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Role of Some Non-rubber Constituents on Thermal Oxidative Ageing of Natural Rubber

H. HASMA* AND ALIAS BIN OTHMAN*

Free tocotrienols isolated from Hevea brasiliensis *latex were shown to protect both raw and vulcanised natural rubber (NR) against thermal oxidative degradation. They conferred a maximum protection against ageing at a level of 0.1% with the* γ*-tocotrienol giving a higher protection than the* α*-tocotrienol. The antioxidant activity of the tocotrienols was retained even when the rubber was subjected to a high drying temperature (110°C) or to bacterial activity which resulted in the rubber being very prone to oxidation. The low resistance of some auto-coagulated rubbers to ageing was found to be associated with a higher free copper content which could be removed by soaking the Heveacrumb in thiourea or phosphoric acid.*

The Hevea *proteins and amino acids, unlike the tocotrienols, did not confer any significant protection against thermal oxidative ageing, although the overall tensile strength values of rubber containing amino acid were comparatively higher.*

Natural rubber (NR) being an elastomer of appreciable olefinic unsaturation, is very prone to thermal oxidative degradation which generally results in deterioration of its physical properties both in the raw and vulcanised forms. Fortunately, being a natural product, NR is endowed with some antioxidants which render it more resistant to oxidation than its counterpart, synthetic polyisoprene. The degree of resistance of NR to oxidation is however not consistent, depending on the methods of processing the rubber. Some rubbers especially the auto-coagulated cuplumps and polybag rubbers are more susceptible to oxidation than the normal acid coagulated ones. This variation, to a large extent, is attributed to the differences in their non-rubber content.

Non-rubber substances although present at a level of about 5% could exert a considerable influence on ageing of NR. The content of some of these substances like the tocotrienols[1,2], proteins[2] and amino acids[3] had been shown to have a positive relationship with the resistance of NR towards oxidation. They could thus act as natural antioxidants for NR. Some inorganic constituents like copper, manganese and iron, on the other hand, were shown to be deleterious to NR by acting as pro-oxidants[4]. The ratio of these two groups of compounds in NR will thus control the susceptibility of NR towards oxidative degradation.

This paper discusses the role of some of these non-rubbers namely tocotrienols, copper, proteins and amino acids on the ageing of NR.

MATERIALS AND METHODS

Materials

Purified rubber was prepared from the rubber phase of ultracentrifuged RRIM 600 fresh latex and washed three times with sodium dodecyl sulphate prior to washing with distilled water. The polybag rubbers were obtained from the RRIM Experiment Station, Sungai Buloh. The amino acids were of commercial grade.

Isolation of Tocotrienols, other Neutral Lipids and B-serum Proteins

Tocotrienols and other neutral lipid fractions were isolated from fresh *H. brasiliensis* latex following the methods outlined by Hasma and Subramaniam[5].

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The B-serum proteins were obtained from the bottom fraction of the ultracentrifuged fresh latex. The bottom fraction was first freeze-thawed three times, recentrifuged and the clear B-serum collected. Ammonium sulphate was added to the B-serum to saturation level and the mixture left in the refrigerator overnight. The precipitated proteins were collected from the recentrifuged mixture, redissolved in water and dialysed against water to remove any ammonium sulphate collected together with the proteins. The dialysed mixture was then freeze-dried to give a powder form of ammonium sulphate precipitated B-serum proteins.

Incorporation of Tocotrienols, other Neutral Lipids, Proteins and Amino Acids into Rubber

The tocotrienols and other neutral lipids were incorporated into acetone extracted rubber by the swelling method. Small pieces of rubber weighing about 10 g were swelled in the chloroform solution of the lipids. The mixture was swirled with a glass rod until no more rubber stuck to the wall of the beaker. The swelled rubber was pressed into sheet and dried in the fume cupboard until free of solvent. The swelled rubber pieces containing tocotrienols and other neutral lipid fractions were subsequently blended with the remaining bulk of the rubber.

The proteins and amino acids were added in aqueous solution to purified latex. They were first dissolved in a minimum of water and then added to purified latex. The mixture was thoroughly mixed before being film dried on glass plates at room temperature. Fans were used to speed up the drying process to overcome the problem of bacterial action on the latices if the mixture was exposed unnecessarily long to the wet condition. The dried films were blended to give rubbers containing the required non-rubber components.

Testing of Rubbers

The oxidisability of raw and vulcanised rubber was assessed by the Plasticity Retention Index (PRI, %) and retention of tensile strength values, respectively. The PRI test involved the measurement of the rapid plasticity before (P_0) and after heating in an air oven at 140°C for 30 min (P_{30}) with the Wallace plastimeter[6]. For the tensile strength test, the vulcanised test pieces were prepared based on the ACS 1 formulation and press-cured to maximum torque. Overcuring was prevented by dipping the cured samples immediately in water after moulding. The vulcanised test pieces were aged at 100°C for one day and the retention of tensile strength was determined using the standard procedure[7].

Determination of Tocotrienol and Copper Content

The amounts of tocotrienols and copper present in the rubber were determined by gas liquid chromatography[5] and atomic absorption spectroscopy[8], respectively.

Infra-red Spectroscopy

The infra-red (IR) spectra were obtained from toluene solution on a Beckman IR 4250 Spectrophotometer.

RESULTS AND DISCUSSION

Tocotrienols

The amount of tocotrienols varied from 0.02% to 0.15% in fresh *H. brasiliensis* latex, depending on the clone. This is comparable with the amount of tocotrienols (0.09%) present in the ammoniated latex concentrate of unspecified *Hevea* clone(s) determined by Dunphy *et al.*[9] However, some of these tocotrienols would be lost during processing of latex to dry rubber.

The amount lost depended on the method of processing the rubber. *Table 1* shows a typical level of tocotrienols present in RRIM 701 latex processed by different methods. All the rubber samples (acid and auto-coagulated) dried at 60°C or 110°C, contained about 0.1% tocotrienols, 0.1% less than normally present (0.2%) in fresh latex. Greater loss was incurred on diluting the latex to 15% d.r.c. to prepare sheet rubbers. The air-dried sheet rubbers, unmatured or matured for one or three weeks

TABLE 1. TOCOTRIENOL CONTENT OF RRIM 701 LATEX PROCESSED BY DIFFERENT METHODS

Rubber sample	Level of free tocotrienols (% of dry weight of rubber)
Acid-coagulated	0.09
Auto-coagulated	0.08
Air dried sheet 1	0.05
Air dried sheet 3	0.06
Heveacrumbs dried at at 60°C	0.09
Heveacrumbs dried at at 110°C	0.09

TABLE 2. COMPARISON OF THE ANTIOXIDANT ACTIVITIES OF γ- AND α-TOCOTRIENOLS

Antioxidant level (% of dry weight of rubber)	PRI γ-tocotrienols	 α-tocotrienols
0	20	20
0.03	83	72
0.06	86	78
0.10	86	81

contained about 0.04% less tocotrienols than the normal acid-coagulated Heveacrumbs. The low tocotrienol content of sheet rubber could be due to the larger proportion of acid used to coagulate the dilute latex and the inability of the rubber particles to coagulate completely. The former action might lead to oxidation of some free tocotrienols by the acid[10], while the latter resulted in some loss of the materials along with the uncoagulated rubber particles which would be washed together with the aqueous serum. The tocotrienols are known to associate with the membrane of the rubber particles[11].

Tocotrienol, a constituent of vitamin E is currently a very important natural antioxidant in the food industry and cosmetology. Its antioxidant activity in NR has been shown by Nadarajah *et al.*[1] and Morimoto[2] who demonstrated a linear correlation between the tocotrienol contents and the PRI values of the raw rubber and the tensile strengths of the vulcanisates, respectively. The study on the antioxidant effect of the tocotrienols was further extended by adding the isolated tocotrienols of fresh NR latex to the antioxidant-deprived NR. *Tables 2* and *3* show the strong antioxidant effect of the tocotrienols. Even at the level of 0.03% it could raise the PRI of acetone-extracted rubber from 20% to 70% *(Table 2).* Further improvement was not significant above a level of 0.1% *(Table 3)* which appeared to be the optimum level of tocotrienols required for the maximum protection of raw rubber against thermal oxidative degradation. Of the two major free tocotrienol isomers in NR, the γ-tocotrienol gave a better protection than the α-tocotrienol *(Table 2).* This is consistent with the finding of Parkhurst *et al.*[12] who observed a similarly higher antioxidant activity of γ-tocopherol over α-tocopherol.

The normal acid-coagulated NR generally has good PRI (>60). The PRI of auto-coagulated rubber however is affected by the type of clone and sites[13]. There were incidences where the PRI of auto-coagulated cuplumps and polybag rubbers were as low as 10% to 20%. This was initially thought to be due to the depletion or inactivation of the tocotrienols. However, results in *Table 4* show that the acetone-extracted neutral lipids of low PRI auto-coagulated rubbers could still protect the antioxidant-deprived acid-coagulated Ribbed Smoke Sheets (RSS 1) indicating that the tocotrienols, the only neutral lipid component behaving as an antioxidant *(Table 3),* were still present in a sufficient active level. There appeared to be other factors inherent in the naturally coagulated rubber, which are responsible for the low resistance of the rubber against ageing and one of these could be the higher pro-oxidant level.

Copper

Copper, manganese and iron are the well known pro-oxidants of NR, with copper being the most active[4]. The normal method of determining copper content in NR[8] did not relate well to the PRI values of the rubber. For instance rubber with a copper content of

TABLE 3. EFFECT OF VARIOUS NEUTRAL LIPID FRACTIONS ON THE PRI OF ACETONE-EXTRACTED RSS 1

Lipid level (% of dry weight of rubber)	PRI (%)			
	Esters	Triglycerides	Tocotrienols	More polar neutral lipids
0	11	9	11	11
0.1	—	10	63	33
0.4	14	17	65	49
0.6	16	24	65	49

TABLE 4. EFFECTS OF ACETONE-EXTRACTED NEUTRAL LIPIDS OF LOW PRI POLYBAG RUBBERS ON THE PRI OF ACETONE-EXTRACTED RSS 1

Rubber sample	Wallace plasticity, P_0	Wallace plasticity after heating at 140°C for 30 min, P_{30}	PRI
Acetone extracted rubber	23	Oxidised	Oxidised
AER + NL of polybag rubber A	22	14	64
AER + NL of polybag rubber B	21	13	62
AER + NL of polybag rubber C	22	15	68

AER — Acetone extracted rubber NL — neutral lipids

Polybag rubbers A, B, and C have PRI of 10, 13, and 14 respectively.

2 p.p.m. could have a PRI of 57% or 9%. This could be due to the inability of the technique to distinguish the actual amount of free copper from the total copper present in the rubber, for only free copper can act as a catalyst in a thermal oxidation process of NR[14].

It is a normal practice of most rubber producers to soak the auto-coagulated Hevea-crumbs in phosphoric acid to boost the PRI of the rubber. Thiourea can also bring about a similar effect but is less used because of its toxicity. The actual mechanisms involved in the improvement of the PRI with soaking is not fully understood. When the copper content of thiourea-treated rubber was analysed, its value was observed to be lower than that of the untreated rubber. For instance, an untreated rubber of PRI 34% had a copper content of 7.2 p.p.m. After soaking in 0.5% thiourea, PRI of the rubber increased to 96% and the copper content decreased to 2.6 p.p.m. Soaking in 0.5% phosphoric acid also reduced the copper content in the rubber. The reduction was however less than by soaking in thiourea and this probably explained the greater efficiency of thiourea over phosphoric acid to boost the PRI of rubber. Both thiourea and phosphoric acid thus appeared to extract the undesirable free copper from the rubber during the soaking process. Results given in *Table 5* confirm this. The amount of free copper extracted by thiourea and phosphoric acid from polybag rubber corresponded roughly to the amount of copper loss after soaking the rubber in the two chemicals.

Soaking the auto-coagulated Heveacrumbs in other copper complexing agents such as amino acids and imidazole however did not give a similar significant increase in PRI. Thiosemicarbazide was the only other chemical observed

TABLE 5. PRI AND COPPER CONTENT OF POLYBAG RUBBER AFTER SOAKING IN THIOUREA AND PHOSPHORIC ACID

Sample	Wallace plasticity, P_0	Wallace plasticity after heating at 140°C for 30 min P_{30}	PRI	Copper (p.p.m.)
Control	64	46	71	4.4
PLR after soaking in water	66	50	71	4.4
PLR after soaking in thiourea	63	59	93	1.7
PLR after soaking in phosphoric acid	60	51	85	2.1
Water extract	—	—	—	0.2
Thiourea extract	—	—	—	2.6
Phosphoric acid extract	—	—	—	1.6

PLR — Polybag rubber

to give a response equivalent to that of thiourea and these two chemicals were reported to complex specifically with free cuprous ions[15].

Copper in fresh latex might complex with proteins and amino acids and in this form, it does not impart any deleterious effect on the ageing of NR. However, when the latex is exposed to microbial activity the microbes degrade the protein and amino acid components of the copper-complex, releasing free copper which is known to be a very active pro-oxidant of NR. This could be a possible explanation to the general susceptibility of auto-coagulated rubber to thermal oxidative degradation compared to the normal acid-coagulated rubber.

The effectiveness of thiourea in boosting the PRI of auto-coagulated rubber however depended on the texture of the coagulum. When they were wet and spongy, the PRI could be raised from 10% to 80% or higher. When they were semi-dried and less spongy the PRI could not be markedly affected by the thiourea; the PRI could only be raised by about 10% to 20%. None could be raised to 80% or higher. This could be due to the inefficiency of thiourea to penetrate the hard textured coagulum to affect a marked improvement in PRI values.

Proteins and Amino Acids

Morimoto[2] showed a linear relationship between tensile strength of acetone-extracted vulcanisate aged at 100°C for one day and the relative peak height of amide band of the rubber as traced by infra-red spectroscopy. The amide band at 1650 cm^{-1} was conferred to the protein absorption band and the positive correlation was interpreted as an antioxidant effect of proteins on ageing of NR vulcanisate. The present study however did not show a similar correlation *(Figure 1)*. The tensile strength of the aged purified rubber vulcanisate generally decreased with increasing levels of protein. This resulted in the retention of tensile strength of the purified rubber containing proteins to be lower than the control. A similar decrease in retention of tensile strengh was observed with the addition of hydrophobic proteins associated with the rubber particles. While some serum proteins would be lost during processing of latex to rubber, most of the hydrophobic membrane proteins will be retained. The results subsequently suggest that the presence of these proteins in NR could not protect the rubber against thermal oxidative degradation.

Infra-red analysis of the purified rubber containing increasing levels of protein showed

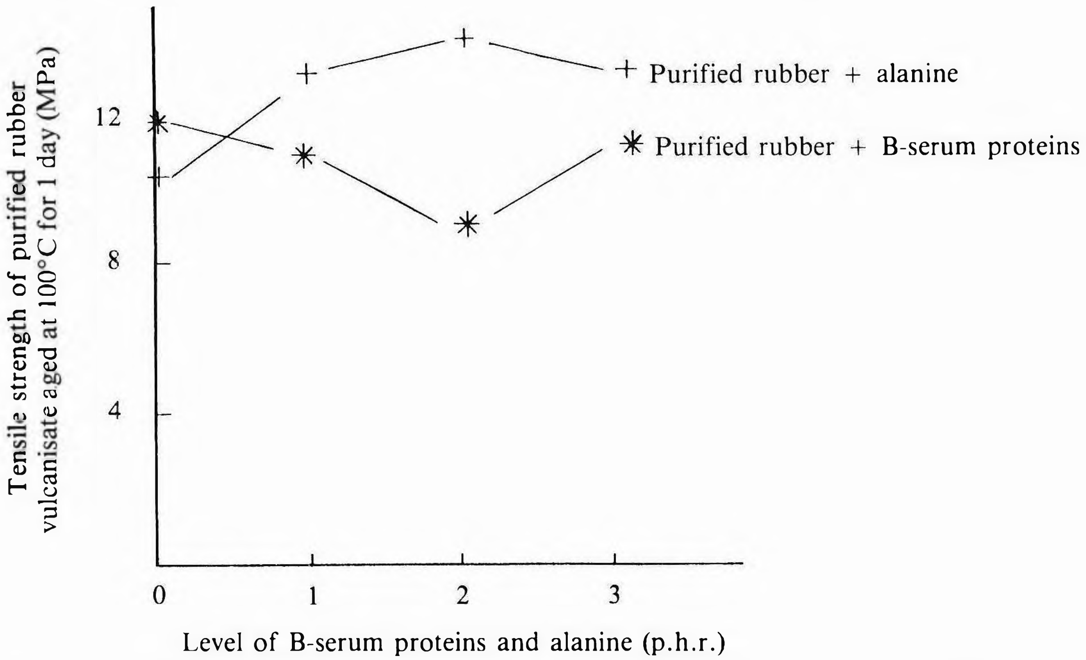

Figure 1. Effect of alanine and B-serum proteins on the tensile strength of aged purified rubber vulcanisate.

characteristic protein absorption bands at 1540 cm^{-1} and 3280 cm^{-1} as reported by the Russian workers[16] and not at 1650 cm^{-1} or 1660 cm^{-1} precisely which was also absorbed by the purified rubber in the absence of proteins *(Figure 2)*. Even the purified rubber containing amino acid showed absorption at 1660 cm^{-1} *(Figure 3)*. However, in the case of the amino acid, there was a positive correlation between the amino acid (alanine) content and the tensile strength of the aged vulcanisate *(Figure 1)*. Although alanine increased the tensile strengths of both aged and unaged vulcanisates, their retention of tensile strength did not increase markedly as that offered by the tocotrienols *(Table 6)*. Similar insignificant effects on retention of tensile strength were observed with other acidic, basic and neutral amino acids such as glutamic acid, arginine and glycine, respectively. Thus the amino acids retained in NR,

TABLE 6. RETENTION OF TENSILE STRENGTH OF ANTIOXIDANT-DEPRIVED RUBBER IN THE PRESENCE OF TOCOTRIENOLS AND AMINO ACID

Rubber sample	Retention of tensile strength (%) (after 1 day ageing at 100°C)
Acetone extracted RSS 1 (AER)	35
AER + 0.7 p.h.r. of tocotrienols	88
Purified rubber (PR)	34
PR + 2.0 p.h.r. of alanine	38

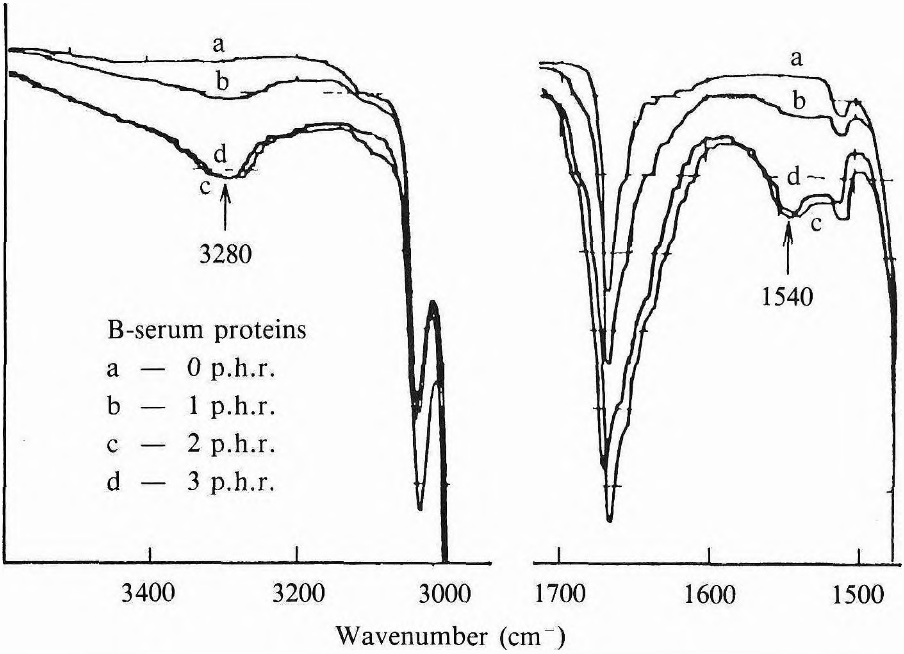

Figure 2. Infra-red spectrum of purified NR containing different levels of B-serum proteins. The arrows mark the characteristic absorption bands of protein (3280 cm^{-1} and 1540 cm^{-1}).

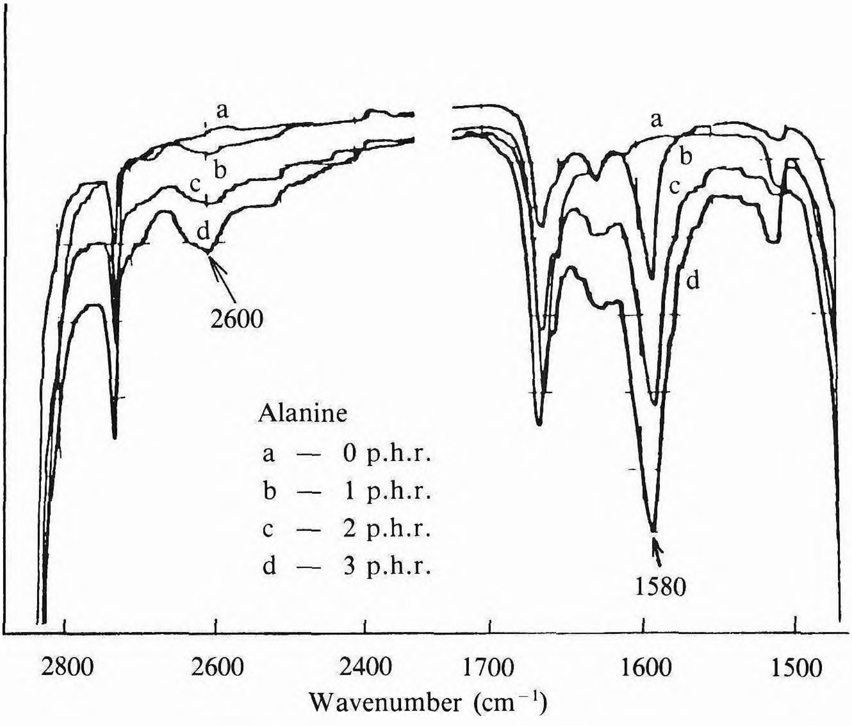

Figure 3. Infra-red spectrum of purified NR containing different levels of alanine. The arrows mark the characteristic absorption bands of amino acid (2600 cm^{-1} and 1580 cm^{-1}).

whether in the original form or as a result of protein hydrolysis, could not act as an inhibitive antioxidant as the tocotrienols. The increase in the tensile strength was due to the accelerator effect of some amino acids during sulphur vulcanisation of rubber[17], which increased the modulus of the rubber and consequently its tensile strength. However, the probable formation of polysulphidic types of network structure rendered the vulcanisate less resistant to thermal oxidative degradation.

CONCLUSION

As reported by the previous workers, the tocotrienols and copper formed the most active natural antioxidant and pro-oxidant for NR, respectively. The amount of tocotrienols in NR remained sufficiently active under normal methods of processing rubber even when exposed to severe microbial attack as in the natural coagulation process. The low PRI values of some auto-coagulated cuplumps and polybag rubbers were more related to the high free copper content of the rubber rather than the depletion of tocotrienols.

The high tensile strength of aged NR vulcanisate was observed to be associated with amino acid, not the presence of protein. Amino acids however could not exhibit the inhibitive antioxidant activity as the tocotrienols.

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Relationship Between Mooney Measurements and Die Swell of Natural Rubber

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Mooney viscometer measurements carried out on carbon black-loaded grades of Standard Malaysian Rubber (SMR) which have been masticated to different extents are shown to give good predictions of their die swells when extruded in a capillary rheometer, the relationship being dependent on the grade of rubber, type of black and conditions of extrusion. A similar linear relationship applies when these measurements are made on single samples of several grades of SMR which were loaded with carbon black in a fixed cycle.

One of the key steps in many rubber product manufacturing processes is extrusion. A major problem often encountered in extrusion is the phenomenon of die swell, or Barus effect, *i.e.* the increase in cross-sectional area (and shrinkage in length) of the extrudate exiting the die. It has to be controlled to within acceptable limits. Die swell also complicates considerably the preparation of extrusion dies for complex extrudate shapes. The magnitude of swell is influenced by the carbon black type and loading, polymer type and oil level as well as the operating conditions. Hence, the extent of die swell cannot be predicted with certainty without knowing the response of the polymer system to the variables of the extrusion process.

In practice it may be useful in many instances to have an advanced idea of the expected die swell of a mix or compound under specified conditions of extrusion. This may, to some extent, be met by a simulated extrusion in a laboratory capillary rheometer or extruder. However, capillary rheometers or laboratory-scale extruders are, as a rule, not standard or common-place equipment in most factories. The Mooney viscometer, on the other hand, is a relatively common piece of quality control instrument and any improvement in its predictive ability will certainly be an added bonus to its traditional usage.

Delta Mooney tests have been found to be correlatable with black incorporation time[1,2]. Giurco and Mills[3] found linear relationships for both delta Mooney (ML6 min + 15 min − ML6 min + 1 min) and Mooney slope (after 4 min) with die swell for solution-polymerised SBR. The current work reports the linear relationships which exist between Mooney measurements on several SMR grades of natural rubber (NR) and their respective die swell when extruded in a capillary rheometer.

EXPERIMENTAL

Four grades of NR, *viz.* SMR GP, SMR CV, SMR L and SMR 20, were individually mixed with 50 p.h.r. of both HAF (N330) black and SRF (N774) black. These black masterbatches were then masticated to different extents on a two-roll mill (for up to 100 passes) to provide a range of Mooney viscosity for each grade. Mooney viscometer measurements, with a preheat time of 5 min, were made on the rubbers at 100°C. Two types of measurements were carried out: in the first, the rubber was sheared continuously for a period of 15 min and the torque was recorded every minute. In the second type of measurement, the rubber was sheared for 4 min, after which the rotor was switched off, and the decaying torque recorded for a further 10 min. Die swell measurements

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were obtained from extrusion at 90°C and 120°C in a capillary rheometer in the range of shear rates from 3.5 s^{-1} to 1181 s^{-1}, using a single capillary of diameter 1.27 mm and a length-to-diameter (L/D) ratio of 20. It is recognised, however, that production dies are normally of lower L/D values and that in such instances, entrance effects will be substantial. The above measurements were also made on unfilled SMR L and SMR CV which had been masticated in the same manner as the black masterbatches.

In a further investigation, single samples of different grades of NR, plus a synthetic *cis*-polyisoprene (Natsyn 2200) and an SBR 1502, were individually mixed with 50 p.h.r. each of HAF black (N330) and MT black (N990) in a Brabender plasticorder. The rotor speed of mixing was 120 r.p.m. and the chamber temperature was set at 60°C. A total mix cycle of 8 min was employed with all the black being added at 1 min. As with the previous investigation, Mooney and die swell of these black mixes were measured.

