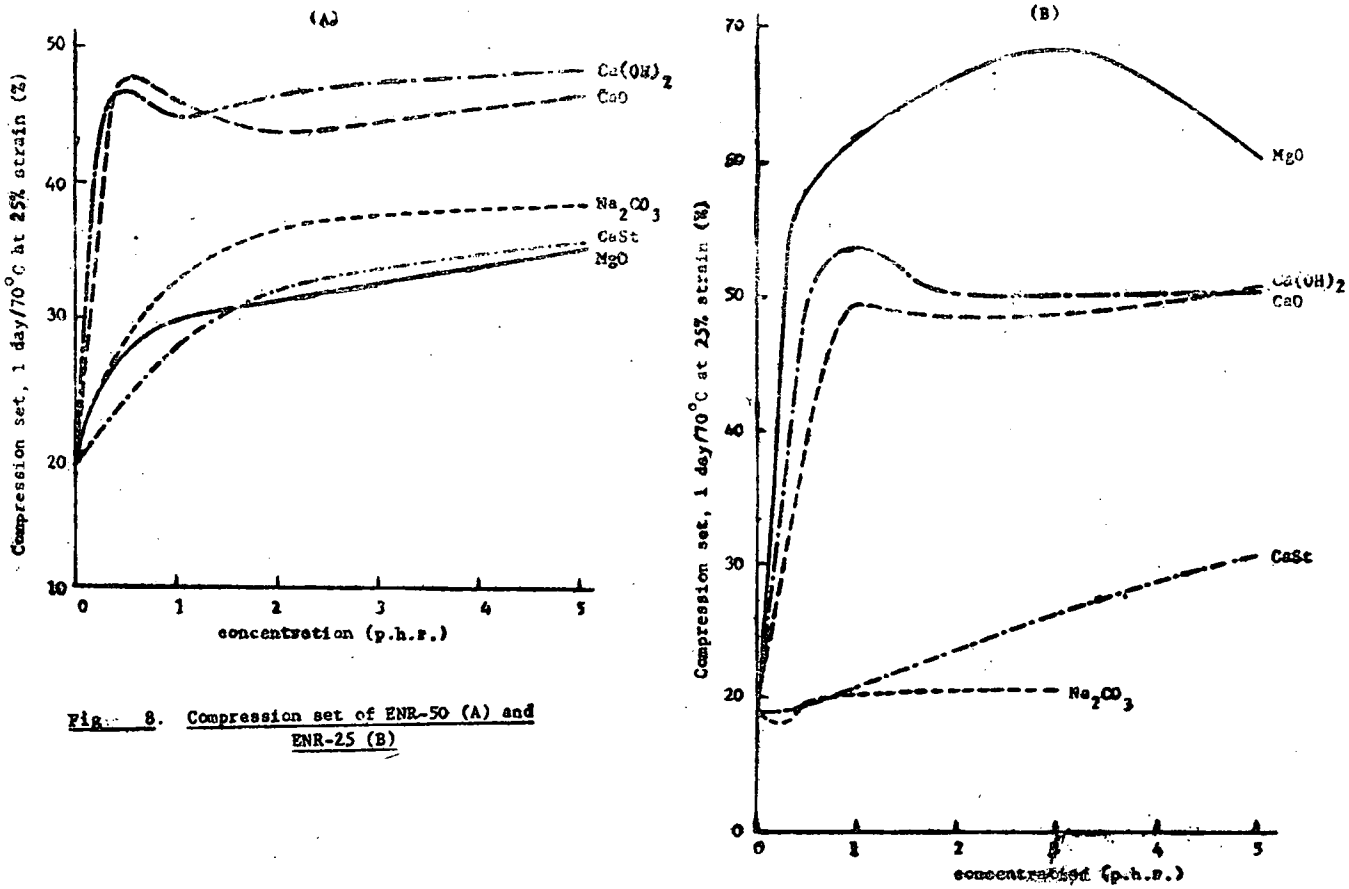


Fig. 8. Compression set of ENR-50 (A) and ENR-25 (B)

gave a narrow band of scorch delay response whilst calcium stearate gave a rather broad scorch delay response with concentrations. Sodium carbonate at high concentration offered the best performance in resisting ageing but at the expense of short scorch time. Hence the choice of the type and level of base for good ageing resistance and processing safety depends on a compromise of these two requirements. For low compression set vulcanisate, an EV system is recommended for ENR-25 and ENR-50 with appropriate level of either sodium carbonate or calcium stearate.

ACKNOWLEDGEMENTS

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REFERENCES

ABU. AMU AND LOH, P. C., (1984). *International Rubber Conference, Moscow*, (1984).

BAKER, C. S. L., GELLING, I. R. AND NEWELL, R. (1984). Rubber Div., *American Chemical Society 1984 Spring Meeting, Indianapolis.*

GELLING, I. R. AND SMITH, J. F. (1979). International Rubber Conference, Venice, (1979).

GELLING, I. R. AND MORRISON, N. J. to be published.

MALAYSIAN RUBBER RESEARCH AND DEVELOPMENT BOARD (1984). *Epoxidised Natural Rubber Bulletin.*

DISCUSSION

Q — A. COOMARASAMY, (RRISL) : (i) What type of effect do you observe when Na_2Co_3, CaO,MgO & calcium stearate are added to unepoxidised NR compounds ?

A — ABU AMU, (RRIM) : We have not done much work on the effect of these bases on unepoxidised NR. However our initial work was based on the effect of NA_2Co_3 on the curing characteristics of NR. This accelerates the cure.

IMPLEMENTATION OF THE COLOUR CODING SYSTEM AND THE MARKETING OF CREPE RUBBER

By

M. D. R. J. GOONETILEKA, W. S. E. FERNANDO AND S. WEERASINGHE
(Rubber Research Institute, Sri Lanka)

SUMMARY

Sri Lanka is the worlds largest producer of quality Pale Crepe. In order to maintain this reputation and to compete with other technically specified light coloured rubbers, a colour coding system was suggested by Rubber Research Institute of Sri Lanka in 1976 and was introduced in 1980. This paper deals with the problems encountered during the past four years, in its implementation.

It has been found that these problems have created an atmosphere which is not conducive to its practical implementation. Therefore, it is felt that certain modifications are necessary in the present system of colour coding if it is to make some impact on the presentation of latex crepes to the consumer.

Latex crepe rubber is considered to be the purest form of natural rubber available in substantial quantities, satisfying stringent requirements laid down by various health regulations. Several instances where such outstanding properties are clearly demonstrated, are highlighted and their usefulness in effective market promotion is also discussed.

Colour coding system

Sri Lanka is the worlds largest producer of high quality latex crepe rubber claiming an out-turn of about 66% of the world latex crepe production. This indeed is a unique distinction for our country since our crepe is purer in quality and lighter in colour compared to any other forms of NR produced. This fact was quite evident from Green Book specifications which states " Latex crepe rubber must be produced from fresh coagula of NR latex under conditions where all the processes are carefully and uniformly controlled ". Factors in favour of Sri Lanka for the production of quality latex crepes are,

(1) Availability of white latex from popular PB 86, and recently introduced RRIC 100 series clones.

(2) Availability of specially controlled, uniform process line for crepe manufacture.

(3) Availability of clean pure water in abundance.

(4) Availability of skilled labour backed by efficient supervisory staff.

Latex crepe is a special purpose rubber used in specific applications such as

(1) Food and pharmaceutical grade rubber goods.

(2) Adhesive industry *e.g.* preparation of rubber solutions, tapes.

(3) Other fields, industrial sole crepe, cut threads, light coloured shoe soles etc.

Since these items contain a high proportion of rubber relative to other additives the final properties would be mainly dependant on the quality of the rubber used. Hence apart from the fact that the rubber is offered as clean and white as possible for these applications, the consumer would welcome consistency in technological properties of latex crepe rubber. Further in the applications of the food & pharmaceutical industry for *e.g.* West German food laws allow only light coloured grades of NR with following additional specifications.

(1) Acetone extract values to be less than 3·5 w/w.

(2) Natural rubber must not contain, Boric acid, p-nitrophenol or sodium pentachloro phenate.

Under these circumstances, only latex crepe, specifically the FB rubber can satisfy these strict requirements. In order to safeguard our reputation as the largest high quality latex crepe manufacturer, RRI put forward this colour coding system embodying their inherent technological and visual properties, based on the method of manufacture.

When compared to the usual operations involved in the manufacture of RSS or block rubber, the latex crepe manufacture involves two important additional set of operations which are unique to it. These are,

(1) Fractionation and (2) Bleaching

As a result of these processes, considerable differences in the processibility and technological properties of fractionated and unfractionated latex crepe rubber could be observed.

Fractional coagulation consists of coagulating the latex in stages to separate, as much as possible, coloured non rubber substance from rubber. This process improves the colour stability, reduces the gel, and in turn increases the solubility of rubber. Due to the removal of a part of non rubber substances the remaining rubber will have lower PRI values, N_2 content and acetone extract values. Since the percentage of the fraction removal varies from estate to estate depending on the clonal distribution, and the use of anticoagulants, it is normally recommended to remove at least 10% as fraction.

Bleaching is a process where yellow carotenoids are deactivated by chemical action resulting in a light coloured product. Bleaching of crepe rubber is carried out using tolyl mercaptan (RRI-7) and this reagent reacts with yellow pigments to interrupt the conjugation of the yellow pigments. The recommend dosage of 35% of tolyl mercaptan solution is in the range of 0·025 — 0·20% on dry rubber. The effective percentage varies, depending on the colour of latex and on an average 0·05% is used. It may be noted that tolyl mercaptan if used excessively would lead to peptization of rubber.

On the basis of the above mentioned processes crepe rubber can be classified into 5 major categories. They are,

(1) UFUB — Unfractionated Unbleached.

(2) FUB — Fractionated Unbleached.

(3) FB — Fractionated Bleached.

(4) UFB — Unfractionated Bleached.

(5) YF — Yellow Fraction.

Of these five groups Sri Lanka produces only three types at present

(1) Unfractionated Bleached (UFB)

(2) Fractionated Bleached (FB)

(3) Yellow Fraction (YF)

It has been observed that the raw rubber properties vary from each other within the three categories considerably.

Table 1. *Raw rubber properties*

	FB	UFB	YF
Dirt (% wt)	0·03	0·03	0·03
V.M. (% wt)	0·60	0·60	0·60
P_o	40	40	40
PRI	70	75	80
N_2 (%wt)	0·35	0·40	0·60
Acetone extract (% wt)	3·0	3·5	7·0
Relaxed modulus	6·0	6·5	8·0

Recently there have been instances where TSR-5L, air dried sheets, and synthetic polyisoprene too, had encroached the field previously dominated by latex crepe. It is believed that this has been mainly due to the following drawbacks. They are,

(1) Lack of uniformity and consistency of latex crepe.

(2) Lack of technologically oriented marketing system.

(3) Poor dialogue between consumer and the producer.

When latex crepe rubber is manufactured by adhering to a specific procedure and marketed in such a way that different categories can be identified easily by a colour coding system the above difficulties could be minimised to a considerable extent.

Implementation of the colour coding scheme

The colour coding scheme of the RRISL was first explained to the rubber producers, brokers and shippers at a seminar in 1977. Further discussions were held in 1978. A booklet entitled " A new presentation method of Sri Lanka latex crepe ", was published with technical details of the three different grades of crepe rubber. Several copies were sent to overseas buyers of crepe rubber through the shipping firms for their comments. Subsequently in 1979 efforts were made to popularize the use of coloured polythene bands (about 4 cm in diameter) to identify the rubber. A further meeting was held in May 1980 with the shippers, brokers and producers, and it was agreed to implement the colour coding scheme from 1 October 1980. Producers were instructed to use the appropriate coloured labels according to the scheme from 1 September 1980. A further innovation in the scheme was the suggestion to the shippers to use polythene bags having coloured labels printed on them. All these efforts however, were not fruitful, due to the following drawbacks of this scheme and the shortcomings in the present marketing system.

(1) Lack of consistency and uniformity of the coloured labels. Due to careless printing the colour of the labels of the same grades differed considerably and most of the time it was hard to recognise the difference between orange, yellow and brown. As a consequence the identification of grades at a first glance was quite difficult.

(2) Lack of interest shown by factory staff, brokers and buyers.

(3) Lack of communication regarding the colour coding system between the producers and consumers. We feel that this may be due to existence of large number of intermediaries between producer and consumer, such as :

Producer— — — — — — — — Broker— — — — — Local buyer— —
Shipper— — — — — — — ——Foreign buyer— — — — — — — — —
Broker— — — — — — — — —Consumer.

The communication gap has to be filled to get a feed back from the consumer to the producer regarding any changes in the existing marketing arrangements.

(4) Differences in raw rubber properties within the same category. It has been also observed the bleaching has no significant effect on raw rubber properties. Therefore bleaching has to be omitted from the colour coding scheme and only fractionation must be considered.

(5) Lack of simple tests to differentiate between FB, UFB, FUB, UFUB, rubber. Sometimes even the technological properties and curing characteristic would

not give enough satisfactory data to identify the grades of rubber, unless the producer sincerely indicate the correct grade. Therefore, there is a probable chance of misleading the ultimate buyer.

(6) Marketing of remilled sole crepe with normal crepe rubber as FB rubber. The sole crepe cuttings are subjected to repeated milling than the normal latex crepe, and the data shows that such remilled rubbers have low Mooney viscosity low PRI and slower cure properties.

(7) Marketing of yellow fraction rubber as latex crepe No. 3. This is misleading, as the yellow fraction rubber differs quite considerably from other grades due to high Mooney viscosity, high N_2 content, high PRI and faster cure.

SUGGESTION AND CONCLUSIONS

To promote our latex crepe rubber along with the colour coding it is necessary to stress the importance of the fractionation, because this step is unique to latex crepe. Visual grading does not highlight the importance of this step in the manufacture of crepe rubber. To highlight this unique step it is suggested that latex crepe rubber should be categorised and marketed as follows.

(1) Fractionated latex crepe rubber.
(2) Unfractionated latex crepe rubber.
(3) Yellow fraction rubber.

Visual grading can take over from here as specified in the Green Book specifications. It is felt that the following colour scheme can alleviate major problems indicated in the discussion.

YELLOW	Fractionated latex crepe
BLACK STRIPES ON YELLOW	Unfractionated latex crepe
BLACK	Yellow fraction

It has been observed that bleaching by tolyl mercaptan (RRI - 7) if done according to the limits specified would not affect the raw rubber properties, other than the colour. Thus to obtain higher grades in the visual grading system bleaching is recommended in the first two categories of crepe rubber *viz*, fractionated and unfractionated latex. In addition the sole crepe cuttings may be marketed as a separate grade of rubber to avoid mis-representation, along with the above grades.

RECENT DEVELOPMENTS IN THE MANUFACTURE OF DEPROTEINIZED NATURAL RUBBER

By

P. A. J. YAPA AND SRIYANI YAPA
(Rubber Research Institute of Sri Lanka, Agalawatta)

ABSTRACT

Deproteinized natural rubber (DPNR) is now a commercial reality. Several methods have been developed for the manufacture of DPNR. Papain treatment of field latex has been reported to produce a low protein rubber with improved technological and dynamic properties.

Methods of manufacture of (a) DPNR from both fresh and preserved Hevea *latex, (b) viscosity stabilized version of DPNR by using chemical and enzyme treatments are reviewed in this paper, with their drawbacks, advantages in relation to technological and dynamic properties.*

INTRODUCTION

Fresh latex of *Hevea brasiliensis* is known to contain approximately 1% of proteins (w/w) among its non-rubber constituents. About 20% of this is absorbed on the rubber particles and a similar amount is associated with the bottom fraction and the remainder is dissolved in the aqueous phase (Archer *et al*, 1963). During recovery of rubber from latex for processing into dry rubber, in addition to proteins of agglomerated rubber particles, the denatured serum proteins also become occluded in the rubber coagulum under normal conditions of coagulation with acid. These proteins are known to adversely affect the dynamic properties of rubber (Smith, 1974). Skim rubber is amongst the worst affected in this respect as it usually contains over 1% nitrogen as compared to 0·3 — 0·4% (w/w) of nitrogen in normal crepe or sheet rubber.

Several attempts have been made during the last decade or so, to produce a rubber with a low protein with a view to improving the dynamic properties of NR thereby enhance its consumer acceptability. This rubber with a low protein content has been generally known as Deproteinized Natural Rubber (DPNR) or sometimes Low Nitrogen Natural Rubber (LNNR). It has also been sometimes referred to as Neorubb PPN by some consumers in order to be more specific of the method of treatment used as there are several of them. Low protein rubbers have been receiving more and more consumer attention and acceptance in recent years, mainly for various engineering applications as anticipated. The purpose of this paper is to review the work carried out by various workers on deproteinization of *Hevea* latex by various methods, particularly in Malaysia and Sri Lanka and also to present the results of some of our recent studies, here in Sri Lanka. I will mainly concentrate on methods of manufacture of low protein rubbers and their raw rubber properties as Dr Sunil Fernando will deal with technological and dynamic properties of DPNR in a later paper at this Conference.

Main advantages of low protein rubber

The removal of proteins from NR has been reported to improve its technological and dynamic properties, particularly the heat-build up. The improved heat performance of low protein rubber makes it highly advantageous in tyre manufacture especially in heavy-duty tyres such as air craft tyres, where the heat build up is very high. Tyre manufacture consumes nearly 60% of the NR produced in the world. The other advantageous of DPNR are (1) low affinity for water due to removal of naturally occurring hydrophillic substances (2) enhanced resilience (3) reduced creep (4) superior fatigue life and (5) uniformity in cure behaviour (Bernard, 1973).

Methods of manufacture

Two methods namely chemical hydrolysis and enzymatic hydrolysis have been successfully investigated for removal of proteins from *Hevea* rubber. Of the two methods, chemical (or alkaline) hydrolysis is known to adversely affect the oxidative resistance of the resulting rubber unless remedial treatments are used. The enzymatic hydrolysis has therefore become established as the most suitable method of enzyme deproteinization of *Hevea* latex.

The basic steps in the manufacture of low protein rubber by enzymatic digestion are as follows :

Latex	— either field or concentrated
↓	— with or without a surfactant
↓	— with little or substantial dilution with water
Enzyme treatment	— normally overnight for breakdown of proteins
↓	
Coagulation	— by the enzyme itself such as in the case of papain and pineapple juice or by the addition of acid.
↓	
Processing	— Coagulam can be processed into any form of rubber desired, block rubber or crepe rubber. It is not recommended for sheet rubber because of the drying problem.

Methods of preparation low protein rubbers from field latex are outlined in Figs. 1, 2 and 3. Methods of preparation of viscosity stabilized version of DPNR are given in Figs. 4 and 5. A method for the preparation of high quality rubber from skim latex by papain treatment is outlined in Fig. 6.

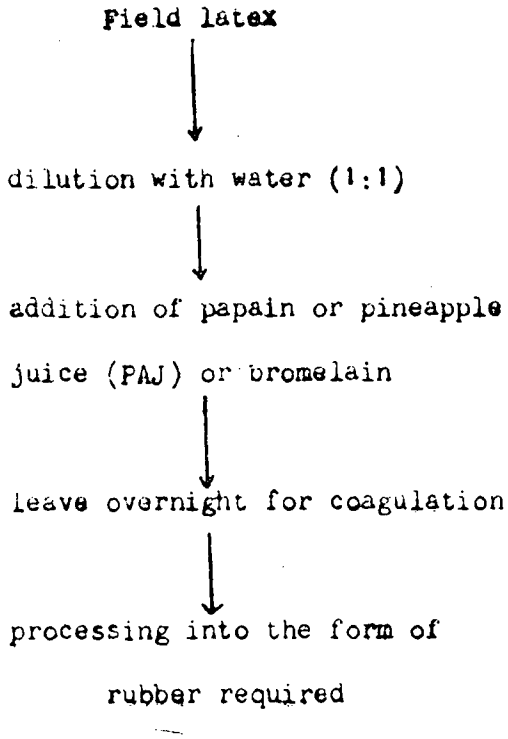


Fig. 1. DPNR from field latex by papain or PAJ treatment.
(Nadarajah et al 1973, Yapa et al 1980)

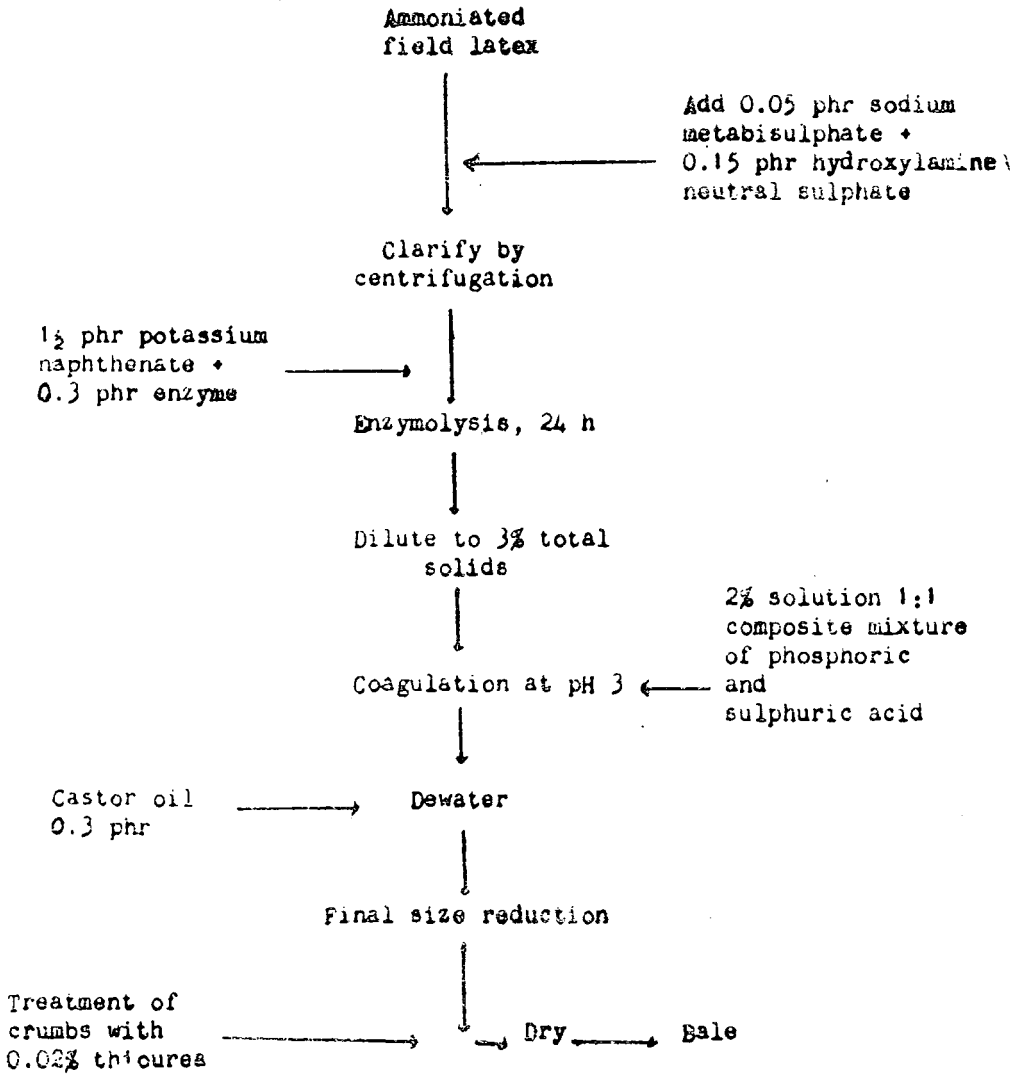


Fig. 2. Viscosity stabilised DPNR from clarified field latex.

(Chang et al, 1977)

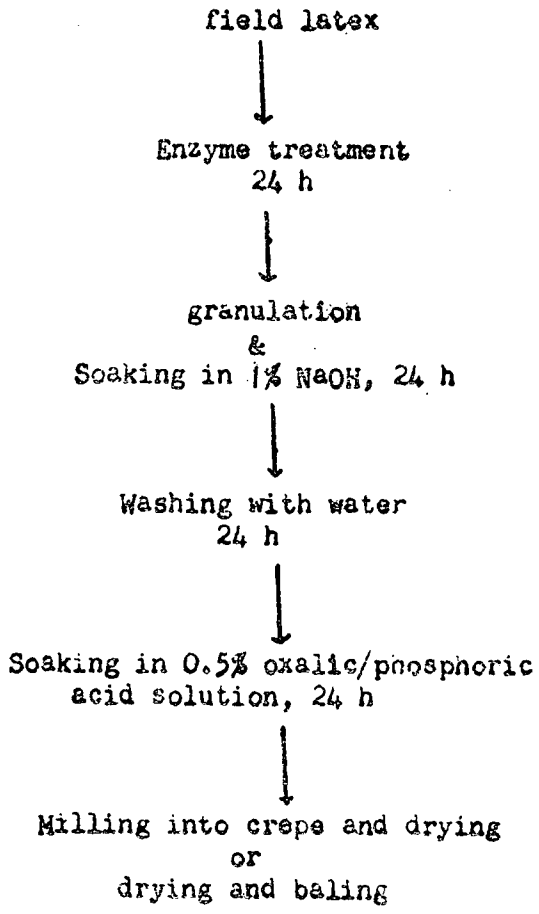


Fig. 3. DPNR from field latex - Alkali method (Yapa, 1977).

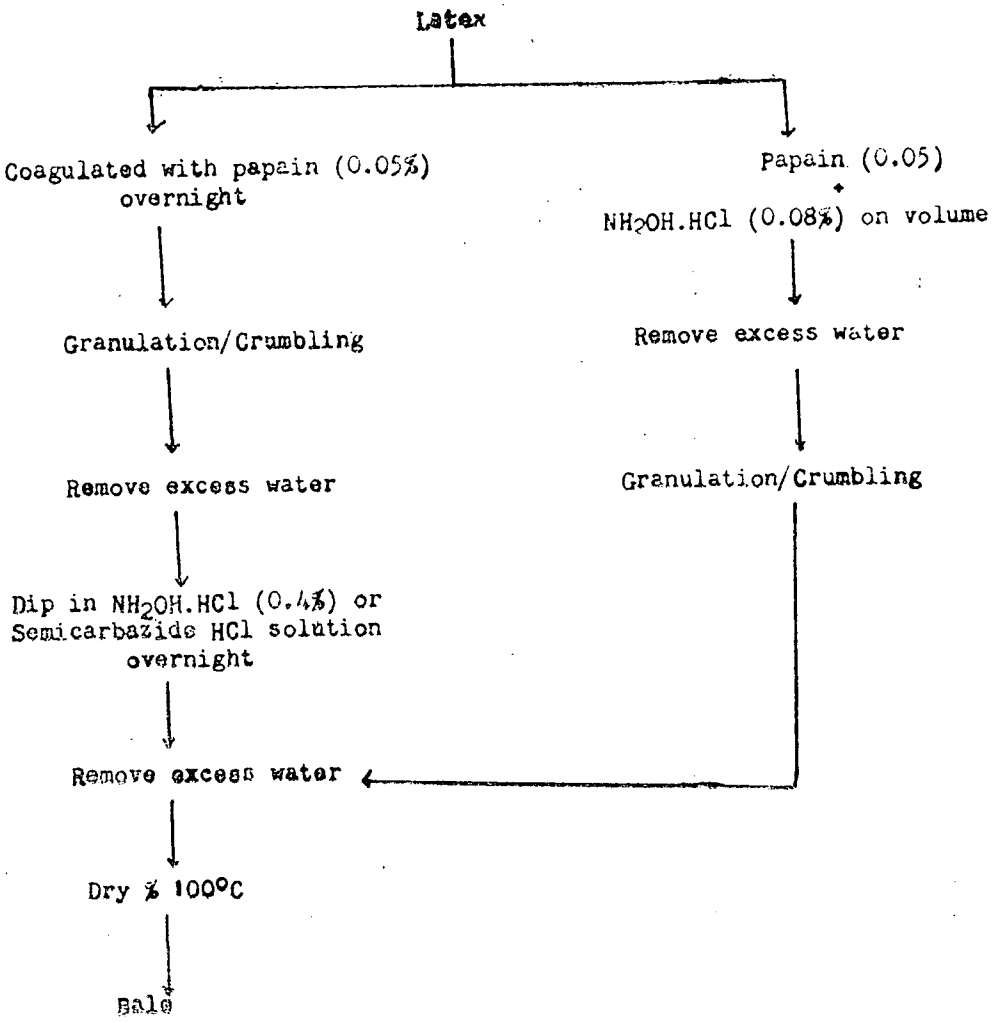


Fig. 4. Low nitrogen cv rubber, papain method (Yapa, 1975).

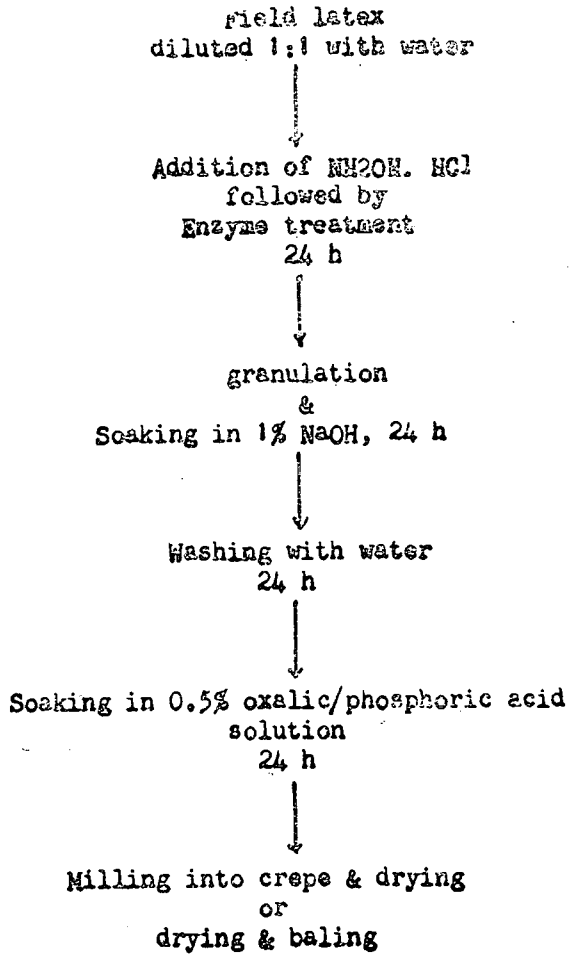


Fig. 5. Viscosity stabilized DPNR - Combined alkali-papain method.

(Yapa, 1977)

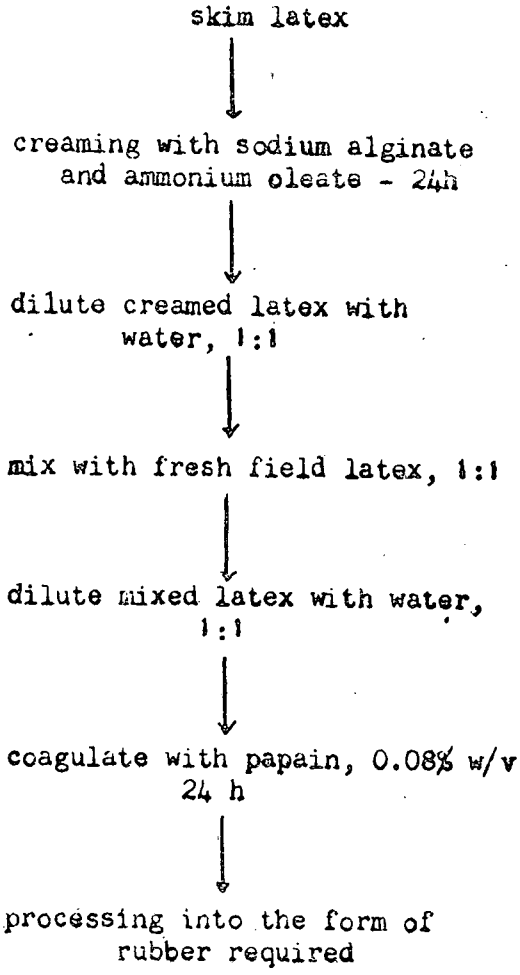


Fig. 6. High quality rubber from skim latex - Papain method.

(Yapa et al, 1978)

A large number of proteolytic enzymes has been tried out. Amongst them are Alcalase, Bacterial Protease Novo (BPN), Esperase (Yapa, 1977) Papain (Yapa & Balasingham, 1974) Bromelain or pineapple juice (Yapa, Prematillake, and Lionel, 1980, Perera & Silva, 1978) Superase (Chin & Smith, 1974, Yapa, 1977), Trypsin (Barnwell, 1957, Yapa, 1977 ; Morris, 1954). These enzymes breakdown the naturally occurring proteins into water soluble products (peptides and amino acids) that are washed away during manufacture of raw rubber. Of these enzymes, two appears to be most popular — papain in Sri Lanka and Superase in Malaysia where they are being used in commercial manufacture of low protein rubber.

One major difference between the method developed by Chin & Smith (1974) and the method now being used in Sri Lanka on a commercial scale is that the former required ammoniated latex where as the papain treatment of latex, used in Sri Lanka can be done on field latex hence comparatively less expensive. Another important difference is that papain treatment does not require additional acid for coagulation as the enzyme itself performs both digestion of proteins and coagulation whereas the ammoniated latex/superase treatment requires additional acid for coagulation of latex hence more expensive.

Nitrogen content

The nitrogen content in low protein rubbers produced by different methods are given in Table 1. Nitrogen content is one of the important parameters in DPNR, that gives an indication of the degree of deproteinization.

Table 1. *Nitrogen content of low protein rubbers*

Method of manufacture	Nitrogen % wt	Reference
Field latex/papain	0·14	(Yapa, 1984)
Field latex/PAJ	0·15	(Yapa, 1984)
Latex concentrate/Superase	0·06	(Chin & Smith, 1974)
Clarified latex/Superase	0·12	(Chang *et al*, 1977)
Skim latex/papain	0·15	(Yapa *et al*, 1978)
Field latex/papain/alkali	0·07	(Yapa, 1977)
Proposed revised specifications max % wt (No sample > 0·15 on test)	0·15	(Chang *et al*, 1976)

The proposed revised specifications for nitrogen value of DPNR is 0·15% wt and no sample to exceed this level on test. This is a relaxation of the earlier maximum level of 0·10% (Chin & Smith, 1974). All the methods reported above satisfy the 0·15% maximum limit although only a few satisfy the original maximum limit of 0·10%. Superase + latex concentrate treatment of Chin & Smith (1974) and Field latex + papain + alkali treatment of Yapa (1977) have yielded rubbers with very low protein contents. The effect of degree of removal of proteins on technological and dynamic properties is not fully known.

Ash content

The ash content of low protein rubbers prepared by different methods is summarized in Table 2. The proposed specification for the ash content is 0·15% and no sample to exceed this value on test. Unlike in the case of nitrogen there has been no change in the maximum level for ash content between the original proposals and the proposed revised specifications.

Table 2. *Ash content of low protein rubbers prepared by different methods*

Method	% wt	Reference
Field latex/papain	0·28	(Yapa, 1984)
Field latex/PAJ	0·23	(Yapa, 1984)
Latex concentrate/Superase	0·05	(Chin & Smith, 1974)
Clarified latex/Superase	0·13	(Chang *et al*, 1977)
Skim latex/papain	0·46	(Yapa *et al*, 1978)
Field latex/papain/alkali	0·16	(Yapa, 1977)
Proposed specification	0·15	(Chang *et al*, 1976 ; Chin & Smith, 1974)
(No sample > 0·15 on test)		

Most of the methods developed with papain and PAJ in Sri Lanka give a higher ash content. Papain treatment of field latex gives a ash content of 0·28% whereas PAJ treatment gives an ash content of 0·23% which are even higher than that of acid coagulated rubber. The RRIM method of superase treatment of latex concentrate gives a very low ash content of 0·05%. The low ash levels are of vital importance in order to reduce the moisture absorption in NR. In Sri Lanka we have carried out extensive studies to bring down the ash levels of low protein rubber produced by papain and PAJ treatments of field latex. I will present the results of these studies later in this paper.

Wallace Plasticity (P_o)

The Wallace Plasticity of low protein rubbers prepared by various methods is given in Table 3. The proposed specification for P_o in 1974 was 30 (minimum). However, this has been taken off in the revised specifications (Chang *et al*, 1977) which has introduced Mooney viscosity, the range of which should be 45 — 55 for low protein rubbers.

Table 3. *Wallace Plasticity of low protein rubbers produced by different methods*

Method	P_o	Reference
Field latex/papain	52	(Yapa, 1984)
Field latex /PAJ	55	(Yapa, 1984)
Latex concentrate/Superase	39	(Chin & Smith, 1974)
Clarified latex/Superase	32	(Chang *et al*, 1977)
Skim latex/papain	52	(Yapa *et al*, 1978)
Field latex/papain/alkali	40	(Yapa, 1977)
Proposed specifications	30 (minimum)	(Chin & Smith, 1974)

Low protein rubbers produced by all the above methods satisfy the P_o requirement of 30. P_o as well as the Mooney viscosity of DPNR produced by papain and PAJ treatments are generally higher than that of acid coagulated rubber. The Malaysian methods seem to give low P_o values. With increased hardness of papain and PAJ treated rubber as indicated by P_o and Mooney viscosity, processing of the rubber also becomes comparatively harder.

Plasticity Retention Index (PRI)

The PRI values of low protein rubbers produced by various methods are given in Table 4. The original specification for PRI was 50 (minimum) Chin & Smith, (1974) It has been raised to 60 (minimum) in the proposed revised specifications (Chang *et al*, 1977).

Table 4. *PRI of low protein rubbers produced by various methods*

Method	PRI	Reference
Field latex/papain	73	(Yapa, 1984)
Field latex/PAJ	72	(Yapa, 1984)
Latex concentrate/Superase	66	(Chin & Smith, 1974)
Clarified latex/Superase	85	(Chang *et al*, 1977)
Skim latex/papain	62	(Yapa *et al*, 1978)
Field latex/papain/alkali	73	(Yapa, 1977)
Proposed specifications	60 (minimum)	(Chang *et al*, 1977)

The PRI of low protein rubbers produced by the above methods are well above the proposed specification limits including that of skim rubber which has a PRI of 62 after the papain treatment. The clarified latex/superase method of Chang *et al*, (1977) has reported the highest PRI, 85 (Table 4). The removal of proteins do not seem to have any adverse effects on PRI and therefore do not seem to require any particular precautions except when alkaline hydrolysis is used for digestion of proteins.

CV version of low nitrogen rubber

Constant viscosity version of low nitrogen rubber (also known as CV-DPNR or CV-LNNR) has also been produced by combined treatment of a proteolytic enzyme and hydroxylamine hydrochloride or hydroxylamine neutral sulphate (Chang *et al*, 1977, Yapa, 1975). In order to obtain very low nitrogen levels, *ie* less than 0·10%, an alkaline hydrolysis has also been introduced, after the enzyme and hydroxylamine hydrochloride treatments (Yapa, 1977).

The nitrogen content, ash content and PRI of CV version of low nitrogen rubber produced by different enzyme treatments are given in Tables 5, 6 and 7 respectively.

Table 5. *The nitrogen contents of CV version of low protein rubber produced by different methods*

Method	Nitrogen % wt	Reference
Field latex/papain/NH_2OH HCl	0·23	(Yapa, 1975)
Field latex/papain/alkali/NH_2OH HCl	0·07	(Yapa, 1977)
Field latex/BPN/alkali/NH_2OH HCl	0·08	(Yapa, 1977)
Field latex/superase/alkali/NH_2OH HCl	0·09	(Yapa, 1977)
Clarified field latex/superase/HNS	0·12	(Chang *et al*, 1977)

Table 6. *The ash content of CV-version of low protein rubber produced by different methods*

Method	Ash content % wt	Reference
Field latex/papain/NH_2OH HCl	0·24	(Yapa, 1975)
Field latex/papain/alkali/NH_2OH HCl	0·11	(Yapa, 1977)
Field latex/BPN/alkali/NH_2OH HCl	0·14	(Yapa, 1977)
Field latex/superase/alkali/NH_2OH HCl	0·12	(Yapa, 1977)
Clarified field latex/superase/HNS	0·13	(Chang *et al*, 1977)

Table 7. *The PRI of CV version of low protein rubber produced by different methods*

Method	PRI	Reference
Field latex/papain/NH_2OH HCl	73	(Yapa, 1975)
Field latex/papain/alkali/NH_2OH HCl	58	(Yapa, 1977)
Field latex/BPN/alkali/NH_2OH HCl	69	(Yapa, 1977)
Field latex/superase/alkali/NH_2OH HCl	65	(Yapa, 1977)
Clarified field latex/superase/HNS	51	(Chang *et al*, 1977)

The nitrogen content of CV version of low nitrogen rubber produced by papain + hydroxylamine hydrochloride treatment is slightly higher than that of papain treated rubber, it has increased to 0·23% from usual 0·15% due to the additional treatment (Yapa, 1975). The introduction of alkali treatment has brought down the nitrogen content considerably with all three enzymes namely papain, Bacterial Protease Novo and Superase, investigated. The reduction in nitrogen content is in the range of 75 — 79%. However, one of the disadvantages of the alkali treatment is that its adverse effect on the PRI. An additional treatment of oxalic acid or oxalic + phosphoric acids is necessary to bring the PRI upto acceptable levels and this makes the final product quite expensive.

The ash content of CV version of DPNR produced by clarified field latex/superase/ HNS method is 0·13% which is comparable with ash content of Sri Lankan methods. The alkali treatment seem to improve the ash content which is usually high after papain treatment (Table 6).

The ash content of all CV low nitrogen rubbers is within the specification limit of 0.15%. No separate specification limits for CV version of low protein rubbers have been introduced yet.

The PRI of CV low nitrogen rubber obtained by papain/alkali/NH_2OH HCl treatment and superase/HNS treatment are 58 and 51 respectively which are below the specification limit for PRI of 60 minimum, set for the normal low protein rubber. This seem to point to the necessity of having a separate specification limit for PRI of CV version of DPNR.

I would now like to present to you results of some of our recent investigations aimed particularly at reducing the ash content of papain treated rubber.

Effect of dilution on nitrogen and ash contents

The effect of dilution of latex prior to enzyme treatment is given in Table 8.

Table 8. *Effect of dilution on nitrogen and ash contents*

Treatment/dilution	N	Ash
1. Acid	·38	·10
2. Papain/1 : 2 dilution	·16	·17
3. Papain/1 : 4 dilution	·15	·14
4. Papain/1 : 6 dilution	·15	·13

Both nitrogen and ash contents decreased on dilution of latex prior to enzymolysis. The nitrogen content was not affected by dilutions larger than 1 : 4. However the ash content continued to reduce on dilution reaching 0·13% at 1 : 6 dilution. Dilutions larger than 1 : 6 were not attempted as it appeared to be impracticable from a commercial point of view and also because of the loss of rubber due to incomplete coagulation.

Effect of dilution and addition of surfactant on nitrogen and ash contents

The effect of dilution and addition of a surfactant on nitrogen and ash content is given in Table 9.

Table 9. *Effect of dilution and addition of surfactant on nitrogen and ash contents*

Treatment	N%	% reduction	Ash %	% reduction
1. Control/HCOOH/1 : 1	0·36	—	0·19	—
2. Papain/1 : 1	0·15	58·3	0·28	—
3. Papain + Nonidet/1 : 1	0·14	61·1	0·21	23·8
4. Papain/1 : 2	0·13	63·9	0·20	26·3
5. Papain + Nonidet/1 : 2	0·12	66·7	0·19	29·8

The addition of surfactant was investigated at two dilutions, 1 : 1 and 1 : 2. The degree of deproteinization was found to improve by the addition of Nonidet. An increase of approximately 3% was observed in the degree of deproteinization at each dilution (Table 9).

A slight improvement in the reduction of ash content was observed by the addition of Nonidet. At 1 : 1 dilution the decrease was nearly 24% but at 1 : 2 dilution the decrease was only 30%, an improvement of 6%, over 1 : 1 dilution plus the addition of Nonidet (Table 9).

Effect of dilution and the addition of surfactant on PRI

The effect of dilution and the addition of surfactant prior to enzymolysis is given in Table 10.

Table 10. *Effect of dilution and addition of surfactant on PRI*

Treatment	Papain	PAJ
1. Control/HCOOH/1 : 1	51	34
2. Enzyme/1 : 1	47	52
3. Enzyme + Nonidet/1 : 1	39	41
4. Enzyme/1 : 2	57	43
5. Enzyme + Nonidet/1 : 2	46	28

Although the addition of surfactant improves the degree of deproteinization and the ash content slightly, it affects the PRI adversely. With papain treatment the PRI came down to 39 from 47 at 1 : 1 dilution, and to 46 from 57 at 1 : 2 dilution (Table 10). A similar drop was observed in PRI with PAJ treatment. The improvement in the degree of deproteinization and in the ash content with dilution + addition of surfactant are really at the expense of a reduction in the PRI.

In Sri Lanka in our recent investigations although we have tried to bring down the ash levels in DPNR we have not attempted to reduce the N levels any further than what we have obtained, the reason being that comparative studies on technological and dynamic properties of different papain treated rubbers have shown that papain coagulation produces the best rubber although the N is not very low. This points to the possibility that the all round improvement of the quality of papain coagulated rubber may not be due to the removal of proteins alone. This is further supported by the finding that the degree of improvement of dynamic properties of DPNR obtained with proteolytic enzymes such as superase is less although the nitrogen content is very low. This may perhaps be due to a maturation of latex during the coagulation process at a higher pH. The coagulation of latex by papain has been reported to occur at a pH of 6·4. Cup lump rubber is generally known to possess excellent heat-build-up properties. Although this has not been attributed to any specific cause, it can again be attributed to the maturation process in both field and factory, during which probably the action of microorganisms also plays an important role.

All these considerations point to the possibility that although the removal of protein from rubber is necessary, it is not the sole factor that contributes to the overall improvement in dynamic properties of DPNR. The importance of maturation and the action of microorganisms is further emphasized by the poor heat-build-up properties of the CV version of DPNR which was prepared by simultaneous addition of hydroxylamine hydrochloride and papain to latex. Hydroxylamine hydrochloride, having some bactericidal properties, would have retarded the action of microorganisms during the papain-coagulation/maturation period.

In view of these observations, the present methods employed in the manufacture of DPNR seem to warrant reconsideration. Maturation of latex coupled with enzyme treatment seems to be the best approach (Fernando *et al* 1984). Alternatively, the coagulum after enzyme treatment can be matured, and this is exactly what we did in one of our recent investigations. The results were very promising and you will hear all about it in a later paper by Dr Sunil Fernando.

In addition to its many advantages in the field of engineering application, papain treated rubber has been reported to be resistant to mould growth. It has been reported that under factory storage conditions, papain treated rubber can be stored for upto 2 years without fungus infection (Anandan and Loganathan, 1984). This is complementary to our earlier reports that papain treated RSS is resistant to mould growth (Yapa and Lionel, 1979).

As far as the commercial prospects for DPNR are concerned, one has to watch the situation carefully and patiently as it takes a considerable amount of time for a new grade of rubber to really catch up, however much they are good. During the last 12 months we in Sri Lanka have supplied papain treated rubber to several customers in Europe. The largest request of them was for a 30 ton batch of papain treated rubber for a West German customer. These rubbers have been used in various engineering applications and their performance will be known in a couple of years time. With the results of these trials in, we are hopeful that DPNR, in our case of course papain treated rubber will fulfil its promise.

REFERENCES

ANANDAN, C. R. AND LOGANATHAN, K. S. (1984). Methods to inhibit mould growth in sheet rubber. *Proc. of the IRMRA 12th Rubber Conf.* 1984, 67 — 72.

BARNWELL, T. H. (1957). Skim latex — The Dunlop Process. *Plrs'. Bull. Rubb. Res. Inst. Malaya*, No. 33, 108.

CHANG, W. P., LAU, C. M. AND NAMBIAR, J. (1977). Deproteinized natural rubber from field latex. *Proc. of the RRIM Planters Conference*, 1977, 295 — 306.

CHIN PEN SUNG AND SMITH, J. F. (1974). DPNR — Preparation and properties. *Rubber in Engineering Conference, Kuala Lumpur*, 1974, Preprint No. 6.