RESULTS AND DISCUSSION

For the purpose of discussion, the following (arbitrary) definitions apply:

MX, MY	—	Mooney torque at the X^{th}, Y^{th} min of shearing, respectively
(*MX* - *MY*)	—	Delta Mooney
XR (*M*4 - *XR*) (*XR* - *YR*)	]	Mooney recovery, where *XR* is the torque *X* min after the rotor is switched off.

Figure 1 shows the two types of Mooney measurements.

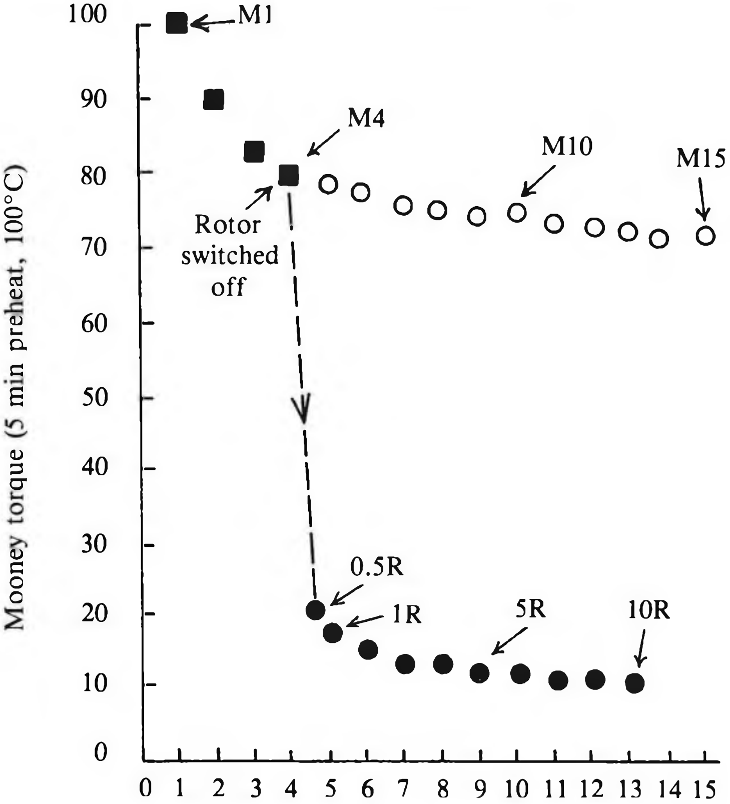

Figure 1. Mooney viscometer measurements.

Single Mooney, Delta Mooney — Die Swell Relationships

Progressive mastication of NR leads to a continuous reduction in the molecular weight of the rubber, which will also be reflected by the progressive drop in conventional Mooney viscosity (*M*4 in this particular instance). Reduction in the molecular weight of the rubber should lead to a reduction in die swell on extrusion and a correlation is therefore expected between die swell and Mooney viscosity under such circumstances. That such a correlation does exist is shown in *Table 1* where the degree of correlation is reflected in the coefficient of correlation *(r)*. The correlation is seen to be remarkably good in most cases. The reason for the poor *r* value of SMR 20 for *M*4 is probably due to the relatively high Mooney viscosity of the rubbers corresponding to five and ten passes on the mill, which were 122 and 115 respectively. Such high viscosity rubbers when extruded gave extrudates which are grossly distorted, which made die swell measurements very imprecise. If these two points are omitted, the *r* value for the *M*4 — die swell of SMR 20 improves from 0.20 to 0.86. It is also seen from *Table 1* that in most cases, delta Mooney has an equally good linear relationship with die swell.

Die swell measurement is only meaningful if the extrudates are not grossly distorted. In each particular grade where the black masterbatches were masticated to different extents, the extrudates of these rubbers were of different degrees of 'smoothness' at any particular shear rate of extrusion, and hence the degree of precision of die swell measurement may be variable. This could affect the degree of correlation between the measured die swell and Mooney measurements. *Table 2* illustrates the degree of correlation between single and delta Mooney with die swell for the same rubbers filled with 50 p.h.r. SRF black at different rates of extrusion. In this case, the correlation between *M*4 with die swell is better than those of delta Mooney with die swell.

In the above computation of the coefficients of correlation, the point corresponding to the unmasticated masterbatch has been omitted. Its inclusion normally leads to a drastic decrease in the value of *r*. This is due to its relatively high value of Mooney viscosity *(Table 3)* as a result of shelf-ageing, which led to the formation of a 'structure', which may or may not be associated with the increase in bound rubber or carbon gel[4]. This shelf-ageing results in a rubber which is more difficult to extrude, but on light mastication, breaks down rather easily[5]. This is confirmed by the rapid drop in Mooney viscosity after just five passes on the mill *(Table 3)*. Typical Mooney — die swell relationships are plotted in *Figures 2* and *3*. It is obvious from these figures that there is a different relation for each grade of NR. *Figure 4* shows that the relationship between die swell and delta Mooney is also dependent on the type of black used.

Mooney Recovery — Die Swell Relationship

Tables 4 and *5* give the coefficients of correlation between Mooney recovery measure-

TABLE 1. COEFFICIENTS OF CORRELATION BETWEEN MOONEY MEASUREMENTS AND DIE SWELL AT 354 s^{-1}, 120°C OF HAF-FILLED NR

NR	Coefficient of correlation			
	M4	(M1-M10)	(M2-M10)	(M1-M15)
SMR L	0.96	0.34	—	0.52
SMR CV	0.93	0.96	0.92	0.97
SMR 20	0.20	0.82	0.92	—
SMR GP	0.96	0.92	0.94	—

TABLE 2. COEFFICIENTS OF CORRELATION BETWEEN MOONEY MEASUREMENTS AND DIE SWELL AT DIFFERENT EXTRUSION RATES OF SRF-FILLED NR

NR	Extrusion rate (s^{-1})	Coefficient of correlation			
		M4	(M1-M10)	(M2-M10)	(M1-M15)
SMR L	118	0.91	0.77	0.73	0.81
SMR CV		0.96	0.75	0.65	0.77
SMR 20		0.82	0.59	0.61	0.53
SMR GP		0.75	0.67	0.67	0.67
SMR L	354	0.87	0.61	0.54	0.71
SMR CV		0.95	0.77	0.71	0.76
SMR 20		0.79	0.58	0.55	0.44
SMR GP		0.91	0.74	0.92	0.78
SMR L	1 181	0.98	0.75	0.70	0.84
SMR CV		0.96	0.79	0.67	0.79
SMR 20		0.93	0.67	0.66	0.59
SMR GP		0.98	0.69	0.91	0.90

TABLE 3. CHANGE OF MOONEY VISCOSITY OF BLACK-FILLED NR ON MASTICATION

No. of passes	M4							
	HAF				SRF			
	SMR L	SMR CV	SMR GP	SMR 20	SMR L	SMR CV	SMR GP	SMR 20
0	96.5	115	101	133	102.5	81	76	94
5	81.5	87	91	121	80	68	64.5	77
8	77.5	82	—	—	—	—	—	—
10	—	—	87	115	71.5	61.5	60	69
20	69.5	72.5	80	107	61	55.5	53	62.5
30	65.5	65.5	79	101	54.5	49.5	47.5	56
40	—	—	78	95	49.4	45	44	51.5
50	—	—	74	93	46	40.5	39.5	47
100	—	—	64	79	32	27	30	33

ments and die swell for HAF and SRF blacks respectively. While *Table 4* shows the Mooney recovery to be equally good as single or delta Mooney for HAF black, *Table 5* shows that for the SRF loaded rubbers, the Mooney recovery values generally show better correlation with die swell than delta Mooney. Typical graphical relationships are shown in *Figures 5* and *6*.

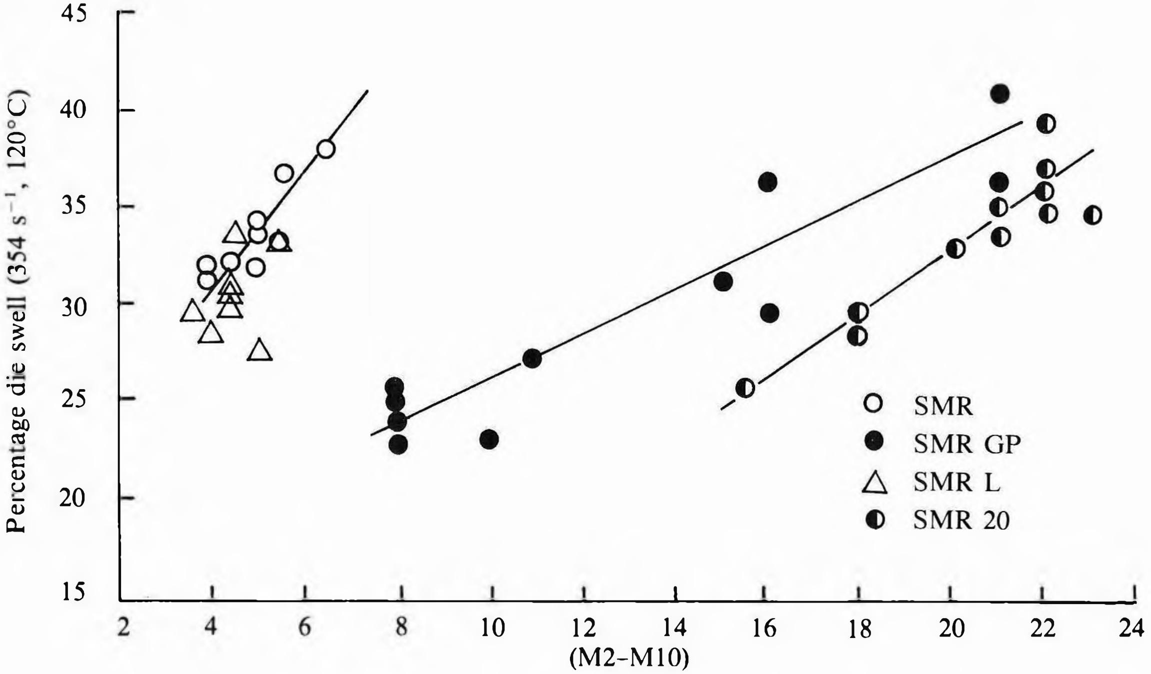

Figure 2. (M2–M10) versus die swell for 50 p.h.r. HAF black.

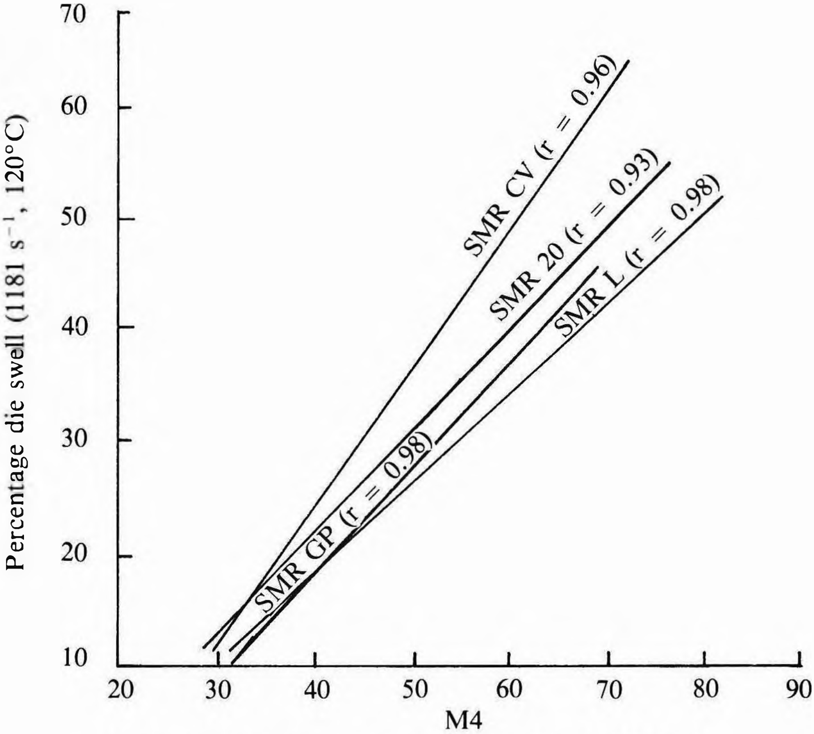

Figure 3. M4 versus die swell, 50 p.h.r. SRF black.

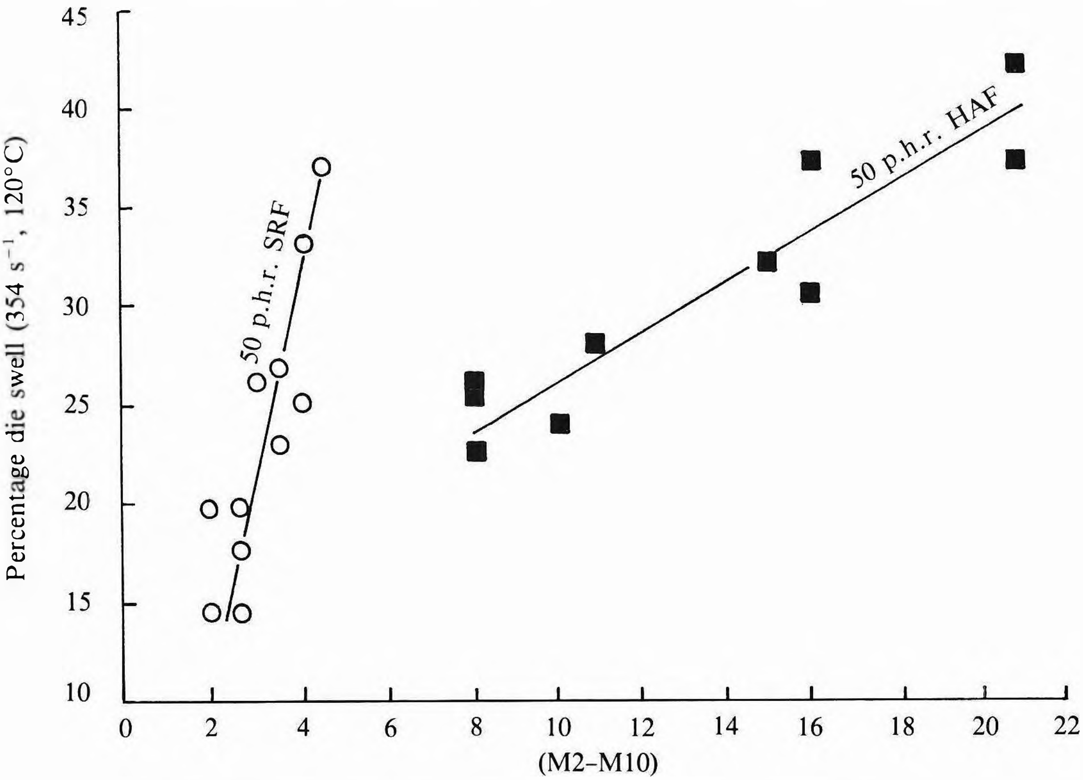

Figure 4. (M2-M10) versus die swell for HAF, SRF blacks (SMR GP).

TABLE 4. COEFFICIENTS OF CORRELATION BETWEEN MOONEY RECOVERY AND DIE SWELL AT 354 s^{-1}, 120°C OF HAF-FILLED NR

NR	Coefficient of correlation					
	0.5R	1R	(M4-1R)	(M4-10R)	(1R-5R)	(1R-10R)
SMR L	—	0.99	0.92	0.93	0.97	0.87
SMR CV	—	0.91	0.93	0.93	0.84	0.86
SMR 20	0.78	—	0.89	0.90	0.93	0.92
SMR GP	0.95	—	0.93	0.97	0.88	0.88

Unfilled-filled Relationship

There is also a correlation between similar Mooney measurements and die swell of unfilled rubbers masticated in the same manner as the black mixes *(Table 6)*. Since die swell is a manifestation of the elastic nature of the rubber and incorporation of carbon black serves to modify the level of swell, the extent of this modification being dependent on the type and loading of black, a correlation between the die swell of the unfilled rubbers and those of the filled rubbers should be expected. This is evident from *Table 7*. In fact, the various

TABLE 5. COEFFICIENTS OF CORRELATION BETWEEN MOONEY RECOVERY AND DIE SWELL AT DIFFERENT EXTRUSION RATES OF SRF-FILLED NR

NR	Extrusion rate (s^{-1})	Coefficient of correlation					
		0.5R	1R	(M4-1R)	(M4-10R)	(1R-5R)	(1R-10R)
SMR L	118	0.92	0.92	0.89	0.90	0.85	0.92
SMR CV		0.97	0.97	0.95	0.95	0.94	0.98
SMR 20		0.88	0.84	0.84	0.85	0.82	0.86
SMR GP		0.74	0.70	0.75	0.75	0.70	0.69
SMR L	354	0.93	0.90	0.85	0.86	0.89	0.90
SMR CV		0.99	0.99	0.94	0.95	0.96	0.97
SMR 20		0.89	0.88	0.80	0.81	0.85	0.86
SMR GP		0.90	0.90	0.91	0.91	0.84	0.79
SMR L	1 181	0.98	0.97	0.97	0.98	0.93	0.97
SMR CV		0.97	0.96	0.96	0.97	0.91	0.97
SMR 20		0.96	0.96	0.93	0.94	0.93	0.95
SMR GP		0.98	0.97	0.99	0.99	0.95	0.92

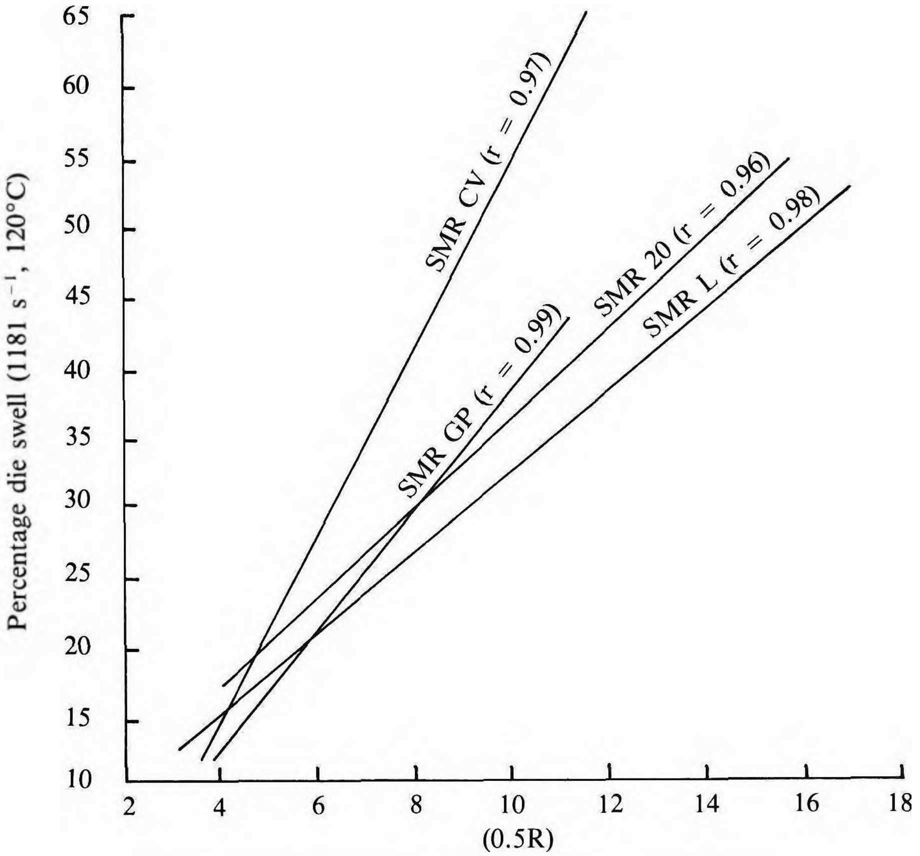

Figure 5. (0.5R) versus die swell, 50 p.h.r. SRF black.

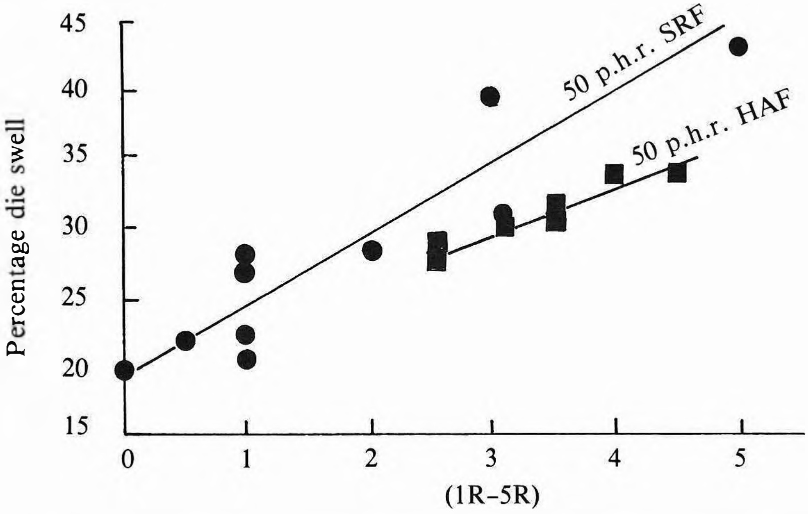

Figure 6. (1R-5R) versus die swell for HAF, SRF black-filled SMR L.

TABLE 6. COEFFICIENTS OF CORRELATION BETWEEN MOONEY MEASUREMENTS AND DIE SWELL AT 354 s^{-1}, 120°C OF UNFILLED NR

NR	Coefficient of correlation				
	0.5R	(M1-M10)	(M1-M15)	(M4-10R)	(1R-10R)
SMR CV	0.94	0.88	0.80	0.87	0.80
SMR L	0.79	0.63	0.69	0.80	0.80

TABLE 7. COEFFICIENTS OF CORRELATION BETWEEN MOONEY MEASUREMENTS AND DIE SWELL OF UNFILLED RUBBERS AND DIE SWELL OF FILLED RUBBER

NR	Coefficient of correlation					
	Die swell	M4	(M1-M10)	(M1-M15)	(1R-5R)	(1R-10R)
SMR CV	0.84	0.80	0.96	0.96	0.88	0.86
SMR L	0.74	0.92	0.82	0.91	0.93	0.93

Mooney measurements made on the unfilled rubbers gave a good prediction of the die swell when carbon black was added to the rubbers (*Table 7* and *Figure 7.)*. This suggests that when the correlation has been established, it may be possible to predict the die swell of the filled rubbers from measurements on the unfilled rubbers.

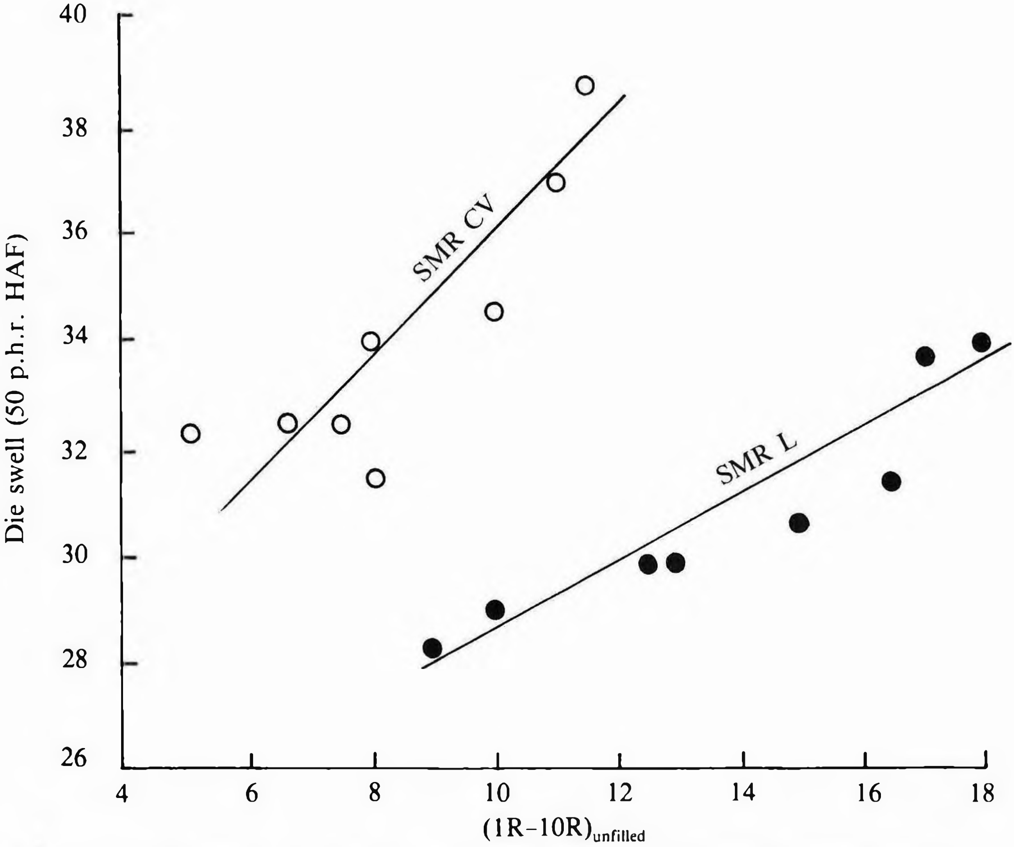

Figure 7. (1R–10R) of unfilled rubbers versus die swell of black-filled rubbers.

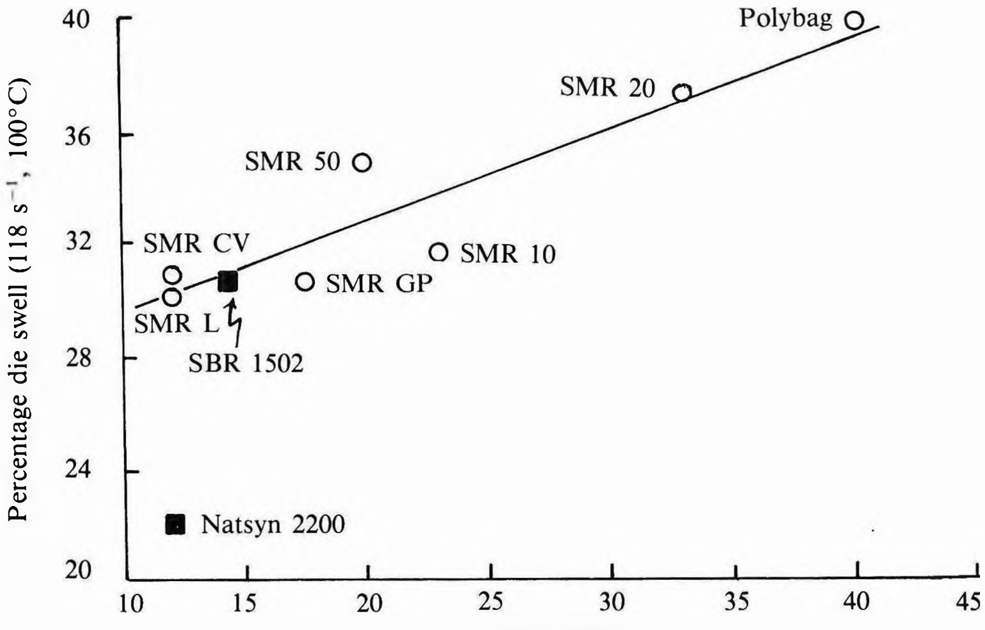

Figure 8. (M1–M10) versus die swell, 50 p.h.r. HAF black.

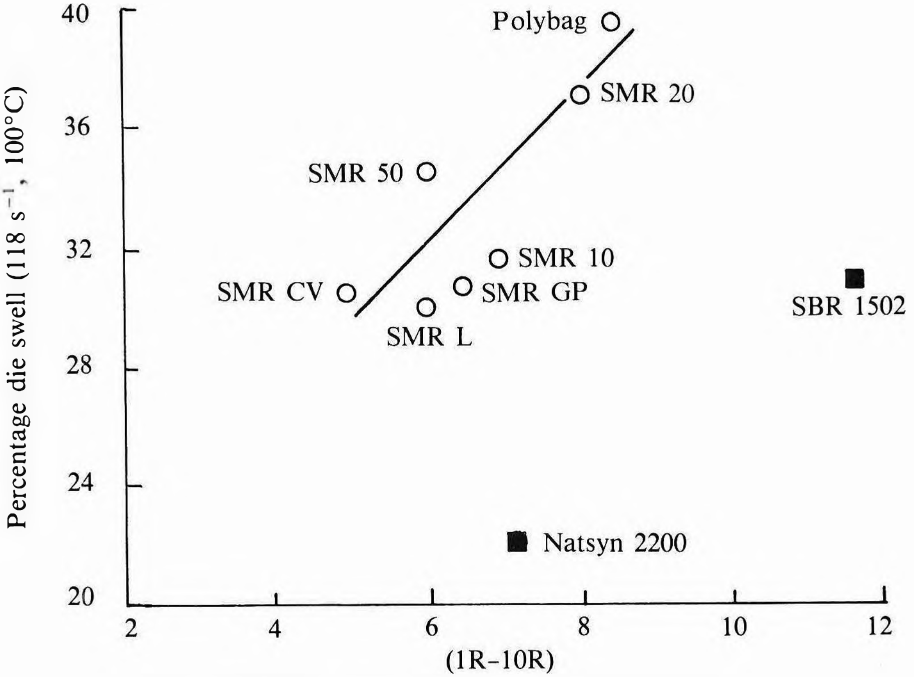

Figure 9. (1R–10R) versus die swell, 50 p.h.r. HAF black.

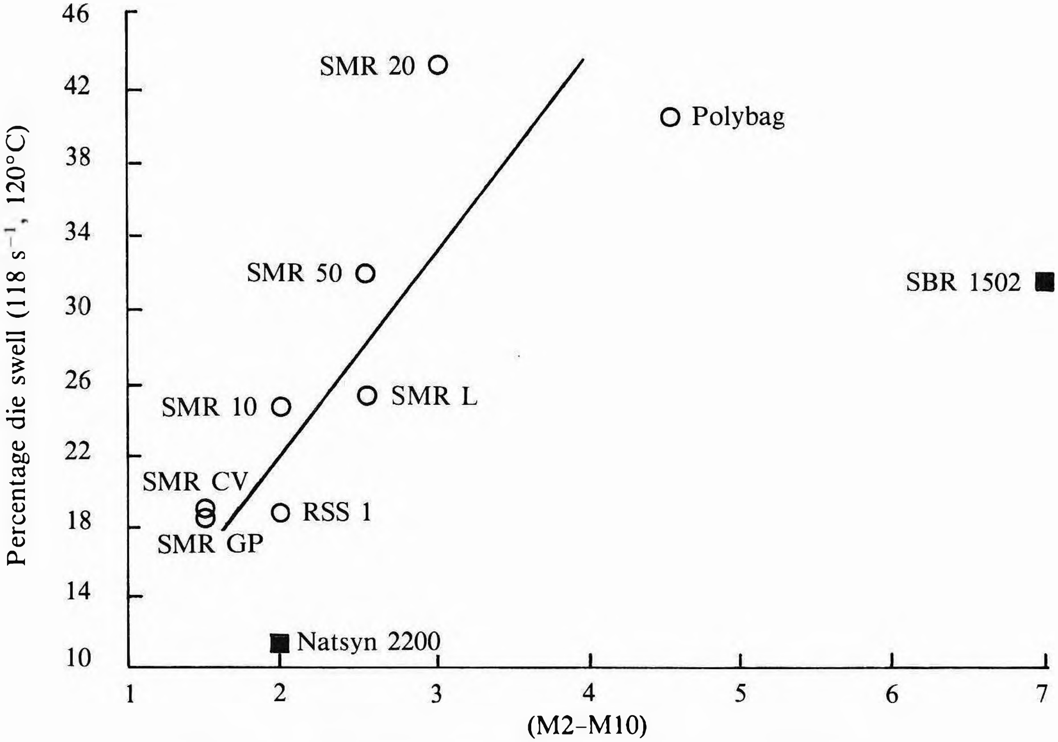

Figure 10. (M2–M10) versus die swell, 50 p.h.r. MT black.

TABLE 8. COEFFICIENTS OF CORRELATION BETWEEN MOONEY MEASUREMENTS AND DIE SWELL FOR DIFFERENT GRADES OF NR

Item	Coefficient of correlation				
	M4	(M1-M10)	(M2-M10)	1R	(1R-10R)
50 p.h.r. HAF	0.73	0.93	0.89	0.91	0.81
50 p.h.r. MT	0.62	0.82	0.86	0.84	0.74

Different Grades of NR

Table 8 and *Figures 8–10* show that for the NR grades, a single relationship exists between a particular Mooney measurement and die swell for each individual black. SBR 1502 and Natsyn 2200 do not fall on this regression line, which appears to be unique to the NR grades.

CONCLUSION

For each grade of natural rubber masticated to different extents, linear relationships exist between Mooney measurements and the die swell of the rubber. This relationship is dependent on the grade of natural rubber, type of black and its loading, and the condition of extrusion. In actual practice where a formulation involves a certain grade of rubber and specific filler type and loading, it may thus be possible to predict the die swell of such a mix at various stages of a process by carrying out Mooney measurements, if this correlation has been previously established.

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Refractive Index Increments of Natural and Synthetic Polyisoprenes

W.S. FULTON* AND K.N.G. FULLER*

Measurements of the refractive index increment of a variety of Hevea *rubber samples and a range of narrow distribution synthetic polyisoprenes have been made at a wavelength of 615 nm and a temperature of 40°C. Evidence that the increment decreased with molecular weight at low values (below 100 kg mol^{-1}) was found for both the natural and synthetic materials. Soluble non-rubbers in the natural material were found to act effectively as a diluent. Otherwise there appeared to be little difference between the natural and synthetic polyisoprene; the average values measured for the refractive index increment were respectively 0.135 mlg^{-1} and 0.133 mlg^{-1}. A high molecular weight fraction of natural rubber gave a figure (0.147 mlg^{-1}) well above that obtained for the other natural polyisoprene samples.*

The refractive index increment *(dn/dc)* is an essential parameter used in the analysis of data obtained from light scattering of polymer solutions. The scattered intensity from a solution depends upon $(dn/dc)^2$, so an accurate determination is particularly desirable. This communication presents the refractive index increments for a series of natural *(Hevea)* and synthetic *cis*-polyisoprenes covering a range of molecular weights. The values were obtained at 615 nm, a wavelength close to the He-Ne gas laser line of 633 nm that is now commonly used in light scattering experiments, but for which there are relatively few *(dn/dc)* values reported. Studies[1–3] at this wavelength for polystyrene, synthetic polyisoprene and polymethyl-methacrylate solutions have recently been reported.

The value of *(dn/dc)* is obtained experimentally from the intercept of the plot of $\Delta n/c$ *versus* c, where Δn is the refractive index difference between the solution (of concentration c) and pure solvent, or the slope of the plot of Δn *versus* c at concentrations low enough for the relationship to be linear, normally assumed to be less than 3% weight/volume[4].

Theoretical calculations of *(dn/dc)* can be made using the Lorenz-Lorentz or Gladstone-Dale equations. The latter expresses the refractive index increment by:

$$dn/dc = v_2(n_2 - 1) - \bar{v}_2(n_o - 1) \qquad \ldots 1$$

where v_2 = specific volume of polymer
$\bar{v}_2$ = partial specific volume of polymer
n_o = refractive index of solvent
n_2 = refractive index of polymer

When additivity of volumes is assumed, *i.e.* $v_2 = \bar{v}_2$, *Equation 1* becomes

$$dn/dc = \bar{v}_2(n_2 - n_o) \qquad \ldots 2$$

The refractive index increments of natural and synthetic *cis*-polyisoprenes have been measured in a number of solvents[1,5–11]. The linear relationship between *(dn/dc)* and the refractive index of the solvent, suggested by *Equation 2,* has been confirmed[6,9]. The gradient of the line, it should be noted, gives an average value for the partial specific volume of the polymer as this parameter varies with the solvent[4].

Comparisons of measurements of *(dn/dc)* made under the same experimental conditions indicate differences between natural and

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synthetic polyisoprenes[6,9] and variations associated with the source and preparation of *Hevea* rubber samples[8]. The present study includes an investigation of the presence of any such differences.

The value of *(dn/dc)* has been found to vary with molecular weight in the case of polystyrene[12]. This study reveals an asymptotic approach of *(dn/dc)* towards a limiting value characteristic of a polymer of infinite molecular weight, the limit being reached with fractions above a molecular weight of 5×10^4 kg mol^{-1}. An investigation of the relationship for natural rubber[11] and synthetic polyisoprene[6] both found *(dn/dc)* to be invariant with molecular weight. However, Hadjichristidis and Fetters[1] using materials covering a wider range of molecular weights found an influence of molecular weight and chain branching on *(dn/dc)* of synthetic polyisoprenes. The present work looks for any similar effects in natural *cis*-polyisoprene.

As well as the possible influence of molecular weight on *(dn/dc)* of natural rubber, factors that may be responsible for variations associated with source and preparation were investigated. These are:

- Type of bale rubber providing source material — SMR L and SMR CV were used
- Solvent for dissolution of bale rubber
- Acetone-extractable non-rubbers
- Proteinaceous material.

The results obtained for the natural rubber materials are compared with those for synthetic *cis*-polyisoprenes with narrow molecular weight distribution.

EXPERIMENTAL

Materials

Natural rubber samples were prepared in the following ways. Several samples were obtained by dissolving the original material in tetrahydrofuran (THF) with gentle rolling of the container to produce a homogeneous solution which included both sol and any gel material present. The sample designated CV was from SMR CV bale rubber, CV/EX from CV bale which had first been acetone extracted to remove soluble non-rubbers, DP from a bale of deproteinised natural rubber and LQ from a low molecular weight, liquid natural rubber.

Various bale rubbers (SMR CV, SMR L and acetone-extracted SMR CV) were separated into sol and gel components by progressive dissolution in dichloromethane. The samples are respectively designated CV/S, L/S and CV/EX/S. A sol component (CV/S/CH) was also obtained from SMR CV bale rubber by progressive dissolution in cyclohexane. The solvent in each case was removed by rotary evaporation.

A sample of sol rubber obtained from SMR CV bale by progressive dissolution in dichloromethane was fractionated by precipitation with methanol. Seven fractions were isolated in this way, five of which were chosen for this study (NRF1-5). One of these fractions (NRF5) contained 22% of acetone-extractable material and therefore an acetone-extracted sample (NRF5/EX) was prepared.

The natural rubber samples tested are listed in *Table 1* together with their molecular weights as measured by GPC in tetrahydrofuran.

The THF used throughout was HPLC grade that had been deoxygenated by purging with dry nitrogen gas. The other solvents were AnalaR grade; the dichloromethane had been redistilled.

The narrow molecular weight fractions (M_w/M_n 1.04 - 1.15) of synthetic *cis* 1, 4 polyisoprene were as supplied from Polymer Laboratories, UK. They ranged in molecular weight from 3.2 kg mol^{-1} to 2.7×10^3 kg mol^{-1} *(Table 2)*.

The synthetic polyisoprenes and the natural rubber samples first prepared with other solvents were dissolved in THF at an initial concentration of approximately 1% weight/volume and left for at least 24 h to ensure complete dissolution. In the case of high molecular weight material, the solutions were

TABLE 1. REFRACTIVE INDEX INCREMENT OF NATURAL RUBBERS IN TETRAHYDROFURAN AT 40°C

Sample	M_w (kg mol^{-1})	M_n (kg mol^{-1})	N (%)	$(dn/dc)_{615}$ (mlg^{-1})
NRF1	2.24×10^3	9.38×10^2	0.29	0.147
NRF2	1.38×10^3	4.80×10^2	0.12	0.135
NRF3	8.29×10^2	3.88×10^2	0.04	0.134
NRF4	4.16×10^2	2.45×10^2	0.03	0.138
NRF5	6.17×10^2	1.93×10^2	0.0	0.121
NRF5/EX				0.136
LQ	26.3	8.13		0.125
CV	9.76×10^2	2.08×10^2		0.136
CV/EX				0.134
CV/S				0.136
CV/EX/S				0.132
CV/S/CH	7.06×10^2	1.24×10^2		0.132
L/S	5.42×10^2	1.56×10^2		0.134
DP	8.76×10^2	1.56×10^2		0.133

TABLE 2. REFRACTIVE INDEX INCREMENT OF LINEAR POLYISOPRENE IN TETRAHYDROFURAN AT 40°C

M_w (kg mol^{-1})	M_n (kg mol^{-1})	$(dn/dc)_{615}$ (mlg^{-1})
3.19	3.07	0.111
34.2	32.8	0.125
60.1	57.7	0.130
1.37×10^2	1.32×10^2	0.133
2.91×10^2	2.81×10^2	0.133
4.53×10^2	4.32×10^2	0.131
1.60×10^3	1.50×10^3	0.135
2.50×10^3	2.22×10^3	0.131

Molecular weight (M_w and M_n) values supplied by Polymer Laboratories Ltd., UK

left for three days. Five dilutions were made during the course of the experiments yielding a final concentration of approximately 0.1% weight/volume. All the rubber solutions and solvent were stored in the dark, under nitrogen, prior to use.

Method

A Brice-Phoenix Differential Refractometer Model BP-2000-V was used to obtain the refractive index differences between solution and solvent. This was obtained from measurements of the lateral displacement of the slit image in the focal plane of the microscope adapted with a filar micrometer.

The measurements were made at the mercury red line, $\lambda = 615$ nm. The mercury vapour lamp was used with a 72B Wratten filter, which has a narrow transmittance region of 590–650 nm. In this region, the line at 615 nm is over ten times more intense than in any other.

The instrument constant k was determined according to the equation:

$$\Delta n = k\Delta d$$

where Δn is the refractive index difference between a solution and its solvent and Δd is the total slit image displacement. The constant was determined from ten separate measurements of Δd using the two positions of the cell and five potassium chloride solutions of known concentration, and hence known Δn. The gradient of the plot of refractive index difference *versus* lateral displacement was calculated by a least squares procedure and gave the calibration constant, $k = (7.7487 \pm 0.0046) \times 10^{-4}$ mm^{-1}.

The measurements were carried out in tetrahydrofuran at 40°C as this was the solvent system and conditions used in related GPC work. The temperature was maintained by a circulating constant temperature bath. The refractometer cell had to be sealed in order to prevent solvent loss by evaporation. The solutions were equilibrated in the cell for at least 15 min prior to measurements. The lateral shift between solution and solvent was determined for six concentrations (1.0% weight/volume to 0.1% weight/volume) of the different rubbers. Five separate measurements of the shift were made for each concentration at the two positions of the refractometric cell.

RESULTS AND DISCUSSION

The lateral shift was plotted against concentration and the gradient of the slope was obtained by a least squares procedure. The refractive index increment for each rubber was calculated from this slope using the instrumental calibration constant.

Tables 1 and *2* summarise the values of *(dn/dc)* found for the different types of natural rubber and the polyisoprene standards. *Table 2* shows that the value of *(dn/dc)* for linear polyisoprene reached a limiting value of approximately 0.133 mlg^{-1} at a molecular weight greater than 6.0×10^2 kg mol. A similar relationship has been revealed for polystyrene in toluene[12] and polyisoprene in cyclohexane[1].

The values of *(dn/dc)* for the natural rubbers are shown in *Table 1*. They correlate fairly well with the limiting value, 0.133 mlg^{-1}, obtained for the narrow distribution polyisoprenes *(Table 2)*, with the following exceptions:

- The low molecular weight liquid rubber (LQ) has a lower *(dn/dc)* than the limiting value. However, it falls on the M_w *versus (dn/dc)* relationship determined from the narrow distribution polyisoprenes.
- A high content (22%) of soluble non-rubbers resulted in a low value of *(dn/dc)* for fraction NRF5; the limiting value was obtained after acetone extraction. Similar extraction of other natural rubber samples with a relatively small soluble non-rubber component (5%) did not greatly affect the value of *(dn/dc)*.
- The high figure of *(dn/dc)* for NRF1 was the only major deviation from the limiting value. This fraction was the highest molecular weight natural rubber sample, and it possibly contained the highest proportion of branched chains. However *(dn/dc)* has been found to be essentially independent of branching for polyisoprene[1]. The fraction contained much more proteinaceous matter (as shown by percentage *N* in *Table 1*) than the others and it is possible that this is responsible for the high value. If that were so, it may have been expected that the value for sample 'CV', prepared from whole bale material, would have been at least similarly high.

The comparison *(Table 3)* between the values given in *Tables 1* and *2* and previously published data has to take account of the differences of wavelength and temperature. The wavelength dependence can be adequately described by the first two terms of the Cauchy dispersion relation[4]:

$$\frac{dn}{dc} = B_1 + \frac{B_2}{\lambda^2} \qquad \ldots 3$$

The refractive index increments in *Table 3* have all been corrected to 633 nm, the wavelength of a He-Ne gas laser, using *Equation 3*. The empirical constant B_2 was determined from the limited data of Angulo-Sanchez *et al*[9]. They gave *(dn/dc)* for three polyisoprenes in THF at two wavelengths. The average value of B_2 obtained from the three pairs of data is 2.0×10^3 mlg^{-1} nm^2.

TABLE 3. COMPARISON OF REFRACTIVE INDEX INCREMENTS FOR NATURAL AND SYNTHETIC POLYISOPRENES IN TETRAHYDROFURAN WITH PREVIOUSLY PUBLISHED DATA ALL SCALED TO λ = 633 NM AND TO A TEMPERATURE OF 40°C

Reference	Material	Published dn/dc	$(dn/dc)^{40}_{633}$
9	*Hevea*	$(dn/dc)_{436} = 0.160$	0.157
9	Natsyn	$(dn/dc)_{436} = 0.153$	0.150
10	Polyisoprene	$(dn/dc)_{633} = 0.123$	0.127
15	*Hevea*	$(dn/dc)_{436} = 0.160^{a}$	0.145
8	Polyisoprene	$(dn/dc)_{546} = 0.128$	0.130
6	Polyisoprene	$(dn/dc)_{546} = 0.116^{b}$	0.118
This work	*Hevea*		0.132 - 0.138
This work	Polyisoprene		0.133
This work	*Hevea*/Polyisoprene		0.133^{c}

[a] This value reported by Bristow[15] is thought incorrect. It was determined from a plot of *(dn/dc)* and solvent refractive index using data presented by Schulz *et al.*[7] Taking $n_{436} = 1.4134$ for THF, a value of $(dn/dc)_{436} = 0.148$ mlg^{-1} should be obtained by extrapolation, and that value is used to determine $(dn/dc)^{40}_{633}$.

[b] Determined from reported data by method used in previous footnote.

[c] Calculated from *Equation 2.*

The correction for temperature can in principle be made by differentiating *Equation 2* to give:

$$\frac{d}{dT}\frac{dn}{dc} = (n_2 - n_o)\frac{d\bar{v}_2}{dT} + \bar{v}_2\left(\frac{dn_2}{dT} - \frac{dn_o}{dT}\right) \qquad \ldots 4$$

Values of the constants in *Equation 4* are listed in *Table 4.* The figure for $\bar{v}_2$ was obtained from plots of *(dn/dc)* against solvent refractive index[7,9] for natural and synthetic polyisoprenes; an average value from the data for both types of material was taken. The temperature dependence of $\bar{v}_2$ was evaluated by assuming:

$$\frac{d\bar{v}_2}{dt} = \bar{v}_2\left(\frac{1}{v}\frac{dv}{dT}\right) \qquad \ldots 5$$

TABLE 4. DATA FOR EVALUATION OF TEMPERATURE VARIATION OF dn/dc

		Reference
Partial specific volume of polymer, $\bar{v}_2$ (mlg^{-1})	1.23	7, 9
Coefficient of volume expansion (°C^{-1})	6.7×10^{-4}	13
$d\bar{v}_2/dT$ (mlg^{-1} °C^{-1})	8.2×10^{-4}	
Refractive indices: n^{25}_{633}		
THF	1.4036	3
polyisoprene	1.5097	9
dn/dT (°C^{-1})		
THF	-4.5×10^{-4}	14
polyisoprene	-3.7×10^{-4}	13

where $(\frac{1}{v}\frac{dv}{dT})$ is the coefficient of volume expansion. Refractive index data for NR and synthetic polyisoprene[9,13] do not suggest a reproducible difference between these two materials. An average value from the work of Angulo-Sanchez *et al.*[9] is quoted after applying a correction based on the Cauchy dispersion relation *(Equation 3)*. The value of *(d/dT) (dn/dc)* obtained by substituting the figures in *Table 4* into *Equation 4* is 1.85×10^{-4} mlg^{-1} $°C^{-1}$.

A value of *(dn/dc)* at 40°C and 633 nm was calculated from *Equation 2* using the data listed in *Table 4* and the above value for the temperature variation.

Table 3 compares the calculated and experimental values of *(dn/dc)* obtained in this study with other published data all scaled to λ = 633 nm and 40°C. This reveals a fair agreement between the present calculated and experimental values and certain previous determinations[8,10], in particular that by Pearson *et al.*[10], the only study performed in THF at 633 nm. There is, however, quite a large difference from both the values reported by Angulo-Sanchez *et al.*[9] and that derived from the data of Schulz *et al.*[7]; the discrepancies could result in up to 40% error in determinations of the values of radius of gyration by light scattering. The lack of agreement is as marked for the synthetic as for the natural polyisoprene. Thus, it seems that differences in the *(dn/dc)* values reported for natural rubbers should not necessarily be ascribed to the variety of source material and sample preparation. Indeed, the present work, with the exception of fraction NRF1, and the data of Angulo-Sanchez *et al.*[9] show relatively small variations in *(dn/dc)* between natural and synthetic polyisoprenes and various types of natural material. The factors found to influence *(dn/dc)* in the present work were molecular weight (in the range below 100 kg mol^{-1}) and, for the natural polyisoprene, soluble non-rubbers which, when present in large amounts, appear to act as a diluent. The reasons for the high value in the natural sample NRF1 remains unclear, though proteinaceous matter is a possibility.

CONCLUSIONS

Values of the refractive index increment for natural and synthetic polyisoprenes for a wavelength of 615 nm and a temperature of 40°C have been obtained. The average figures, 0.135 mlg^{-1} and 0.133 mlg^{-1} respectively, indicate little difference between the two materials. The only samples showing significant departure from these values were those of low molecular weight, whether synthetic or natural, and a high molecular weight fraction of natural rubber.

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Peroxide Prevulcanisation of Natural Rubber Latex

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The peroxide prevulcanisation of natural rubber (NR) latex using a range of commercially-available organic peroxides in both activated and non-activated systems, has been investigated. A few reactive peroxyesters have been found to be effective as prevulcanising agents at 100°C. A range of activators for promoting peroxide decomposition in NR latex has been evaluated. Fructose-activated hydroperoxide and fructose-activated peroxyester systems were found to be effective at temperatures above 50°C. The effectiveness of these systems is further enhanced in the presence of a ferric ion complex. The physical properties of films from peroxide-prevulcanised latex were evaluated.

Prevulcanisation of NR latex by heating the latex containing an organic peroxide has been known for many years[1]. However, there are relatively few publications available on the subject[1-9]. The re-investigation of peroxide prevulcanisation of NR latex was initiated by a great concern about the possibility of carcinogenic nitrosamines and nitrosatable amines being present in products from conventional sulphur-vulcanised latex[10]. The nitrosamine problem is particularly significant for products such as baby teats and soothers. Gorton *et al.*[11] have reported some sulphur-accelerator vulcanising systems for NR latex that meet regulatory limits for nitrosamines. However, these systems are generally slower curing than the conventional sulphur-dithiocarbamate systems.

The mechanism of peroxide prevulcanisation of NR latex is not understood. However, it is likely that the actual crosslinking of the polyisoprene molecules within the rubber particles occurs by reactions which are similar to those by which the peroxide vulcanisation of dry NR occurs[12,13]. The peroxide prevulcanisation of NR latex also involves the diffusion of peroxide molecules or radicals generated from the decomposition of the peroxide, from the aqueous phase to the rubber phase.

In the previous published work on the peroxide prevulcanisation of NR latex, the investigations were limited to a few organic peroxides that were commercially available at that time. This paper evaluates the effectiveness of various peroxide prevulcanising systems for NR latex, their prevulcanisation behaviour and the properties of films from the prevulcanised latex.

EXPERIMENTAL

High-ammonia (HA) latex concentrates which met the requirements of specification *ISO 2002* for NR latex concentrates were used. Texofor FP170, a non-ionic surfactant, was used as the peroxide emulsifier when attempting to vulcanise the latex at temperatures below 90°C. Potassium oleate was used as the emulsifier when attempting to vulcanise the latex at 100°C. The amount of surfactant used was generally in the range 15%–30% weight/weight on peroxide. Ferric ion was used in the form of ferric ion-pyrophosphate complex. Most peroxyesters and hydroperoxides were used on the basis of peroxide contents assayed by iodometric analysis. Others were used on the basis of the peroxide contents indicated by the suppliers.