FERNANDO, W. S. E., YAPA, P. A. J., MEDAGAMA, D. D. AND DE SILVA, DAYANTHA (1984). Technological properties of DPNR. *Paper presented at the International Rubber Conference, Sri Lanka,* 1984.

MORRIS, J. E. (1954). Improved rubbers by enzymatic deproteinization of skim latex. *Proc. 3rd Rubb. Technol. Conf. London,* 1954, 13.

NADARAJAH, M., YAPA, P. A. J., BALASINGHAM, C. G. AND KASINATHAN, S. (1973). Papain as a coagulant for natural rubber latex. *J. Rubb, Res. Inst. Sri Lanka,* **50,** 134 — 142.

PERERA, C. AND DE SILVA, T. (1978). Extraction of bromelain and its use in the reduction of nitrogen content of rubber latex. *Proc. of the 7th Annual Sessions of Inst. of Chemistry, Sri Lanka,* 1978, 61 — 65.

YAPA, P. A. J. AND BALASINGHAM, C. G. (1974). The proteolytic action of papain on proteins in *Hevea* latex. *J. Rubb. Res. Inst. Sri Lanka.* **51,** 1 — 12.

YAPA, P. A. J. (1975). The preparation and properties of low nitrogen constant viscosity rubber. *J. Rubb. Res. Inst. Sri Lanka,* **52,** 1 — 9.

YAPA, P. A. J. (1977). Enzyme deproteinization of *Hevea* latex I. Preparation and properties of DPNR and viscosity stabilized DPNR. *J. Rubb. Res. Inst. Sri Lanka,* **54,** 508 — 519.

YAPA, P. A. J., NADARAJAH, M. AND LIONEL, W. A. (1978). High quality low protein rubber from skim latex. *IRRDB Symposium, Kuala Lumpur,* 1978, Preprint.

YAPA, P. A. J. AND LIONEL, W. A. (1979). Enzyme deproteinization of *Hevea* latex II. The use of papain in RSS manufacture. *J. Rubb. Res. Inst. Sri Lanka,* **56,** 34 — 41.

YAPA, P. A. J., NADARAJAH, M. AND LOGANATHAN, K. S. (1980). Use of papain treatment of NR latex to produce superior quality rubbers. *Plastics & Rubber : Materials & Applications* Feb. 1980, 32 — 36.

YAPA, P. A. J., PREMATILLAKE, S. P. AND LIONEL, W. A. (1980). Proteolytic action of bromelain on *Hevea* proteins. *Proc. Internat. Rubb. Conf. India,* 1980.

TECHNOLOGICAL PROPERTIES OF DEPROTEINIZED NATURAL RUBBER

By

W. S. E. FERNANDO*, P. A. J. YAPA*, D. D. MEDAGAMA*
AND
DAYANTHA DE SILVA**
*(*Rubber Research Institute of Sri Lanka*)
**(*Sri Jayawardenapura University, Sri Lanka*)

INTRODUCTION

Natural Rubber (NR) is still the most versatile general purpose elastomer having good mechanical properties low creep and hysteresis in the important low strain region of the stress strain curve. It is now widely known that dynamic properties can be further improved by reducing the nitrogen content of the raw rubber (Yapa, 1977, Yapa & Lionel, 1980).

Since nitrogen comes mainly from natural proteins, the methods proposed to reduce it, ranges from alkaline hydrolysis to the use of micro organisms and to preferential enzymatic treatments (Yapa & Yapa 1984). However there is no universally accepted procedure to prepare low nitrogen rubbers.

This paper evaluate the relative merits of low nitrogen rubber prepared by using two known proteolytic enzymes, *viz* papain and bromelain in pineapple juice (PAJ) and coagulum maturation.

Experimental

The low nitrogen rubbers were obtained by enzymatic treatments using procedure described in the literature (Yapa, 1977, Yapa & Lionel 1980). For coagulum maturation techniques the coagulum obtained by acid coagulation of field latex using 2% formic acid solution was matured with trapped serum for predetermined length of time before processing into latex crepe rubber. For comparative purposes the coagula obtained by enzyme treatments too were similary matured with trapped serum for similar lengths of time, before processing.

The notation used for such treated rubbers are as follows :—

Acid 1 — Field latex coagulated with formic acid and processed overnight.

Papain 1 — Field latex coagulated with papain and processed overnight.

PAJ 1 — Field latex coagulated with bromelain in pineapple juice and processed overnight.

Acid 8 — Coagulum from Acid 1 was matured for 8 days before processing.

Papain 8 — Coagulum from papain 1 was matured for 8 days before processing.

PAJ 8 — Coagulum from PAJ 1 was matured for 8 days before processing.

The following compound formulation was used for evaluation of raw rubber.

Table 1. *Compound formulation for technological evaluation of low nitrogen rubbers*

Rubber	100·0
Zinc Oxide	5·0
Stearic acid	1·0
Antioxidant IPPD	1·0
Accelerator CBS	0·7
Sulfur	2·5
HAF Black	30·0

Test equipment used :— The Wallace Rapid Plastimeter, SPRI Shearing Disc Mooney Viscometer were used for the determination of plasticity and Mooney viscosity of raw rubbers.

Tensile and hysteresis studies were conducted using Instron Universal Tester 1196.

Heat built up studies were conducted at 250 rpm in compression (22½%) at 28°C.

The metal ion concentration of raw rubbers was determined by atomic absorption spectrophotometer using ash samples obtained by combustion of raw rubbers.

RESULTS AND DISCUSSION

The enzymatic treatment of field latex gave lower nitrogen values in the raw rubber, than coagulum maturation of acid coagulated latex. Maturation of enzyme treated coagulum does not result in further improvement in the efficiency of break down of rest of the proteins in the coagulum Table 2. In general the plasticity and the Mooney viscosity increases with the decrease in the nitrogen content of the raw rubbers. The ash content too showed an upward trend along with decrease in the PRI of raw rubber Table 3. Analysis of ash for metal ions show an increase in the Mg^{+2} content of raw rubber, except for the acid maturated sample, Table 4. This indicates an accumulation of magnesium in raw rubber, probably due to complex formation with liberated free amino acids resulting in a drop in the plasticity retention index of raw rubber.

Table 2. *Effect of the coagulant and maturation on the nitrogen content of raw rubber*

Sample	Coagulant	Coagulum maturation Time in day	N2 % by wt
Acid 1	Formic acid	1	0·38
Acid 8	Formic acid	8	0·22
Papain 1	Papain	1	0·12
Papain 8	Papain	8	0·12
PAJ 1	Pineapple juice	1	0·13
PAJ 8	Pineapple juice	8	0·13

Table 3. *Raw rubber properties*

Sample	P_0	PRI	Ash	ML (1 + 4) @ 100°C
Acid 1	48	73	0·14	74
Acid 8	62	32	0·20	88
Papain 1	61	61	0·21	84
Papain 8	62	42	0·22	85
PAJ 1	56	30	0·20	81
PAJ 8	62	29	0·24	86

Table 4. *Metal ion concentration of raw rubbers*

	Mg^{+2}/ppm	Cu^{+2}/ppm	Mn^{+2}/ppm
Acid 1	61·0	3·0	1·0
Acid 8	58·0	1·0	1·0
Papain 1	137·0	2·0	1·0
Papain 8	159·0	1·0	1·0
PAJ 1	160·0	1·0	1·0
PAJ 8	143·0	1·0	1·0

The tensile properties of vulcanizates appear to be independent of the method of manufacture Table 5. However low nitrogen rubbers obtained by enzymatic treatments show poor retention of tensile properties on oxidative ageing Table 6. There is a direct correlation between the Mg^{+2} content of raw rubber and the aged tensile data of the respective vulcanizates, where high magnesium raw rubber offering lower resistance to ageing.

Table 5. *Tensile properties of vulcanizates cure 20 mins at 145°C*

	M_{100}	Tensile strength MPa	Hardness IRHD
Acid 1	2·3	25·4	53
Acid 8	2·7	25·7	54
Papain 1	2·4	29·0	55
Papain 8	2·5	29·0	56
PAJ 1	2·3	28·9	56
PAJ 8	2·4	28·6	55

Table 6. *Aged tensile data, 3 days @ 100°C*

	Percentage retention of TS
Acid 1	50·0
Acid 8	49·0
Papain 1	28·0
Papain 8	26·0
PAJ 1	31·0
PAJ 8	36·0

The difference between the behaviour of vulcanizates of low nitrogen rubbers and the control is evident in the resilience and hysteresis tests. Even a loss of 43% nitrogen in Acid 8 compared to the control is adequately reflected in the resilience and hysteresis data Table 7. However these results clearly indicate that the method of preparation of low nitrogen rubbers play a major role in determining the response of the vulcanizates to deformation at low strains, than the extent to which nitrogen has decreased in the raw rubber. When both hysteresis data and resilience values are taken into account papain treated rubber gives vulcanizates which perform best under dynamic deformation.

Table 7. *Rebound resilience and hysteresis of vulcanizates*

Sample	Resilience at 28°C	Resilience at 70°C	Relative area of hysteresis loop
Acid 1	63	69	1·7
Acid 8	68	74	1·1
Papain 1	68	72	1·0
Papain 8	70	76	0·8
PAJ 1	67	73	1·2
PAJ 8	69	73	1·1

It is possible to distinguish three distinct sets of rubbers when heat build up data is evaluated ; the control sample showing higher faster rate of build up. The enzyme treated rubber show lower rate of build up than the control. Maturation of coagulum with trapped serum has a profound effect on heat build up properties even at reasonably higher nitrogen levels in rubber as shown by the sample Acid 8 Fig. 1.

These results are indicative that other non rubber components apart from those containing nitrogen play an important role in determining energy loss in vulcanizates during deformation. In a cross linked net work the following components of the structure determine its behaviour under dynamic deformation.

(a) Chemical nature of cross link structure and cross link density.

(b) Inter and Intra molecular forces.

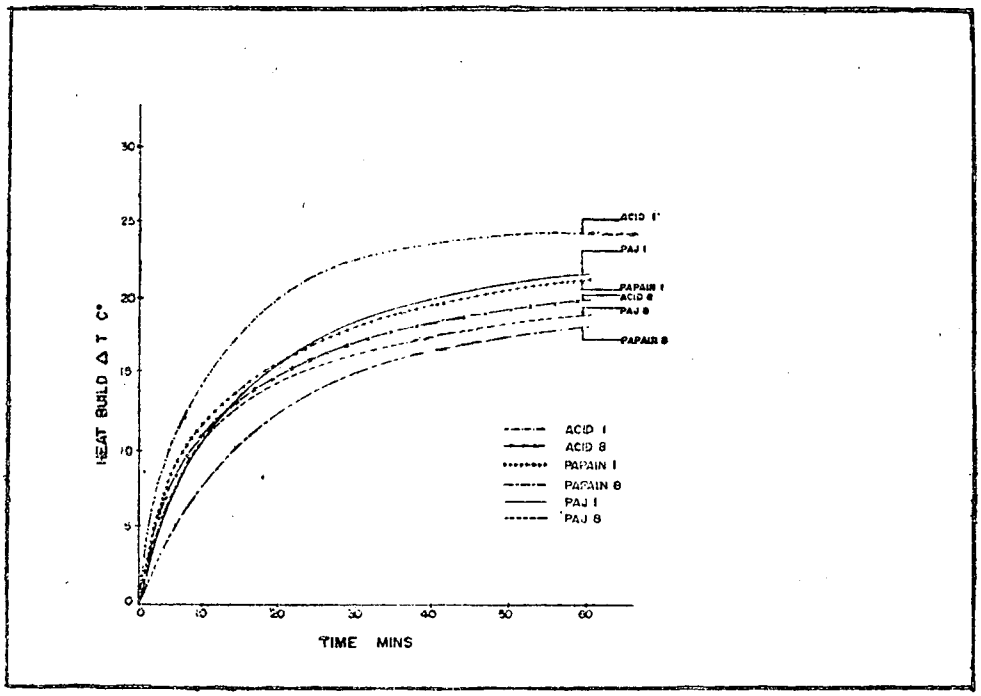


Fig. 1. **Heat build up Data**

For a given elastomer if (a) is kept constant then the performance of the vulcanized net work under deformation (cyclic or otherwise) at low strains will depend mainly on the short range, molecular forces such Vander Walls forces, of electronic origin. The presence of polar non rubbers can thus greatly influence the relaxation characteristics of large molecules by delaying the normal process of relaxation due to molecular forces. Of the polar non rubber proteins are just one component. The presence of new types of non rubbers in low nitrogen rubbers apart from carbohydrates and phenolic components, are indicated by the high ash content of the raw rubbers. Since polar materials have a higher affinity for water, absorption of water by rubber could influence relaxation processes in the network structure.

The measurement of compression set both in air and in water is thus indicative of the performance of low nitrogen rubber under dynamic conditions Tables 8 and 9. This measurement together with the absorption of water by raw rubbers is useful in assessing the performance of low nitrogen rubbers under dynamic deformation (Fig. 2). Thus, vulcanizate of raw rubber obtained by papain treatment followed by maturation was found to show better dynamic behaviour of the rubbers tested. This rubber absorbed the least amount of water in raw rubber, form. The compression set of vulcanizate immersed in water was also found to be lower than other rubbers tested. Thus for low nitrogen rubbers, the measurement of water absorption by raw rubber together with the measurement of compression set in water can be used to predict their performance under dynamic deformation at low strains.

Table 8. *Compression set (%) 30°C, 25% compression in air*

Sample	Recovery time 30 mins	Recovery time 24 h	% N_2 in raw rubber
Acid 1	5·7	2·6	0·38
Acid 8	5·1	2·3	0·22
Papain 1	5·2	2·2	0·12
Papain 8	4·8	1·8	0·13
PAJ 1	5·6	2·9	0·13
PAJ 8	5·1	2·3	0·14

Table 9. *Compression set (%) 28°C, 25% compression in water*

Sample	Recovery time 30 Mins	Recovery time 24 h	% N_2 in raw rubber
Acid 1	7·7	5·2	0·38
Acid 8	5·0	2·5	0·22
Papain 1	5·4	2·6	0·12
Papain 8	4·9	1·9	0·13
PAJ 1	5·5	3·8	0·13
PAJ 8	5·5	2·8	0·14

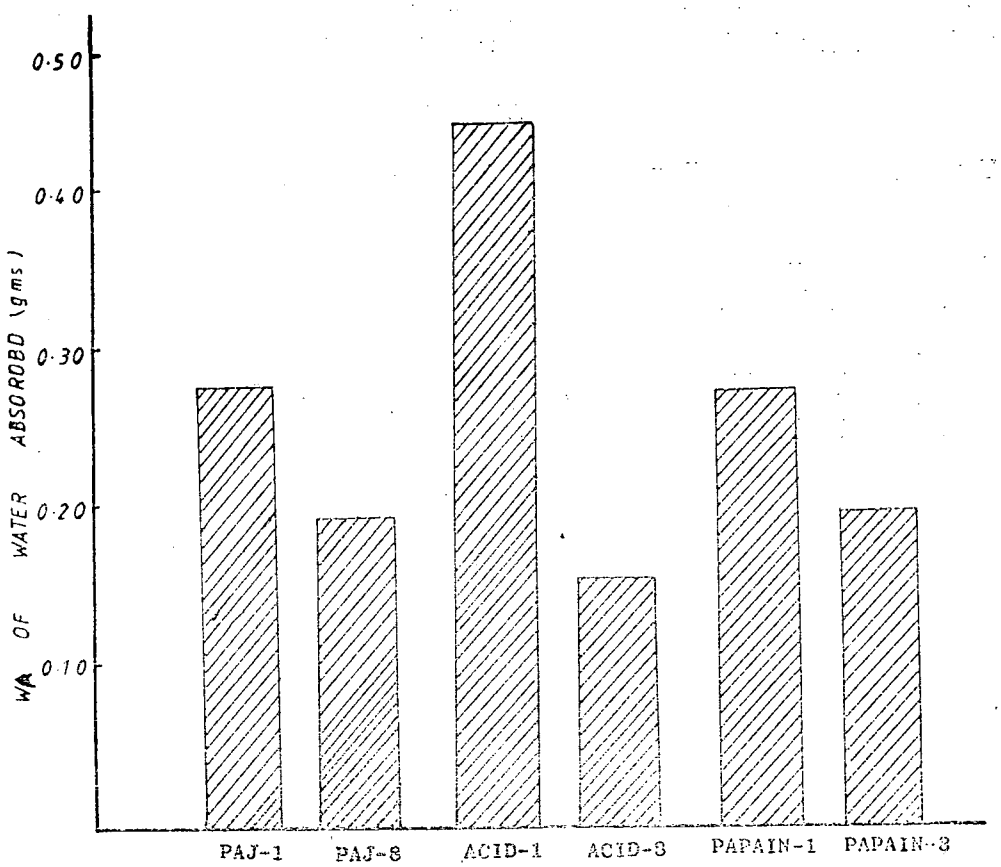


Fig. 2. Water Absorption by raw rubbers

CONCLUSIONS

The proteolytic enzymes used in these investigations were equally effective in reducing the protein content of raw rubber.

However, the properties of low nitrogen rubbers differed to a considerable extent with papain giving the best low nitrogen raw rubber.

Maturation of coagulum was found to improve dynamic properties in acid and papain coagulated rubber. It was observed that water absorption by raw rubber and compression set measurement in water can be used as a means of predetermining the performance of vulcanizates of low nitrogen rubbers under dynamic deformation.

REFERENCES

YAPA, P. A. J. (1977). Enzyme deproteinisation of *Hevea* latex. *J. Rubb. Res. Inst. Sri Lanka*, **54**, 508 — 519.

YAPA, P. A. J. AND LIONEL, W. A. (1980). Some studies on cyclisation of Bromelain treated Rubber. *J. Rubb. Res. Inst. Sri Lanka*, **57**, 7 — 12.

YAPA, P. A. J. AND YAPA, S. Recent developments in the manufacture of deproteinized NR. *Paper presented at the International Rubber Conference*, 17 — 19th September, 1984, Colombo, Sri Lanka.

CHARACTERIZATION OF THE MECHANICAL BEHAVIOUR OF RAW UNFILLED RUBBER BY MEANS OF RELAXATION MEASUREMENTS

By

K. N. G. FULLER

(*Malaysian Rubber Producers' Research Association, Hertford, UK*)

INTRODUCTION

For the efficient production of a consistent final article the rubber manufacturer should be able to predict how his feedstock will behave during the various processing stages, and be able to allow for a certain variability in the feedstock. This requirement has led to the search for parameters able to characterize the ' processability ' of rubbers.

Rheological properties are perhaps the most important, but certainly not the only factor determining processability. The Mooney viscosity is commonly used as a simple measure of the flow behaviour of uncrosslinked rubbers. Not surprisingly, a measurement of the viscosity at one strain rate sometimes fails to give a reliable indication of the response to a processing operation, even when comparing feedstocks all based on the same polymer (Bristow, *et al*, 1983). Raw rubbers are viscoelastic materials, and would be expected to display both the viscous and the elastic facets of their rheological behaviour during processing operations. For example, the phenomenon of die swell is likely to be strongly influenced by the elastic character of the material. An additional complication is provided by the large strains and high strain-rates produced in many processing operations ; the non-linearities of stress with strain and strain-rate must therefore be considered. The complex nature of the rheology of raw rubbers means that any simple test is likely to give only a crude indication of behaviour during processing. Nevertheless attempts to find tests that offer some advantage over the Mooney viscometer have continued.

Stress relaxation measurements have been proposed as a basis for a simple processability test, and an instrument developed (Leblanc, 1980). It gives two parameters — a stress and a relaxation time — and thus some indication of both the viscous and the elastic properties is made possible. The objective of the present paper is to examine the basic assumption that flow behaviour can be predicted from relaxation measurements.

An approach more precise than one which merely looks for correlations between relaxation properties and other flow behaviours has been adopted. A single-integral, non-linear viscoelastic theory able to account for the results of stress relaxation experiments was chosen. The response throughout other flow histories was calculated by means of the theory, the parameters of which could be completely determined from the relaxation data, and the predicted behaviour compared with that observed experimentally.

The relaxation measurements were carried out on two uncrosslinked, unfilled rubbers : a natural rubber (NR) and a synthetic cis-polyisoprene (IR). Three deformation modes — extension, uniaxial compression and simple shear — were investigated so that the influence

of strain geometry on the relaxation behaviour could be studied. Some stress relaxation measurements on polyisoprene rubbers have been reported elsewhere (Montés & White, 1982, Arai & Niinomi, 1971., Djiauw & Gent, 1974). However, the use of relaxation data to test whether viscoelastic theories can successfully predict the response to other deformations, appears to be mainly confined to other polymers such as polyisobutylene (Taylor & Ferry, 1979), plasticized PVC (Zapas & Craft, 1965), polyethylene melts (Wagner & Laun, 1978, Wagner & Stephenson, 1979) and styrene-butadiene copolymer (Wu, *et al*, 1978). One study involving natural and synthetic isoprene has been made (Fuller, 1982) ; predictions of creep and recovery in shear were compared with experimental observations, and found to agree quite well. The present paper extends these comparisons in the case of IR to two other types of flow history, again applied in simple shear ; the different apparatus used here enabled the experiments to cover larger stress levels. In the first type of deformation history the rubber was loaded and unloaded at a controlled strain-rate ; a reversal in the direction of straining was included because it is associated with die swell and other processes involving recovery. The second type of history was double-step relaxation with the second step being applied in the opposite sense to the first. Although this history has been found to provide a severe test of viscoelastic theories (Doi, 1980), its use has mainly been in experiments with polystyrene solutions (Osaki, *et al*, 1981).

Experimental details

The rubbers used were RSS1 grade natural rubber (NR) and Natsyn 2200 synthetic polyisoprene (IR). Each was masticated to a similar Mooney viscosity, and degassed before being moulded (100°C for 1 hr) into flat sheets from which individual testpieces were cut. The Mooney values ($M_L1 + 4$, 100°C) were 40 for the NR and 37 for the IR. From the one batch of NR two sheets 8 mm thick and one 2 mm thick were moulded ; each sheet provided specimens for one deformation geometry. Only one sheet (8 mm thick) of the IR was moulded.

The stress relaxation tests required the sudden application of a fixed strain to the test-piece and the monitoring of the subsequent decay of the stress. The interval over which useful measurements could be made was typically between 1s and 10^4s after loading. The lower limit was set by the time taken to load the test-piece — a period five times this was allowed before readings were taken. The length of the test was limited by the necessity to ensure that the effects of either any loading introduced whilst setting up the experiment, or a previous test remained negligible throughout. Shorter relaxation tests were also carried out specifically to investigate the form of the stress-strain behaviour at a certain relaxation time. This could be done at a short relaxation time because, as the overall results will show, the form of the isochronal stress-strain dependence did not depend upon the reference time chosen.

The experiments performed in simple shear used the test-piece geometry shown in Fig. 1. The rubber specimens (strips about 7 cm long and 1·5 cm wide cut from sheets nominally 8 mm thick) were glued to the loading plates with cyanoacrylate adhesive. The rubber was strained in an Instron 1122 testing-machine. Care was taken in setting up the test jig in the Instron in order that any load this introduced on to the rubber should be kept to a minimum. The presence of such a ' pre load ' was of concern because, even

after being allowed to decay for some time, it could still be changing enough to limit the period over which accurate measurements of the relaxation load were possible. In fact measurements were not allowed to extend beyond the time at which the estimated change in the pre-load was more than 3% of the relaxation load, this being taken as the indicated load less the pre-load acting just prior to the test itself. The shear strains investigated ranged up to 140%. The maximum speed (1000 mm/min) of the Instron crosshead resulted in a time $\lesssim 0{\cdot}7$ s for the application of the strain. Several tests were performed with each rubber specimen, particular care being taken that there was a sufficiently long interval between tests to allow the rubber to recover. The tests were carried out at a temperature of 23 $\pm$ 1°C.

The uniaxial compression tests (Fig. 1) used disc specimens of diameter 3·7 cm cut from 8 mm sheet. In order to improve the accuracy with which the applied strain could be measured some thicker test-pieces made up of two or three discs were also used. The rubber specimens were deformed in the Instron testing-machine between loading-platens lubricated with silicon grease, which was found to be more effective than less viscous lubricants as these tended to be completely squeezed out of the contact. Nevertheless the degree of lubrication required for the deformation to be perfectly uniaxial was not reached. Examination of the discs after the high strain tests suggested that part of the side of the test-piece had been brought into contact with the loading-platens. The procedure adopted for the tests ensured that complete contact between the nominally flat discs and the platens was obtained before the application of the test strain. Establishing complete contact inevitably imposed a ' pre-load ' on to the rubber, and thus introduced a limitation on the length of the relaxation test similar to that described above for the shear experiments.