Table 1 shows a typical peroxide prevulcanisation formulation. Peroxide emulsion was

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TABLE 1. A TYPICAL PEROXIDE PREVULCANISATION FORMULATION

Ingredient	Parts by weight, wet
60% D.r.c. latex	167
75% tBPIB	1.185[a]
20% Texofor FP170	1.0
20% Fructose	5.0[a]
Water	

[a] Equivalent to 5.55×10^{-5} gmol/g rubber

prepared by mixing the peroxide, surfactant and water. The peroxide emulsion was added to the latex contained in a beaker, at room temperature, the latex being continuously stirred. The remaining ingredients were then added to the latex. Prevulcanisations at 40°C–80°C were carried out in a beaker immersed in a water-bath. The beaker was covered with polyethylene, a stirrer shaft passed through a hole in the polythene, and the latex was continuously stirred. Prevulcanisations at 100°C were carried out under reflux in a round flask heated by a heating mantle. At the end of the heating period prevulcanised latex samples were quickly chilled to prevent further vulcanisation. For ageing experiments, antioxidant dispersions for emulsions were added to the prevulcanised latex.

Crosslink concentration and the physical properties of prevulcanised latex films were determined from cast films which had been leached in distilled water at room temperature for 24 h and then dried at room temperature. The dried films were kept at ambient conditions prior to determination of the crosslink concentration and the physical properties. The chemical crosslink concentration, $[X]_{chem}$, was determined by equilibrium solvent (toluene) swelling measurement, using the modified Flory-Rehner equation[14] and Mullins[15] relationship which relates the concentration of physically-effective crosslinks to that of chemical crosslinks. The value of 0.391 for the rubber-toluene interaction parameter reported by Bristow and Watson[16] was used in the Flory-Rehner equation. However, it is noteworthy that the Mullins' correlation of physically-effective crosslinks with chemical crosslinks was carried out using bulk rubber vulcanisates and vulcanisation temperatures above 100°C. In the present investigation, latex prevulcanisates and prevulcanisation temperatures of 100°C and below are used. Under these conditions, the above Mullins' correlation may not necessarily be valid. An equilibrium swelling index Q, the ratio of the weight of solvent to the weight of rubber in the swollen vulcanisate, was also used to give a measure of crosslink concentration. For lightly crosslinked vulcanisates, the Q-value was found to discriminate better than $[X]_{chem}$ between vulcanisates having different crosslink concentrations.

Modulus, tensile strength and elongation at break of the prevulcanised latex films were determined according to *ISO 37,* using *Type 2* dumb-bell test-pieces. The MRPRA's *Type 3* dumb-bell test-pieces were used in cases where breakage tended to occur at the grips. These test-pieces have 25 mm tab, and 30 mm length and 4.0 mm width of the narrow section. The median of three test results was taken. Tear strength was determined according to *ISO 34,* using 'trousers' test-pieces. Tension set (100% strained for 22 h, relaxed for 30 min) was determined according to *ISO 2285.* For ageing tests, dumb-bell test-pieces were heated in a circulating hot-air oven at 70°C for seven days. The aged test-pieces were conditioned for 24 h at 23°C before determining tensile properties.

RESULTS AND DISCUSSION

Diacyl Peroxides, Peroxydicarbonates, Dialkyl Peroxides and Peroxyketal Systems

Dioctanoyl peroxide, didecanoyl peroxide and bis-2-ethylhexyl peroxydicarbonate were found to be ineffective vulcanising agents for NR latex *(Table 2).* At least 50% of these peroxides should have decomposed after 6 h at 70°C. This is because the half-life times for the unpromoted decomposition of these peroxides are less than 3 h at 70°C. The ineffectiveness of these peroxides in vulcanising NR latex is probably due to the generation of radicals of low reactivity.

TABLE 2. RESULTS OF LATEX PREVULCANISATION EXPERIMENTS[a] USING DIACYL PEROXIDES AND A PEROXYDICARBONATE

Peroxide[b]	Q (g/g)
Unvulcanised latex film	> 25
Dioctanoyl peroxide	> 25
Didecanoyl peroxide	> 25
Bis-2-ethylhexyl peroxydicarbonate	> 25

[a] Prevulcanisation was carried out at 70°C for 6 h

[b] Using 5.55×10^{-5} gmol/g rubber of peroxide. Ferric ion (0.1 p.p.h.r.) was added as catalyst for diacyl peroxide systems.

A relatively low crosslink concentration was obtained after 24 h of prevulcanisation at 100°C using di-t-butyl peroxide (tBP) *(Table 3)*. Certain quaternary ammonium chlorides have been found to activate the decomposition of di-t-butylperoxyketal[17]. However, the presence of benzyltrimethyl ammonium chloride in the di-t-butyl peroxyketal system did not result in any prevulcanisation after 6 h at 80°C. The commercial peroxyketals and tBP would probably be effective as vulcanising agents for NR latex at elevated temperatures[3,18].

Hydroperoxide and Peroxyester Systems

A low crosslink concentration was obtained after 24 h of prevulcanisation at 100°C using t-butyl hydroperoxide (tBHP) *(Table 4)*. However, since the half-life time for the non-promoted decomposition of tBHP at 100°C is very long (more than 1500 h), it is probable that there is some promoted decomposition of tBHP by the non-rubber substances present in NR latex. Peroxyesters are significantly more effective than tBHP at 100°C *(Table 4)*. The effectiveness of the peroxyesters as vulcanising agents for NR latex appears to increase with increasing reactivity of the peroxyesters.

Activators for Peroxide Prevulcanising Systems

The results shown in the previous section and those of other workers[6-9], indicate that the decomposition of hydroperoxides and peroxyesters in NR latex can be promoted by using suitable activators. Various reducing agents and chemical agents that are known to promote peroxide decomposition in latex vulcanisation[6-9], in polyester curing[19] and in emulsion polymerisation[20-24] have been evaluated. The effectiveness of these activators was assessed from the crosslink concentration obtained after 6 h of prevulcanisation at 60°C using tBHP and activators. Among the activators investigated, fructose was found to be the most effective for tBHP. *(Table 5)*. It also has other advantageous properties compared with other activators. It is non-toxic, non-irritant, does not affect latex stability like hydroxylamine hydrochloride[8] due to the effect of ammonium chloride formed by reaction of hydroxylamine hydrochloride with ammonia and does not impart poor ageing properties to the prevulcanised latex films like metal salts[7]. The results in *Table 5* show that

TABLE 3. RESULTS OF LATEX PREVULCANISATION EXPERIMENTS USING A DIALKYL PEROXIDE AND A PEROXYKETAL

Peroxide[a]	Activator[b] (p.p.h.r.)	Reaction Temp. (°C)	Reaction Time (h)	Q (g/g)
tBP	—	100	24	12.8
tBPTCH	TEP (1.05)	80	6	> 25
tBPTCH	BZTAC (1.03)	80	6	> 25
tBPTCH	Fructose (1.0)	80	6	> 25

[a] tBP is di-t-butyl peroxide, employed at 6.48×10^{-5} gmol/g rubber. tBPTCH is 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, employed at 2.77×10^{-5} gmol/g rubber.

[b] TEP is tetraethylenepentamine and BZTAC is benzyltrimethyl ammonium chloride.

TABLE 4. RESULTS OF LATEX PREVULCANISATION EXPERIMENTS USING A HYDROPEROXIDE AND PEROXYESTERS

Peroxide	[Peroxide] × 10^5 (gmol/g rubber)	$[X]^a_{chem}$ × 10^5 (gmol/g rubber)
tBHP	11.1	0.04
tBPEH[b]	11.3	3.55
tBPIB[c]	11.2	2.88
tBPIC[d]	11.1	1.39
tBPAC[e]	11.0	0.96
tBPBO[f]	10.6	0.05

[a] For films from latex prevulcanised for 24 h at 100°C

[b] t-butyl peroxy-2-ethylhexanoate

[c] t-butyl peroxyisobutyrate

[d] t-butyl peroxyisopropylcarbonate

[e] t-butyl peroxyacetate

[f] t-butyl peroxybenzoate

activators which are easily oxidised, *i.e.*, strong reducing agents, tend to be less effective in promoting peroxide prevulcanisation of NR latex than those which are less easily oxidised. However, this does not take into account the effectiveness of other reducing agents such as hydroxylamine[8].

Fructose Activated Hydroperoxide and Peroxyester Systems

Figure 1 shows the changes in the crosslink concentration with time of prevulcanisation for tBHP-fructose and tBPIB-fructose systems at 60°C. The slope of the curve in *Figure 1* indicates the rate of crosslink insertion, and the maximum chemical crosslink concentration indicates the efficiency of crosslinking for the system. The results show that the tBPIB-fructose system is more efficient than the tBHP-fructose system. This is probably because of differences in the extent of unimolecular homolytic decomposition, fructose-activated decomposition and the decomposition activated by the non-rubber substances.

Table 6 shows the crosslinking efficiency (f_∞) and rate coefficient for crosslink formation (k'') for fructose-activated peroxyester systems at 60°C. The crosslinking efficiency f_∞ is the ratio (× 100) of maximum chemical crosslink concentration ($[X]_\infty$) obtained to the initial peroxide concentration. Crosslink formation during peroxide prevulcanisation of NR latex was found to be a first-order reaction, for the various systems investigated. The rate coefficient for crosslink formation can be obtained from the slope of $\ln[X]_t/[X]_\infty$ against time (t) plot, where $[X]_t$ is the chemical cross-

TABLE 5. EFFECTIVENESS OF ACTIVATORS IN PROMOTING tBHP PREVULCANISATION[a] OF NR LATEX AT 60°C

Activator	Q (g/g) after 6 h
Fructose	5.9
Tetraethylenepentamine (TEP)[b]	12.9
Maltose, lactose, catechol	$> 10 < 20$
Ascorbic acid, quinol, p-hydroxyethoxy benzaldehyde, 1,3-dibutyl-2-thiourea + n-dodecyl mercaptan[c], phenylphosphinic acid, NN-dimethyl-p-toluidine, anisaldehyde, 2,6-dimethylphenol, p-hydroxydiphenyl, o-hydroxydiphenyl, 8-hydroxyquinoline	> 20

[a] Using 11.1 × 10^{-5} gmol/g rubber each of tBHP and activator

[b] Q value obtained after 24 h using 7.89 × 10^{-5} gmol/g rubber of tBHP and 0.22 p.p.h.r. of TEP

[c] Using 0.49 p.p.h.r. of thiourea and 1.12 p.p.h.r. of mercaptan

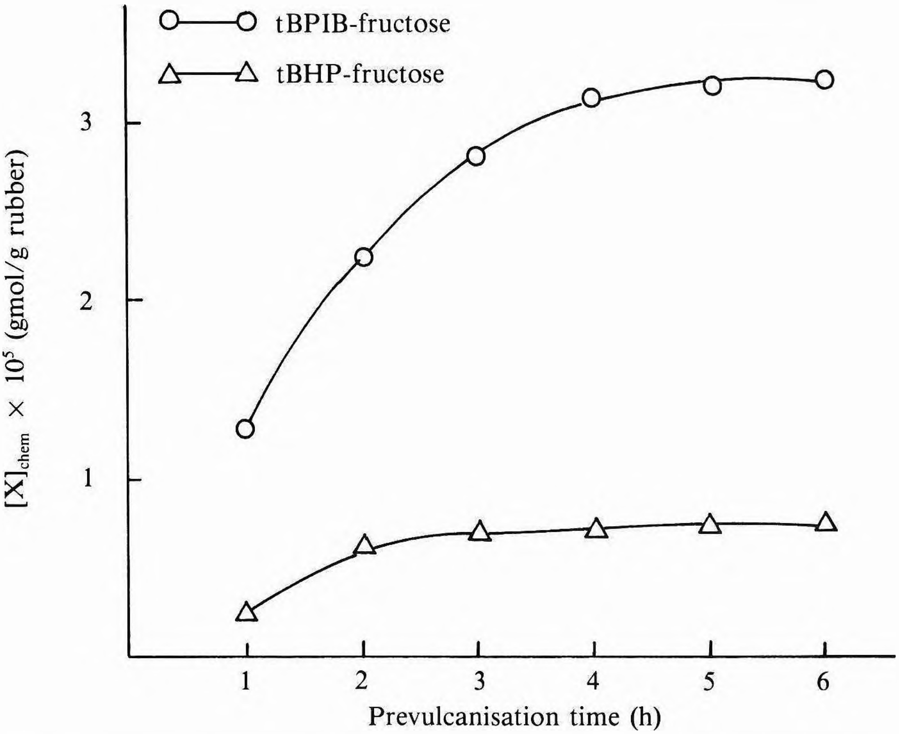

Figure 1. $[X]_{chem}$ versus prevulcanisation time for tBHP-fructose and tBPIB-fructose systems using 1.11×10^{-4} gmol/g rubber of peroxide and 2 p.p.h.r. of fructose at 60°C.

TABLE 6. CROSSLINKING EFFICIENCY AND RATE COEFFICIENT FOR CROSSLINK FORMATION OF PEROXYESTER-FRUCTOSE SYSTEMS[a] AT 60°C

Peroxyester	f_∞(%)	$k'' \times 10^5$ (s^{-1})
tBPND[b]	5	10.1
tBPPV[c]	6	6.6
tBPEH[d]	15	11.5
tBPIB[e]	13	23.1
tBPAC[f]	6	16.1
tBPBO[g]	8	7.4

[a] Using 5.55×10^{-5} gmol/g rubber of peroxyester and 2 p.p.h.r. fructose

[b] t-butyl peroxyneodecanoate

[c] t-butyl peroxypivalate

[d] t-butyl peroxy-2-ethylhexanoate

[e] t-butyl peroxyisobutyrate

[f] t-butyl peroxyacetate

[g] t-butyl peroxybenzoate

link concentration obtained after prevulcanisation time, *t*. *Figures 2–4* show plots of ln $[X]_t/[X]_\infty$ against prevulcanisation time at various temperatures for systems which initially contained different concentrations of tBPIB and fructose. The results in *Table 6* show no clear-cut relationship between the chemical structure of the peroxyesters and the effectiveness of the fructose-activated peroxyester prevulcanising systems. Fructose-activated tBPIB and t-butyl peroxy-2-ethylhexanoate (tBPEH) are more effective than other systems investigated. The efficiency of crosslinking of the fructose-activated tBPIB system increases with prevulcanisation temperature *(Figure 5)*. The initial fructose concentration has little effect upon the crosslinking efficiency. The crosslinking efficiency appears to increase with increasing initial peroxide concentration (compare results for tBPIB in *Figure 1* and *Table 6)*. The rate coefficient for the crosslink formation

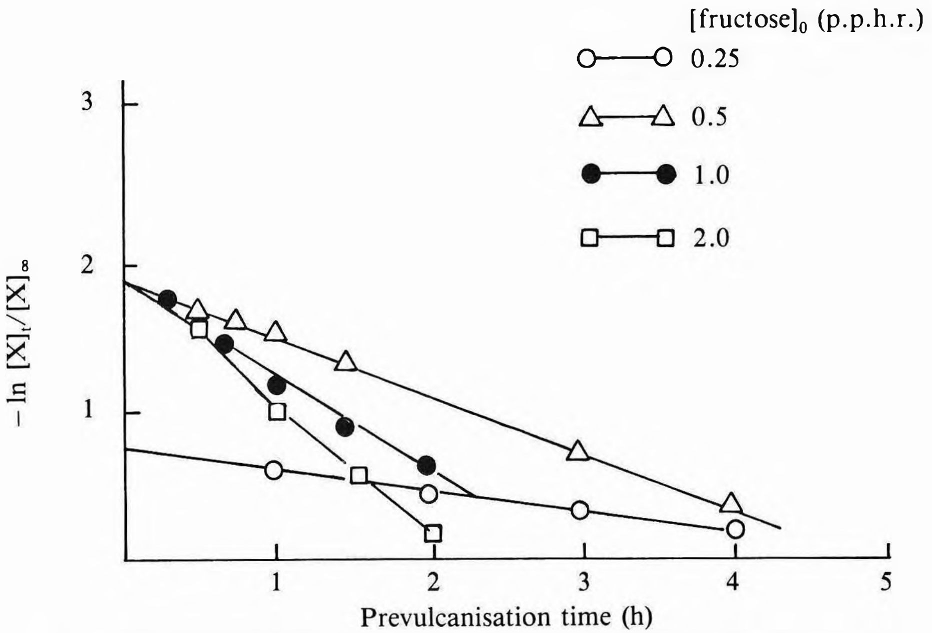

Figure 2. Plots of $-\ln [X]_t/[X]_\infty$ against prevulcanisation time at 60°C for systems which initially contained 5.56×10^{-5} gmol/g rubber tBPIB and different concentrations of fructose.

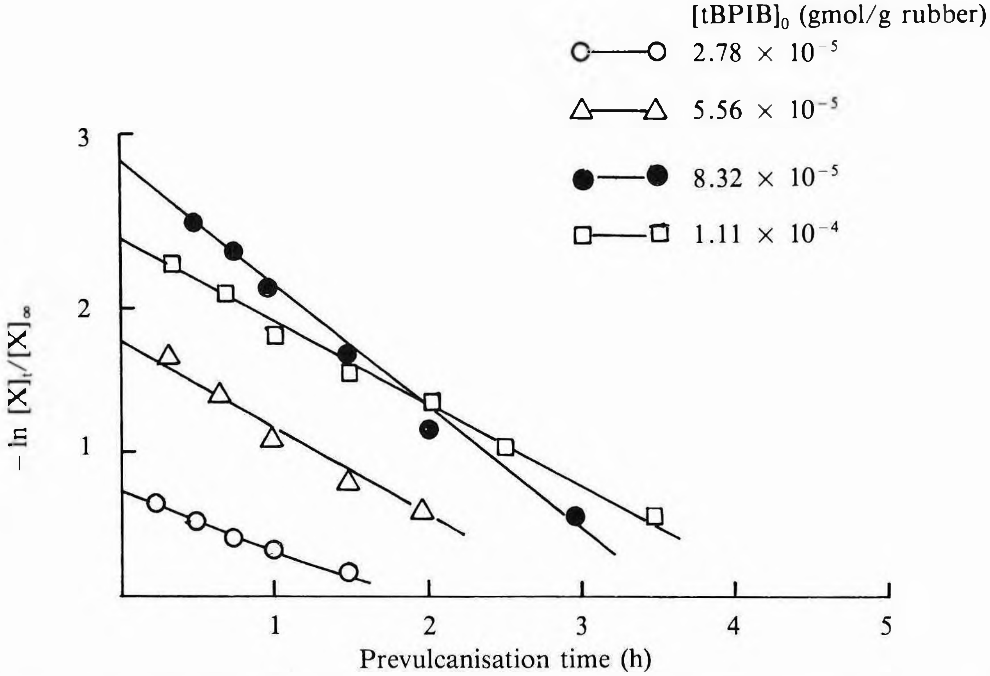

Figure 3. Plots of $-\ln [X]_t/[X]_\infty$ against prevulcanisation time at 60°C for systems which initially contained 1.0 p.p.h.r. fructose and different concentrations of tBPIB.

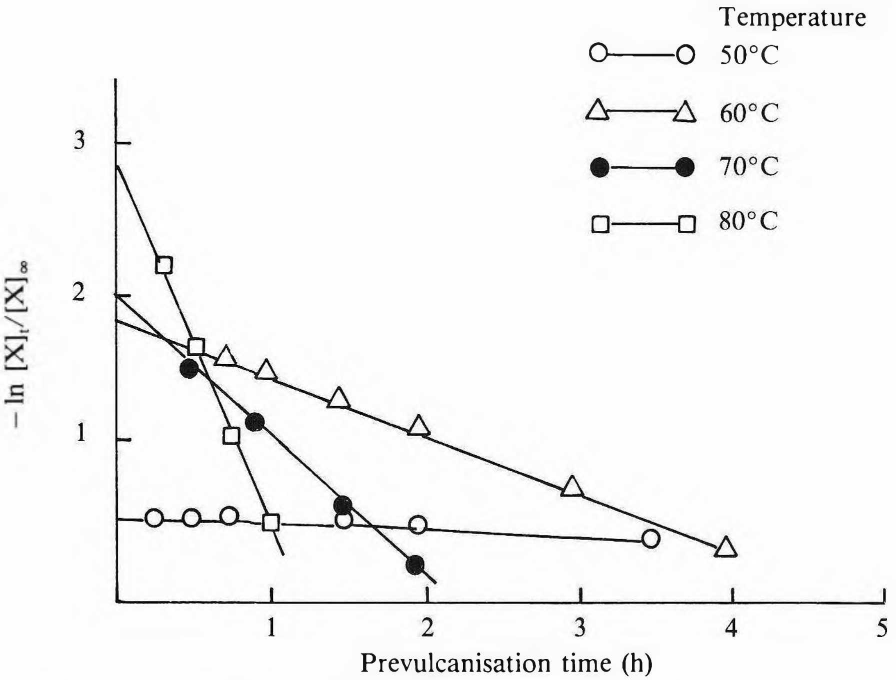

Figure 4. Plots of $-\ln [X]_t/[X]_\infty$ *against prevulcanisation time at various temperatures for systems which initially contained* 5.56×10^{-5} *gmol/g rubber tBPIB and 0.5 p.p.h.r. fructose.*

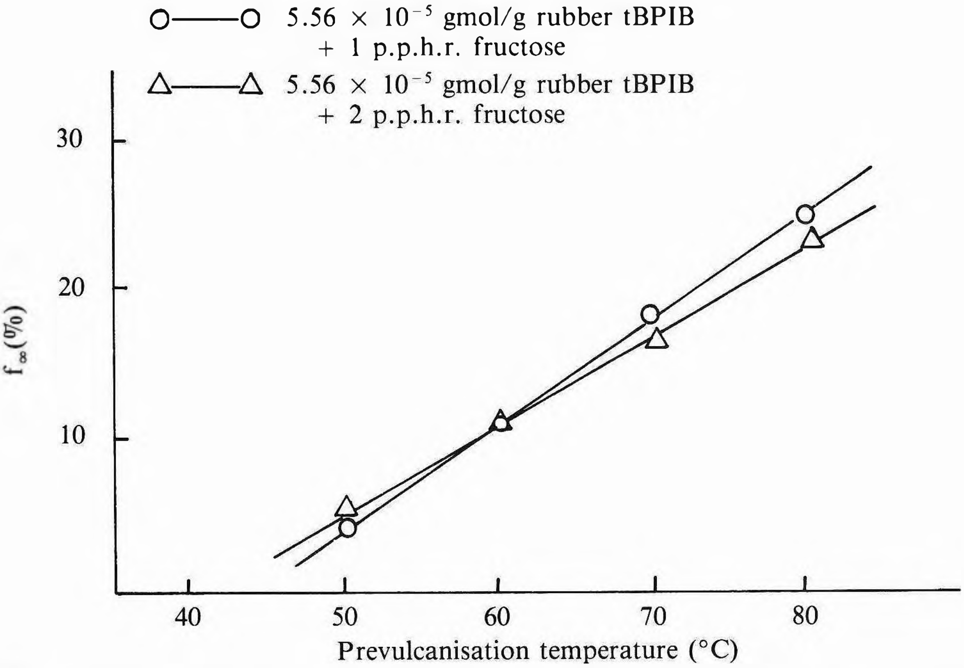

Figure 5. Effects of prevulcanisation temperature and initial fructose concentration at constant initial tBPIB concentration on the value of f_∞.

increases with increasing temperature and initial fructose concentration *(Figure 6)*.

Peroxyester-fructose-ferric Ion Systems

Prevulcanisation at 40°C using the tBPEH-fructose system proceeds at a very slow rate *(Table 7)*. However, a significant increase in the rate of prevulcanisation was observed when a trace amount of ferric ion-pyrophosphate complex was added to the system. Although transition-metal elements are present in trace amounts in NR latex, the peroxyester-fructose system became reasonably activated at 40°C when a ferric ion complex was added to the latex. This is probably because metal ions differ in their ability to perform catalysed reactions of peroxide[25]. The reactivity of a metal ion also depends upon its form[26,27]. The role of fructose in the above system is probably in converting ferric to ferrous ion, which is in a more appropriate oxidation state to activate the decomposition of peroxide. In the absence of fructose, a direct utilisation of ferrous ion may not be effective as it could be rapidly oxidised by the oxidising agents in NR latex and by oxygen[21,22].

Physical Properties of Films from Peroxide-prevulcanised NR Latex

The tensile strength of films from peroxide-prevulcanised NR latex increases and then decreases with increasing crosslink concentration *(Figure 7)*. The maxima in tensile strength and also the crosslink concentrations at which these maxima occur are generally lower for peroxide-prevulcanised latex films than for sulphur-prevulcanised latex films[27,28]. Bristow *et al.*[29] found that the maxima in tensile strength of bulk rubber vulcanisates are dependent upon the vulcanisate structure and the higher maxima occur at higher crosslink concentrations. Thus, a vulcanisate which contains

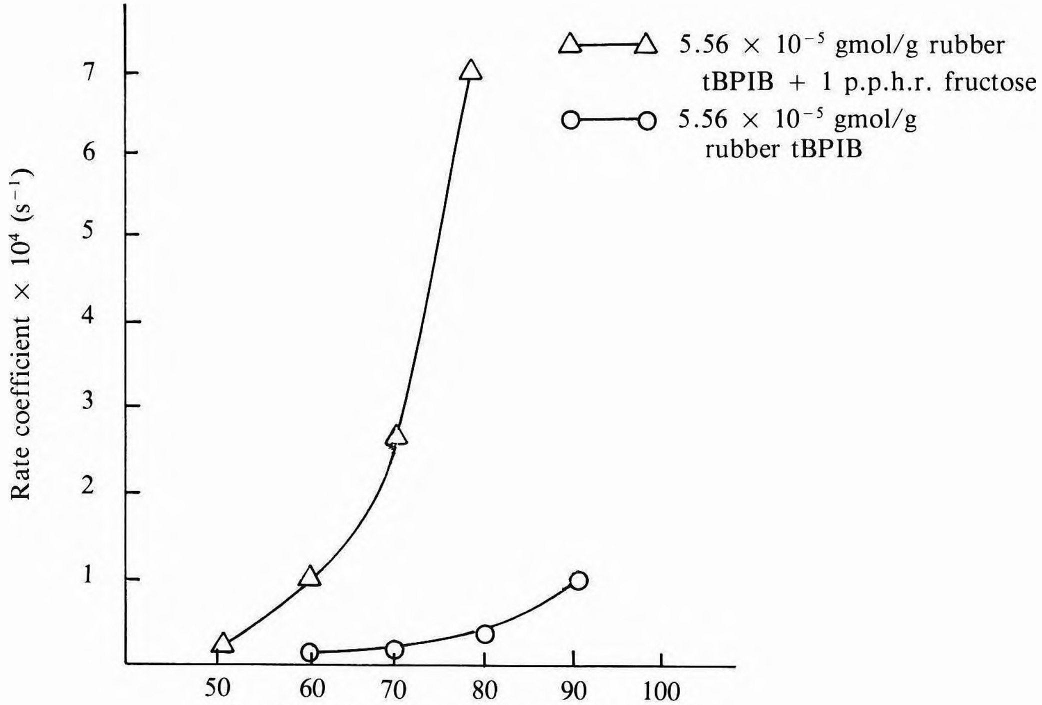

Figure 6. Effects of prevulcanisation temperature and fructose/tBPIB concentrations on the rate coefficient of crosslink formation.

TABLE 7. EFFECTS OF FERRIC IONS ON THE PREVULCANISATION OF NR LATEX USING tBPEH-FRUCTOSE SYSTEM AT 40°C

Prevulcanising system	Prevulcanisation time (h)	Q (g/g)
1.09×10^{-5} gmol/g rubber of tBPEH + 2 p.p.h.r. fructose	1	61
	2	46
	3	42
	4	35
	5	32
	6	26
1.09×10^{-5} gmol/g rubber of tBPEH + 2 p.p.h.r. fructose + 0.02 p.p.h.r. ferric ion	1	16.6
	2	9.3
	3	7.6
	4	6.1
	5	5.3
	6	4.8

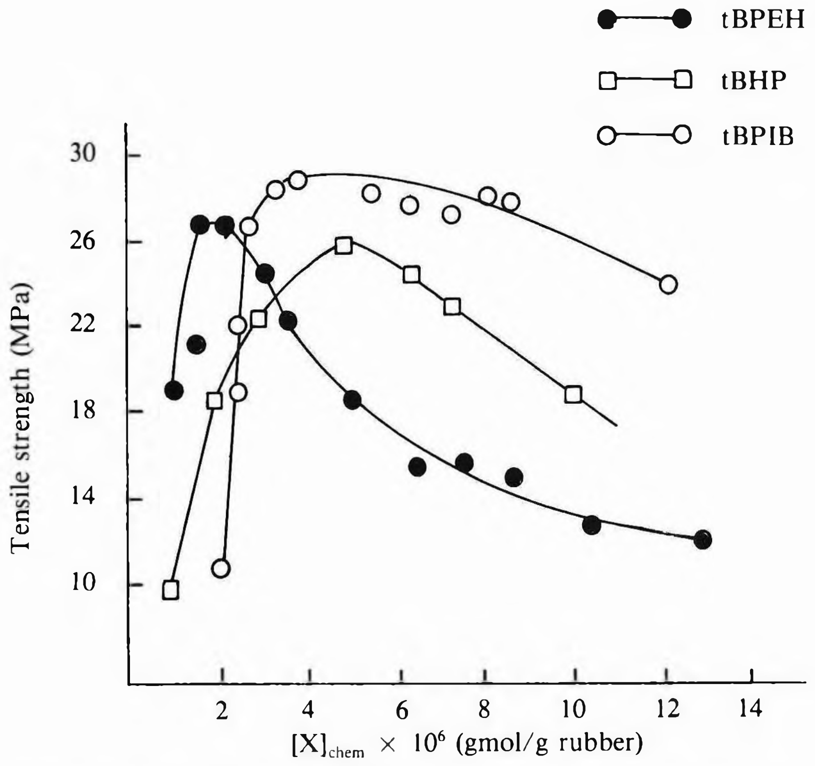

Figure 7. Tensile strength as a function of $[X]_{chem}$ *for films from various peroxide-prevulcanised NR latices.*

a high concentration of polysulphidic crosslinks was found to have a higher tensile strength maximum, that occurs at a higher crosslink concentration, than a vulcanisate which contains carbon-carbon crosslinks. The effect of polysulphidic crosslinks in enhancing tensile strength is attributed to the ability of sulphur-sulphur bonds to rupture and reform at the elongations[29]. The above explanation is probably also applicable to account for the differences in the tensile strength properties between a peroxide prevulcanisate which contains carbon-carbon crosslinks and a sulphur prevulcanisate which contains predominantly polysulphidic crosslinks. In addition to this, sulphur-prevulcanised latex film is probably more coherent than peroxide-prevulcanised latex film. This is because in the case of sulphur-prevulcanised latex film, inter-particle crosslinks[30,31] could form, and redistribution of crosslinked structures[31] between latex particles could occur during film formation and drying.

Films from peroxide-prevulcanised NR latex generally show 'medium' modulus *(Figures 8* and *9).* The tension set of films from peroxide-prevulcanised NR latex decreases quite rapidly with increasing crosslink concentration *(Figure 10).* The tear strength of films from peroxide-prevulcanised NR latex increases and then decreases with increasing crosslink concentration *(Figure 11).* The maximum tear strength appears to occur at a rather higher crosslink concentration than the maximum tensile strength.

The ageing properties of unprotected films from peroxide-prevulcanised NR latex are poor. This is because the natural antioxidants in NR latex have been oxidised during prevulcanisation, and probably also due to the presence of pro-oxidants in the films. The addition of certain antioxidants into the peroxide-prevulcanised NR latex helps improve the ageing properties of the films *(Table 8).* Among the antioxidants studied, bis-[beta-(3,5-ditert-butyl-4-hydroxybenzyl) methylcarboxyethyl] sulphide (Irganox 1035), was found to give good retention of tensile strength after ageing. Some of the antioxidants are much more effective on their own than when combined with other antioxidants.

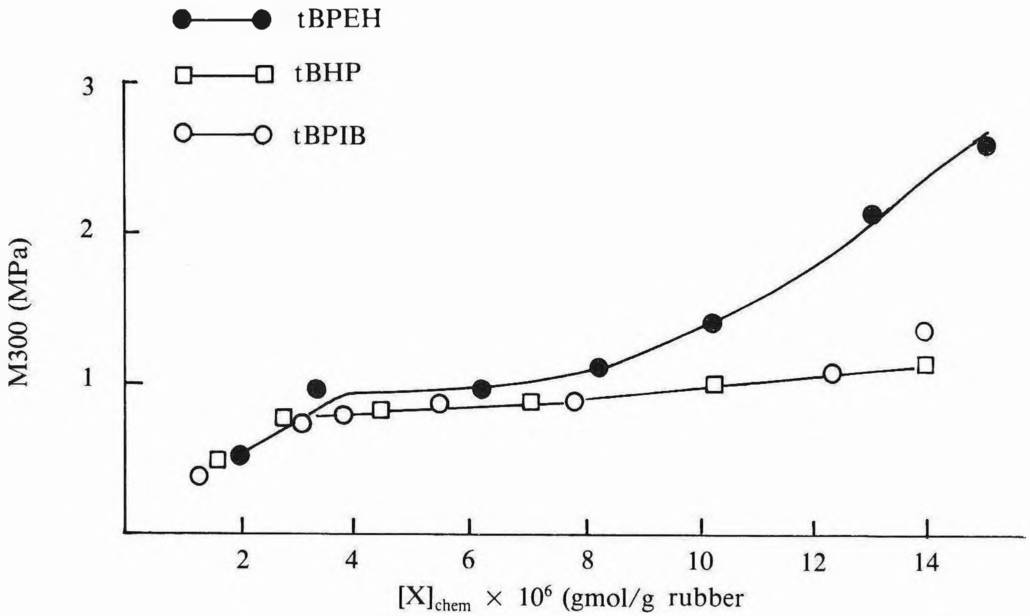

Figure 8. M300 as a function of $[X]_{chem}$ for films from various peroxide-prevulcanised NR latices.

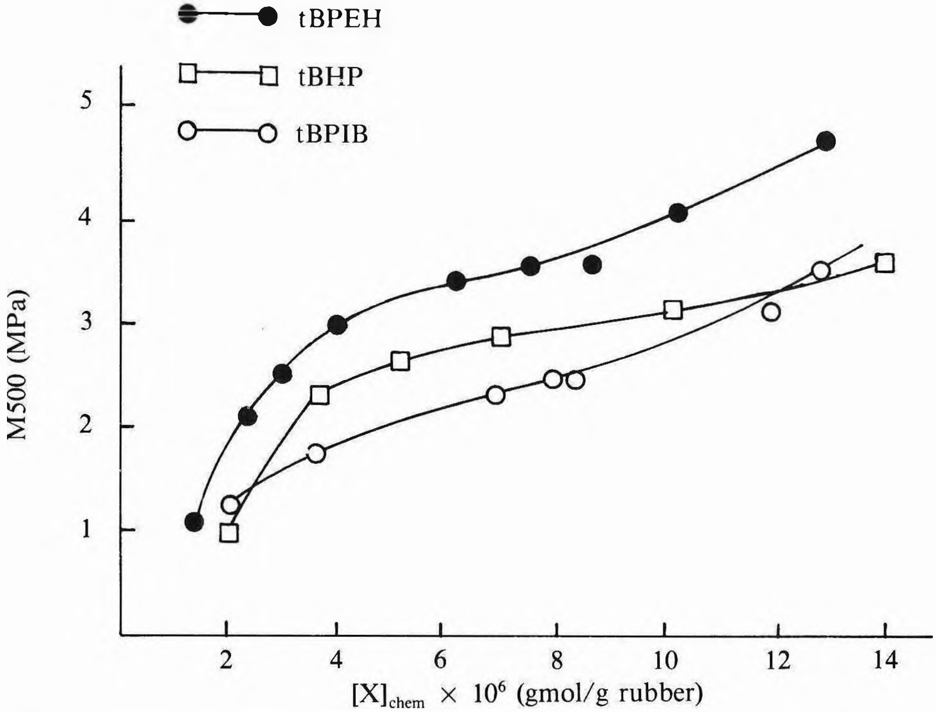

Figure 9. M500 as a function of $[X]_{chem}$ for films from various peroxide-prevulcanised NR latices.

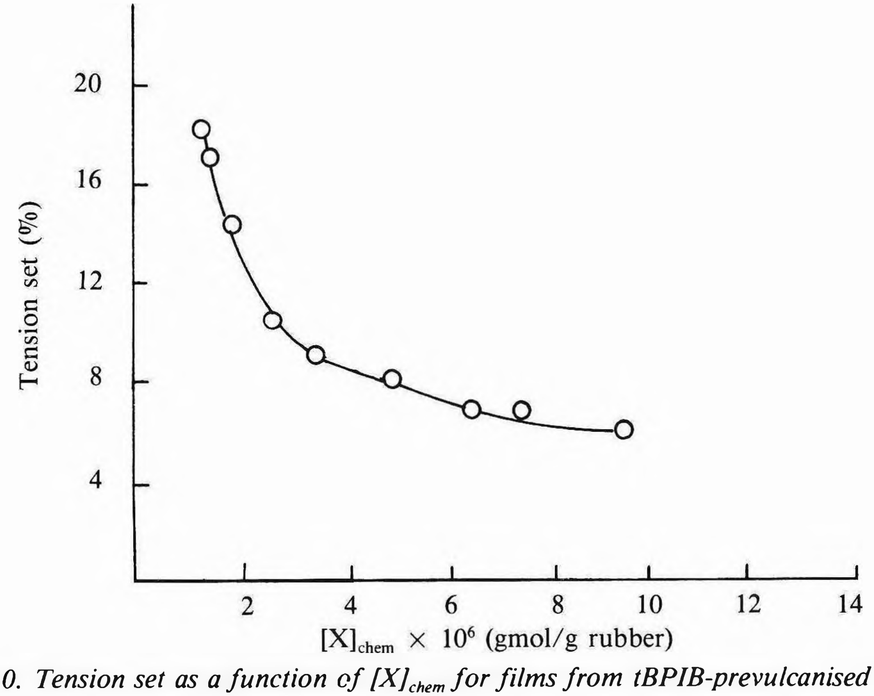

Figure 10. Tension set as a function of $[X]_{chem}$ for films from tBPIB-prevulcanised NR latex.

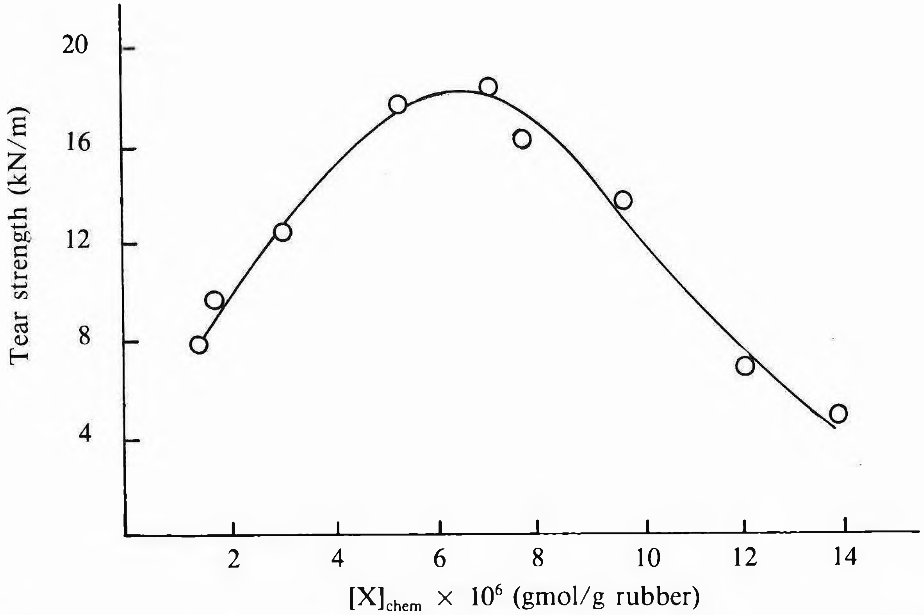

Figure 11. Tear strength as a function of $[X]_{chem}$ for films from tBPIB-prevulcanised NR latex.

TABLE 8. EFFECTS OF ANTIOXIDANTS ON AGED (70°C FOR 7 DAYS) PROPERTYES OF FILMS FROM PEROXIDE-PREVULCANISED NR LATEX[a]

Antioxidant	Percentage retention of property after ageing		
	M500	TS	EB
Without antioxidant	36	5	60
ZDEC (1 p.p.h.r.)	76	130	127
Antioxidant 2246[b] (1 p.p.h.r.)	52	17	79
Irganox 1035 (1 p.p.h.r.)	65	87	119
Irganox 1093 (1 p.p.h.r.)	59	41	103
Irganox 1010 (1 p.p.h.r.)	65	56	105
Irganox 1076 (1 p.p.h.r.)	62	49	104
Irganox PS802 (1 p.p.h.r.)	70	49	101
Irgafos TPP (1 p.p.h.r.)	61	41	90
Cadmium diisopropyl thiophosphate (1 p.p.h.r.)	65	58	107
EDTA (1 p.p.h.r.)	61	41	90
Antioxidant 2246 (0.5 p.p.h.r.) +			
Irganox PS802 (0.5 p.p.h.r.)	60	38	93
EDTA (0.5 p.p.h.r.)	61	30	90
Irganox 1076 (1 p.p.h.r.)	58	28	90
Irgafos TPP (0.5 p.p.h.r.)	56	19	79
Antioxidant 2246 (0.5 p.p.h.r.) +			
Irganox PS802 (0.5 p.p.h.r.) +			
EDTA (0.5 p.p.h.r.)	68	67	107
Irganox 1076 (0.5 p.p.h.r.)	57	33	95
Irgafos TPP (0.5 p.p.h.r.)	61	20	81

[a] Latex prevulcanised at 60°C for 4 h using 5×10^{-5} gmole/g rubber tBPIB and 1 p.p.h.r. fructose. Unaged film properties: M500 = 3.03 MPa, TS = 21.1 MPa, EB = 849.

[b] Discolouration of all samples using Antioxidant 2246.

CONCLUSION

The fructose-activated peroxyester systems, particularly the fructose-tBPIB system, are generally more effective (higher prevulcanisation rate and prevulcanisation efficiency) prevulcanising systems than others investigated. Peroxide-prevulcanised NR latex films having tensile strength in the range 20–25 MPa can be obtained. The tensile strength maxima of films from peroxide-prevulcanised NR latex occur at lower crosslink concentrations than those of films from sulphur-prevulcanised NR latex. The ageing properties of films from peroxide-prevulcanised NR latex are poor. Some antioxidants added to the prevulcanised latex improve the ageing properties of films obtained from it. Peroxide-prevulcanised NR latex has potential in applications such as baby teats, soothers and certain medical products. However, some knowledge of the fate of reaction by-products of peroxide is required to establish the toxicity credentials of the product. Further improvement in the ageing properties of the prevulcanised latex films is necessary.

ACKNOWLEDGMENT

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Effect of Process Aids on Surface Friction of Raw Rubber

E.L. ONG* AND A.D. ROBERTS**

The efficacy of various commercially available process aids as surface lubricants of raw natural rubber was examined using a simple friction apparatus. The aids were either spread on the hard counterface or incorporated in the raw rubber. Experiments were carried out over a range of temperatures from 25°C to 120°C at modest sliding speeds in order to follow changes in friction levels, surface morphology of the rubber and film transfer. In general, the presence of any process aid at the sliding interface led to a reduction in the surface friction.

Over the past decade or so, the rubber industry has become increasingly interested in the automation of machinery, and to accomplish this it requires rubber grades with predictable processing characteristics. To this end, process aids have a role to play. They are materials which can be added in small amounts to a rubber compound to improve processability in factory operations prior to vulcanisation, without adversely affecting the physical properties of the vulcanisate. For example, materials are available to provide lubrication so as to aid extrusion and moulding. Fatty acids and their derivatives, such as esters and metal soaps, increasingly find use as suitable materials. How such aids bring about processing improvements is not always clear, although there is evidence that they can lubricate molecules within the rubbery bulk. For example, measurements of stress relaxation in tensile testpieces of raw rubber indicate faster relaxation when an aid such as Dutrex 729 or Struktol A60, is incorporated into the rubber[1]. This can only be 'internal' lubrication.

Different process aids may act differently, perhaps depending on circumstances. They may be both internal and external lubricants. In mixing, it may be a balance between sufficient external friction and sufficient internal lubrication that is important and calls for an appropriate process aid. In die extrusion, however, the action of the aid may be essentially a surface effect to provide external lubrication[2].

A study of the surface friction of polypropylene showed that additives can have a profound effect[3]. As originally made, the polymer had high friction, but after storage the friction decreased. Reversion to the original friction could be obtained by washing the sample, indicating that the low friction was due to surface bloom of the additive. Such lubricants can be deliberately added to a polymer, or may be purely adventitious. The effect can be marked with only small quantities of additive, at the 0.1% level in the case of some surfactants.

A rheometer study[4] of the flow of unvulcanised rubber has shown that high levels of incorporated stearic acid reduce the friction at rubber-metal interfaces. It was inferred that a low viscosity/low shear strength phase separates out onto the rubber surface. The phenomenon is referred to as lubricated wall slip. Rubber compound formulations which retain lubricated wall slip at high shear rates do exhibit extremely smooth surfaces when extruded. Commercial stearic acid is a mixture of fatty acids with a range of carbon atom numbers. The rheometer study[4] was extended to examine the effect of fatty acid molecular weight on wall slip and it was found that the higher the molecular weight, the greater was the

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**Malaysian Rubber Producers' Research Association, Brickendonbury, Hertford SG13 8NL, United Kingdom wall slip. It appeared that the lower molecular weight fatty acids less readily separated out to the surface. These results have control implications for factory operations.

This paper reports experiments on the lubricating effect of some commercial process aids by making friction measurements of unvulcanised Malaysian natural rubber sliding against a hard substrate with either an aid incorporated into the rubber or precipitated as a thin film on the substrate. In addition, tests are reported on using palm oil as an aid. Reduction in friction levels of up to 70% was found with certain types of process aid.

EXPERIMENTAL

Details of the process aids used in this study are given in *Table 1.* The raw natural rubber grades employed were SMR CV and SMR L. The formulations of the commercial process aids are not disclosed but they are believed to consist of mixtures of esters or metal soaps of long-chain fatty acids with melting points ranging from 50°C to 100°C. The mixing of any aid into a rubber was done on a laboratory two-roll mill (Brabender preparative mill). The roll surface was maintained at around 90°C. The addition of process aids (usually 5 p.p.h.r.) was carried out after the rubber had formed a continuous band on the mill surface, and the mixing process was continued for another 5 min.

Friction measurements were taken as an indication of the effectiveness of a particular process aid to act as a surface lubricant. The measurements were made with a simple apparatus[5]. A raw rubber hemisphere or hemicylinder was slid against a flat substrate of either 'Perspex' (polymethylmethacrylate), mild steel or a thin sheet of raw rubber supported on a hard substrate. Rubber hemicylinders and hemispheres were made by compression moulding at elevated temperatures[5]. When a 'Perspex' plate was used the sliding interface could be examined directly, and when

TABLE 1. TYPES OF PROCESS AIDS AND OTHER LUBRICANTS

Process aid	Chemical description	Melting point (°C)	Manufacturer
A	Esters mixture on inert carrier	50	S & S
B	Mixture of high molecular weight fatty acid derivatives	—	S & S
C	Water in oil emulsion	—	Kettlitz
D	Peptiser, water in oil emulsion	—	Kettlitz
E	Disperator	—	Kettlitz
F	Mixture of fatty acid soaps, mainly of calcium	95	S & S
G	Zinc soap of high molecular weight fatty acid	—	S & S
H	Zinc soap of high molecular weight fatty acid	—	Bozzetto
I	Zinc soap based on long- and branch-chain fatty acids	75-85	S & S

S & S = Schill and Seilacher

Many melting points cannot be quoted because the commercial process aid is carried on silica or other materials.

a mild steel plate was used its temperature could be raised to 120°C by an electric heater. A process aid was either put on a substrate surface as a thin film (spread, or precipitated from a solvent), or mixed into a rubber. Temperature measurements were made with a thermocouple probe touched onto a track surface. A sufficiently long contact dwell-time was allowed for the rubber sub-surface to warm up[5].

Under a normal load, W, the sliding friction force, F, was measured at a given speed and the friction coefficient, $\mu = F/W$, used to compare the efficacy of various process aids as surface lubricants of raw rubber. Unless otherwise stated, hard substrate surfaces were cleaned by wiping with tissue paper moistened with pure isopropanol, then allowed to dry. All rubber surfaces were tested as moulded without solvent treatment. The friction apparatus arrangement for measurements on a hot steel surface is shown in *Figure 1.*

Capillary Rheometry

Supplementary studies to examine the lubricity of process aids were carried out using a capillary rheometer (Monsanto Processability Tester) over a range of temperature and extrusion speeds[2]. The die capillary diameter was 2 mm and its length/diameter ratio was 20. This tends to give steady extrusion flow.

RESULTS

Sliding on 'Perspex' Track

A number of commercially available process aids were tested at room temperature for their lubricant action at the sliding interface of a raw SMR CV hemisphere (radius 21 mm) in contact with a length of 'Perspex' plate (polymethylmethacrylate), the track surface being smooth (surface roughness less than 0.1 μm Centre Line Average). A film of an aid was cast onto the 'Perspex' track. The various aids were compared for a fixed normal load at constant sliding speed. In general, the results *(Table 2)* show that all the process aids tested reduced the friction of a dry, clean track. The presence of water led to the lowest values of friction, and the least deformation or damage of the rubber surface.

Smooth-surfaced 10 mm thick sheets of raw SMR CV were laid on a 'Perspex' plate to form rubber tracks. Various aids were cast in turn

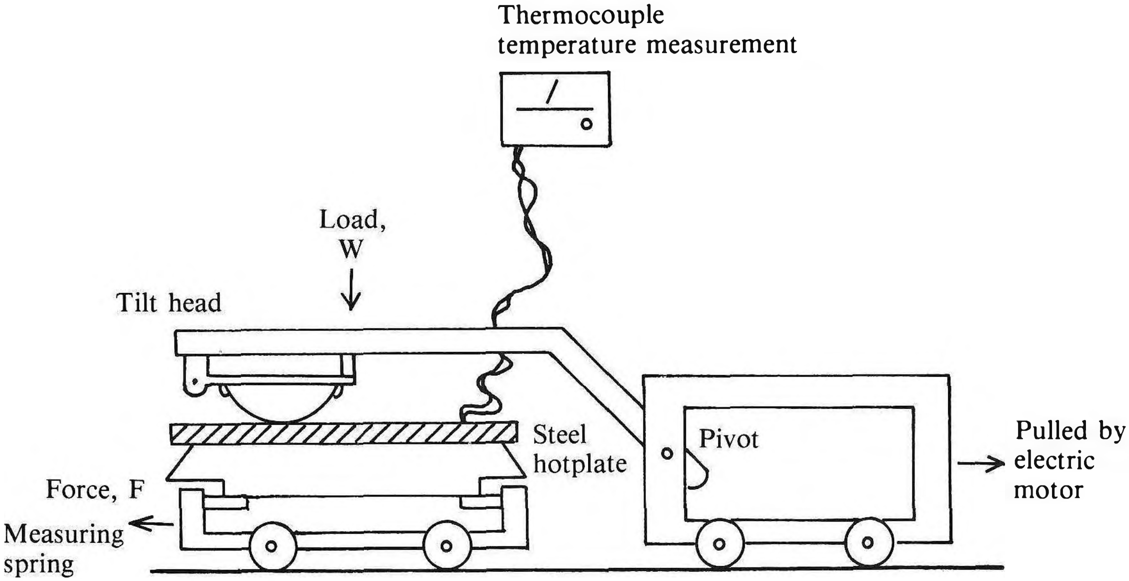

Figure 1. Apparatus for friction measurements against hot steel.

TABLE 2. EFFECT OF PROCESS AIDS ON SURFACE FRICTION OF SMR CV ON PERSPEX TRACK

Process aid	Track treatment	Friction coefficient	Observations on rubber surface
None	Dry	3.4	Ridge formation
A	Cast film	2.1	Some damage to the rubber
	Repeat cast	2.0	
	+ dist. H_2O	1.9	No damage
B	Cast, recast	2.0	Slight damage
	+ dist. H_2O	1.7	No damage
C	Cast, recast	1.7	Tiny ridges
	+ dist. H_2O	1.5	No damage
D	Cast film	2.1	Some scuffing
	Repeat cast	1.6	Slight scuffing
	+ dist. H_2O	1.4 ave.	No damage
	Cast film	1.1	No damage apparent
	Repeat cast	0.9	
	+ dist. H_2O	0.9	

Normal load 3.43 N; sliding speed 0.2 mms^{-1}, T = 22°C–24°C   SMR CV hemisphere

onto the fresh tracks. Their lubricant effects, at room temperature, were compared when a hemisphere (radius 21 mm) of raw SMR CV was drawn over the track. All the process aids reduced the friction of untreated surfaces, some more than others *(Table 3).*

Sliding on Mild Steel

Various process aids were tested by either putting them, in turn, on the mild steel track surface (surface roughness 0.2 μm CLA) or incorporating them into the raw rubber

TABLE 3. EFFECT OF PROCESS AIDS ON SURFACE FRICTION OF SMR CV HEMISPHERE ON SMR CV TRACK

Process aid	Track treatment	Friction coefficient	Observations on rubber surface
None	Dry	10	Severe surface damage
A	Cast film	5.1	Some slight damage
B	Cast film	9.4	Considerable damage
F	Cast film	6.3	Pulled out area of rubber
E	Cast film	3.2	Ridges on hemisphere, track damaged
D	Cast film	4.6	Ridges on hemisphere, track marks
C	Cast film	5.2	Ridges on hemisphere, track marks
Zinc stearate film		3.7	Ridges on hemisphere, track marks
G		2.1	Only slight surface damage
H		3.4	Slight surface damage

Normal load 3.43 N; sliding speed 0.2 mms^{-1}, T = 22°C–24°C.