The extension ratio, λ, applied in each test is given by :—

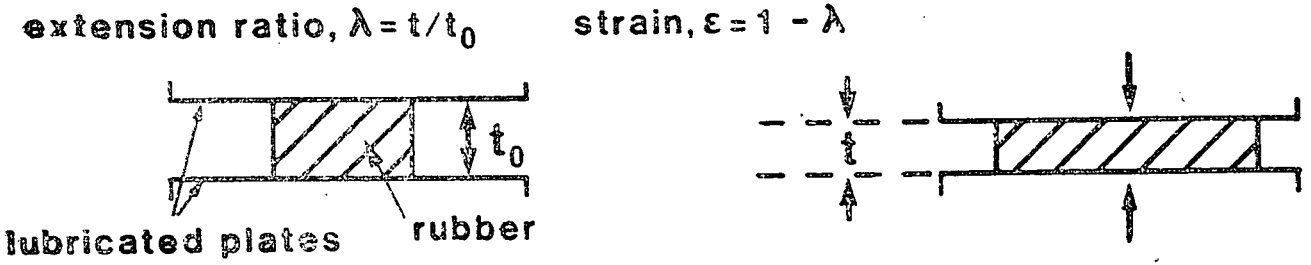
$$\lambda = t/t_o,$$

where t_o was the thickness of the test-piece after the pre-load was applied. The value of t_o was taken as the separation of the platens less the thickness (1/4 mm) of the two grease layers. This approximate figure was determined in subsidiary experiments ; it was found to decrease only slightly as the contact stresses increased from those applied during the pre-loading to those of the main test. Thus the final test-piece thickness, t, could be obtained with sufficient accuracy by subtracting the displacement of the Instron crosshead from t_o. Consistent with the above definition of λ, the cross-sectional area used to calculate the nominal stress was that appropriate to the thickness, t_o. The extension ratios ranged in value down to 0·3. The deformations were applied in a time $\lesssim 0{\cdot}3$ s using a crosshead speed of 100 mm/min. A short relaxation test at a small strain ($\lambda \simeq 0{\cdot}9$) was also carried out for each test-piece in order to obtain a value for the small strain modulus. Preliminary experiments had found the moduli to be rather irreproducible, and it was hoped that obtaining a small strain value for every test-piece would help to circumvent this difficulty.

The relaxation experiments performed in tension used strips (width $\simeq 1{\cdot}0$cm) cut from the 2 mm thick, NR sheet. The gauge length was provided by two lines at a distance from each grip about equal to the strip width. The test-pieces were glued to the grips

LOADING GEOMETRIES

uniaxial compression



simple shear

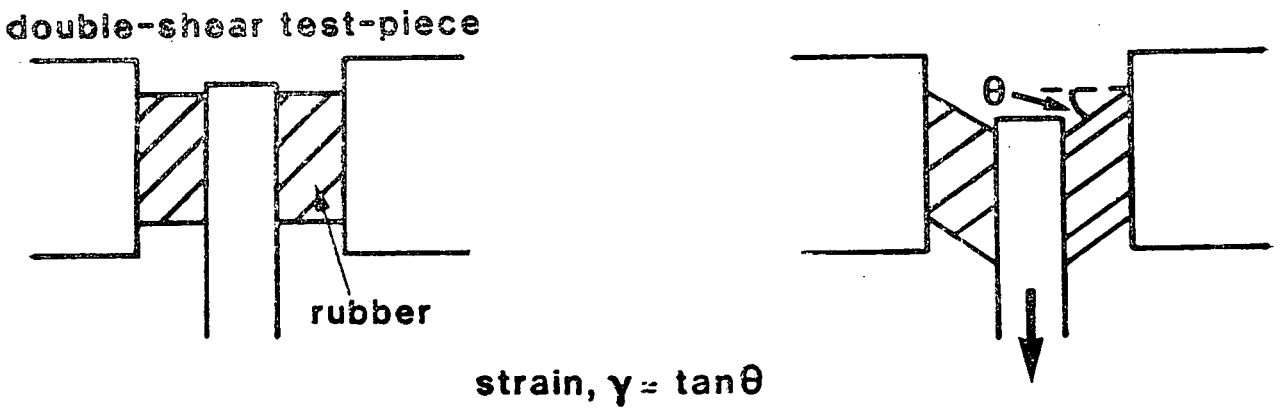


Fig. 1. Schematic diagram of the loading geometries for the uniaxial compression and simple shear tests.

with cyanoacrylate adhesive ; mechanical grips were not used to reduce the possibility of isolated flow in the region of clamping. The strips were strained in the relaxometer shown schematically in Fig. 2. The extension was applied manually in $\sim$0·2 s by sliding the lower grip down. With the lower grip then held in position against the stops, the position of which could be adjusted to provide a range of extensions, the strain on the test-piece was held constant. The subsequent relaxation of the load was followed as a function of time by monitoring the deflection produced at the end of the rigid beam, which was supported from a short strip of spring steel. The earthed plate attached to the beam enabled a capacitive distance probe to measure the deflection. The movement of the upper grip was kept insignificant by mounting it close to the supported end of the beam. Attaching the test strip to the grips sometimes introduced a ' pre-load ', the effect of which was accounted for in the fashion described earlier in reference to the shear tests. In order that several values of the small strain modulus could be obtained, each strip was tested at 10% extension as well as a higher strain. The procedure normally followed was first to carry out the relaxation test for 10% extension, and simply to leave the rubber extended for a time (in fact at least 7 h) sufficient for the load to decay to a small, slowly changing level. The new dimensions were taken as the initial length and cross-section for the test at the higher extension ; the load still acting was treated as a new ' pre-load '. The experiments were carried out at 27°C ; the slight difference compared to the temperature of the other tests was thought not to have a significant influence on the observations. The range of extensions covered was up to 70% ; in such circumstances strain crystallization was not expected to occur.

The measurements which provided the observations to be compared with theory were carried out with the IR. Two types of simple shear deformation history were applied using the same apparatus as for the single-step relaxation tests. The first loaded the rubber at a constant rate up to a shear strain of just over 100% (this is well into the non-linear region of behaviour) ; after a few seconds the strain was removed at the same or a lower rate. The crosshead rates for loading ranged from 1 to 20 mm/min (strain rates ($\dot{\gamma} \sim 2 - 40 \times 10^{-3}\ s^{-1}$), and for unloading 0·05—5 mm/min ($\dot{\gamma} \sim 0{\cdot}1 - 10 \times 10^{-3}\ s^{-1}$); the latter was sometimes carried out in steps because the maximum negative load measurable with one of the load-cells was rather small.

The second deformation history applied (at a crosshead speed of 1000 mm/min) a step strain to the rubber and after a certain interval applied a reverse step of either equal size or half the size. The tests involving equal steps investigated both the effect of varying the size of the step whilst keeping the interval fixed (at about 22s), and of varying the intervals (from 3·5 to 300 s) for a fixed step strain of about unity.

Single-step relaxation results

The data obtained in three of the simple shear tests of IR are seen in the double-logarithmic plot of Fig. 3. The observations form a set of virtually parallel curves. Although each test generally gave results forming quite a smooth curve, there was slight differences between the slopes of the curves from test to test. The differences, however, do not appear to form any systematic variation with the shear strain if the data from all these tests is considered. The percentage spread in the slopes of the curves decreased from about 4% at short times (5 s) to about 2% at long times (1000 s). The fact that the relaxation

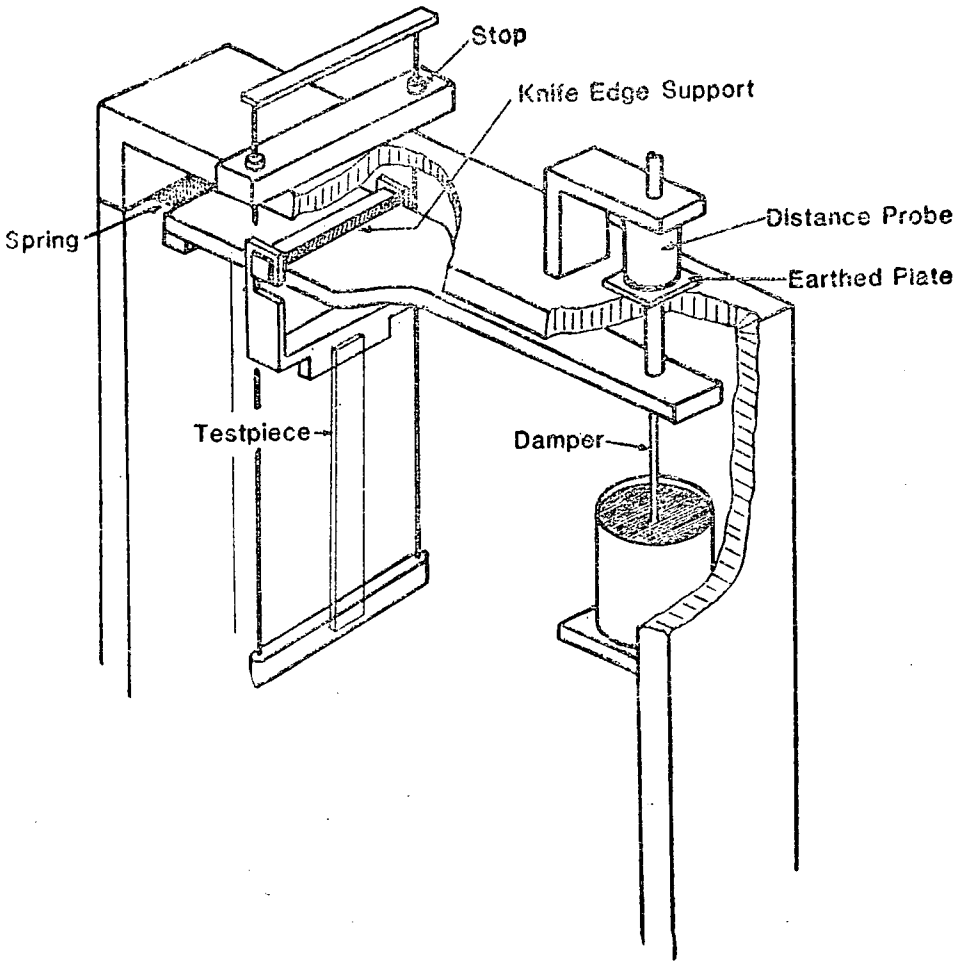


Fig 2. Schematic diagram of the apparatus used for the relaxation tests in tension.

curves for different strains are parallel leads to the important conclusion that the relaxation stress, $\tau(r, t)$, can be expressed as separate functions of the strain, r, and the time, t :—

$$\tau(\gamma, t) = g(\gamma).f(t)$$

Fig. 4 shows some of the results obtained with NR. Data from the three deformation geometries studied are presented as double — logarithmic plots of shear modulus, G, against time. The statistical theory relationships between stress and deformation are used for each geometry to calculate an apparent shear modulus. Thus for simple shear :—

$$G(t) = \frac{\tau(t)}{\gamma}$$

where τ (t) is the shear stress after time, t, and r the shear strain. For uniaxial extension or compression.

$$G(t) = \frac{\sigma(t)}{(\lambda - 1/\lambda^2)}$$

where λ is the extension ratio, and σ (t) the stress referred to the initial cross-section.

The most important feature of these results is that the plots again all form a set of approximately parallel curves regardless of either the deformation geometry or the strain. As with the IR data there were slight differences between the shapes of the curves from test to test. A consideration of all the NR relaxation data obtained, however, did not indicate that the slopes of the curves systematically varied with either deformation geometry or with strain. The differences appeared to be attributable to experimental scatter, which, expressed as a percentage variation in the slope of the relaxation curves, was $\pm$ 10 % at all relaxation times. Thus the separability of the time — and strain — dependence of the relaxation behaviour is seen to apply to NR as well as IR. Moreover, the NR results indicate that the same time-dependence applies whatever the mode of deformation.

Support for the finding that the relaxation stress can in some circumstances be factorized into two separate functions is provided by rheological theory and other experiments. The Doi-Edwards theory predicts separability beyond a certain molecular equilibration time (Doi, 1980). Experiments (Monté's & White 1982) performed in shear on guayule rubber at 100°C were found to give separable behaviour down to times of 0·5 s ; the applied strains ranged up 15. The tension measurements of Arai and Niinomi (1971) suggested, however, that, for polyisoprene, separability could not be applied at temperatures below room temperature. The relaxation dependence of other rubbers has also been found to be factorizable over a reasonably wide range of conditions (Djiauw & Gent, 1974., Kimura *et al*, 1981). The results of Kimura *et al.*, (1981) on polybutadiene showed furthermore that the time-dependence found from shear and tension measurements was the same, a finding similar to that reported here for NR.

A comparison of the IR and NR relaxation curves in Figs. 3 and 4 shows the NR to relax much more slowly despite the two rubbers' having a similar Mooney viscosity. Montés and White (1982) also found *Hevea* rubber to exhibit the slowest relaxation amongst a range of polyisoprenes. They suggested that the presence of gel or long-chain branching

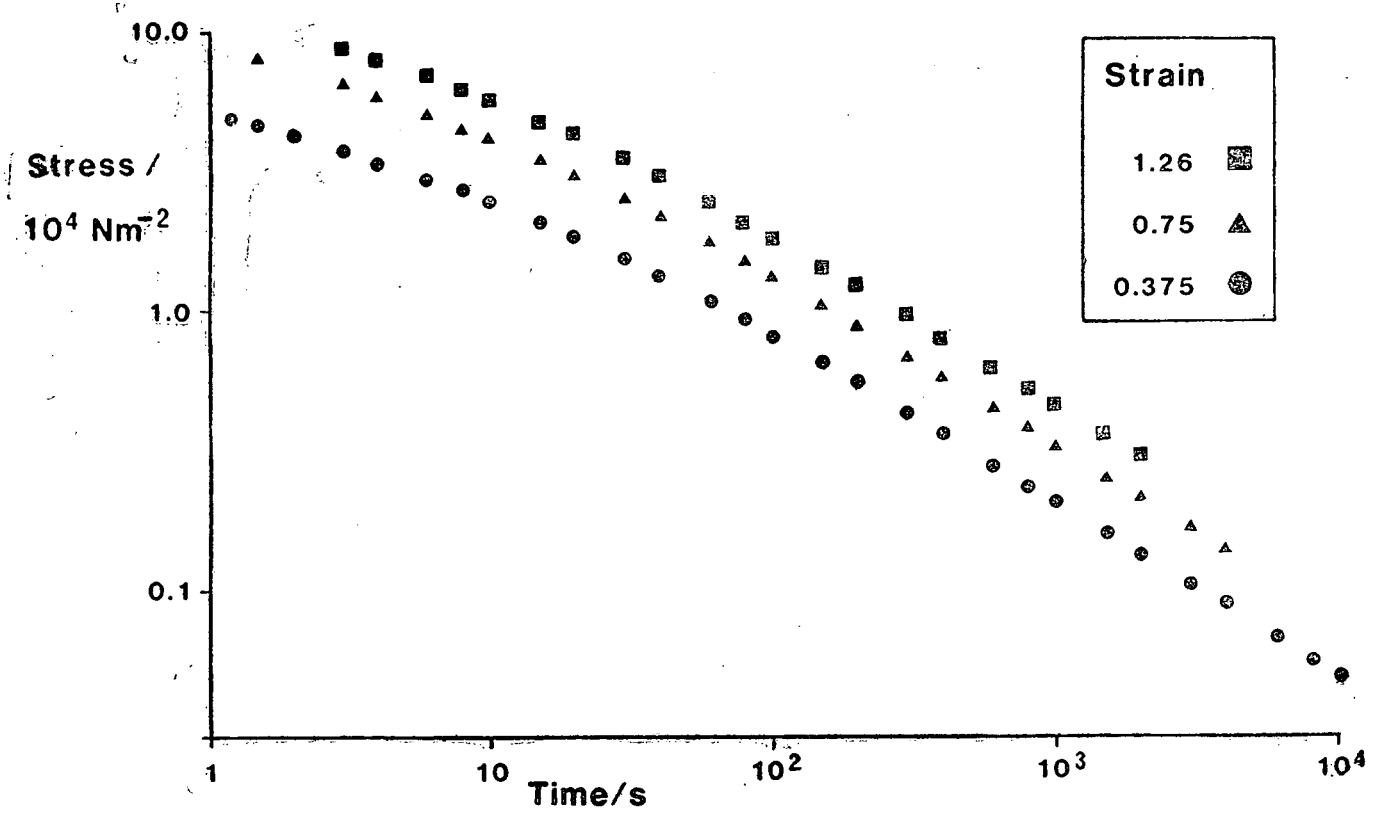


Fig. 3. Variation of the relaxation stress with time for IR deformed to the shear strains indicated.

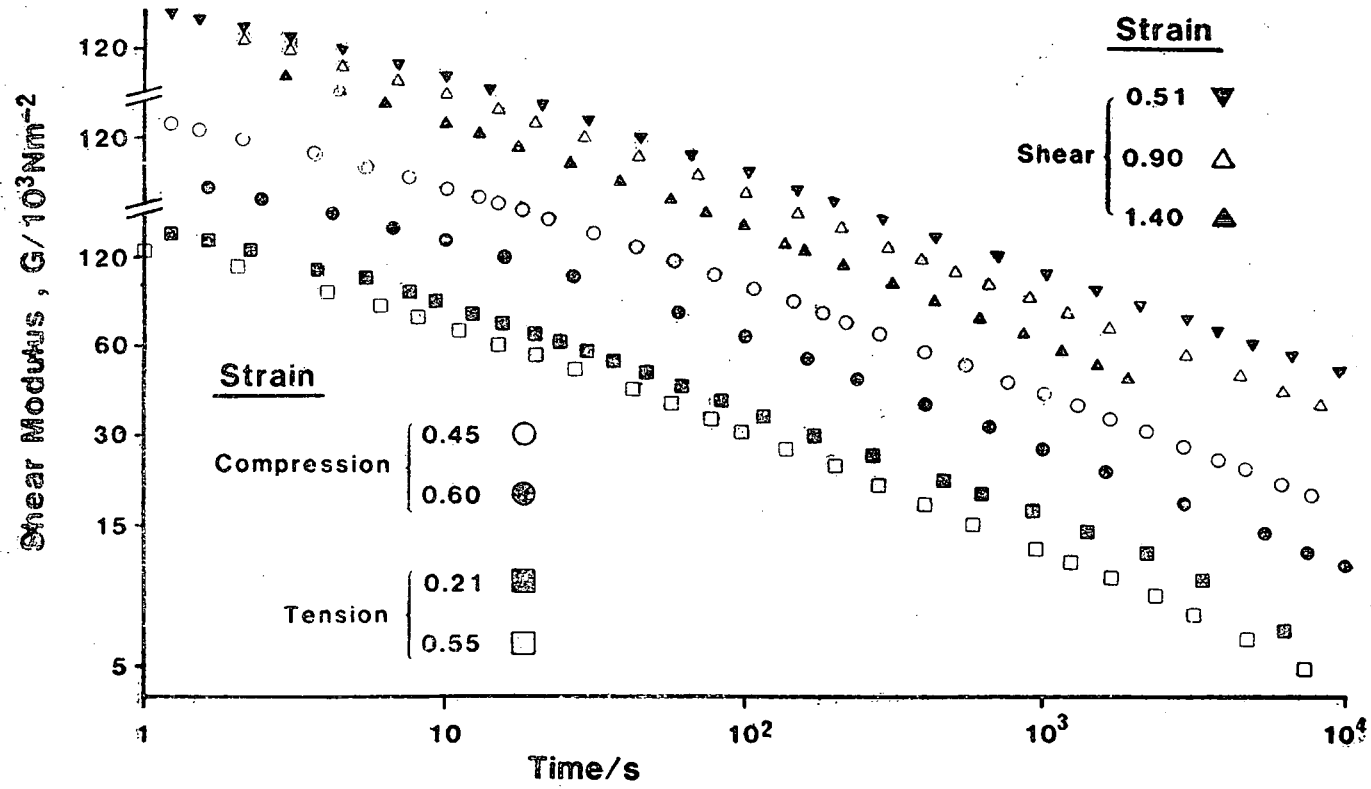


Fig. 4. Variation of the relaxation modulus with time for NR. The shear modulus (calculated assuming statistical theory elasticity) is shown for all the deformation modes.

in the *Hevea* offered an explanation of its behaviour. However, relaxation measurements on sol fractions of *Hevea* indicate that the presence of gel material does not necessarily influence the rate of relaxation (Campbell & Fuller, 1984).

The strain-dependent of the relaxation behaviour is here considered in terms of the variation of the apparent shear modulus, G, with strain. For each deformation geometry, the value of G at some reference time, t_r, was calculated for the various test strains, and normalized by G_0 (t_r) — the value at a small strain. The normalization had the advantage of mitigating the effects of various experimental uncertainties that became apparent when moduli obtained from different test-pieces were compared. The major source of these uncertainties appear to depend upon the deformation geometry. For the shear and compression tests the modulus obtained at high strain with a given test-piece correlated strongly with the value at low strain. Thus in both these geometries the normalizing factor for a given G was taken as the value of G_0 obtained for the same test-piece. For the tension tests, however, the largest spread in the modulus values occurred at the low extension. Thus in this case each modulus, G was normalized by the average of all the G_0 values obtained. The value of the small strain modulus at a relaxation time of 10 s is given for each deformation geometry in the table. The tension figure is perhaps too

Deformation	$G_0(10)/10^4$ Nm^{-2}
Shear	$10{\cdot}4 \pm 0{\cdot}2$
Tension	$8{\cdot}6 \pm 0{\cdot}5$
Compression	$8{\cdot}8 \pm 0{\cdot}9$

low as it is possible that an extension below the 10% value used was necessary to establish a small strain modulus.

Fig. 5 shows the variation of G/G_0 with the strain for the three deformation geometries ; results for IR were only obtained in simple shear. The reference time chosen was 10 s, but because the relaxation curves are parallel, the form of the dependences for G/G_0 should be independent of the choice of t_r. It is apparent that the constant modulus expected for a rubber obeying statistical theory is not obtained. For all the deformation modes the normalized modulus decreases markedly with strain, though the decrease is preceded by a short plateau in the case of compression and shear. As the modulus calculated from each deformation mode is simply plotted as a function of the appropriate strain it is not surprising that the three curves differ. The dependence of G/G_0 upon the shear strain is seen to be very similar for the IR and NR, despite the two rubbers' exhibiting different time behaviour. Other experiments (Wu *et al.* 1978) in uniaxial compression have shown these two rubbers to exhibit a variation of G/G_0 very similar to each other. The suggestion that different isoprene rubbers show a similar strain-dependence is supported by the shear experiments of Montés & White (1982) who studied *Hevea*, guayule and two synthetic isoprenes. Shear relaxation measurements on a range of polybutadiene rubbers, however, found the strain-dependence to depend upon the molecular weight and molecular structure (Vrentas & Graessley, 1982).

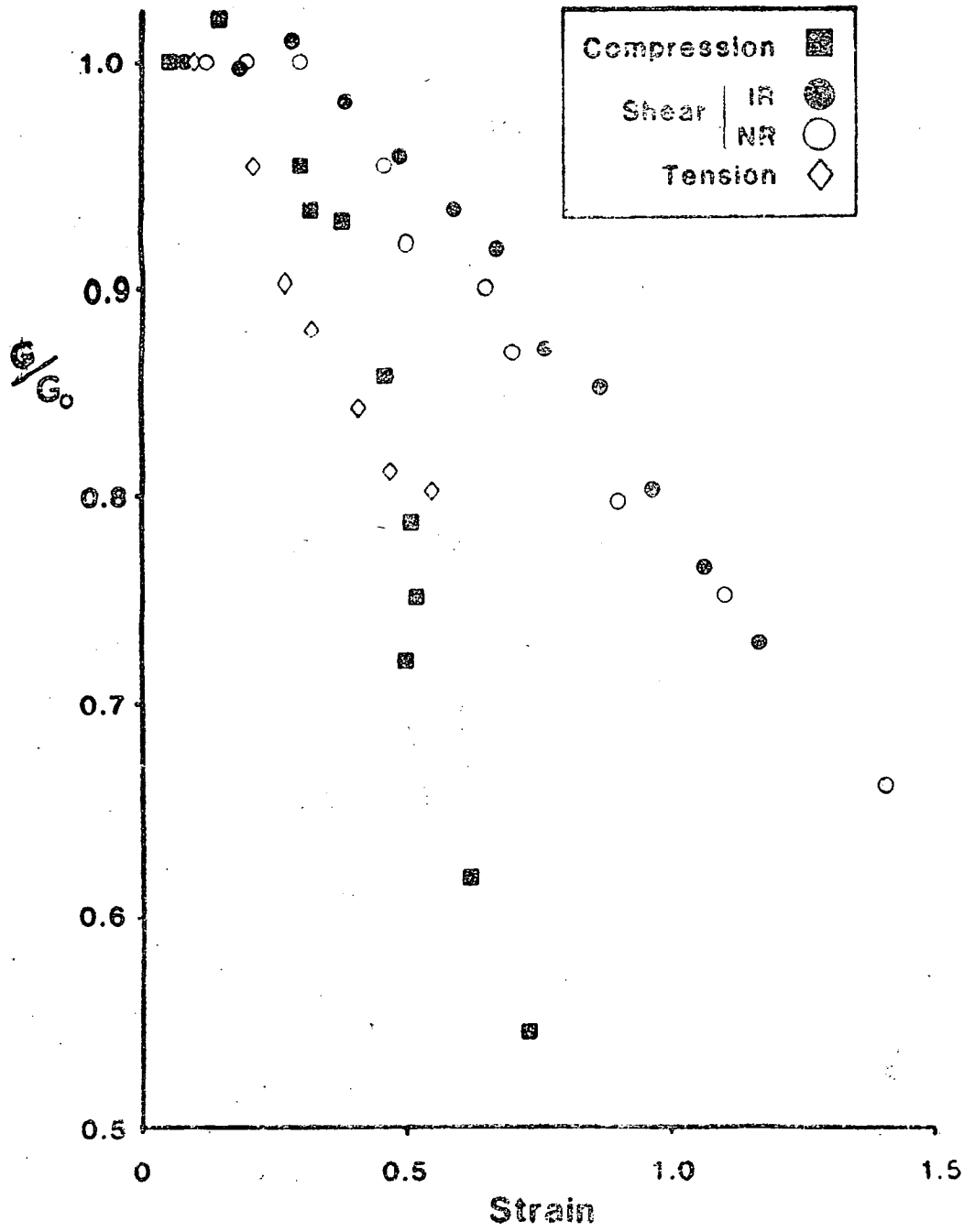


Fig. 5. The normalized isochronal (reference time 10s) shear modulus as a function of compressive, tensile and shear strains. The shear modulus was calculated for each deformation mode by assuming statistical theory elasticity.

Theory

A single-integral constitutive equation of the BKZ-type (Bernstein *et al*, 1963., Bernstein 1966) is used here to model the rheological behaviour. The fact that the time-dependence of the relaxation behaviour was, at least for the range of conditions covered here, independent of the magnitude and the mode of the deformation means that the form of the equation is greatly simplified. For a general strain, the true stress, S_{ij}, at time, t, can be expressed as :—

$$S_{ij}(t) = -p\,\delta_{ij} + 2\int_{-\infty}^{t} m(t-t')\left[h_1 B_{ij}(t,t') - h_2 B_{ij}^{-1}(t,t')\right]dt'$$

where p is an arbitrary hydrostatic pressure, δ_{ij} the Kronecker delta, B_{ij} the left Cauchy-Green tensor, m(t-t') a memory function dependent on the interval between the current time, t, and past time, t_1, and h_1 and h_2 are both functions of the two strain invariants, I_1 and I_2.

At small strains $h_1 + h_2$ equals unity, and thus the shear relaxation modulus,

$$G_o(t) = 2\int_{-\infty}^{\infty} m(t-t')\,dt'.$$

At larger strain, the modulus in simple shear becomes :—

$$G(\gamma,t) = G_o(t)(h_1 + h_2)$$

and in uniaxial deformation :—

$$G(\lambda,t) = G_o(t)(h_1 + h_2/\lambda)$$

The data presented here is too limited to make a unique determination of the functional dependence of h_1 and h_2. In a study (Kimura, *et al*, 1981) of polybutadiene in tension and shear it was suggested that h_1 be made a function of I_1 alone and h_2 of I_2 alone. If these assumptions are followed equations (1) and (2) can provide a reasonable fit to the three (G/G_o curves of figure with $h_1(\cdot) = 7h_2(\cdot)$.

The comparisons between theory and experiment were made only in simple shear. The shear stress, T, at time, t, developed by a shear strain history, $r(t')$, is given by :—

$$\tau(t) = 2\int_{-\infty}^{t} m(t-t')\;H(|\gamma(t)-\gamma(t')|)\left[\gamma(t)-\gamma(t')\right]\,dt',$$

where $H(= h_1 + h_2)$ is assumed to depend upon only the absolute value of the strain difference. The function m is simply related to the relaxation modulus $G_o(t)$, and the function $H(r)$ is given by the dependence of G/G_o upon the shear strain. Thus the stress T,

for any shear strain history can be predicted from the single-step relaxation behaviour without any parameter remaining to be adjusted.

Complications arise in predicting the response to a strain history which involves a turning-point in the strain. The difficulties are reduced in the case of simple shear because of the symmetry between positive and negative strains ; such symmetry is not found with uniaxial deformations as can be seen from the tension and compression results in Fig. 5. Another question arises, however, in any strain geometry. According to the BKZ theory the function H is simply a function of the instantaneous strain difference. The function H can, however, be regarded as representing some sort of strain-aided structural breakdown. In this case Wagner and Stephenson (Wagner & Stephenson, 1979) suggested that the function, H, should be replaced by a functional, H ; for shear,

$$H(|\gamma(t) - \gamma(t')|) = \min \; H(|\gamma(t) - \gamma(t'')|) : t'' = t', t$$

Thus H is assigned the minimum value attained as t″ is varied between t′ and t. In their study of the elongational recovery of polyethylene melts, Wagner and Stephenson found the functional to give predictions closer to the observed behaviour. An investigation of shear recovery of polyisoprene rubbers (Fuller, 1982) also concluded that behaviour was better predicted using the functional. In the next section the stresses calculated with both the function, H, and the functional, *H* are compared to observed responses.

Comparison of predicted and observed responses

As described in the preceding section, equation (3) gives an expression for the shear stress during any shear strain history. The functions m and H are known from the single-step relaxation tests, and hence the behaviour of the IR during the controlled strain-rate and the double-step relaxation tests could be predicted. The time-dependence of m was calculated from an average log (modulus) — log (time) curve. This represented the best single composite curve that could be found by vertically shifting all the individual relaxation plots. The function m also depends upon the value of G_0 at some reference time ; it was found preferable to measure G_0 for each test-piece used.

Every comparison involved the computation of two calculated responses. That designated (1) used equation (3) with the functional H in place of *H*, whereas that designated (2) used the original equation. The two calculated responses only differ the strain has passed through a maximum ; before the turning-point H and *H* are indistinguishable.

Controlled strain-rate tests

Figs. 6 and 7 show the observed and calculated stresses for two of the controlled strain-rate tests. The agreement during the loading stage is seen to be good. In the other tests rather larger discrepancies between theory and experiment were found during loading. The percentage difference never exceeded 10%, however ; normally it was less than 5%. The largest percentage figure for an individual test usually occurred at the end of loading, and invariably the sense of any disagreement was to make the calculated stress too low.

The unloading was carried out in stages for the tests in Figs. 6 and 7. The two calculated responses (1) and (2) are seen to differ during this part of the strain history, though only by a small amount. The observed stresses lie close to the two calculated lines, but neither of these offers agreement significantly superior to the other. A similar conclusion can be drawn from the tests carried out at other strain rates. Thus it appears that either of the calculated responses can provide an equally reasonable fit to the observations. As the stresses pass through zero it is misleading to assign a percentage error to the discrepancy between the calculated and observed stresses. The absolute differences seen in Figs. 6 and 7 are quite small in comparison to the stress levels at the end of loading. In the remaining tests the differences were broadly similar ; larger ones (up to 3800 Nm^2) did occur but, with the exception of one test, they appeared at the beginning of the unloading, where the stresses were high.

Double-step relaxation tests

The results given in Fig. 8 are from tests in which the same strain (1·17) was rapidly applied to the rubber, and, after the interval indicated, completely removed. The figure shows double-logarithmic plots of stress against time, the instant the strain was removed being taken as zero time. Only one calculated stress line is drawn as the two predicted responses are very similar. Although the observations initially lie close to the theoretical lines, they begin to diverge towards higher values at a time comparable in each case to the period for which the strain was applied. Expressed in percentage terms the largest divergence (about 40%) occurred in the test for which the strain was imposed for the shortest time. Times of straining additional to those indicated in Fig. 8 were investigated, but the results all followed the same basic pattern of behaviour. The effect of applying smaller strains in this type of double-step test was also studied. For a given time of straining (about 22 s) the percentage difference between calculated and observed stresses decreased with the strain imposed.

Fig. 9 compares the observed and calculated response to a double-step test in which the second, reverse step was about half the magnitude of the first. The graph is a semi-logarithmic plot of stress against time ; the latter is again measured from the moment the second step was applied. For this strain history the two calculations do give slightly different predictions. The observed stresses are seen to lie between the two theoretical lines, neither of which can be preferred if the full time span of the test is considered. Nevertheless, as with the controlled strain-rate tests, either of the calculations gives a reasonable prediction of the observed stresses. The largest absolute err r in the stress is about 2000 Nm^2 which is comparable to that typically found in the unloading portion of the controlled strain-rate tests.

DISCUSSION

The comparisons between theoretical and observed responses show that the single-integral constitutive equation used here is generally able to model the behaviour during a variety of deformation histories quite well. For the histories investigated here, there appears to be no advantage in describing the strain-dependence in terms of the functional H rather than the simple function, H. Consistent departures between predicted and experimental stresses have been found during certain types of double-step tests. Similar

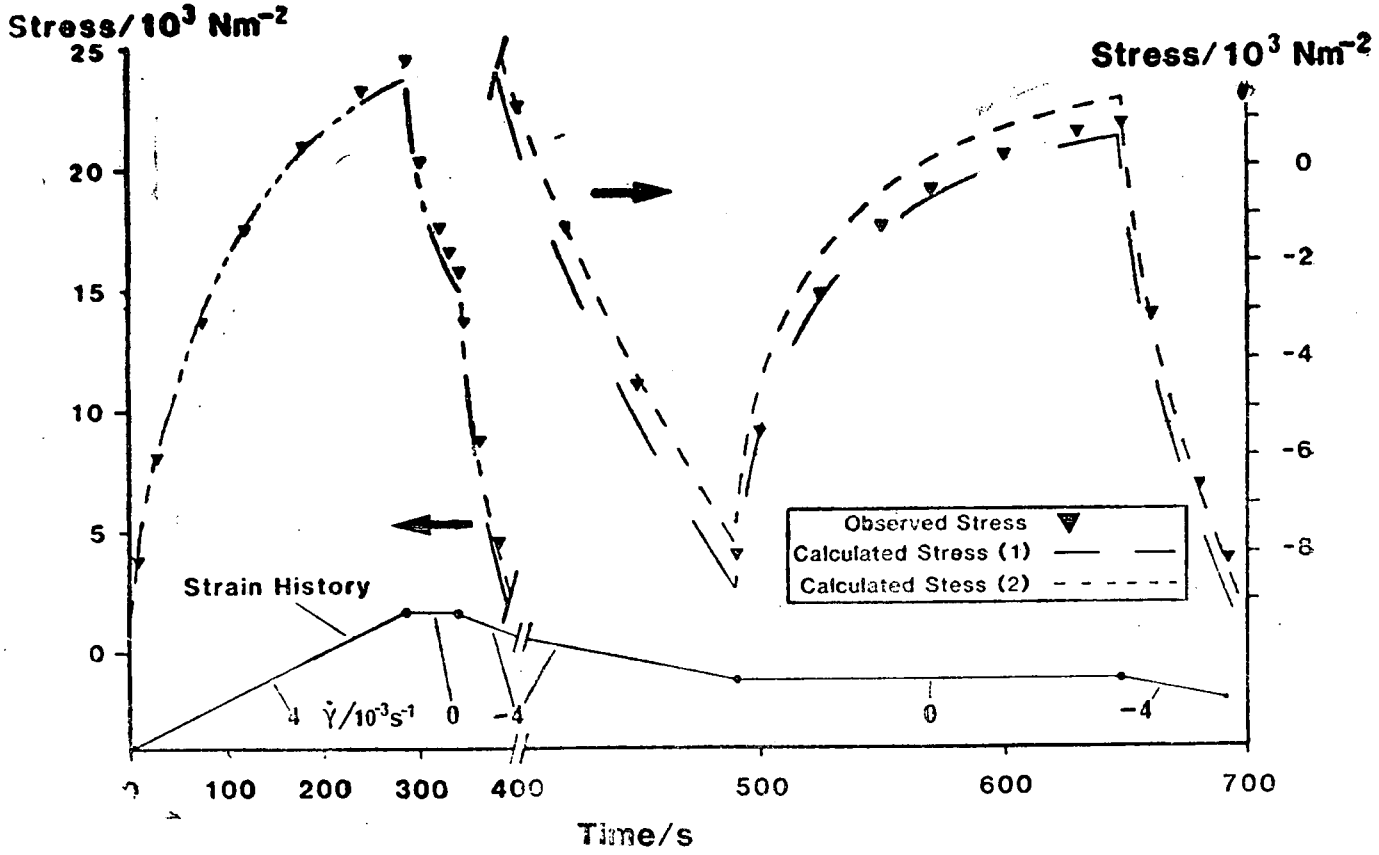


Fig. 6. Comparison between predicted and observed shear stresses for the shear strain-rate history drawn schematically at the bottom of the figure ; the strain rates, $\dot{\gamma}$ at the various parts of the history are indicated. The stress responses are drawn in two parts : the first is referred to the left-hand axis, and the part after the break to the much expanded right-hand scale. Note the scale of the time axis also changes at the break.

For the difference between calculated responses (1) and (2) refer to text. Material used : IR.

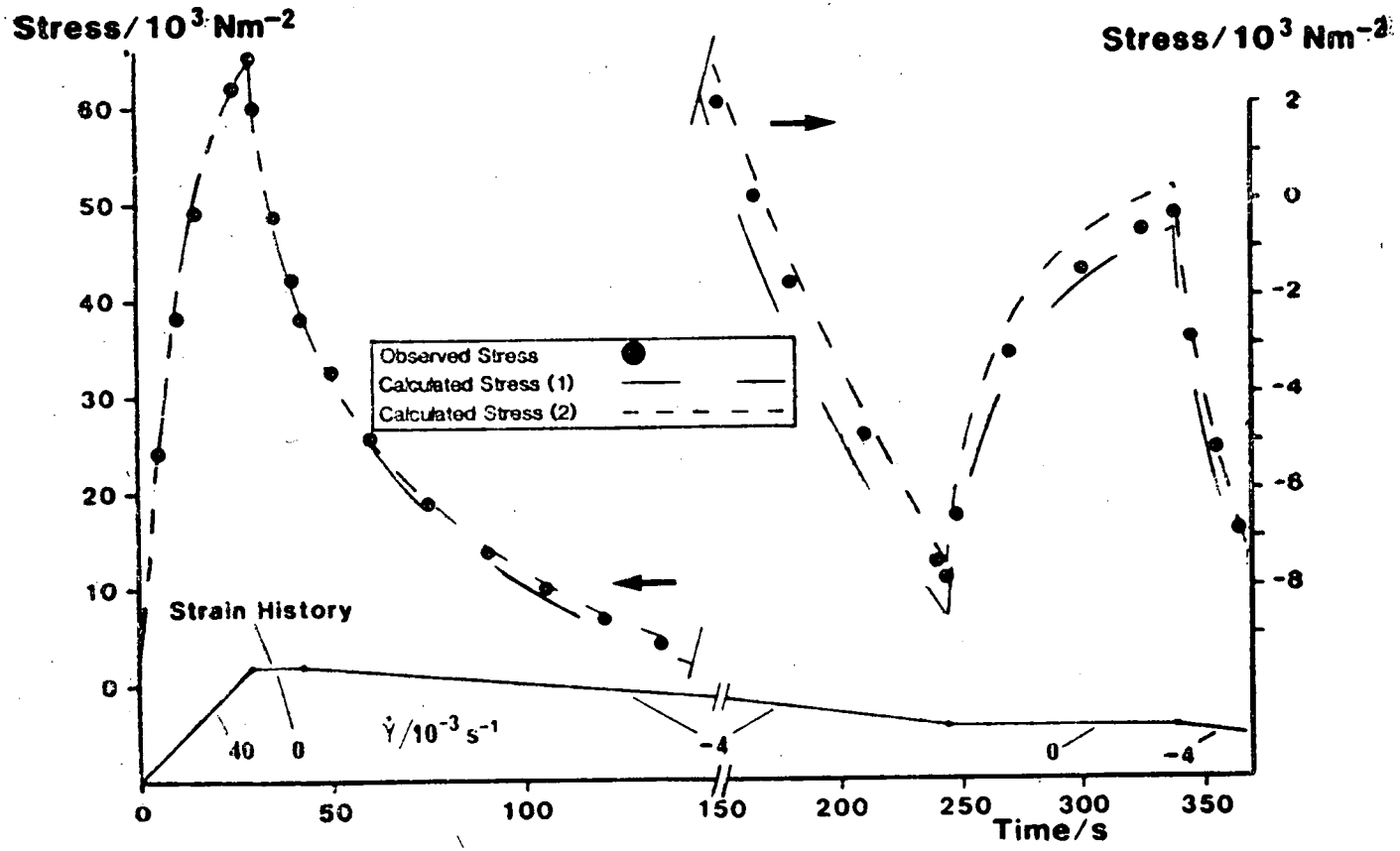


Fig. 7. Comparison between predicted and observed stresses for the strain-rate history shown. As in figure 6 the stress responses are drawn in two parts, and the time-axis is changed at the break. Material used : IR.

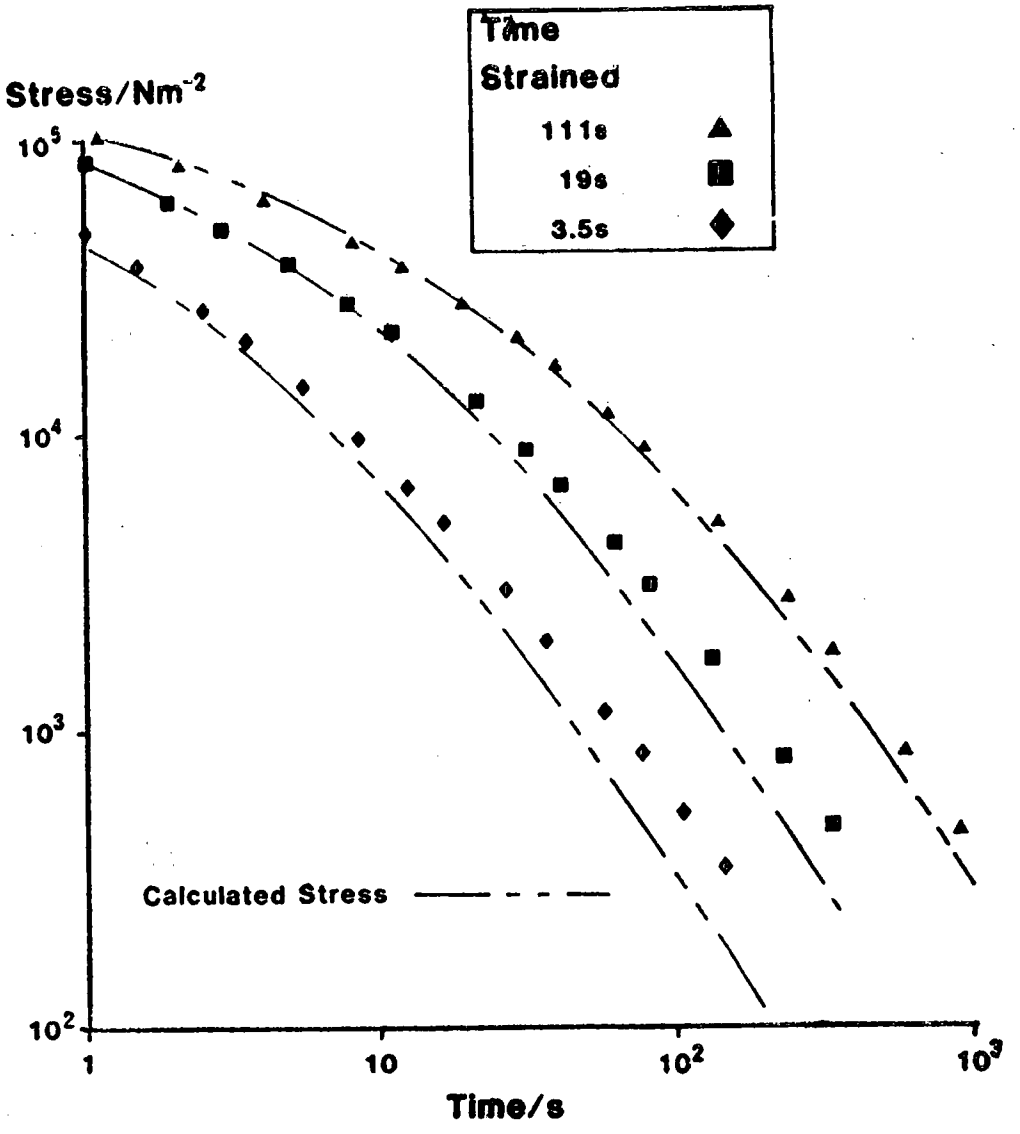


Fig. 8. Calculated and observed variations of shear stress with time after application of two equal, but opposite shear strain steps (+ 1.17, — 1.17). Time origin is taken from instant second step applied. The interval between the steps — ' time strained ' — is indicated. The observations are shown as points, and the calculated stresses are the lines. Material used : IR.