(SMR CV). The rubber samples were in the form of moulded smooth-surfaced hemicylinders, (radius 21 mm). Friction measurements were carried out at room temperature and at selected elevated temperatures. The results *(Table 4)* indicate that at room temperature the reduction in the friction due to a process aid was generally greater when the aid was put on the steel track, than when it was incorporated into the rubber. With increasing temperature, the trend was for the difference in friction between surface deposition and rubber incorporation of an aid to become less. At higher temperatures, above the approximate melting point for the aids, surface or incorporated aid gave the same surface lubricating effect, absolute values of friction being noticeably less than at room temperature

TABLE 4. FRICTION ON MILD STEEL IN PRESENCE OF PROCESS AIDS

Process aid	Temperature of track (°C)	Friction coefficient		Friction stress (KPa)	
		For surface deposit	For rubber incorporation	For surface deposit	For rubber incorporation
F	24	0.7	2.4	28.0	77.4
	40	0.6	3.8	20.1	76.6
	60	0.5	2.0	10.5	18.3
	90	0.3	0.8	5.5	2.6
	120	0.2	0.4	2.5	1.2
G	24	1.7	2.1	74.7	53.1
	40	1.1	4.5	28.9	20.2
	60	1.5	2.0	25.4	5.4
	90	0.7	0.5	8.6	1.0
	120	0.8	0.3	7.1	0.5
I	24	1.9	2.0	55.6	49.2
	40	1.7	3.8	43.6	20.1
	60	0.7	1.3	12.3	3.4
	90	0.5	0.7	6.2	1.0
	120	0.4	0.3	3.7	0.6
H	24	1.2	2.1	51.6	85.4
	40	1.2	3.9	35.4	25.2
	60	1.6	1.6	23.0	5.2
	90	0.3	1.3	5.2	3.1
	120	0.2	0.4	2.5	0.9
No aid	24	3.7		392	
	40	3.5		261	
	60	2.8		133	
	90	1.8		52.1	
	120	1.2		13.6	

Normal load 3.43N; sliding speed 0.2 mms^{-1}

(Figure 2). With increasing temperature, surface damage due to sliding of rubber samples became less.

A peak in the friction coefficient that occurred at 40°C was observed for all aids when they were incorporated into rubber *(Table 4, Figure 2).* This appears to be due to a softening effect. When an aid was incorporated into a rubber sample, the body of the sample readily deformed upon loading against the steel track, with the result that the real contact area was much enlarged compared to a similar sample without aid incorporated. This enlarged contact area is believed to be the reason for the peak friction at 40°C. An examination *(Figure 3)* of contact areas after sliding was found helpful to interpretation. A plot of the friction stress (friction force/contact area) shows the efficacy of a process aid above its melting temperature *(Figure 4).* When allowance is made for the actual contact area a 'cross-over' in friction levels is found, the lower level at high temperature resulting from process aid incorporated into the rubber. One might surmise that the cross-over in frictional stress levels above 80°C could be due to the aid-incorporated rubber having a softer bulk. For a given load, this would lead to a relatively higher real area of contact and hence high friction. This result, obtained in the laboratory for a rubber hemisphere slid against a steel plate, may not be borne out in practical situations of different contact geometry.

Capillary Rheometry

The aim of these rheometry studies was to see the amount by which the apparent capillary shear stress is reduced at a given shear rate by the incorporation of different process aids. In an earlier study[2] of flow curves, it was found that the viscosity was reduced by the addition of a particular process aid. The results *(Table 5)* of this study show that an incorporated process aid can reduce the shear stress considerably, particularly at high temperature and low shear rate under conditions of steady extrusion. For

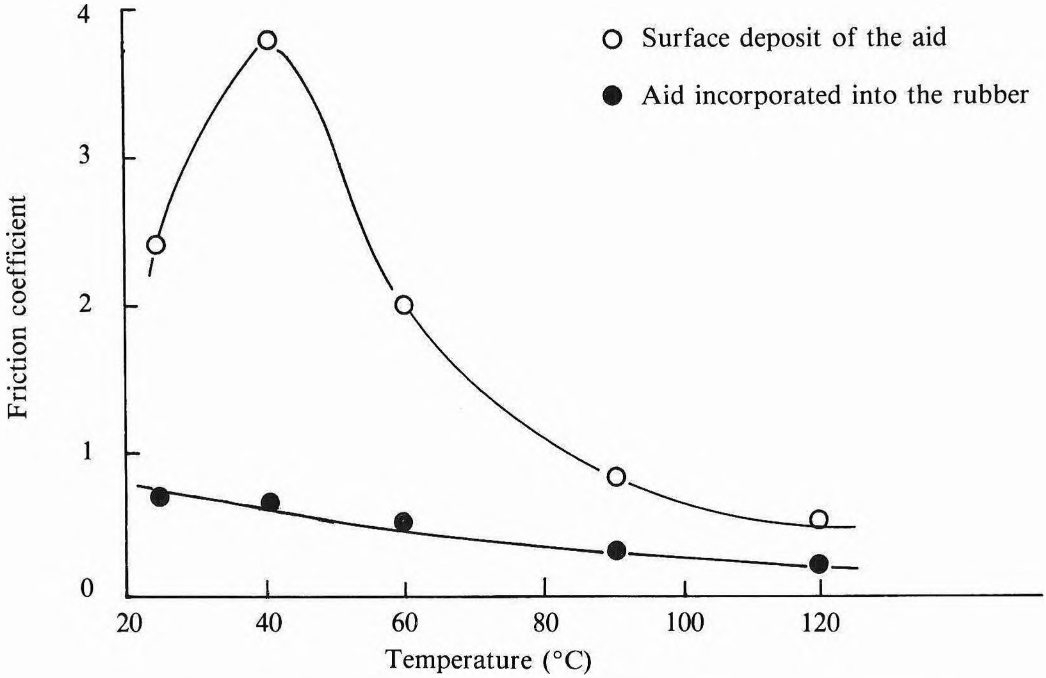

Figure 2. Effect of process aid F on friction of SMR CV against steel.

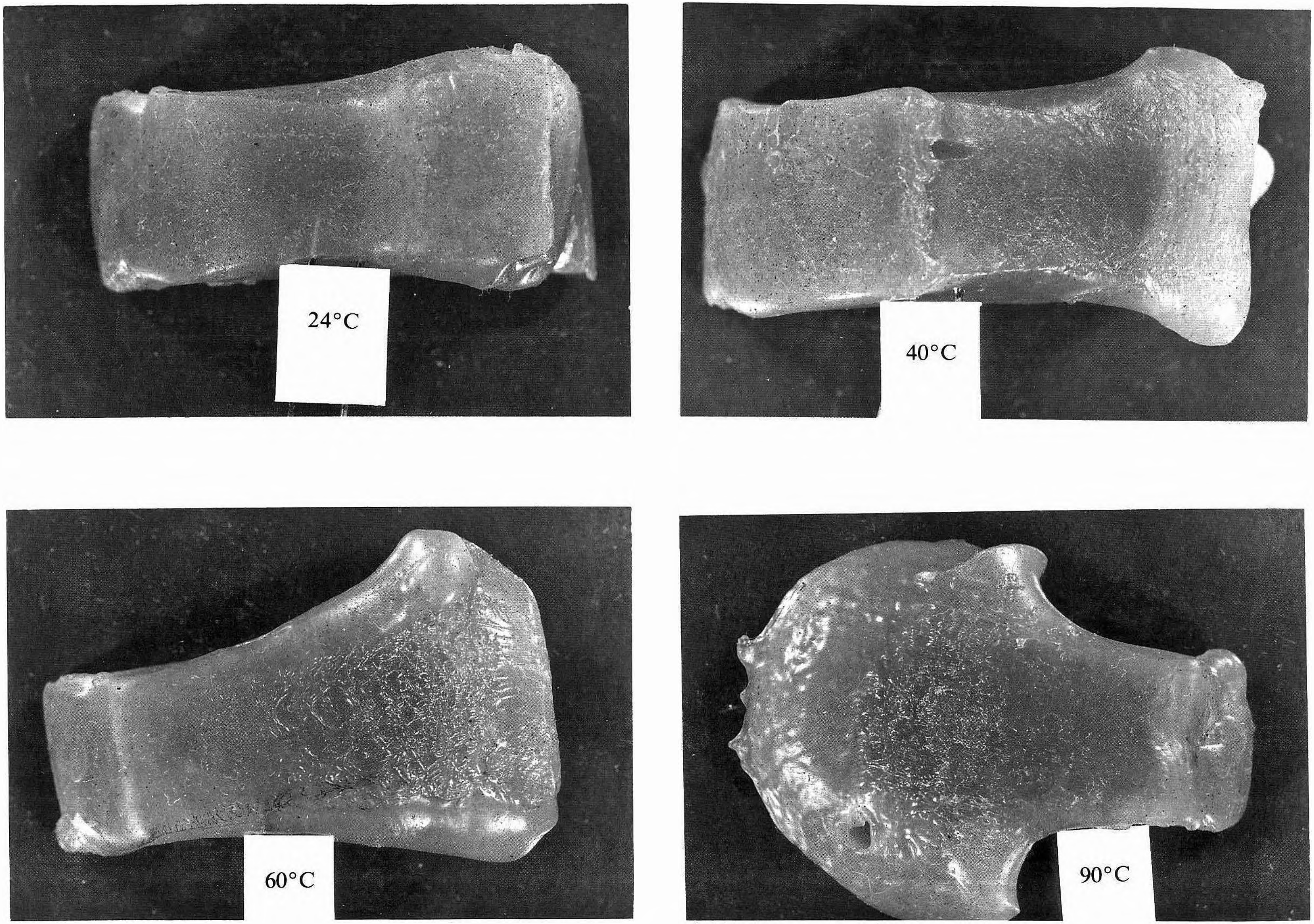

Figure 3. Contact areas as seen after sliding of SMR CV against steel. The rubber contained the process aid F incorporated into its bulk. Steel surface temperatures were 24°C, 40°C, 60°C and 90°C.

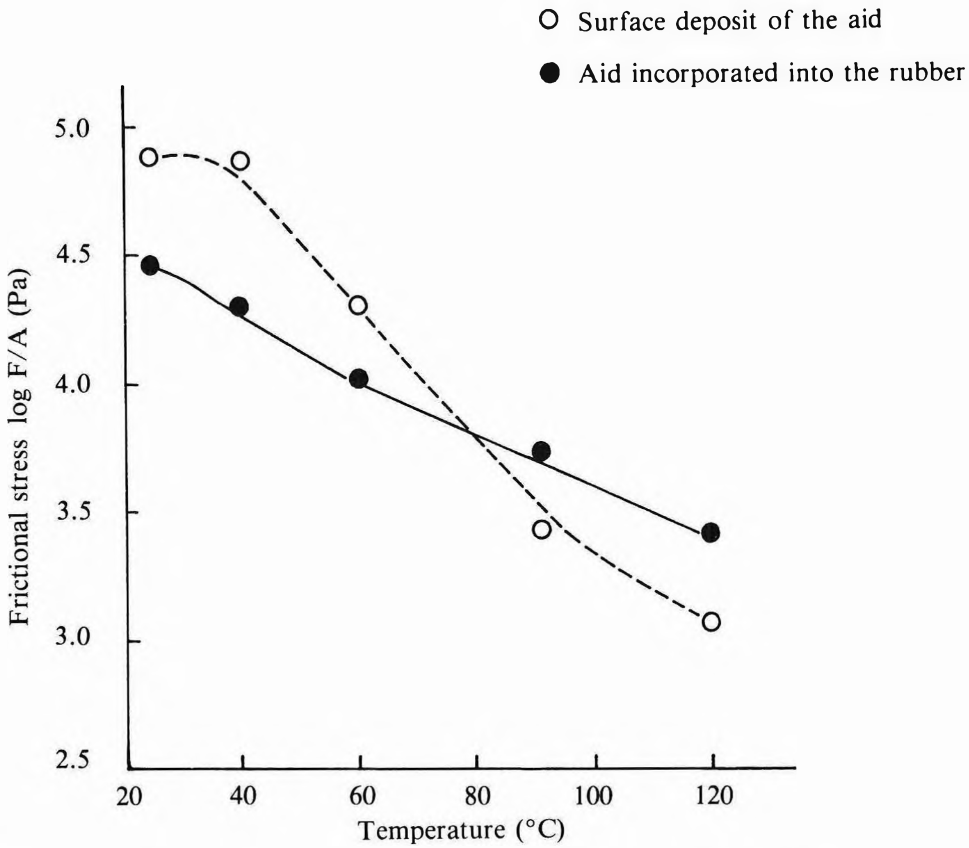

Figure 4. Plot of friction stress to show efficacy of the process aid F above its melting point.

TABLE 5. EXTRUSION STRESS AT DIFFERENT APPARENT SHEAR RATES OF SMR CV WITH VARIOUS PROCESS AIDS INCORPORATED

Process aid	Temperature (°C)	Extrusion stress (MPa)			
		1.5 s^{-1}	7.6 s^{-1}	15.1 s^{-1}	76 s^{-1}
I	60	0.072	0.127	0.149	0.243
	90	0.039	0.071	0.086	0.143
	120	0.017	0.042	0.057	0.101
G	60	0.075	0.140	0.172	0.303
	90	0.034	0.061	0.084	0.144
	120	0.012	0.026	0.039	0.084
NR (control)	60	0.269	0.582	0.765	1.045
	90	0.140	0.194	0.216	0.280
	120	0.107	0.162	0.194	0.248

Conditions: L/D = 20, diameter 2 mm

these circumstances, the measured friction stress for incorporated process aid *(Table 4)* mirrors this behaviour.

Palm Oil

The objective was to discover whether palm oil might provide effective surface lubrication of raw natural rubber, and whether it also plasticises the rubber. Accordingly, testing of SMR L hemicylinders sliding against mild steel was done. Palm oil in various states of refinement was either deposited onto the steel surface, or it was incorporated into the rubber bulk. Friction measurements were obtained at different temperatures, and a comparison made with epoxidised soya bean oil which is used industrially to plasticise various plastics such as PVC. The results *(Table 6)* suggest that crude palm oil acts as a good lubricant when incorporated into the rubber. Refined states or components do not show any improvement in lubricity. The surface deposit was particularly effective because a lot of oil was used. It seems surprising that rubber incorporated soya bean oil which is less compatible with rubber than palm oil gives higher friction values at high temperatures *(Table 6)*. It is possible that there

TABLE 6. FRICTION COEFFICIENTS FOR PALM OIL AS A PROCESS AID FOR SMR L

Oil	Temperature (°C)	Friction coefficient	
		Surface deposit	Rubber incorporation
Zero oil	24		4.1
Epoxidised crude palm oil	24	0.22	1.5
	40		0.8
	60		0.3
	90		0.3
Epoxidised RDB palm oil	24	0.09	1.5
	40		0.4
	60		0.6
	90		0.4
Epoxidised RDB palm stearin	24	0.11	1.5
	40		0.7
	60		0.6
	90		0.3
Epoxidised RDB palm olein	24	< 0.01	1.6
	40		0.7
	60		0.3
	90		0.3
Soya bean oil (epoxidised)	24	0.11	1.5
	40		0.5
	60		0.5
	90		0.5

RDB — Refined de-odourised bleached

Sliding speed 0.2 mms^{-1}

TABLE 7. EXTRUSION STRESS OF SMR L WITH VARIOUS OILS INCORPORATED AT VARIOUS APPARENT/SHEAR RATES

Oil	Extrusion stress (MPa)							
	3.6 s^{-1}	10.8 s^{-1}	21.6 s^{-1}	36.0 s^{-1}	108.0 s^{-1}	218.0 s^{-1}	360.0 s^{-1}	720.0 s^{-1}
None (control)	0.237	0.284	0.315	0.345	0.491	0.717	0.872	1.138
Crude palm oil	0.197	0.235	0.257	0.278	0.345	0.483	0.707	1.000
Epoxidised crude palm oil	0.198	0.234	0.252	0.269	0.322	0.427	0.528	0.976
RBD palm olein	0.200	0.233	0.248	0.265	0.315	0.425	0.500	0.961
Epoxidised RBD palm oil	0.198	0.237	0.259	0.276	0.339	0.465	0.612	0.974
RBD palm oil	0.190	0.222	0.240	0.254	0.303	0.384	0.481	0.871
Epoxidised RBD palm olein	0.200	0.248	0.267	0.284	0.338	0.447	0.690	1.045

RBD = Refined de-odourised bleached

Extrusion at 100°C

is a smaller amount of soya bean oil being incorporated at the mix stage of the rubber to migrate to the surface to lower the friction. Its compatibility may also change with temperature. This will be studied further.

The capillary rheometer (Monsanto Processability Tester) was employed to examine the effect of palm oil on extrusion flow. The results *(Table 7)* show that crude palm oil can reduce extrusion stresses but no further reductions result from refinement of the oil. Thus the friction and extrusion data indicate that crude palm oil is quite sufficient as a process aid, without any refinement.

Effect of Presence of Water

From time to time, there are reports that the presence of 'knuckles' or wet spots in raw rubber can give rise to processing problems due to slip during mixing. This can affect the dispersion of formulation ingredients. A simple study shows *(Table 8)* by how much the friction might change. Knuckles were deliberately introduced by dipping the surface of rubber hemicylinders in distilled water for 72 h. The surface was then wiped dry before friction experiments were conducted.

DISCUSSION

Whatever the operating temperature, the presence of a process aid at the sliding interface leads to a reduction in friction. However, it is apparent that such materials are most effective above their melting point. For example, at room temperature, the majority of the process aids studied could about half the friction, but at 120°C, the friction typically fell to a fifth of the value in the absence of an aid at the same temperature. A comparison of frictional stresses further shows that at high temperatures, an aid is more effective when incorporated into the rubber.

Water lubrication by 'knuckles' reduces the friction at room temperature by a factor of two, but at elevated temperature (90°C), there is only a 20% difference. This lack of lubrication at high temperatures may be contrasted with the behaviour of process aids.

Palm oil appears capable of providing reasonable surface lubrication when incor-

TABLE 8. EFFECT OF 'KNUCKLES' ON FRICTION

Temperature (°C)	Knuckles in rubber	Friction coefficient
25	None	4.1
90	None	2.0
25	With knuckles	1.9
90	With knuckles	1.5

Mild steel track, sliding speed 0.2 mms^{-1}, normal load 3.43 N porated into raw rubber. No advantage is gained from refining it. Whether it can be considered a viable alternative to currently used process aids may depend upon precise operating circumstances, but at least it is more compatible with rubber than some other oils. The effects of palm oil and its derivatives on the physical properties of rubber vulcanisates need to be studied before definitive recommendations can be made. It is interesting to note that some of the commercially available process aids are in fact derived from palm oil.

CONCLUSION

It is found that commercial process aids are most efficient above their melting point when they form a lubricating film at the rubber interface. This may result in a fall in friction by up to six times. Crude palm oil can act as a process aid and might merit further consideration for industrial use.

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Clonal Characterisation of Latex and Rubber Properties

ESAH YIP*

Properties of latex and bulk rubber from Hevea *clones of commercial interest have been studied. These include the* Class I, Class II *and some new* Class IIIA *clones described in the Rubber Research Institute of Malaysia (RRIM) Planting Recommendations.*

Latices, collected under standard conditions from about 100 trees of each clone and processed into latex concentrates and bulk rubbers using a fixed procedure, were investigated. Clonal differences have been observed in almost all the properties examined. Possible influences of various latex components and other factors on the variability of some of the properties are discussed.

Generally, most clones produce latex concentrates with fairly good latex stability, although added soap is needed in some cases. The mechanical stability of a few unstable clones however remain low due to poor response to the soap treatment. All other properties tested meet the specifications for latex concentrate.

While the RRIM clones often yield rubbers with low to medium viscosities, those from the PB (Prang Besar) clones generally tend to be of relatively high viscosity. The inclusion of comparatively few rubber clones with low viscosity in the Recommendations is noted. Latices from all clones are suitable for commercial production of SMR non-viscosity-stabilised rubbers, while clones which can be processed into SMR CV60 grade without blending with other latices have been identified. Twenty-five clones have been observed to yield light-coloured rubbers consistently.

Good correlations are observed between Mooney viscosity and initial Wallace plasticity of both non-CV and CV rubbers of these clones. Their cure characteristics, such as the torque change (ΔT) and the relaxed modulus (MR100), are also significantly correlated.

In the general breeding and selection programme of *Hevea brasiliensis* clones, emphasis has always been placed on the high yielding capacity and good growth characteristics of the trees, as well as their resistance to leaf diseases and wind damage. However, a high yielding clone with vigorous growth does not always produce latex and rubber of suitable properties as desired by the producers. More emphasis is now being placed on the properties of the latex and rubber obtained from individual clones. Although information of this type had been reported earlier in the RRIM Planting Manual of 1965[1], it referred mainly to the older clones, many of which are no longer planted. Information on the modern clones is somewhat scattered.

The present work was therefore undertaken to study, on a laboratory scale, the properties of latices and rubbers from clones that are of current interest to the industry. The *Class I, Class II* and some new *Class IIIA* clones, as indicated in the RRIM Recommendations for conventional planting[2] were thus investigated. The properties examined included those of fresh field latex, latex concentrate and raw

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rubber, all of which are related to the specifications required for concentrate and dry rubber production.

Classification of Clones

According to the RRIM Recommendations for conventional planting, clones are classified based on the growth and yield characteristics of the trees:

Class I clones : High performance materials recommended for large-scale planting.

Class II clones : Promising materials, suitable for moderate-scale planting.

Class IIIA clones : Experimental materials planted up to 10 ha per clone.

Class IIIB clones : New materials planted in one-task-size blocks only, selections of which have only been tested in small-scale trials.

EXPERIMENTAL

All the clones studied are planted in the RRIM Experiment Station, Sungai Buloh. The trees were all on the ½S d/2 tapping system. They had not been stimulated nor subjected to any special fertilising practices. The parentage of each clone, its location and panel of tapping during the investigation are shown in *Table 1.*

Latices were collected and pooled from approximately 100 trees of each clone, lightly ammoniated (0.08% for preparation of bulk rubbers, 0.4% for latex concentrates) and brought back to the laboratory as soon as possible. Latex from each clone was then processed immediately into latex concentrate and dry rubber (both viscosity-stabilised and non-viscosity-stabilised). For each clone, a total of at least six cycles of sampling and testing were carried out over a period of one to two years for each of the properties examined. Results are expressed as means of all the values obtained in each case.

Dry Rubber Content of Field Latex

This was determined using the standard method[3] involving the coagulation of a known weight of a representative sample of latex, with dilute acetic acid and determining the weight of the sheeted coagulum after drying at 75°C.

Acetone Extraction of Total Solids Film

Total solids film, obtained by drying latex on glass plates at room temperature for 24 h, was cut into very small pieces and extracted using a Soxhlet extracter for 16 h. The acetone was removed and the extract dried and weighed[3].

Elemental Analysis

Chemical analyses of field latex, latex concentrate and dry rubber were carried out using the methods described in the 'Manual of Laboratory Methods for Chemical Analysis of *Hevea brasiliensis* Rubber' published by the RRIM[4]. Values are expressed as percentage of total solids, except for copper and manganese which are in parts per million (p.p.m.) in view of their very low levels.

Preparation and Testing of Latex Concentrate

This was prepared by centrifuging field latex containing about 0.4% ammonia in a latex separator to give a concentrate of approximately 60% dry rubber content, which was then preserved with 0.7% ammonia as a high-ammonia (HA) concentrate.

The mechanical stability time (MST), potassium hydroxide (KOH) number and volatile fatty acid (VFA) number were determined according to procedures set out in *ISO 35, ISO 127* and *ISO 506* respectively.

Preparation and Testing of Bulk Rubbers

The dry rubbers tested were prepared from field latices following the SMR procedures of coagulation using formic acid at pH 5–5.2, after which the coagula were crumbled and dried at 100°C. In the case of viscosity-

TABLE 1. PARENTAGE, LOCATION AND PANEL TAPPED DURING INVESTIGATION OF FORTY-THREE CLONES PLANTED AT THE RRIM EXPERIMENT STATION, SUNGAI BULOH

Clone	Parentage	Field planted	Panel tapped
Class I			
GT 1	Primary clone	54	BO-2
RRIM 600	Tjir 1 × PB 86	28	BI-1
RRIM 712	RRIM 605 × RRIM 71	28	BI-1
PR 255	Tjir 1 × PR 107	45B	BO-1
PR 261	Tjir 1 × PR 107	28	BO-2
PB 217	PB 5/51 × 6/9	45A	BO-2
Class II			
RRIM 623	PB 49 × Pil B 84	20C	BI-1
RRIM 628	Tjir 1 × RRIM 527	14B	BI-1
RRIM 701	44/553 × RRIM 501	28	BI-1
RRIM 703[a]	RRIM 600 × RRIM 500	68	BO-2
RRIM 725[b]	F × 25 (ill)	34	BO-2
RRIM 728	GT 1 × RRIM 623	34	BO-2
RRIM 729	RRIM 623 × FX 25	34	BO-2
RRIM 805	RRIM 628 (selfed)	60C	BO-1
RRIM 901	PB 5/51 × RRIM 600	45A	BO-2
RRIM 905	PB 5/51 × RRIM 600	45A	BO-2
PB 28/59	Primary clone	34	BO-2
PB 230[c]	PB 5/51 × PB 49	34	BO-2
PB 235	PB 5/51 × PB s/78	28	BI-1
PB 254	PB 5/51 × PB s/78	38	BO-2
PB 255	PB 5/51 × PB 32/36	27	BO-2
PB 260	PB 5/51 × PB 49	27	BO-2
PB 280	PBIG seedling	34	BO-2
RRIC 100	RRIC 52 × PB 86	45C	BO-1
RRIC 110	LCB 1320 × RRIC 7	45C	BO-1
IAN 873[b]	PB 86 × F 1717	38	BO-2
PM 10	Primary clone	60C	BO-1
BPM 24	GT 1 × AVROS 1734	45C	BO-1
Nab 17	Tjikadu seedling	35	BI-1
Class IIIA			
RRIM 709[c]	RRIM 605 × RRIM 71	28	BI-1
RRIM 710[c]	RRIM 605 × RRIM 71	28	BI-1
RRIM 717[c]	PB 49 × RRIM 603	27	BO-2
RRIM 730[c]	LCB 1320 × RRIM 623	34	BO-2
RRIM 803	RRIM 501 × RRIM 623	38	BO-2
RRIM 804	RRIM 501 × 44/553	38	BO-2
RRIM 806	RRIM 600 × RRIM 701	45C	BO-1
RRIM 809	RRIM 600 × RRIM 623	45C	BO-1
PB 242	PB 5/51 × PB 32/36	28	BI-1
PB 274	PB 28/59 × PB 32/36	38	BO-2
PB 312	RRIM 600 × PB 235	60C	BO-1
PM 8	Primary clone	60C	BO-1
RRIC 101	Ch 36 × RRIC 7	45C	BO-1
RRIC 102	RRIC 52 × RRIC 7	45C	BO-1

ill : Illegitimate

BO-1, BO-2 : Virgin panels

BI-1, BI-2 : Renewed panels

[a] Clone withdrawn from recommendation due to wind damage

[b] Clone withdrawn from recommendation due to Corynespora attack

[c] Clone withdrawn from recommendation due to poor yield

stabilised (CV) rubbers, 0.15 p.p.h.r. of hydroxylamine neutral sulphate (HNS) was added before coagulation.