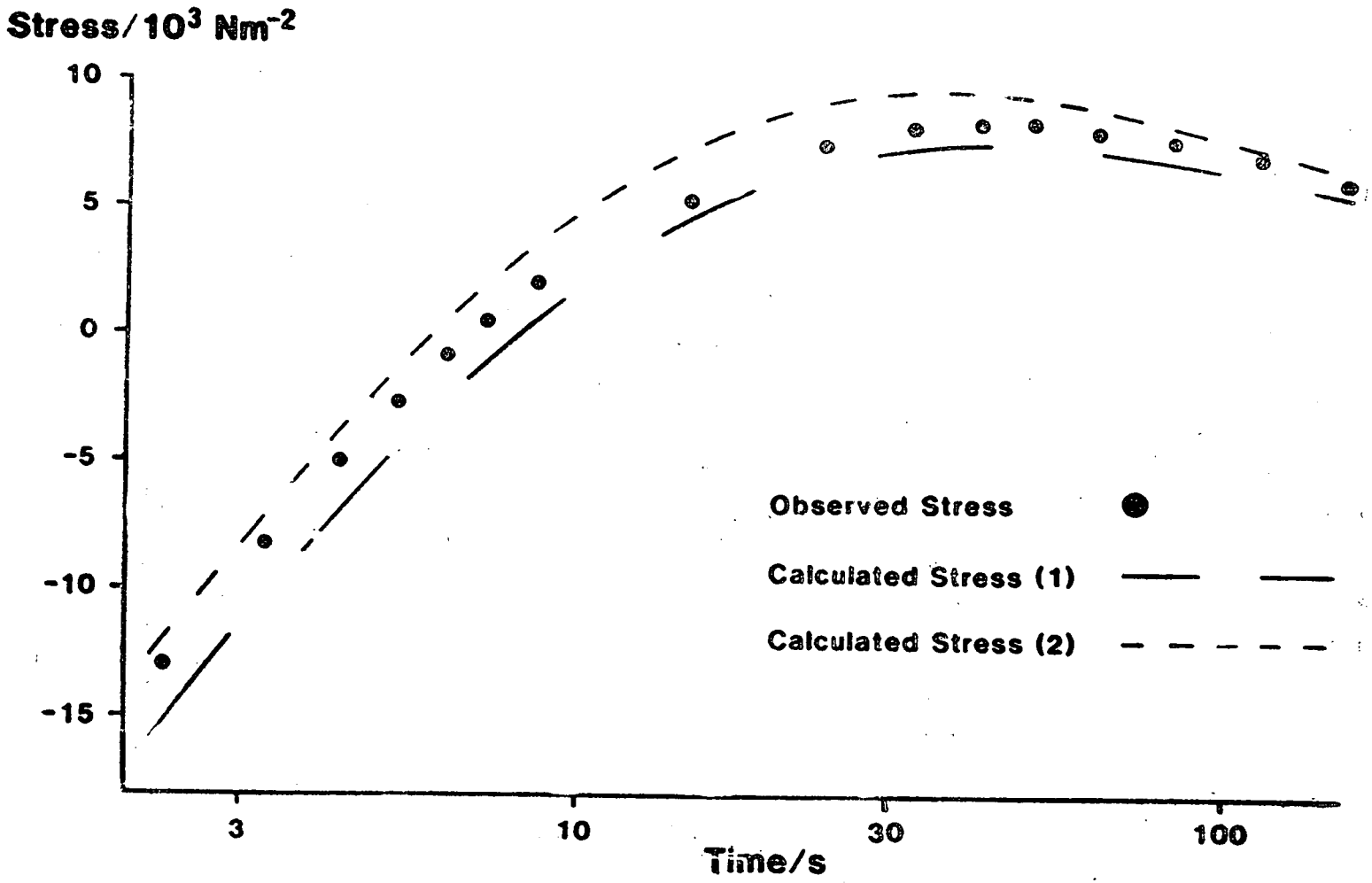


Fig. 9Caq. culated and observed variations of shear stress with time after application of two shear steps (+0.99, —0.49) spaced by 23.7s. Time origin is taken from instant second step applied. For the difference between calculated.

experiments on polystyrene solutions (Osaki, *et al*, 1981) have also shown that the type of equation used here has some inadequacies. Unfortunately it appears likely that any attempt to improve the predictions would require a considerably more complex theory, resulting in much more elaborate tests to determine the parameters of the theory.

CONCLUSIONS

The response of isoprene rubber to the types of deformation history studied has been predicted reasonably well from a knowledge of the stress relaxation behaviour. The predictions were made using a single-integral constitutive equation whose parameters were completely determined from relaxation tests. These measurements had to cover the range of strains and times appropriate to the other deformation histories.

Extrusion is an example of a processing operation where the major flow history is sometimes fairly straight-forward. In some circumstances the rubber may be regarded as being primarily subjected to an extensional deformation for a period determined by the time of travel through the die. The results presented here suggest that in such a case a reasonable prediction of die swell should be possible from a knowledge of the relaxation properties.

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REFERENCES

ARAI, K. & NIINOMI, M. (1971). *Kogyo Kogaku Zasshi.* **74**, p. 2525.

BERNSTEIN, B., KEARSLEY, E. A. & ZAPAS, L. J. (1963). *Trans. Soc. Rheol.* **7**, p. 391.

BERNSTEIN, B. (1966). *Acta Mech.* II/4, p. 329.

BRISTOW, G. M., FULLER, K. N. G. AND THOMAS, A. G. (1983). *Scandinavian Rubber Conference, Bergen Norway*, May, 1983.

CAMPBELL, D. S. & FULLER, K. N. G. (1984). *Rubber Chem. Tech.* **57**, p. 104.

DJIAUW, L. K. & GENT, A. N. (1974). *J. Polym. Sci. : Symp.* **48**, p. 159.

DOI, M. (1980). *J. Polym. Sci. : Polym. Phys.* **18**, p. 1891.

DOI, M. (1980). *J. Polym. Sci. : Polym. Phys.* **18**, p. 1005.

FULLER, K. N. G. (1982). *Proc. Int. Rubber Conf., Paris, 1982.*

KIMURA, S., OSAKI, K. & KURATA, M. (1981). *J. Polym. Sci. : Polym. Phys.* **19**, p. 151.

LEBLANC, J. L. (1980). *Eur. Rubber J.* **162**, p. 20 (1980).

MONTES, S. & WHITE, J. L. (1982). *Rubber Chem. Tech.* **55**, p. 1354.

OSAKI, K., KIMURA, S. & KURATA, M. (1981). *J. Rheol.* **25** p. 549.

TAYLOR, C. R. & FERRY, J. D. (1979). *J. Rheol.* **23**, p. 533.

VRENTAS, C. M. & GRAESSLEY, W. W. (1982). *J. Rheol.* **26**, p. 359.

WAGNER, M. H. AND LAUN, H. M. (1978). *Rheol. Acta* **17** p. 138.

WAGNER, M. H. & STEPHENSON, S. E. (1979). *J. Rheol.* **23**, p. 489.

WU, L., MEINECKE, E. A. & TSAI, B. C. (1978). *Rubber Chem. Tech.* **51**, p. 117.

ZAPAS, L. J. & CRAFT, T. (1965). *J. Res. Natl. Bur. Stand.* **69**A p. 541.

DISCUSSION

Q— K. P. FERNANDO, (University of Moratuwa) : It is surprising to see that your compression and tensile stress relaxation results fall into the same cure, since the ' strain' does not have a significance to the mode of compression. Note that rubbers are mainly sheared up radially. What do you think are the reasons ?

A — K. N. G. FULLER, (MRPRA) UK : The question itself contains the answer. Regardless of the overall deformation the rubber experiences a shear. Therefore it is not strange that the tensile & compression stress relaxation data follow the same curve.

ENGINEERING WITH RUBBER

By

LEONARD MULLINS
(Unido Consultant, UK)

Almost 60% of all the rubber used both natural and synthetic goes into the production of tyres. This figure has remained surprisingly constant since the advent of the pneumatic tyre at the end of the last century. There is no question that the growths of the rubber producing industries, the tyre industry and the automotive industry have been and still are closely inter-dependent.

For natural rubber, however, this percentage has increased steadily during recent years, and now tyres take over 70% of its production.

This dominating position of tyres is a source of both strength and weakness for the producers of natural rubber. Strength in that natural rubber is a preferred material in a giant market; weakness in that it is readily susceptible to changes and difficulties in the automotive industry.

Thus the development of the radial ply tyre and its widespread adoption during the 1960's and 1970's have, on the one hand, provided car owners with tyres which last up to twice as long, but, on the other hand, resulted in the tyre industry making only about half as many tyres and consuming only about half as much rubber as would otherwise be required. The concurrent oil crises and economic recession have also had direct effects on the automotive industry and the usage of cars and have strongly reduced the anticipated increase in demand for tyres and thus for rubber.

It is hoped that these changes and difficulties have been largely accommodated, but they have had an adverse and lasting effect on the natural rubber producing industry and the projected optimistic expansion envisaged in the 1970s has been replaced by a much less confident one of limited growth. As a result of scarcity of supply it appears that the percentage of available natural rubber used in tyres will increase even further in the years ahead. This increase, will also be reinforced by the continuation of the radialization of tyres and the drift of the growth of the tyre industry towards developing countries in which the mix of tyres involves a greater proportion of truck tyres.

This has the inevitable consequence that smaller proportions will be available for other applications. This situation could, of course, be altered either by a higher than anticipated rate of growth of natural rubber production, or by an unexpected reduction in the requirement of natural rubber for tyres. But both of these conjectures can be ruled out for the foreseeable future.

Thus for the many non-tyre applications there will be further progressive substitution of natural rubber by synthetic rubber, and natural rubber will only provide say 20% to 25% of the rubber required. Even though natural rubber is eminently suitable for many of the applications and for some its unique balance of properties makes it an ideal material.

It is not my purpose to comment on the desirability of much increased production of natural rubber, or of the wisdom of taking natural rubber off the market to protect its price. But it is self-evident that restriction either of its production, or of its use, provides additional markets for synthetic rubbers.

Out of a total current consumption of approximately 12 million tonnes of rubber about 5 million tonnes is used in non-tyre applications and of this rather more than 1 million tonnes is natural rubber. Latex applications account for about 0·3 million tonnes of natural rubber and this leaves only about 0·7 million tonnes available for all of the other non-tyre uses.

There are good grounds for claiming that, given the availability, a much larger portion of non-tyre articles could be made from natural rubber, and that, in view of its limited supply, there is a need to concentrate on extending the use of natural rubber into those non-tyre applications which are technically demanding and for which it is most appropriate, and in this way to strengthen its market position.

Such a development must be of special importance to natural rubber producing countries. All of which are seeking to achieve greater industrialization to increase their national wealth and to improve the living standards of their populations. This involves moving from a position in which they were essentially suppliers of raw rubber to the industrialized countries, to one in which a much larger proportion of their national income is generated by the manufacture and export of finished products.

With rubber the manufacture of tyres is obviously the first consideration ; but these are relatively sophisticated products and major companies in America, Europe and more recently Japan supply the world markets. As a result the export market for ty es is a difficult one to enter, and currently there is too much production capacity chasing too little demand. A much greater opportunity exists in the less developed and expanding outlets for the use of rubber as an engineering material.

Although the use of rubber in engineering applications predates the discovery of the pneumatic tyre, as evidenced by the illustration taken from Hancock's book dated over 150 years ago which catalogues its use among others for axle springs, buffer stops and pipe seals. The development of its wider use was severely limited by lack of information on the mechanical properties of rubber expressed in terms which the engineer could employ in the design of components. Its use depended on the ingenuity and patience of practising engineers and rubber technologists who had perforce to follow laborious methods of trial and error to achieve their furial designs.

In the past 20 to 30 years great studies have been taken in overcoming the problems which hindered the fuller exploitation in this area of application. These have involved not only the provision of a body of information which enables design problems to be tackled rationally and the service performance of components to be satisfactorily forecast, but also the development of a real measure of understanding of how the detailed composition and structure of rubber vulcanizates is related to the mechanical properties which determine their performance service. This enables compounds to be chosen with the optimum combination of properties such as stiffness, strength, resilience and durability, and permits the proper exploitation of the latest developments in compounding, processing, and vulcanizing.

There is now an accumulation of experience of the most satisfactory performance of rubber in a wide range of engineering products which provides assurance that it can be used with the same degree of confidence as traditional engineering material such as steel and concrete.

In all of the many civil and mechanical engineering applications of rubber the real reason for its use is because it is highly deformable elastically. As a result it can function either (i) as a resilient seating which allows relative movement between adjacent parts of the structure ; and cushions impact, or (ii) as a spring which isolates a structure from a source of vibration ; or (iii) as a universal coupling which allows the transmission of rotational movement and accommodates lateral displacement.

It is used widely in transport systems to isolate passengers from noice, vibration and shock or for power transmission. Illustrative examples are :

(i) the replacement of coil and leaf springs on rail vehicles. The London Transport underground introduced natural rubber suspension systems about 1957 to connect the axle box to the underframe. This produced enormous benefits from a maintenance point of view. Hitherto suspension bearings were checked every 3 days, inspected every 3 to 4 weeks and replaced in major overhauls every 2 to 3 years. The rolling stock now returns for overhaul every 9 years and even then no work is carried out on the bogies and suspension gear. In these laminated rubber bearings the mode of deformation is combined shear and compression both horizontally and vertically and in this way the stiffness can be different in the two horizontal directions, with a third different stiffness vertically. Such systems are now widely used, and the advent of high speed trains in which smooth ride is of extreme importance has provided the opportunity for the extensive use of interleaf natural rubber springs.

(ii) in automobiles where rubber springs have important advantages to steel leaf springs in terms of longer life, superior ride and reduced maintenance. The most well documented is the Moulton Hydrolastic unit used in British Leyland cars. Rubber springs have also been used with particular success in buses and coaches. The most recent success was the use of hollow natural rubber springs in the primary suspension of the Project Trust car which last year broke the world land speed record. The response to these springs is non-linear, and these rising rate springs help to maintain the stability of the vehicle at high speed. Similar springs were earlier successfully used in the suspension of a Formula 1 racing car. Until now the relative expense of these rubber suspensions has militated against their widespread adoption in passenger cars. However continued cooperation between vehicle manufactures and rubber suspension manufactures promises to result in the development of more economic rubber systems to replace leaf springs in standard suspensions.

(iii) the development of natural rubber steel laminated bearings for helicopter motor systems. The conventional motor head originally contained 408 parts to transmit the various blade motions and loads, while only 48 parts were necessary to serve the same purpose with rubber bearings. Further an additional 233 parts to provide for lubrication were completely unnecessary.

Further in addition to reduced maintenance and the possibility of visual inspection without disassembly the rubber bearings last 3 to 5 times longer.

These are just three examples with different degrees of complexity and are merely illustrative of a host of examples of the growing use of rubber in mountings, bearings, couplings, shock absorbers, bushes and seals in mechanical engineering applications.

An important impetus to the use of rubber in civil engineering applications occurred with the development of laminated rubber steel bearings to support bridges. The first use of such bearings was in England some 25 years ago ; the bearing replaced a relatively cumbersome system of metal rollers that presented problems of corrosion and of maintenance. The success of this development — the rubber bearings are currently functioning perfectly are in rather better condition than the bridge they support, and require no maintenance — has led to the adoption of the system world-wide. The future of bridge bearings will be limited only by the rate of road construction.

The bridge bearing is *not* basically an anti-vibration device. It did, however provide the design engineer with a basic unit which had all of the requirements of an isolation spring. Used to support a building on a site subject to ground-borne vibrations the physical characteristics of the spring can be so designed as to alter the natural frequency of the building spring combination and thus suppress any resonance with the disturbing frequency. The major advantage of building mounts is to allow the use of sites that would otherwise be unusable owing to vibration. Once again this type of component has achieved world-wide application.

This concept of using rubber bearings as base isolators to buildings provides a most promising and elegant method of protecting life and property against earthquake hazards. The need is obvious. An estimated 2000 earthquakes occur in the world every day. Most cause little or no damage or occur in unpopulated regions. But each year they kill thousands of people and result in enormous destruction. Extensive experimental work so far carried out has fully confirmed the potential of rubber mounts to handle the massive vibrations caused by earthquakes and demonstrated that the maximum destructive forces developed in medium rise buildings may readily be reduced as much as tenfold. Some buildings have already used this principle. The most recent, and the first in the USA is in the construction of a civic low centre in San Bernardino in California on a site within 16 km of the San Andreas fault. This building incorporates the latest knowledge and experience on base isolation.

An important extension to this concept is the protection of sensitive equipment within a building by mounting such equipment on rubber bearings. Obvious areas where such protection will be of value are in isolating vulnerable parts of nuclear reactors.

Architects and engineers who design buildings are rightfully cautious and afraid of failure. Reasons for delay in applying this base isolation technique are no longer scientific or technical but are associated with resistance to change. However there are encouraging signs of increasing interest and confidence and it is anticipated that this method of greatly increasing earthquake safety will soon gain wide acceptance.

The offshore oil industry is using wide ranging technologies to solve its new problems. One proposed application for natural rubber is in a totally novel type of oil rig designed from drilling in deep water up to 1000 m in depth. The tower rests on a fixed base through an articulated joint with acts through the deformation of curved rubber steel laminated pads. On the topside rubber is used in more conventional applications as fenders to protect against accidental impact ; as mountings to living quarters to reduce the effect of waves ; as shock cells, cushions and blow out preventers in oil riser pipes ; all to protect against damage.

So far we have mentioned just a few of the many and wide ranging applications of rubber in engineering applications. These have been selected merely to illustrate the versatility and development potential of rubber in this area of use. I would like to conclude by mentioning two novel applications which are currently emerging from the " drawing board " stage.

It seems unfortunate that the energy expended in getting vehicles moving should be wasted as heat when the vehicle is braked. Typically in urban travel with one or two stops a mile half of the energy is dissipated in braking. Several suggestion for regenerative braking systems have been made ; and rubber with an energy storage capacity two orders of magnitude (100 times) higher than that of a steel spring is a very suitable candidate for such applications. Road trials have already been carried out on a device that allowed the engine of an automobile to be stopped as at traffic lights and automatically restarted by the energy stored in a rubber spring. Laboratory tests on another device winding up an extended rubber rod in torsion have confirmed the potential for storing energy for much larger systems such as railcars.

Many potential sources of power are being canvassed to replace fossil fuel. If wave power is used, rubber has many predictable roles to play in sluice seals, gaskets and flexible connectors. But the elastic properties of rubber suggest a more active role such as to use wave movements, to operate a battery of hose pumps connected to a flexible floating mattress in which the cyclic deformation of rubber hose produced by waves pumps water through a turbine. A device 50 metres long 10 metres wide could generate 250 watts of electricity, enough for a remote coastal community.

For all of the applications discussed natural rubber is the polymer of choice. It possesses the desired combination of properties of high extensibility, high strength, high fatigue resistance, low creep, high energy absorption with high resilience and good electrical, liquid, gas and thermal resistance.

The engineer can be offered materials with a very wide spectrum of properties by compounding natural rubber with appropriate fillers, vulcanizing agents, protective chemicals and processing aids. There is now promise that with suitable chemical modification of natural rubber an even wider range of properties will be available.

With the proper exploitation of scientific and technical skills currently available mechanical and civil engineers can rely on properly desinged rubber components performing their function year after year without the need for constant and costly attention.

The question which needs to be asked is " Will the natural rubber required be available " ? The answer must be " Yes " but the industry will be short-changing itself if it means the removal of natural rubber from other applicational areas.

Most of the applications mentioned represent relatively small tonnage off takes of natural rubber, but in total they provide a significant proportion of the amount of rubber going into non-tyre uses. Already about 150,000 tonnes of natural rubber are used annually in steel — rubber bonded engineering components, together with rubber used in other engineering applications is, next to latex applications, the second largest area of non-tyre use of natural rubber and promises to grow rapidly in the years ahead. It is also an area in which natural rubber producing countries seeking greater industrialization of their resource-based industries could correctly and effectively develop. It provides an opportunity to be grasped. The task is certainly easier than entering the highly sophisticated manufacture and highly developed export market for tyres. But it also has an additional challenge. It involves ascertaining, predicting, and satisfying consumer requirements for novel solutions to both new and existing applicational problems in which the fullest use is made of composites with natural rubber as one of its components.

DISCUSSION

Q — K. P. FERNANDO, (University of Moratuwa) : It is reported that NR is susceptible to biological degradation. The water industry in UK has now abandoned the using of sealing rings made of NR and are using EPDM as a substitute. Has MRPRA taken any action to improve the microbiological resistance of NR.

A — L. MULLINS, (UNIDO, UK) : The wisdom of replacing NR sealing rings with EPDM has been questioned in the UK because the seals are inferior to NR in sealing qualities although the microbiological resistance is higher.

The MRPRA has done work on this and is confidant that formulations are available which make NR perform well in this application. Details of these formulations could be obtained from MRPRA.

Q — DHARMASENA : Could you elaborate on how power is generated using NR ?

A — L. MULLINS, (UNIDO, UK) : When a rubber hose is stretched the volume inside the hose decreases. So when a hose filled with water is stretched, water gets squeezed out of the hose. This water is used to drive the turbine. A hose 50m long and 10m wide will generate enough electricity for a fishing village.

Q — R. WIJEWANTHA, (EDB) : (i) Would you expand on the subject of energy storage using NR ?

(ii) Is data available for practical applications ?

A — L. MULLINS, (UNIDO, UK) : (i) An extended rod of rubber is twisted in torsion. When the energy stored is released it can be used to drive a rail car or an automobile.

(ii) No published data is available on the practical applications. There has been experimental work by two groups of workers where large amounts of energy are stored.

THE USE OF RUBBER BEARINGS FOR VIBRATION ISOLATION AND EARTHQUAKE PROTECTION

By

C. J. DERHAM AND K. N. G. FULLER
(Malaysian Rubber Producers' Research Association Brickendonbury, Hertford SG 13 8NL, England)

ABSTRACT

Vibration in buildings has become an important problem owing to increased heavy road traffic and the development of sites previously thought unsuitable because of their proximity to roads and railways. This paper describes the use of large rubber bearings to isolate the superstructure of buildings from the vibrations experienced by the foundations. It also deals with the extension of this concept of base isolation to the protection of buildings from earthquakes. Studies have shown that rubber bearings can be constructed to isolate the superstructure from the ground accelerations produced during an earthquake, and that such a system offers distinct advantages over existing methods of protection.

Rubber Bearings

During the mid - 1950's research led to the development of multilaminar rubber and steel bearings to replace the mechanical bearings then used to support bridge decks. The bearings have to be soft in shear so that the thermal expansion of the bridge deck imposes low loads on the supporting piers, and yet very stiff vertically to minimize any movement in that direction. Rubber bearing can be readily designed to meet these requirements.

The compression characteristic of rubber blocks are normally considered in terms of the shape factor, S, of the block, defined as the ratio of the loaded cross-section to the total force free area. Thus for a rectangular block of thickness, D, length, L, and width, B :

$$S = LB/[2D(L + B)]$$

The compression modulus E_c of the block is given by

$$E_c = 3G(1 + 2S^2) \qquad (1)$$

where G is the shear modulus at the appropriate strain ; a working strain has to be specified in order to take account of the non-linear stress-strain characteristics of filled rubbers. For high shape factors the bulk compressibility of the rubber is no longer negligible, and the value of E_c given by equation (1) must be divided by $(1 + E_c/K)$, where K is the bulk compression modulus. The dependence of E_c on the shape factor enables the verticle stiffness of a block of given size to be substantially increased by the inclusion of horizontal metal plates in the block. Provided the plates are firmly bonded to the rubber, they divide the block into a number of layers of high shape factor whilst the overall shear stiffness is unaltered.

Rubber-steel bearings are now widely used to support bridge decks. Natural rubber and polychloroprene are the most commonly used polymers in this application ; the former, however, can better withstand exposure to low temperature (0°C) without stiffening due to crystallization.

Vibration Isolation

Principles

The use of rubber-steel laminated bearings as vibration isolation springs for entire buildings began during the mid-1960's.

The principle of vibration isolation is one of detuning. This is achieved by mounting the structure on springs so that its natural frequency, n_f, is lower than the disturbing frequency, n. The transmissibility, t, of a spring is given by :

$$t = \left\{ \frac{1 + \tan^2\delta}{(1 - n^2/n_f^2)^2 + \tan^2\delta} \right\}^{\frac{1}{2}}$$

where tan δ is the loss tangent of the spring. Fig. 1 shows the transmissibility as a function of n/n_f for a value of tan δ of 0·14 — a figure typical of an engineering natural rubber. It is seen that for efficient attenuation the natural frequency need to be less than about one-third of the disturbing frequency, which is usually in the range 20 — 50 Hz. For a structure, mass m, mounted on an ideally eleastic spring of stiffness Y the natural frequency is

$$n_f = \frac{1}{2\pi} (Y/m)^{\frac{1}{2}}$$

Natural rubber-steel laminated bearings can readily be designed to have a vertical stiffness so that the mounted structure has the required natural frequency. Each bearing might typically support a load of 200 tonnes. Although other systems such as steel springs could meet the requirements of equation (3), the natural rubber bearings are preferred because they eliminate direct transmission at audio frequencies, and they provide the desired level of internal damping – too little results in the possibility of resonance whereas too much reduces the degree of isolation attainable (see equation (2).)

A study (Derham & Waller, 1975) of the first building mounted on rubber bearings has shown that in the frequency band 3 — 30 Hz the vibration velocities were only about a quarter of those observed in the previous building on the site. The performance of the bearings has been monitored since construction. No physical deterioration has occurred, and current estimates confidently predict a service life in excess of a hundred years.

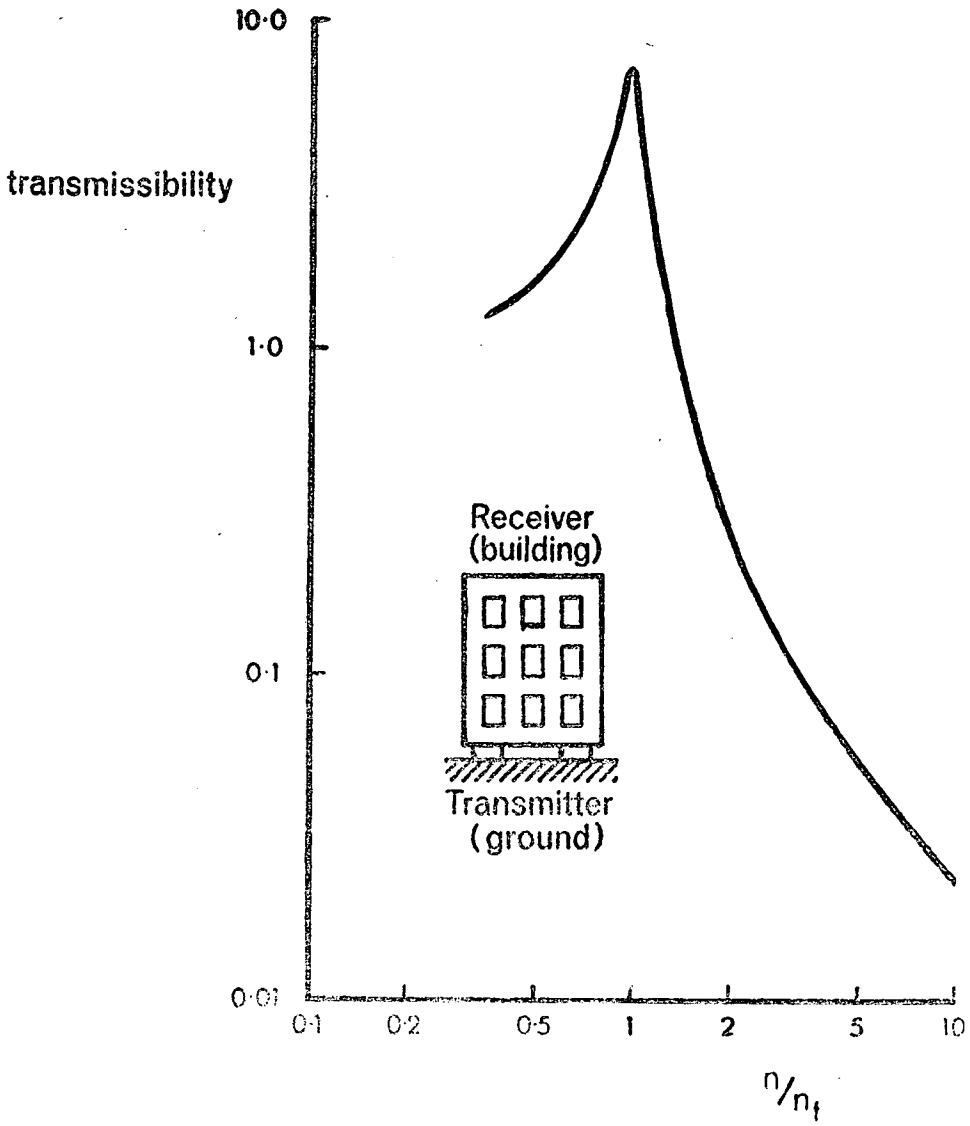


Fig. 1. The transmissibility of a spring as a function of (disturbing frequency) / (natural frequency) - n/nf. Curve is for a spring with a loss tangent of 0.14.

Rubber properties and the design of building mounts

The most important rubber parameter in the design of bearings for vibration isolation is the value of the stiffness to be used in equation (3). Filled rubbers are non-linear in their stress-strain behaviour. This is evident from Fig. 2 which shows schematically the load-deflection characteristic of a rubber bearing as measured by applying a continually increasing deformation. The effect of vibrations is to apply small cyclic deformations to the bearing about the static load deflection, P. The cycling produces the ellipse, S, drawn schematically in Fig. 2. The incremental or dynamic stiffness appropriate to the cyclic deformation is given by the slope of the major axis of the ellipse. It can be seen that this slope is not given by the tangent to the load-deflection curve at the working deflection, P. Effects associated with the presence of the filler result in the incremental stiffness being larger than the tangential stiffness — the so-called ' dynamic/static ' ratio. It should be emphasised that even if the cyclic deformation is applied quasistatically a ratio significantly above unity is still obtained.

It is convenient from the designer's viewpoint for the incremental stiffness to be constant over the range of frequencies and amplitudes associated with the vibrational disturbances. For a typical natural rubber engineering compound the incremental stiffness changes little with the frequency of cycling (for cycles of amplitude 2%, it increases by only about 10% as the frequency is raised from 0·1 to 3 Hz), or with amplitude (for values ranging up to about 10%). The corresponding variations for other polymers can be considerable. For the bearings to function effectively the incremental stiffness should remain constant over the range of service temperatures. Thus the fact that low temperature stiffening occurs less readily with natural rubber gives it another advantage over most of the synthetics.

Other properties of the rubber have to be considered in order to ensure that the bearings perform satisfactorily throughout their service life. Rubbers can be extremely durable materials and in fact atmospheric attack on the steel plates occurs more easily than attack on the rubber. Thus the rubber/steel laminates are encased by an outer layer of rubber which protects both the plates and the steel-to-rubber bonding. The large volume to surface ratio of the rubber in the bearings offers protection from degradants, such as oil or oxygen, able to diffuse into the rubber. The addition of antioxidants gives further protection against oxidative attack. Ozone cracking, to which rubber is susceptible, can also be prevented by chemical additives ; even without such protection the growth of cracks in bearings loaded in compression is confined to a thin surface layer, for it is only there that the tensile stresses necessary for the growth of ozone cracks exist.

Creep of the rubber can occur due to both visco-elastic (*i.e.* physical) effects and chemical effects such as oxidation. Natural rubber has a low physical creep rate, so that with this polymer there should be no difficult in reducing the total amount of creep over the design life of the bearings to an acceptably small value. This view has been confirmed by the study (Derham & Waller, 1975) of a building mounted on bearings. The total creep after 8 years was less than 1 mm (*i.e.* 10% of the initial deflection) — a figure agreeing well with projections based on laboratory experiments lasting a few days.

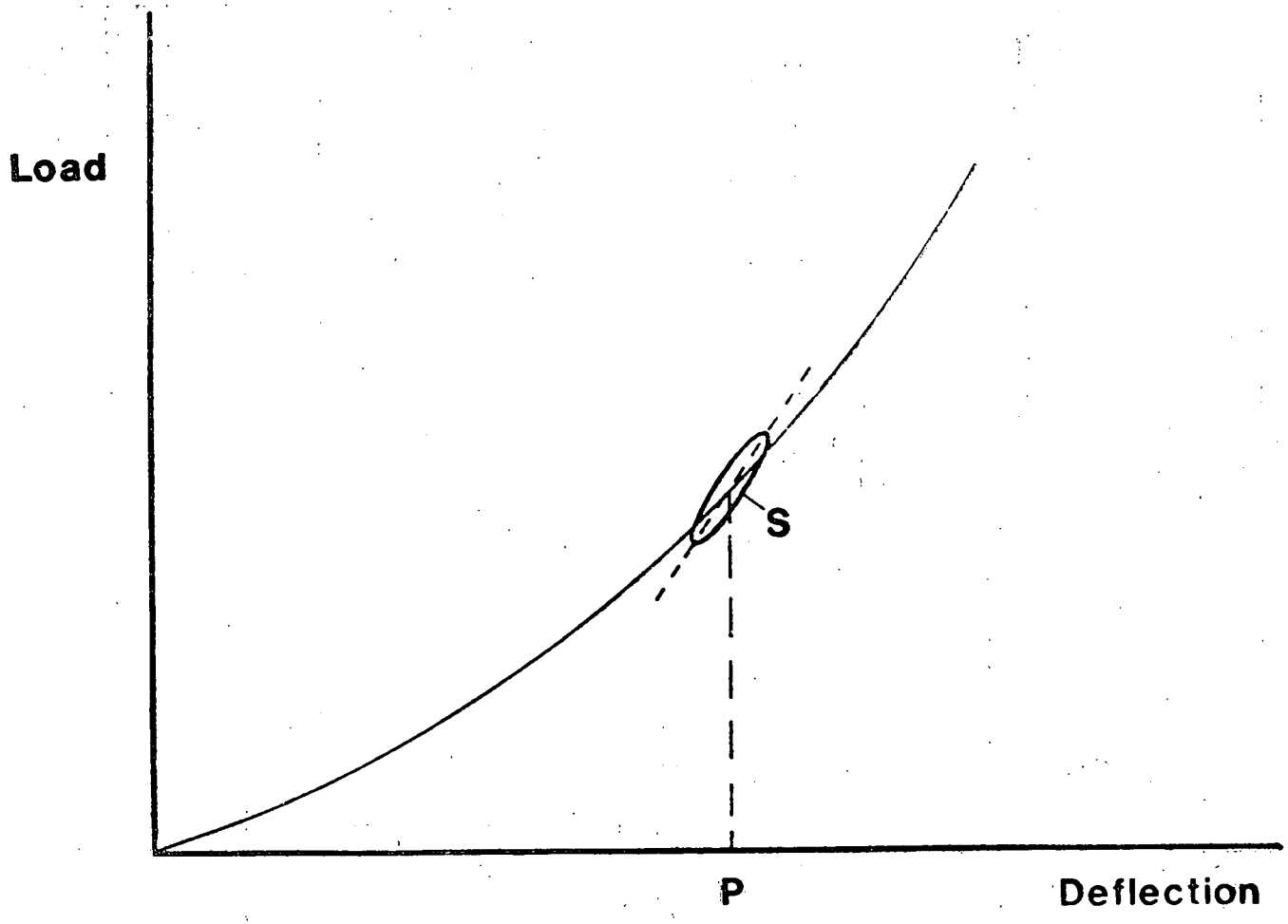


Fig. 2. Load-deflection characteristic of a rubber bearing. The ellipse, S, represents a small cyclic deformation applied about the static deflection, P.

Strong rubbers such as natural or polychloroprene can withstand very large deformations without failure. They should therefore have more than adequate strength to accept the shear strains that develop in the bearings at the edge of the bond to the plates. Care must be taken in design, however, to ensure that any overturning moments do not put significant tensile stresses on the bearings. Such stresses would lead to the development of negative hydrostatic strains in the thin bonded sections of rubber, and if the stresses reach levels approximately equal to the Young's modulus, rupture of the rubber due to cavitation can occur.

The stability of the bearings is an important factor to be considered. It is necessary to ensure that the imposed load, P, is small compared to the load, P_c, that will produce buckling. For circular bearings of large shape factor, the safety factor, P_c/P can be expressed as (Derham & Thomas, 1983) :

$$\frac{P_c}{P} \simeq \frac{30 n_f^2 h}{g}$$

where n_f is the vertical natural frequency, h the thickness of each rubber layer and g the acceleration due to gravity. Interestingly, stability for a given n_f requires a certain minimum rubber layer thickness.

Earthquake protection

Base isolation

The success of rubber-steel laminated bearings in providing isolation from noise led to research aimed at extending their use to seismic protection. Earthquakes are simply ground oscillations of very large amplitude and rather low frequency. The predominant mode of excitation is horizontal, not vertical as in normal ground-borne noise. The dominant frequencies depend on a number of factors and must be evaluated for each site. Past seismic records indicate that local site conditions strongly influence the frequency spectrum of an earthquake (Seed, *et al*, 1976). Rock and stiff soils typically result in most energy being associated with frequencies of 2 — 5 Hz ; softer soil conditions lead to the energy being spread over a broader range with a considerable component associated with frequencies of 1 Hz or less.

Many stiff medium-rise structures have a natural frequency in the range of 2 — 5 Hz, and thus could actually resonate in sympathy with an earthquake. The response of the structure to earthquake disturbance should be greatly reduced by mounting it on bearings with a low shear stiffness ; the horizontal natural frequency of the structure could thus be brought down to a value below the predominant frequency range of the earthquake. Rubber-steel laminated bearings can be designed to give a mounted structure a horizontal frequency down to 0·4 Hz, and yet provide sufficient vertical stiffness to prevent rocking of the structure. Valus below 0·4 Hz are not likely to be achieved for reasons associated with stability of the bearings. This frequency limit means that effective base isolation could be provided for buildings on rock or stiff soil sites ; the system is less feasible on soft soil sites, where disturbances at frequencies below 1 Hz are experienced.

Preliminary calculations of response of base-isolated structure

The initial theoretical studies (Atkins research and Development report 1977) calculated the accelerations experienced by a five-storey shear wall structure when subjected to a typical earthquake having a peak ground acceleration of 0·3 g. Comparison was made between the response for the structure fixed firmly to the ground (*i.e.* conventionally built) and for the structure mounted on springs such that it had a natural frequency of 0·5 Hz. A figure of 10% was used for the internal damping of the springs and structure.

The accelerations experienced at various levels of the structure are shown for the two cases in Fig. 3. For the fixed base condition the accelerations increase with height to reach a maximum about three times that of the input acceleration. The mounted structure in contrast behaves essentially as a rigid body moving with an acceleration about only one-third of the peak input. Thus the reduction in the natural frequency to around 0·5 Hz results in the maximum forces experienced by the structure being reduced about ten-fold.

This preliminary study confirmed the feasibility of markedly reducing the accelerations experienced during an earthquake by a structure built on stiffer soil sites. The reduction in the accelerations offers several important advantages for the technique of base isolation over the conventional method of earthquake protection by reinforcement of the structure. Not only does the building itself require less strengthening, but the occupants and the internal fixtures are likewise protected from large accelerations. For buildings such as hospitals it is as important to safeguard the equipment as the structure. The reduction of differential movement within the structure also lessens the problems of shedding of external cladding, and breaking of window glass and outside fixtures ; the safety of people in the street is thus improved.

Experimental tests of base-isolated model structures

The performance of rubber-steel bearings has been assessed in tests carried out on the shaking table at the Earthquake Engineering Research Center, University of California, Berkeley. The table can be excited either by sinusoidal inputs or by inputs derived from earthquake records ; it is able to move vertically as well as in one horizontal direction.

Two highly instrumental model structures have been tested. Some results obtained with the 20 tonne, three-storey single bay structure shown in Fig. 4 are summarized here ; a more detailed description of the experiments is given elsewhere (Derham *et al*, 1977). The model was subjected to various earthquake inputs both with a conventional foundation (*i.e.* bolted directly to the shaking table) and when mounted on rubber bearings. Because of the difficulty of producing stable bearings which would give a horizontal natural frequency of 0·5 Hz when supporting a load of only 5 tonnes, special low modulus vulcanizates had to be developed (Teo and Pond, 1977).

Fig. 5 shows the floor displacements at the various levels for the model when fixed directly to the shaking table. The input was the N-S horizontal component of the 1940 El Centro earthquake ; the peak input acceleration was 0·30 g. The dominant response of the structure is at its first mode natural frequency of 2 Hz. The displacements increase

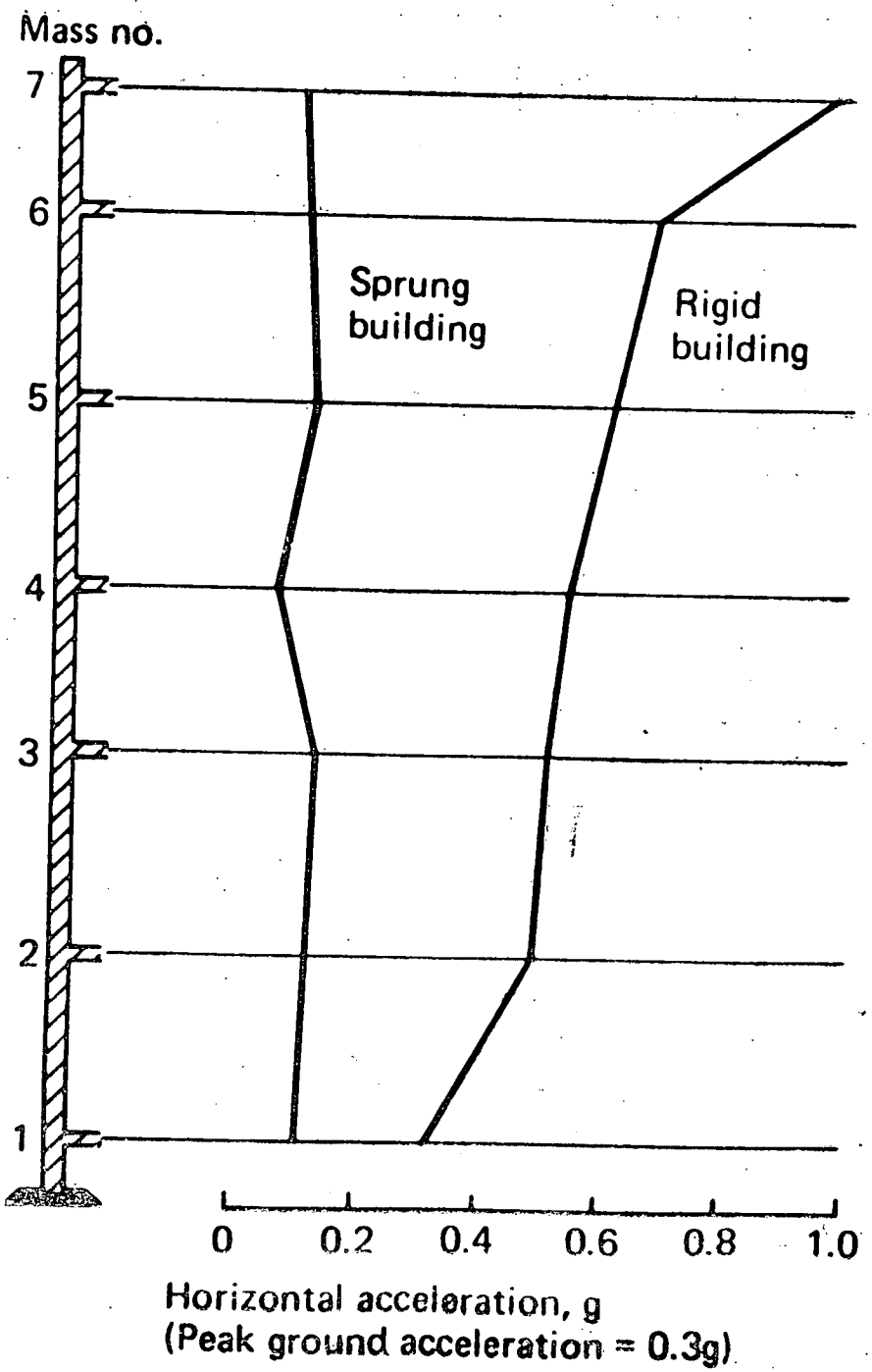


Fig. 3. Computed response to a typical earthquake for a five storey structure a) mounted on springs, b) conventional, fixed foundation.

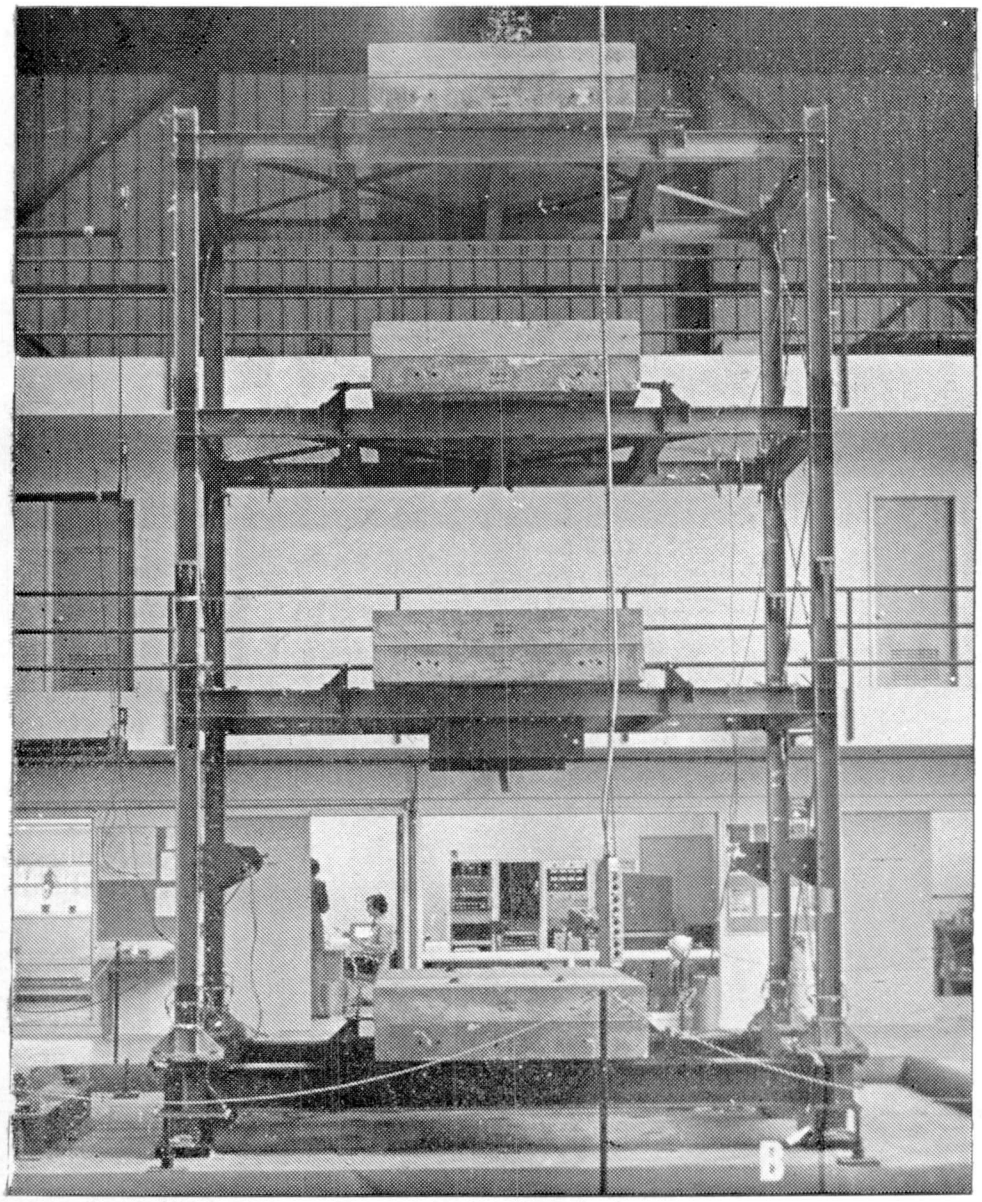


Fig. 4. 20 tonne model structure on the shaking table of Earthquake Engineering Research Center, Berkeley, California. One of the rubber bearings, B, is indicated.