Mooney viscosity *(V_R)*, Wallace plasticity *(P_0)*, Plasticity Retention Index (PRI), degree of storage hardening and colour were all determined using recommended methods[5].

The cure behaviour of each rubber was assessed by measuring the torque required to oscillate a biconical disc at an angle of ± 3° in the ACS 1 mix at 160°C, using a Monsanto rheometer, according to *ISO 3417*. The torque was recorded autographically as a function of time.

Assessment of cure characteristics was also done by determining the relaxed modulus at 100% extension (MR100) measured on test-pieces prepared using the ACS 1 mix, and vulcanised at 140°C for 40 min[5].

RESULTS AND DISCUSSION

Field Latex Properties

Hevea latex as obtained from the tree consists not only of rubber hydrocarbon particles, but also non-rubber substances which include lipids, proteins, carbohydrates, acids, amines and some inorganic constituents. It is generally known that some of these non-rubbers can affect the properties of latex concentrates and bulk rubber derived from the field latex. Relevant field latex properties such as dry rubber content (d.r.c.), acetone soluble-non-rubber content (acetone extract) and elemental composition were therefore investigated. Results for the various clones studied are as shown in *Tables 2* and *3*.

Dry rubber content. This is a highly variable property. When a tree of any one clone or seedling is first tapped, it produces an unstable

TABLE 2. DRY RUBBER CONTENT OF FRESH *HEVEA* LATEX FROM CLASS I, CLASS II AND CLASS III CLONES

Class	D.r.c. of fresh *Hevea* latex Below average 31%-34%	 Average 34%-38%	 Above average 38%-41%	 High > 41%
I	—	GT 1 RRIM 600 RRIM 712	PR 255 PR 261 PB 217	—
II	—	RRIM 725 RRIM 728 RRIM 729 RRIM 805 IAN 873	RRIM 701 RRIM 703 RRIM 905 PB 230 PB 255 PB 260 RRIC 100 BPM 24 Nab 17	RRIM 623 RRIM 628 RRIM 901 PB 28/59 PB 235 PB 254 PB 280 RRIC 110 PM 10
III A	RRIM 710 PB 274	RRIM 709 RRIM 804 RRIM 806 RRIM 809 PB 312 PM 8 RRIC 101	RRIM 717 RRIM 803 PB 242 RRIC 102	RRIM 730

latex with a high rubber content. As the tapping is continued with a regular tapping system, the latex stability increases and the d.r.c. falls to a steady level which can vary between 25% and 45%, depending on the nature of the planting material. Changes in d.r.c. can also be brought about by other factors such as the tapping system, seasonal variation and yield stimulation[6,7,8]. For example, a full-spiral cut gives a lower d.r.c. than a half-spiral cut, and alternate daily tapping results in a higher d.r.c. than daily tapping. Higher d.r.c. is also observed for latex obtained from high-panel tapping compared with that from low-panel tapping. Furthermore, intensive tapping or drastic tapping causes marked decrease in d.r.c.

The high d.r.c. occurring at the end of a dry season is an effect of seasonal variation. Although an inverse relationship between productivity and d.r.c. is generally found for any one tree, no such correlation has been reported for different clones[6,9]. Lower d.r.c. is often found to result from application of yield stimulants to the tree, although d.r.c. generally increases again after some time[7,10].

In view of these variables, all the latices studied were collected from trees grown in one area, tapped on the same tapping system and without yield stimulation. Samplings were also made at intervals over a period of a year to include any variation due to seasonal changes. The dry rubber contents of six *Class I,* twenty-three *Class II* and fourteen *Class IIIA* clones were determined. By classifying the average d.r.c. values into ranges[1], the results shown in *Table 2* were obtained.

It can be seen that while most of the clones have average to above average d.r.c. (34%-41%), ten clones yield latices with high d.r.c. (more than 41%). Only two clones, RRIM 710 and PB 274, both of *Class IIIA,* give below average d.r.c. (31%-34%). None of the clones examined produce latices with d.r.c. lower than 25%, below which the latex is unsuitable for latex concentrate production due to decreased efficiency in the latex concentration process.

Acetone extract of total solids film. Unlike the d.r.c., this property has not been extensively studied. However, it has been shown[7] to increase after yield stimulation using 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), and to decrease with the age of the tree. Generally, acetone extract varies between 3% and 6% in films from field latex and 2% and 5% in dry rubber.

Table 3 gives mean values for the forty-three clonal latices. These fall in a range between 3.25% and 6.11%, with PM 10 having the lowest content and PB 274 having the highest. Acetone extract consists of non-rubbers, some of which, particularly the lipids[11,12], are responsible for the stability of the rubber particles. This has probably contributed to the good stability of the concentrate of PB 274, but the low content of lipids of PM 10 does not give rise to an unstable concentrate (see later). The reason for this rests on the fact that many other factors besides lipids also exert influence on the stability of latex and its concentrate.

Nitrogen content. The nitrogen content of field latex is largely associated with the proteinaceous materials present. It has been reported[13] that about 30% of these materials are present in the rubber hydrocarbon phase and about 70% in the non-rubber phase. Most of these have been shown[6,14] to play an important role in the stability of *Hevea* latex. Certain influence of seasonal changes on this parameter had also been observed by Resing[6] in his study of some of the older clones. A range of 0.53%-0.80% (on total solids film) was reported for some latices[1,6,7]. Results from the present study indicate a very similar nitrogen content, varying from 0.51% to 0.87% *(Table 3).*

Phosphorus and magnesium. Approximately one-third of the phosphorus in latex is found in the rubber hydrocarbon phase and the rest in the non-rubber phase[15]. Magnesium, on the other hand, is found mainly in the non-rubber fractions (C- and B-sera)[16]. Both phosphorus and magnesium have been shown to affect latex stability. While phosphorus compounds exert a stabilising effect, magnesium, in the form of divalent cation, is destabilising[17,18]. It has been shown that although the ratio of phosphorus/magnesium is correlated with the stability of

TABLE 3. ACETONE EXTRACT, NITROGEN, PHOSPHORUS AND MAGNESIUM CONTENTS OF FIELD LATEX OF FORTY-THREE CLONES PLANTED IN THE RRIM EXPERIMENT STATION (TOTAL SOLIDS FILMS)

Clone	Acetone extract (%)		Nitrogen content (%)		Phosphorus content (%)		Magnesium content (%)	
	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Class I								
GT 1	4.18	0.27	0.80	0.06	0.19	0.04	0.09	0.01
RRIM 600	3.92	0.61	0.74	0.05	0.23	0.04	0.16	0.03
RRIM 712	3.40	0.77	0.71	0.02	0.22	0.02	0.15	0.05
PR 255	4.06	0.94	0.61	0.05	0.13	0.03	0.04	0.01
PR 261	3.74	0.66	0.64	0.08	0.22	0.05	0.13	0.02
PB 217	5.81	0.13	0.57	0.09	0.17	0.06	0.07	0.03
Class II								
RRIM 623	3.41	0.23	0.60	0.08	0.23	0.07	0.06	0.01
RRIM 628	4.33	0.26	0.64	0.04	0.22	0.04	0.07	0.02
RRIM 701	5.38	0.56	0.56	0.03	0.18	0.01	0.08	0.01
RRIM 703	3.49	0.57	0.69	0.07	0.30	0.03	0.10	0.01
RRIM 725	5.84	0.52	0.87	0.04	0.27	0.11	0.11	0.07
RRIM 728	3.68	1.06	0.73	0.06	0.22	0.03	0.16	0.02
RRIM 729	5.59	0.39	0.64	0.08	0.17	0.02	0.08	0.02
RRIM 805	3.89	0.50	0.64	0.09	0.21	0.05	0.10	0.02
RRIM 901	5.25	0.35	0.68	0.03	0.24	0.03	0.08	0.01
RRIM 905	4.99	0.72	0.68	0.05	0.26	0.06	0.12	0.03
PB 28/59	5.36	0.43	0.61	0.04	0.20	0.07	0.08	0.05
PB 230	3.86	0.52	0.73	0.06	0.24	0.09	0.16	0.08
PB 235	4.96	0.74	0.53	0.05	0.22	0.02	0.06	0.02
PB 254	4.21	0.18	0.68	0.10	0.24	0.05	0.09	0.02
PB 255	4.16	0.55	0.53	0.03	0.21	0.03	0.07	0.01
PB 260	4.40	0.37	0.53	0.03	0.19	0.02	0.06	0.02
PB 280	3.67	0.19	0.66	0.02	0.16	0.03	0.10	0.03
RRIC 100	3.66	0.80	0.70	0.07	0.16	0.04	0.09	0.02
RRIC 110	3.65	0.45	0.62	0.08	0.12	0.01	0.07	0.04
IAN 873	4.04	0.60	0.84	0.07	0.29	0.06	0.12	0.04
PM 10	3.25	0.86	0.62	0.07	0.22	0.04	0.14	0.03
BPM 24	4.22	0.43	0.73	0.05	0.17	0.03	0.11	0.02
Nab 17	3.91	0.37	0.69	0.04	0.27	0.02	0.07	0.02
Class IIIA								
RRIM 709	3.84	0.61	0.68	0.11	0.17	0.03	0.07	0.03
RRIM 710	4.06	0.52	0.85	0.05	0.28	0.06	0.11	0.04
RRIM 717	3.67	0.39	0.64	0.03	0.20	0.03	0.14	0.02
RRIM 730	3.64	0.15	0.51	0.05	0.13	0.01	0.05	0.02
RRIM 803	3.38	0.45	0.67	0.04	0.22	0.03	0.11	0.01
RRIM 804	4.02	0.42	0.78	0.05	0.22	0.03	0.09	0.02
RRIM 806	3.94	0.50	0.76	0.06	0.21	0.06	0.06	0.02
RRIM 809	3.83	0.16	0.52	0.14	0.21	0.05	0.07	0.01
PB 242	3.94	0.55	0.68	0.05	0.21	0.05	0.09	0.04
PB 274	6.11	1.40	0.85	0.07	0.33	0.03	0.12	0.06
PB 312	3.87	0.69	0.76	0.14	0.27	0.07	0.15	0.04
PM 8	3.65	0.46	0.74	0.07	0.25	0.05	0.14	0.04
RRIC 101	3.46	0.28	0.58	0.22	0.19	0.04	0.12	0.02
RRIC 102	3.64	0.62	0.68	0.06	0.18	0.03	0.06	0.01
L.S.D.		0.93		0.12		0.07		0.05
S.D.		0.58		0.07		0.05		0.03

L.S.D. — Least significant difference at 5% probability level
s.d. — Standard deviation, S.D. — overall s.d.

latex to a certain extent, it is by no means the only influencing factor[15]. Nevertheless, in the processing of latex concentrate, diammonium hydrogen phosphate is sometimes added to precipitate the undesirable free magnesium ions to ensure better stability of the concentrate produced.

Analyses of latices from the various clones revealed a phosphorus concentration ranging from 0.12% to 0.33% *(Table 3)*. Lower concentrations were detected in the case of magnesium, which varied from 0.04% to 0.16%. These levels are consistent with those reported earlier for some selected clones[7,14,19], although a lower phosphorus content of 0.08% and a lower magnesium content of 0.03% were reported for a very old clone of AVROS 50[7].

Copper and manganese. These two elements are known to be present in latex in relatively low concentration compared to other metals, such as potassium, magnesium, calcium and sodium. A range of 1–7 p.p.m. of copper and a concentration of less than 2 p.p.m. of manganese were detected in the clonal latices analysed.

Both copper and manganese ions are known to enhance oxidation of the rubber polymer[20,21], copper ion being the more potent one. It is believed that these two metals are present in latex in an inert form which could be activated to catalyse the degradation process during storage of rubber. So far, all the observations reported[20,21] concerned only the effect of copper and manganese ions added to the latex system. No study has yet been carried out on the action of the naturally occurring copper and manganese. Such a study could be interesting and informative.

Latex Concentrate Properties

The latex concentrates studied were those of the centrifuged type preserved with high ammonia. This is the predominant latex type produced in Malaysia. Of the important properties required by the specifications as stated in *ISO 2004,* the mechanical stability time, the KOH number and copper and manganese contents are of interest in view of their sensitivity to clonal variation[6,7,15,17].

KOH and VFA numbers. The KOH number is a measure of the content of anions in latex. These include those of the volatile fatty acids, higher fatty acids, phosphates, carbonates and bicarbonates. The volatile fatty acids are the products of bacterial action on latex due to inadequate preservation, and are normally measured separately by the VFA number, which is the number of grammes of potassium hydroxide equivalent to the volatile fatty acid contained in 100 g of total solids. The presence of carbonates and bicarbonates may be due to the absorption of carbon dioxide during exposure of the latex to air. The other anions are inherent components of the latex system, the contents of which may vary from clone to clone. The KOH number is therefore defined as the number of grammes of potassium hydroxide equivalent to the acid radicals combined with ammonia containing 100 g of total solids. A high KOH number and a high VFA number indicate inadequate preservation of latex.

Measurement of the KOH number showed that clonal variation in this property was not marked as indicated by the somewhat small range of 0.56–0.75 *(Table 4)*. Even less variation was observed in the case of the VFA

TABLE 4. POTASSIUM HYDROXIDE, VOLATILE FATTY ACID NUMBERS AND CONTENTS OF COPPER AND MANGANESE FOR LATEX CONCENTRATES FROM FORTY-THREE CLONES

Property	Range	ISO 2004 specification
KOH No.	0.56 — 0.75	Not to exceed 1.0
VFA No.	Less than 0.04	Not to exceed 0.2
Copper	Less than 3 p.p.m.	Maximum 8 p.p.m.
Manganese	Less than 1 p.p.m.	Maximum 8 p.p.m.

All KOH and VFA values were obtained from samples after three months' storage numbers which remained very low for all the clones, showing that preservation of all the concentrates examined had been adequate. In view of these very low VFA numbers, it can be concluded that the KOH number reflects the concentrations of long-chain carboxylates and inorganic anions in the various clonal latex concentrates. Magnitudes of both KOH and VFA numbers are well within the latex concentration specifications *(Table 4)*.

Mechanical stability time (MST). This is a measure of the colloidal stability of latex concentrate. It is assessed by a measure of the resistance of the latex particles to irreversible flocculation or coagulation when subjected to mechanical stirring. The MST of a freshly prepared latex concentrate is always low. During storage at ambient temperature, it increases very rapidly for three to four weeks, after which the rise becomes more gradual for the next one to two months. The initial rapid increase in MST has been correlated to the increasing content of higher fatty acid soaps with time, arising from the hydrolysis of some lipids (mainly phospholipids and glycolipids) on the surface of the rubber particles[22]. As most of these soaps are absorbed on the surface of the latex particles, this gives rise to higher surface electrical charge density, greater particle repulsion forces, and hence higher MST. The subsequent slow rise in MST is due to exposure of latex to oxygen in air[23]. According to the specification limit, a minimum MST of 650 s is required below which the latex is considered unstable.

Mechanical stabilities of all the clonal concentrates studied are shown in *Table 5* which refers to values after three months' storage. Generally, most of the clones are capable of producing good stabilities although soap treatment has to be used in some cases for improved MST.

It was observed that the following clonal latex concentrates exhibited low latex stabilities (MST < 650 s) even after three months' storage:

Class I : RRIM 600, RRIM 712, PR 255, PR 261 and PB 217

Class II : RRIM 703, RRIM 729, RRIM 905, PB 254, RRIC 100 and RRIC 110

Class IIIA : RRIM 717, RRIM 803, RRIM 804, RRIM 806, RRIM 809, PB 242 and PM 8

Various factors which are associated with the inherent properties of the latex system could be responsible for the low latex stabilities of these clones. These factors include the lower concentration of higher fatty acid soaps, lower contents of proteins and saponifiable lipids on the rubber particle surface, and excessive quantity of inorganic cations in the serum phase. In order to identify the influence of the individual factors on the instabilities of the above clonal latices, a separate and systematic study is required.

Parentage of clones also appears to play a role in latex stability in view of the following observations. One of the parents of each of the three low-stability *Class I* clones — PR 255, PR 261 and RRIM 712 — had been found to yield unstable latex concentrates. They are PR 107 for clones PR 255 and PR 261 and RRIM 605 for clone RRIM 712 *(Table 1)*. Similarly, RRIM 703 of *Class II* and RRIM 806 and RRIM 809 of *Class IIIA* have the unstable RRIM 600 as one of their parents. Parentage is obviously not the only influencing factor since the RRIM 600 clone which gives unstable latex concentrates, has parents (Tjir 1 and PB 86) which both show high concentrate stabilities. This is also the case with the unstable RRIM 803 clone of *Class IIIA,* whose parents, RRIM 501 and RRIM 623, are known to produce latex concentrates of high MST. Possible influence of parentage on the other low stability clones (with the exception of PM 8 which is a primary clone) would not be discussed due to insufficient information on the MST values of their parent clones, many of which are either very old clones or are garden materials grown only for breeding purposes.

Anionic long-chain fatty acid soaps, when added to latex concentrates, are known to

TABLE 5. MECHANICAL STABILITY TIME OF LATEX CONCENTRATES FROM DIFFERENT CLONES AFTER THREE MONTHS' STORAGE

Class	MST (s)			
	< 650	650–900	900–1200	> 1200
I	PR 255[a] PB 217	GT 1 RRIM 712[a] PR 261[a]	RRIM 600[a]	—
II	RRIM 703[a] RRIM 729[a] RRIM 905[a] RRIC 100[a]	RRIM 728 RRIM 805 PB 254[a] PB 280 IAN 873 BPM 24	RRIM 623 RRIM 628 RRIM 901 PM 10 PB 255	RRIM 701 RRIM 725 PB 28/59 PB 230 PB 235 PB 260 RRIC 110[a] NAB 17
IIIA	RRIM 804[a] RRIM 806[a]	RRIM 710 RRIM 803[a] PB 242[a] PB 312 RRIC 102	RRIM 709	RRIM 717[a] RRIM 730 RRIM 809[a] PB 274 PM 8[a] RRIC 101

[a] Latices treated with 0.02% ammonium laurate

increase their mechanical stabilities[6,24]. This is mainly due to the adsorption of the surface-active soap molecules on the rubber particle surface. It is interesting to note that when 0.02% ammonium laurate (on latex weight) was added to the above-mentioned low-stability concentrates, different responses were obtained. While some clonal latices showed a marked increase in MST, others gave a smaller change, as illustrated in *Figure 1*. Of the seventeen clonal latices tested after three months' storage, ten responded well, elevating their MST from below 650 s to above this specification limit. The other seven clones also indicated some response, but their MST remained below 650 s under the experimental conditions. The exact causes for this behaviour are not yet fully understood, but it is likely that the nature and composition of the protein and lipid components on the rubber particle surface are implicated. Latices from these latter clones are obviously not suitable for latex concentrate production, unless perhaps higher soap concentrations can be used to improve their stabilities further.

Latices of low stabilities are often associated with high KOH numbers which usually have high VFA numbers (due to inadequate preservation of latex). In the present study, a relationship between MST and KOH has not been obtained, as shown by the statistical analysis of data from the forty-three clones which indicated that the correlation between these two parameters was insignificant: $\mathrm{MST} = -1520\ \mathrm{KOH} + 1806$ ($r = -0.19$). This lack of correlation could probably be partly explained firstly, by the fact that not all the acidic anions as measured by the KOH number exert destabilising effects on latex particles. Those of the higher fatty acids, for example, when adsorbed onto the rubber surface, can in fact confer latex stability. Secondly, as reported by Yip and Subramaniam[15] and also briefly mentioned earlier, the MST is greatly influenced by a number of other inherent latex properties which show variability between clones.

Copper and manganese. As expected, the levels of these two elements in latex concentrates are lower than those in field latex. About

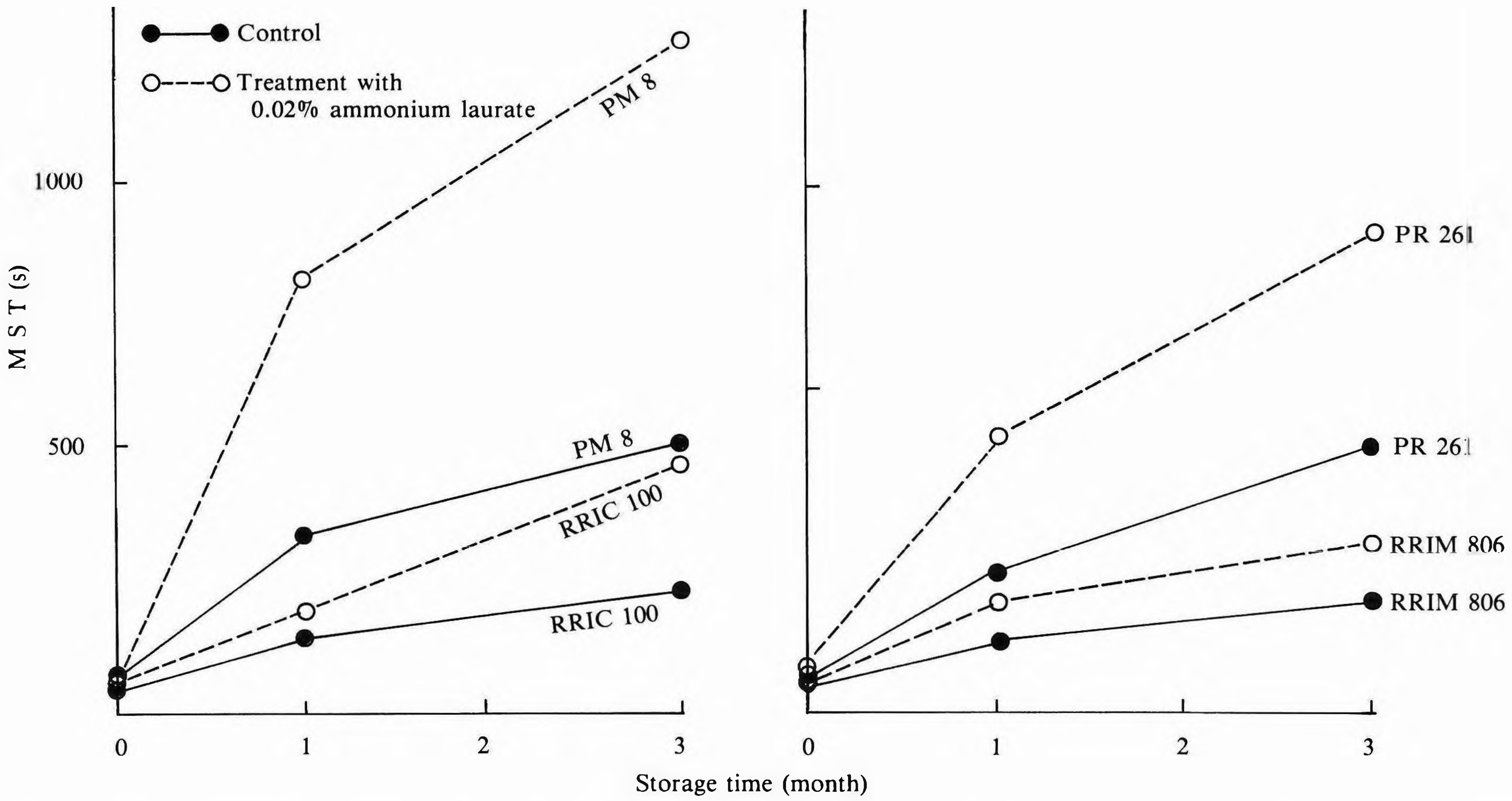

Figure 1. Effect of 0.02% ammonium laurate on the mechanical stability of different clonal latex concentrates in the form of HA latices.

3 p.p.m. or less of copper and 1 p.p.m. or less of manganese were detected in the concentrates from the various clones *(Table 4)* as compared to 1-7 p.p.m. of copper and about 2 p.p.m. of manganese in their corresponding field latices. The difference is probably due to the partial removal of some of the non-rubber substances during the centrifugation process.

Bulk Rubber Properties

The dry rubbers tested in this study were those of the Standard Malaysian Rubber — whole field latex (SMR WF) and the constant-viscosity (SMR CV) grades, and the properties examined are those included in the specifications for SMR production[25]. As all the rubbers were prepared using the same processing procedure, any variation detected in the properties studied could be considered as mainly due to differences between clones, except for dirt and volatile matter contents which are actually influenced by the processing of rubber.

Mooney viscosity. This parameter is universally used in all the rubber consumer countries. It gives an indication of the amount of mechanical work required on the raw rubber to give mixes with consistent rheological properties after standard plastication, compounding and mixing. This means that a rubber with very high Mooney viscosity, for example, may require long premastication times or need expensive peptisers to obtain a product of a workable and consistent viscosity, whereas the soft rubbers with low Mooney viscosities require no prior mastication.

Mooney viscosity of rubber sometimes changes during storage. This is due to the fact that natural rubber often hardens, resulting in higher bulk viscosity, when it is stored at ambient temperature and humidity over a period of time. This hardening process is accelerated at elevated temperatures and dry conditions. It has been postulated to be mainly due to the crosslinking reaction between the rubber molecules involving the aldehyde or carbonyl groups[26,28,29] and certain aldehyde condensing groups in the non-rubber phase including some amino acids[30,31]. Addition of a monofunctional carbonyl reagent, such as hydroxylamine, to latex before coagulation inhibits this reaction, *via* the deactivation of the carbonyl group hence rendering the rubber less prone to hardening[32,33]. Such is the case of the CV rubbers. It may therefore be mentioned that Mooney viscosities of the CV rubbers may be regarded as having values closer to the true values as produced by the trees.

Although in the SMR Scheme, Mooney viscosity is not specified for any of the non-viscosity-stabilised grades, this property is very important in the case of the viscosity-stabilised (or CV) rubbers, which require different viscosity ranges for different CV grades[2,5], e.g. the most demanded CV grade of SMR CV 60 requires a range of 55–65 Mooney units.