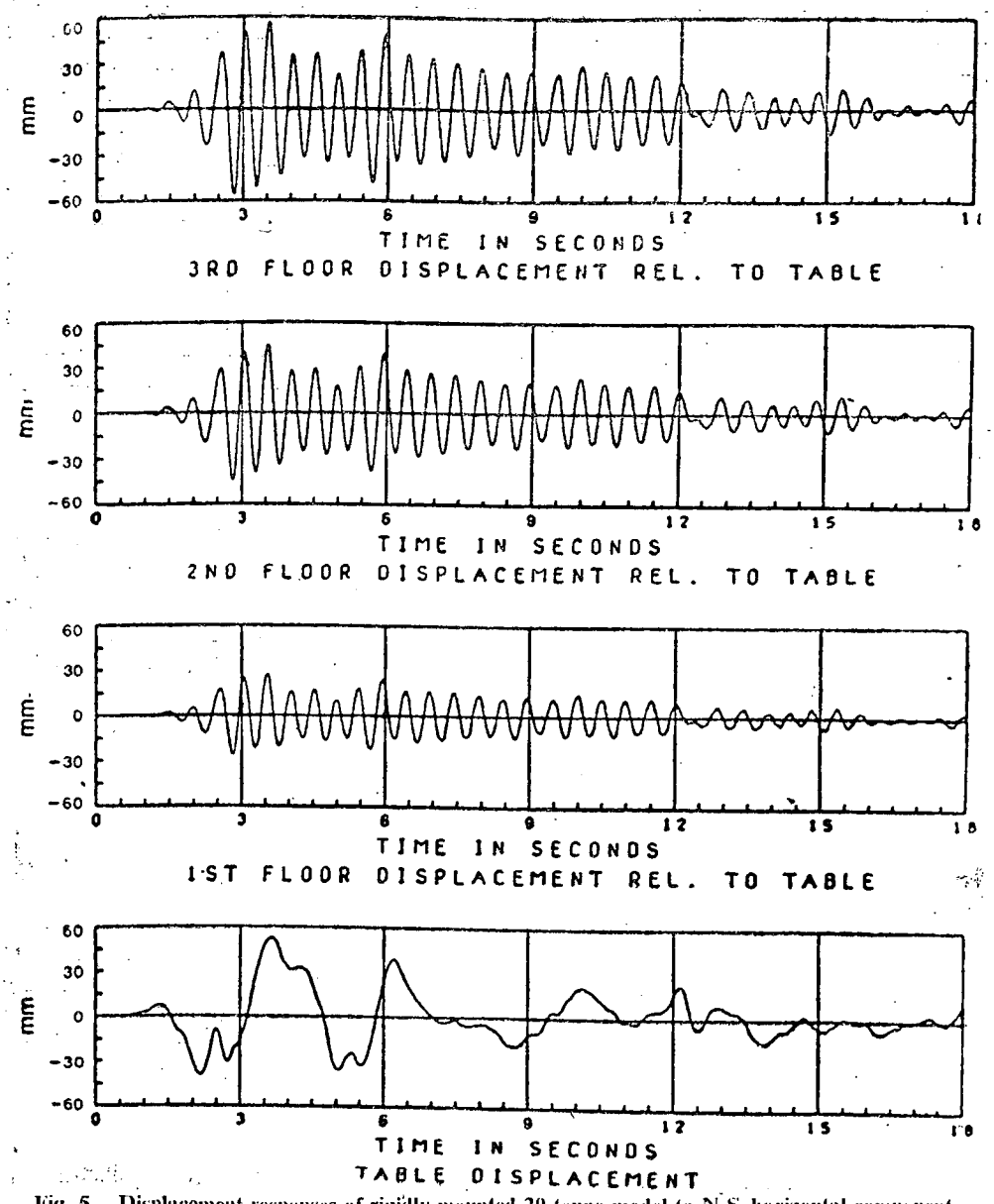


Fig. 5. Displacement responses of rigidly mounted 20 tonne model to N-S horizontal component of 1940 El Centro earthquake.

with height, as expected for a rigid foundation, to a maximum of 5·8 cm. The accelerations experienced at 1st, 2nd and 3rd floor levels are respectively 0·6, 0·9 and 1·2 g; the amplification of the input acceleration is similar to that predicted in the preliminary theoretical study discussed earlier. Mounting the model on rubber bearings and imposing the same input resulted in the displacement response shown in Fig. 6. The dominant response is now at the reduced natural frequency — about 0·55 Hz. Although the maximum displacement of the structure has increased to 8 cm, the much lower frequency of movement reduces the maximum acceleration experienced to about 0·12 g — a ten-fold reduction compared to the fixed-base model. The peak shear forces and overturning moments are also much reduced (by a factor of about eight) in the mounted structure, as is seen in Fig. 7. The results given in Figs. 6 and 7 were obtained using bearings constructed with an NR vulcanizate having a loss tangent of 0·10 at 0·6 Hz and 100% shear strain. Similar tests using a rubber with the same stiffness characteristic but a loss tangent of 0·03 showed that the higher damping rubber led to a much faster attenuation in the displacement response. Higher damping also acts to prevent resonance; this might otherwise occur because the broad frequency spectrum of earthquakes is likely to result in some energy input at the natural frequency of the mounted structure. Although high damping is beneficial in these two respects, excessive damping would vitiate the system as it relies not on adsorption of the vibrational energy of the disturbance but on isolation.

The experimental tests, like the preliminary theoretical study, show that the technique of base isolation by mounting a structure on rubber bearings is capable of dramatically reducing the destructive forces experienced during an earthquake. The test results also confirm that the displacements and acceleration responses at all levels are nearly the same, and thus the mounted structure behaves as a rigid body. Such a response makes the detailed analysis of real structures much more tractable.

Vertical earthquake component

The base isolation system discussed above is designed to attenuate only horizontal earthquake disturbances. Although there may be a vertical component to an earthquake it is potentially less damaging for two reasons. First, in most cases the vertical accelerations are substantially less than the horizontal ones, and secondly, structures are intrinsically strong vertically. An attempt to reduce vertical earthquake forces by making the rubber bearings of a very low vertical as well as horizontal stiffness would undoubtedly lead to coupling between the horizontal and vertical motions and thus to unacceptable rocking of the structure. Moreover the construction of bearings with a vertical stiffness low enough (*i.e.* over 100 x less than those typically used in vibration isolation) to give significant attenuation is not practicable.

As the rubber bearings are not designed to protect against vertical earthquake movements, it was necessary to check that they would not amplify the vertical component. A shaking-table test was performed with both horizontal and vertical accelerations applied to the 20 tonne model mounted on bearings. The vertical accelerations experienced by the model were virtually identical to those of the input signal. Furthermore the horizontal response of the model was barely distinguishable from that recorded in the absence of a vertical component.

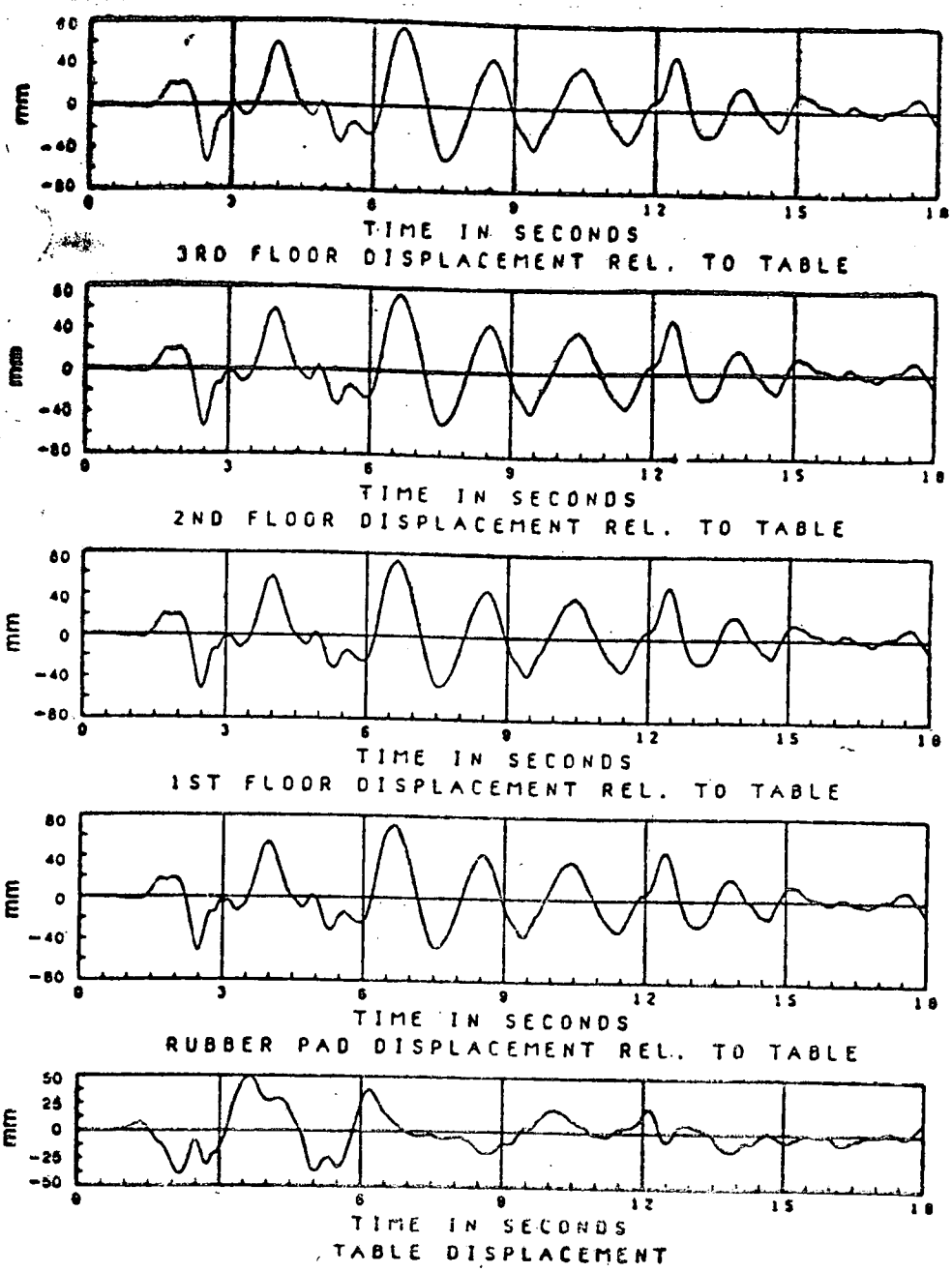
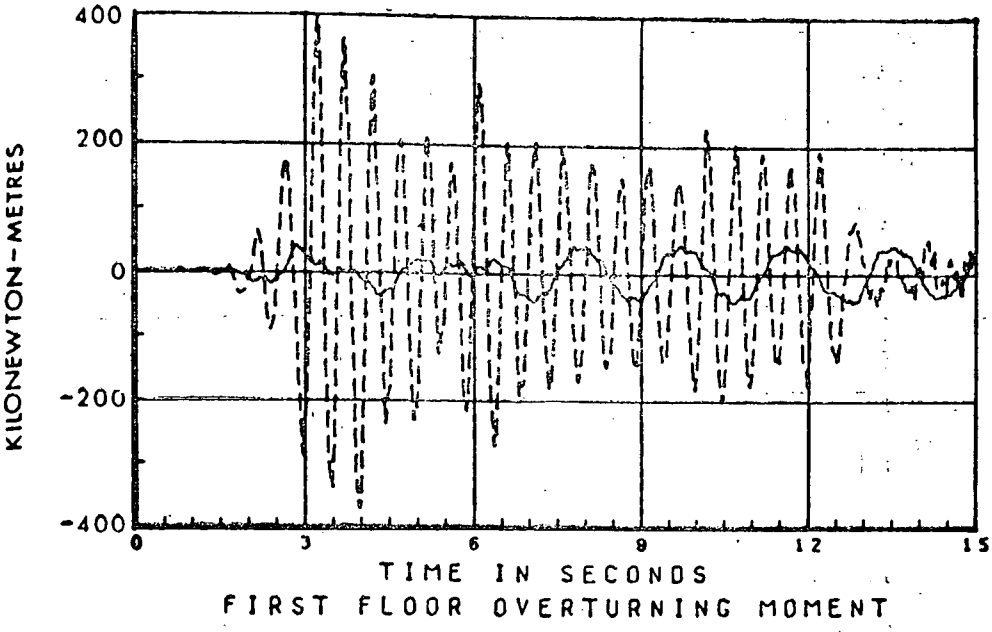


Fig. 6. Displacement responses relative to table of 20 tonne model mounted on rubber bearings. Input as for Figure 5.



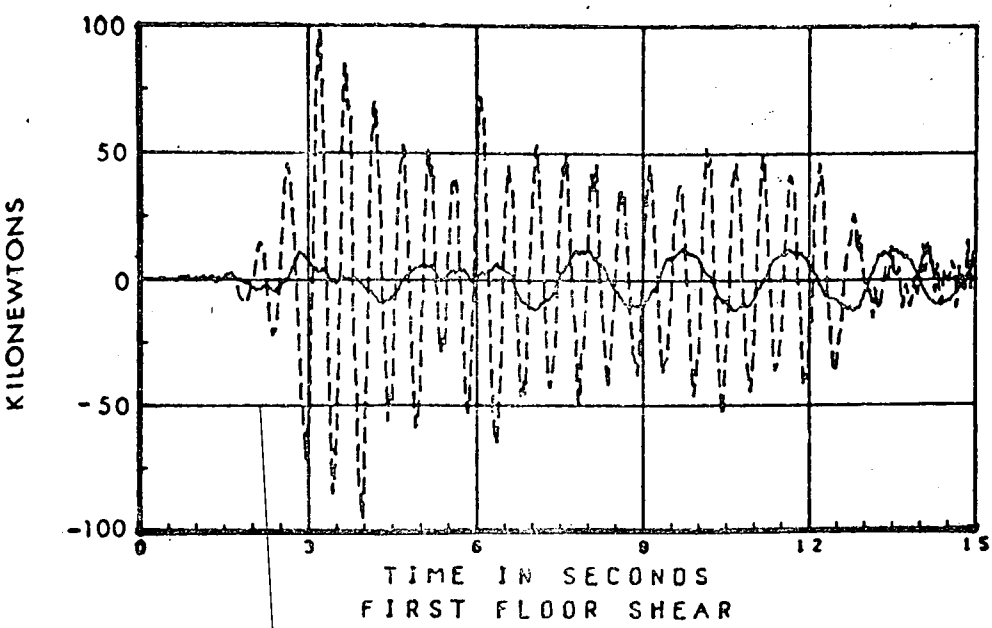


Fig. 7. Horizontal shear forces and overturning moments for 20 tonne model excited by same input as for Figure 5. Full line is for model mounted on rubber bearings; broken line is for rigidly mounted case.

Elastomer characteristics

Modelling the rubber for design studies

The prediction of the response of a conventionally protected building to an earthquake is an uncertain exercise, as the response is likely to be strongly dependent upon the quality of the on-site workmanship. Moreover, should it be necessary to take account of yielding and the plastic response the calculations would become extremely difficult. A base-isolated structure will essentially respond as a rigid body, and the forces transmitted to the structure will be sufficiently low for them to fall well within the elastic range. Thus, provided the behaviour of the rubber bearings can be accurately modelled, the prediction of the response of the structure as a whole is a more straightforward and reliable exercise than for a conventionally protected structure.

The rubber bearings have been successfully modelled (Derham, *et al*, 1978) by the standard linear solid, which consists of an elastic element in parallel with a single Maxwell element (a viscous and an elastic element in series). Predictions of the response of a mounted structure have been compared with results from the shaking table. Very close agreement between calculation and experiment was obtained for two rubbers with different loss tangents. It was found that the damping of the loaded bearings was higher than expected from the loss tangent of the rubber components. The reason for the increase is associated with the small height change that occurs when a large shear deformation is applied to a bearing subjected to a constant vertical load (Thomas, 1982).

Non-linear behaviour : wind restraint

Although the rubber is well approximated by a linear viscoelastic model at the large shear strains expected during an earthquake, the stress-strain behaviour does show significant non-linearities. At small deformations, strains of a few percent, the rubber has a substantially higher modulus than at large strains. By special compounding NR vulcanizates can be produced with a low strain stiffness sufficient to prevent a building mounted on rubber bearings from moving excessively under wind loading (Derham, *et al.* to be published). The necessity to incorporate special wind restraints, which would be designed to break if an earthquake occurred, can thus be removed by exploiting the non-linear character of the rubber.

Design of bearings

The manner in which the vertical stiffness of rubber-steel laminated bearings can be determined from the shape factor has already been discussed in section 2.

The horizontal stiffness, K, of bearings of plan area, A, and z rubber layers each of height h is given by

$$K = GA/zh \qquad (4)$$

where G is the average shear modulus in the appropriate strain range. Equation (4) applies provided the bearing is subjected to a vertical load, P, well below the critical load,

P_c, for buckling. For circular bearings of large shape factor, P_c is approximately given by (Thomas, 1982) :

$$\frac{P_c}{P} = \frac{8\pi^4}{\sqrt{2}} \frac{Pz\, n_f^4}{Gg^2}$$

where n_f is the horizontal natural frequency of the mounted building, and g the acceleration due to gravity. The equation shows that an adequate safety factor (say at least 2) becomes more difficult to obtain for low loads, P, and particularly for low frequencies, n_f. There should be no stability problems, however, associated with a bearing designed to support a load of 100 tons or more and give a natural frequency of 0·5 Hz. An additional factor that may be thought important in assessing the stability of the bearings is the degree of parallelism of the outer plates. A theoretical and experimental study (Thomas 1982) has shown that misalignment of 1° does not decrease the critical load.

During a severe earthquake the rubber bearings are expected to undergo large horizontal deformations. Experimental studies (Derham, *et al* to be published) suggest that displacements of up to 80% of the least plan dimension can be safely withstood. Bending moments set up under a large shear produce hydrostatic tensile stresses. The safe maximum shear suggested ensures that the hydrostatic tensions are insufficient to produce significant cavitation.

Implemented base-isolation schemes

The earliest example of a building mounted on rubber is a school built in 1969 in Skopje, Yugoslavia (Hubacher, *et al*, 1970). The bearings were made entirely of natural rubber with no metal laminations ; this resulted in a low vertical natural frequency (2 Hz) as well as a low horizontal one (0·6 Hz). As discussed in section 4D such a low vertical stiffness is considered unnecessary and may well be undesirable. Another school, completed in France in 1978, has been built on conventional rubber-steel laminated bearings (Delfosse, 1972).

The particular base-isolation system advocated here relies on bearings manufactured from special NR vulcanizates so that wind restraint and high damping are provided without any additional devices. These ideas have been incorporated into the bearings designed for a large local government building now under construction in San Bernardino County, California, 21 km from the San Andreas fault. The building, a $ 30 m Law and Justice Center, is to be mounted on 98 bearings of diameter 76 cm and height 38 cm. The bearings are not all of identical construction as the load supported by each ranges from 100 to 400 tonnes. The steel plates used to make up the laminations are 3·2 mm thick ; the end plates are 32 mm thick. There are 15 to 21 plates incorporated into each bearing. Fig. 8 shows a general view of the bearings after installation. Analysis of the response to the design earthquake showed that the maximum relative displacement at the corner bearings should be 38 cm. Prior to approval of the system four bearings were tested repeatedly up to a displacement of 38 cm, and were found to perform satisfactorily. Afer the test one bearing was sectioned ; no sign of internal damage could be seen.

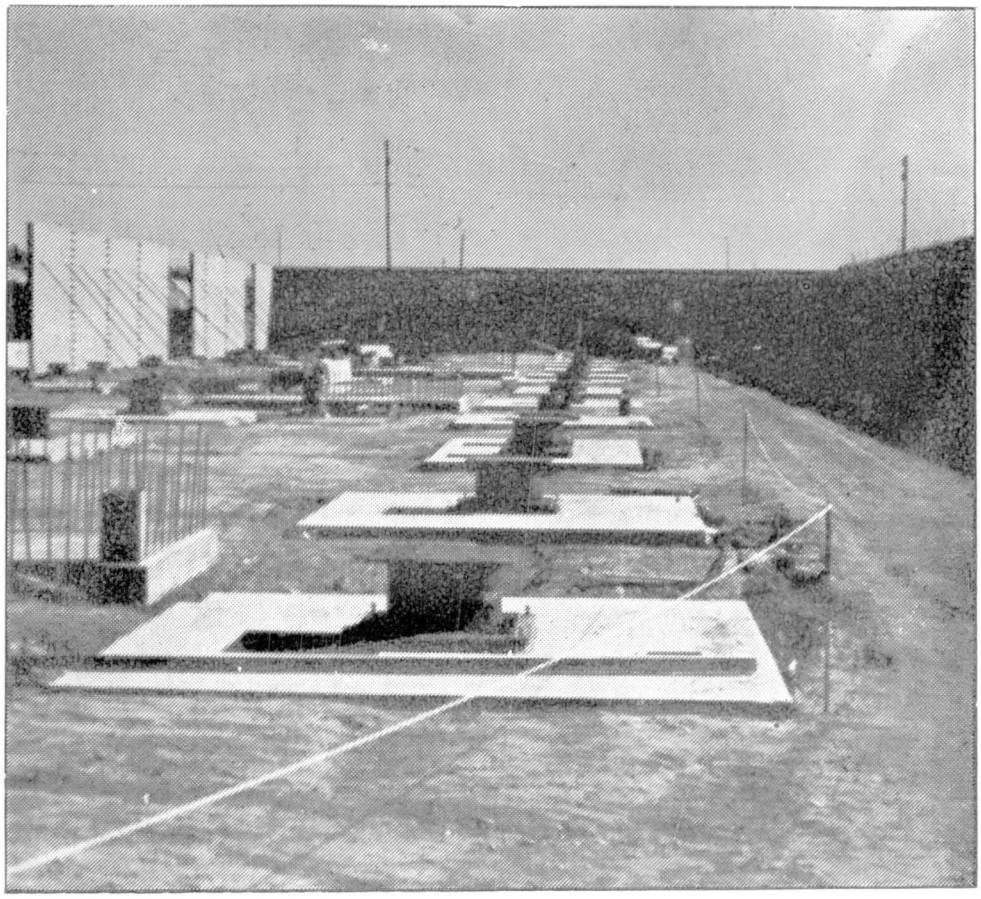


Fig. 8. A view of the rubber bearings after installation on the site of the Foothill Communities Law and Justice Center, San Bernardino, California.

CONCLUSIONS

The use of rubber-steel laminated bearings for the vibration isolation of buildings is now of proven success. The extension of the principles of base isolation to earthquake protection has been shown to be both feasible for stiff soil sites and clearly advantageous when compared with existing methods relying on reinforcement. A major advantage is the protection offered to occupants and internal equipment, as well as the structure itself, because of the marked reduction in the forces experienced during an earthquake. Despite its superiority base isolation should lead to cost savings over a conventionally strengthened structure, particularly as the size of the earthquake designed against is increased.

REFERENCES

ATKINS RESEARCH AND DEVELOPMENT, (1974). Report to MRPRA on the use of rubber springs to protect buildings in earthquake zones.

DELFOSSE, G. C. (1972). *Proc. 6th International Conf. on Earthquake Engineering*, New Delhi, India.

DERHAM, C. J. AND WALLER, R. A. (1975). *The Consulting Engineer*, **39**, 49.

DERHAM, C. J. AND THOMAS, A. G. (1983). *NR Technology*, **14**, 52.

DERHAM, C. J., EIDINGER, J. M., KELLY, J. M. AND THOMAS, A. G. (1977). *NR Technology* **8, 41.**

DERHAM, C. J., THOMAS, A. G. AND KELLY, J. M. (1978). *Proc. of Conf. on Engineering Design for Earthquake Environments*, I. Mech. E., London, 1978.

DERHAM, C. J., KELLY, J. M. AND THOMAS, A. G. Nuclear Eng. & Design, to be published.

HUBACHER, D., STAUDACHER, E. AND SEIGENTHALER, R. (1970). Neue Zurcher Zeitung Technikbeilage, 9·2.

SEED, H. B., UGAS, C. AND LYSMER, J. (1976). *Bull. Sismological Soc. Am.* **66**, 221.

TEO, S. C. AND POND, T. J. (1977). *NR Technology*. **8**, 62.

THOMAS, A. G. (1982). *Proc. of Conf. on NR for Earthquake Protection of Buildings. Kuala Lumpur, Malaysia.*

DISCUSSION

Q — G. SCOTT, (University of Aston in Birmingham) : Have the earthquake bearings being tested for fatigue resistance under service conditions ?

A — C. J. DERHAM, (MRPRA) : Under service conditions one does not expect the bearings to move unless there is an earthquake and hence the bearings will not go through many strain cycles. They have been tested over a few strain cycles and found to be satisfactory. It is not just fatigue in the conventional sense. It is just to ensure that if they are subjected to a very large shear deformation they do have to remain in one piece to be ready for the next earthquake.

A — G. SCOTT, (University of Aston) UK : The shear must be extraordinarily high and there might be breaking of a lot of rubber bonds which would subsequently lead to a process of slower oxidation. I am concerned about the long term effects of the short term shear.

A — K. N. G. FULLER, (MRPRA) : In terms of oxidation resistance, most of the rubber is protected by the rubber outside. In terms of the strength requirements during the large shear, with NR there is no problem.

COMMENT BY DR. MULLINS : In an earthquake we do not see it as a fatigue problem. If the bearing is subjected to a large shear in the earthquake and if the building is protected and does not fall down, then the bearing would have done its job. The buildings can be organised such that the bearings can be replaced after an earthquake.

Q — P. P. JAYASINGHE, (RRISL) : What is the minimum and maximum thickness of rubber between laminations in bridge bearings ? Are there any limitations ?

A — C. J. DERHAM, (MRPRA) : There are no limitations on the maximum thickness except in regard to the stability of the bearings. As far as minimum thickness is concerned you can have a block of steel which will make the rubber very thin.

Q — R. SAMARASINGHE, (IDB) : What is the lifetime of the building bearings ? Are they replaceable ?

A — C. J. DERHAM, (MRPRA) : (i) 100 years or more. Probably longer than that of the building.

(ii) There is no reason why bearings could not be replaced.