Table 6 shows the results obtained for CV rubbers from *Class I, Class II* and *Class IIIA* clones. The average Mooney viscosity is 55–83 units for the six *Class I* clones, 39–89 units for the twenty-three *Class II* clones and 46–78 units for the fourteen *Class IIIA* clones. By classifying the viscosity values into five arbitrary ranges as illustrated in *Table 7,* it is apparent that although there are some clones producing rubbers with the preferred medium viscosity range, about one-half and more than one-half the number of the good yielding clones recommended in *Class I* and *Class II* respectively produce medium-hard to hard rubbers. There are indeed very few soft or medium-soft rubber clones. It may be mentioned that unless these softer rubber clones are also selected for planting, the production of SMR CV 60 grade from the harder rubber clones, using the usual practice of blending latices with high and low V_R to give the required viscosities, would encounter some difficulties in the future. This would particularly be so when the existing softer rubber clones such as the RRIM 501 becomes unavailable due to wind damage. Fortunately, three more low V_R clones are identified among the newer ones in *Class IIIA*. They are RRIM 804, RRIM 806 and PB 312. Although these are still experimental planting materials, they have the potential to be promoted to *Class II* if they continue to show good yield and growth performances and no secondary defects. CV 60 can nevertheless be

TABLE 6. RAW RUBBER PROPERTIES OF FORTY-THREE CLONES IN THE RRIM EXPERIMENT STATION

Clone	V_R (CV rubber)		P_o		PRI (%)		Ash (%)		Nitrogen (%)		Colour
	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	
Class I											
GT 1	58	2	45	3	90	6	0.38	0.03	0.56	0.03	
RRIM 600	55	4	42	2	91	3	0.37	0.02	0.50	0.02	L
RRIM 712	59	4	45	3	93	6	0.44	0.04	0.48	0.02	L
PR 255	69	5	48	3	83	5	0.30	0.05	0.48	0.03	
PR 261	73	4	53	2	92	5	0.35	0.09	0.47	0.03	L*
PB 217	83	5	59	3	80	8	0.21	0.02	0.41	0.06	
Class II											
RRIM 623	63	4	49	5	92	4	0.37	0.02	0.43	0.01	
RRIM 628	84	8	57	6	85	6	0.38	0.09	0.43	0.01	
RRIM 701	55	3	39	3	99	8	0.43	0.06	0.44	0.04	
RRIM 703	56	8	42	7	94	7	0.41	0.06	0.49	0.04	
RRIM 725	72	8	49	5	83	3	0.42	0.03	0.50	0.04	
RRIM 728	39	3	31	3	105	8	0.38	0.09	0.52	0.04	L
RRIM 729	66	6	47	4	90	2	0.34	0.04	0.48	0.02	
RRIM 805	55	4	40	4	93	7	0.28	0.08	0.49	0.02	
RRIM 901	61	3	46	4	89	3	0.41	0.04	0.46	0.01	L*
RRIM 905	65	4	48	4	91	3	0.38	0.01	0.45	0.02	L*
PB 28/59	87	6	58	3	85	3	0.36	0.05	0.40	0.03	
PB 230	64	4	48	4	89	5	0.39	0.04	0.45	0.03	
PB 235	76	7	55	3	85	7	0.37	0.06	0.38	0.02	L*
PB 254	83	4	59	3	84	4	0.32	0.03	0.44	0.03	L*
PB 255	72	6	55	3	89	8	0.38	0.04	0.39	0.01	
PB 260	63	7	48	3	91	8	0.36	0.04	0.38	0.02	L
PB 280	87	6	61	5	82	2	0.35	0.05	0.42	0.03	
RRIC 100	69	8	46	6	87	6	0.30	0.04	0.52	0.05	
RRIC 110	67	5	49	2	91	5	0.28	0.08	0.46	0.01	L*
IAN 873	89	5	60	4	85	4	0.28	0.02	0.50	0.04	L*
PM 10	86	7	59	5	84	5	0.29	0.10	0.43	0.04	L*
BPM 24	50	3	39	3	97	8	0.41	0.08	0.48	0.06	
Nab 17	72	5	51	3	89	5	0.37	0.06	0.47	0.02	
Class IIIA											
RRIM 709	69	4	49	3	83	5	0.37	0.09	0.47	0.04	L
RRIM 710	58	2	43	4	96	6	0.33	0.04	0.54	0.04	L
RRIM 717	47	2	36	4	105	9	0.49	0.08	0.44	0.04	L*
RRIM 730	67	3	51	4	87	4	0.31	0.05	0.39	0.02	L*
RRIM 803	60	5	46	4	103	6	0.41	0.07	0.47	0.02	L
RRIM 804	53	4	40	4	103	4	0.34	0.04	0.57	0.03	L
RRIM 806	46	2	34	2	91	8	0.24	0.06	0.52	0.03	L*
RRIM 809	55	2	43	3	90	7	0.25	0.05	0.49	0.01	L*
PB 242	67	1	51	2	91	3	0.30	0.07	0.43	0.01	L
PB 274	72	3	56	2	91	4	0.31	0.04	0.51	0.06	L*
PB 312	52	2	37	3	88	9	0.27	0.08	0.54	0.07	L*
PM 8	57	3	44	6	90	10	0.31	0.03	0.49	0.03	
RRIC 101	77	8	53	5	90	6	0.30	0.08	0.47	0.03	L*
RRIC 102	78	3	53	3	88	4	0.22	0.03	0.48	0.03	L*
L.S.D.	8		6		9		0.09		0.05		
S.D.	5		4		6		0.06		0.03		

L.S.D. : Least significant difference
S.D. : Standard deviation
L : Colour less than six Lovibond units
L* : Colour less than six Lovibond units on treatment with sodium metabisulphite

TABLE 7. MOONEY VISCOSITY OF RAW RUBBERS FROM CLASS I, CLASS II AND CLASS IIIA CLONES

Raw rubber viscosity (CV)	V_R range [ML (1 + 4) min, 100°C]	Number of clones		
		Class I	Class II	Class IIIA
Low	< 45	nil	1	nil
Medium-low	45–55	nil	1	4(1)
Medium	55–65	3	8(2)	4(1)
Medium-hard	65–75	2	6(1)	4(2)
Hard	> 75	1	7(2)	2

Figures within brackets indicate the number of clones withdrawn from the recommendation, see *Table 1*.

produced with clonal latices which give medium rubber viscosities, and do not require blending with other latices. These clones are:

Class I : GT 1, RRIM 600 and RRIM 712

Class II : RRIM 623, RRIM 701, RRIM 703, RRIM 805, RRIM 901, RRIM 905, PB 230 and PB 260

Class IIIA : RRIM 710, RRIM 803, RRIM 809 and PM 8

It is also observed that while 70% of the RRIM clones studied (fourteen out of twenty) produced low to medium viscosity rubbers, 70% of the PB clones (seven out of ten clones) gave medium-hard to hard rubbers. The influence of genetic factors on rubber viscosity is complex but the following relationships may be worth noting. A closer examination of the PB clones reveals that, except for PB 28/59 which is a primary clone (V_R = 87 units), all the other harder PB clones have a common parent of either PB 5/51 (V_R = 91 units) or PB 28/59. This parentage effect perhaps is responsible for the high viscosity observed in these clones. It is however interesting to note that clones PB 230, PB 260, RRIM 901 and RRIM 905, which also have PB 5/51 as one of their parents, yielded rubbers of medium viscosities. In these cases, the influence of their other parents may be more prevailing. PB 312, the only PB clone that gives medium-soft rubber, on the other hand, does not have PB 5/51 nor PB 28/59 as one of its parents *(Table 1)*. Similarly, none of the RRIM clones has a PB parent, with the exception of RRIM 901, RRIM 905 and RRIM 600. It may be of interest to point out that RRIM 600 rubber has lower V_R (55 units) than those of both its parents, *i.e.* PB 86 (V_R = 76 units) and Tjir 1 (82 units)[27].

Wallace plasticity. Besides Mooney viscosity, the important property of bulk viscosity of rubber is also measured by Wallace plasticity using the Wallace plastimeter. Unlike Mooney viscosity, there is a specification limit for this parameter in the SMR production of non-viscosity-stabilised rubber grades[25]. A minimum of 30 units is required, below which the rubber is considered to be too soft.

The plasticity values determined for the same forty-three clones are shown in *Table 6.* A range varying from 42 to 59 units was indicated for the *Class I* clones, 31–61 units for the *Class II* clones and 34–56 units for the *Class IIIA* clones, all of which are above the limit specified.

Correlation between Mooney viscosity and Wallace plasticity. These two parameters are known to be related. Their relationship however is dependent on the history of the rubber samples involved since differences in processing, drying conditions and mastication could affect it. The somewhat different relationships reported for total solids rubbers, viscosity-stabilised and non-stabilised crepes, and masticated rubbers[26,34–37] are a case in point.

Statistical analyses of the present data obtained from crumb rubbers of forty-three clones (with no mastication) showed the following correlations between the two parameters. For non-viscosity-stabilised SMR WF type rubbers:

$V_R = 1.33\ P_o + 7.93$ where the coefficient of correlation $r = 0.93$

For the viscosity stabilised SMR CV type rubbers:

$V_R = 1.38\ P_o + 7.01$ where $r = 0.95$

The coefficient *'r'* in both cases is significant at $P < 0.001\%$. The relationships are also expressed graphically as shown in *Figure 2.* The slightly higher gradient of the straight-line relationship for CV rubbers compared to that for the non-CV rubbers is consistent with that observed by Subramaniam[26] who, in his study of crepe rubbers, attributed this to the presence of different gel contents which could give rise to varying increases in the P_o and V_R values.

Comparison of the V_R values obtained from the above equations with those estimated from equations reported for crepe rubbers[26] indicated a difference of 1.8% to 7.6% when the P_o value of non-CV rubbers varied from 30 to 60 units. A smaller difference of 0.002% to 6.2% was observed in the case of the CV rubbers for the same P_o range.

Correlation between Mooney viscosity and storage hardening. The hardening phenomenon of natural rubber is usually assessed by the 'accelerated storage hardening' test in which the rubber is stored at 60°C over phosphorus pentoxide in vacuum for 48 h, and the degree of storage hardening is expressed in terms of the resulting increase in Mooney viscosity, ΔV_R, or the increase in the Wallace plasticity number, ΔP.

In the present investigation, the influence of the initial bulk viscosity *(V_R)* on the degree of storage hardening (ΔV_R) was examined. V_R as measured, is the difference between the viscosity after storage hardening *(V_{SH})* and the initial bulk viscosity of the non-viscosity-stabilised rubber before the test, *i.e.*

$$\Delta V_R = V_{SH} - V_R$$

Analyses of the data of the forty-three clones gave the following correlation *(Figure 3)* between ΔV_R and V_R:

$$\Delta V_R = -0.85\ V_R + 101.88$$

$$r = -0.81\ (P<0.001\%)$$

Since V_R of non-CV rubbers tends to increase somewhat during or after their preparation, due to the presence of the aldehyde groups, a more accurate way to present the value of ΔV_R would perhaps be

$$\Delta V_R{}^1 = V_{SH} - V_{R(CV)}$$

where $\Delta V_R{}^1$ denotes the intrinsic extent of storage hardening of the rubber sample, the initial viscosity of which is not affected by any crosslinking reaction prior to the test, and can thus be represented by V_R of the corresponding viscosity-stabilised sample, $V_{R(CV)}$. This gives a relation with a better correlation coefficient *(Figure 4),* expressed by the following equation:

$$\Delta V_R{}^1 = -0.89\ V_{R(CV)} + 105.86$$

$$r = -0.86\ (P<0.001\%)$$

Clonal rubbers with lower initial bulk viscosities are associated with greater extents of storage hardening and *vice versa.* This is in agreement with the higher aldehyde group concentration generally found in the softer clonal rubbers, compared to the harder clonal rubbers[26].

The initial bulk viscosity is also correlated to the storage hardening index (SHI) which is defined as:

$$\text{SHI} = \frac{\text{Viscosity after storage hardening}}{\text{Original viscosity}}$$

Figure 5 shows the relationship which is also represented by

$$\text{SHI} = -0.024\ V_R + 3.40$$

where $r = -0.88\ (P<0.001\%)$

This is somewhat different from that reported for crepe rubbers[26] where

$$\text{SHI} = -0.017\ V_R + 2.8.$$

V_2 values in both cases are those of the CV rubbers. The difference is again likely to be related to the history of the samples.

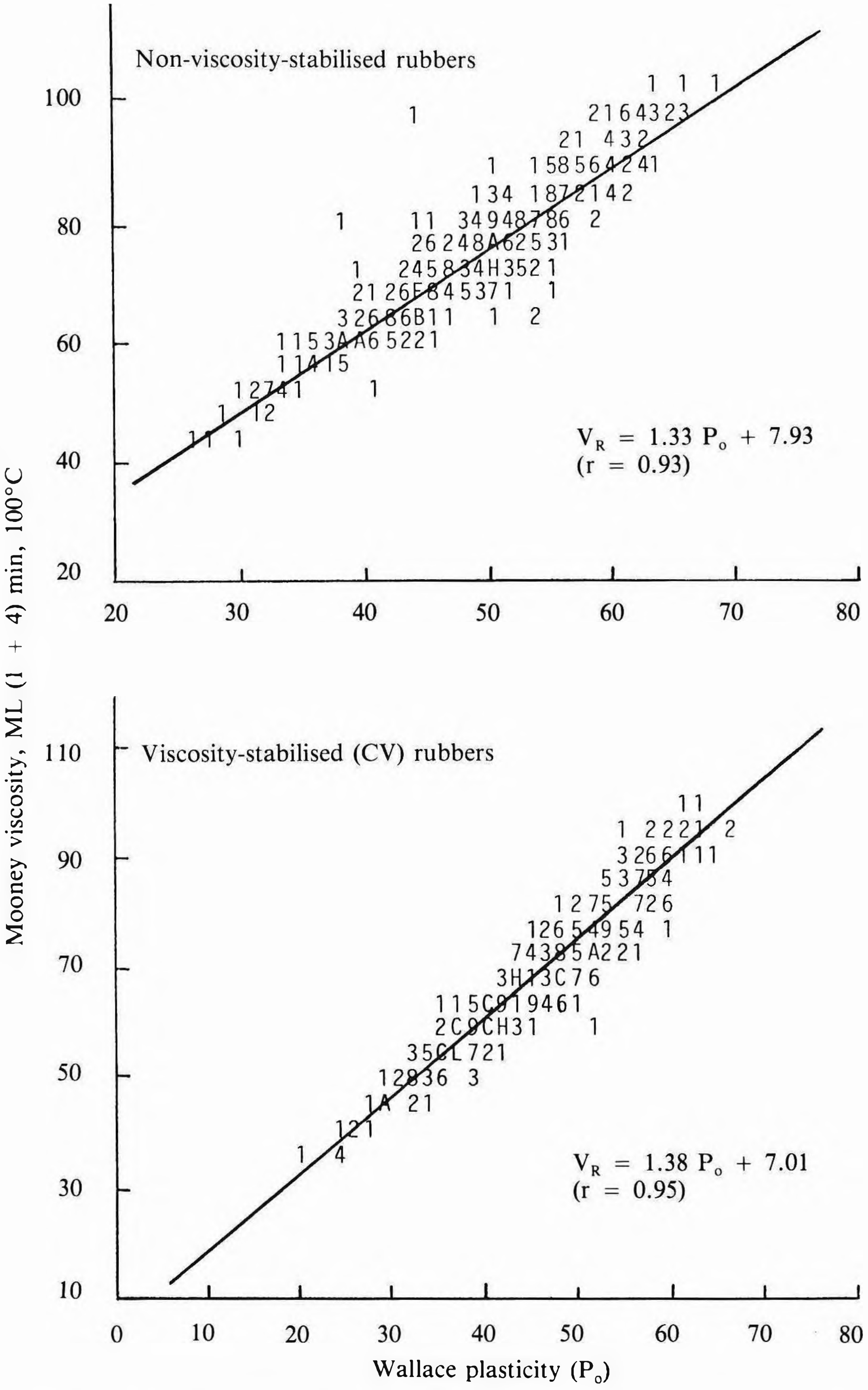

Figure 2. A plot of Mooney viscosity against Wallace Plasticity of raw rubbers from forty-three clones. The numbers 1–9 stated in the graph denote the number of points plotted in a given position. Similarly the alphabets A, B, C .... L represent 10, 11, 12 .... 16 points respectively.

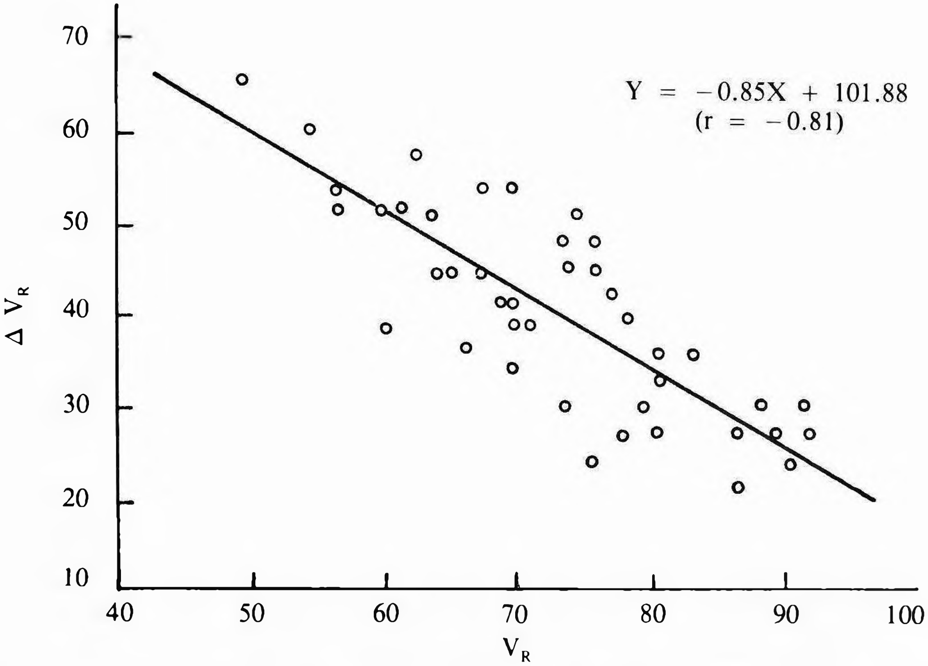

Figure 3. Correlation between the extent of storage hardening, ΔV_R, and the initial bulk viscosity of clonal rubbers.

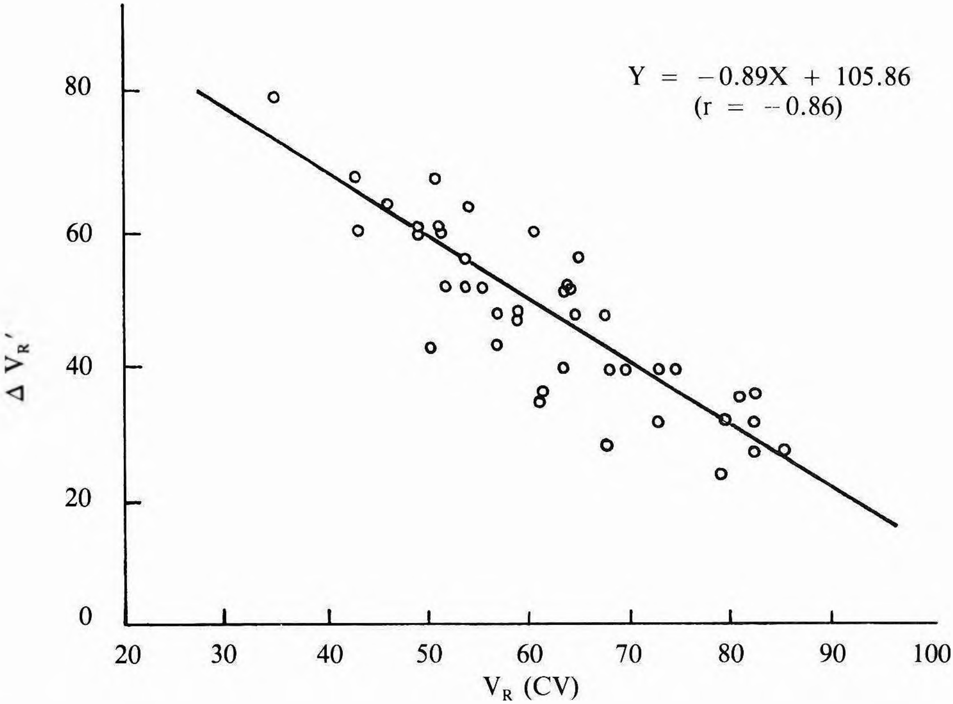

Figure 4. Correlation between the intrinsic extent of storage hardening, $\Delta V_R'$ and the original bulk viscosity, $V_{R(CV)}$, for the same clonal rubbers as in Figure 3.

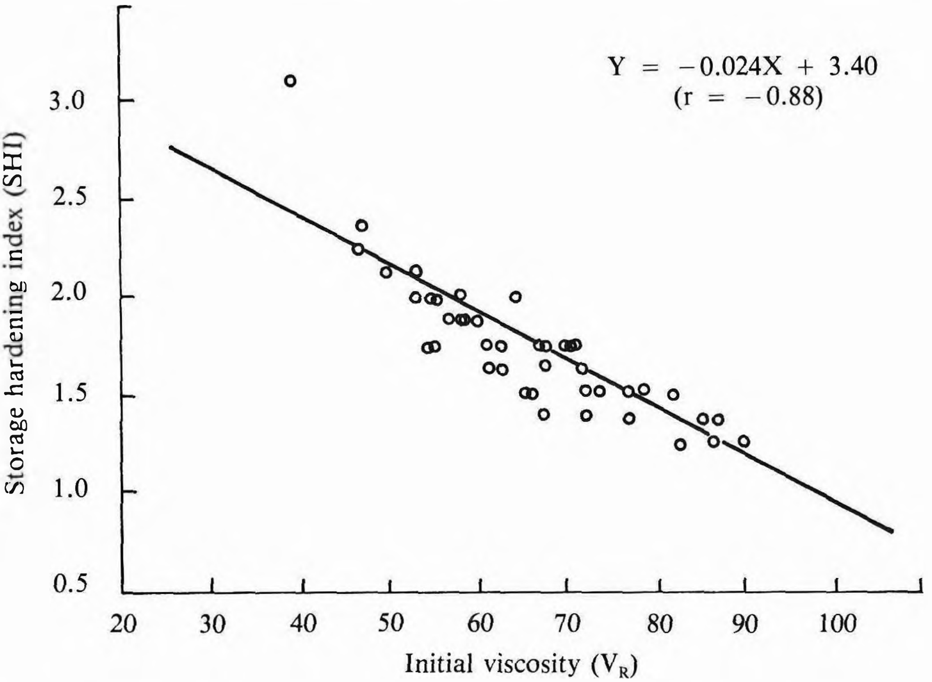

Figure 5. Relationship between initial bulk viscosity, $V_{R(CV)}$, and the storage hardening index (SHI) for forty-three clonal rubbers.

Plasticity retention index. This is a measure of the resistance of rubber to molecular breakdown by heat. It is assessed by the percentage change of the original plasticity when the rubber is heated at 140°C for 30 min, *i.e.*

$$\text{PRI (\%)} = \frac{P_{30}}{P_o} \times 100$$

where P_o is the original plasticity

P_{30} is the aged plasticity

High values correspond to good heat resistance. PRI determinations of the forty-three clonal rubbers indicated a value ranging from 81% to 105% *(Table 6)*, all of which are within the SMR specification which requires a minimum of 60% for all latex grades[25].

As P_o values exhibit clonal differences, they are expected to induce certain variation in the plasticity retention index measurements. The following equations were obtained for the clonal rubbers:

Non-CV rubbers, $\text{PRI} = -0.52\,P_o + 115.23$

($r = -0.46$, significant at 0.001%)

CV rubbers, $\text{PRI} = -0.09\,P_o + 88.59$

($r = -0.16$, significant at 0.01%)

That rubbers with lower plasticity have higher PRI and those with higher plasticity tend to have lower PRI is suggested in the case of the non-CV rubbers in spite of the somewhat low *'r'* value. Three reactions are known to occur during the PRI test: degradation; some crosslinking by free radicals; and, a certain amount of hardening due to the aldehyde groups and the aldehyde-condensing groups. The correlation between the two parameters for the non-CV rubbers is mainly attributed to the hardening reaction since such correlation is very much reduced or absent[26] in the case of the viscosity-stabilised (CV) rubbers.

Ash and nitrogen contents. The ash content represents the amount of mineral matter present in the rubber, such as carbonates and phosphates of potassium, magnesium, calcium, sodium and other trace elements. A high ash content in rubber could result from contamination during latex collection or processing. The nitrogen content of dry rubber, on the other hand, indicates the quantity of proteins present. Among them, certain proteinacous materials had been shown to exert various effects on the technological properties of rubber[38-41].

The SMR specification limits for these two characteristics are a maximum of 0.50% for ash and a maximum of 0.60% for nitrogen. *Table 6* shows the results obtained from the present investigation, indicating that all the forty-three clonal rubbers have ash contents varying from 0.21% to 0.49%, and nitrogen level ranging from 0.38% to 0.58%. These clonal rubbers should all meet the specification requirements if they are not contaminated during processing.

Colour. This is an essential property in the production of light-coloured rubbers, such as the SMR L grade which requires a colour limit of six units or less on the Lovibond colour scale[25].

The discolouration of raw rubber is usually due to the polyphenol oxidases in latex reacting with the naturally occurring phenolic substances in the presence of atmospheric oxygen, forming certain coloured products. It is sometimes due to the presence of non-rubber particles which are coloured, particularly the brightly coloured carotenoid Frey-Wyssling bodies. The browning of rubber which occurs in some cases, is often associated with the naturally occurring amines in the presence of divalent metal ions[6]. It therefore appears that all the known causative factors for the discolouration of rubber involve the non-rubber components of the latex system, the composition of which varies from clone to clone, and to a certain extent also, from day to day[6,14]. It is thus not surprising that such changes could induce variability in the colour of the derived rubber. Furthermore, this property could also be affected by differences adopted in the processing conditions of rubber, such as the preservation and dilution of latex, the coagulation method, the maturation and drying temperature.

Under the conditions employed in the present study, in which all the rubber samples were subjected to a single set of processing conditions, nine clones were found to yield rubbers with a consistently light colour (< 6 Lovibond units). A further sixteen clones produced rubbers which satisfied the colour requirement when the latex was treated before coagulation with 0.04 p.h.r. sodium meta-bisulphite — a compound normally added to latex to inhibit the enzymic darkening *(Table 6).* In these latter cases, a dominant role by the oxidases is implied. As the above-mentioned non-rubber components involved in the discolouration process have not been investigated in this study, it is not possible to identify the extent of their influence on the colour of the various clonal rubbers. Such a study should be informative.

Curing characteristics. Although not a specified property, consistency in cure behaviour is important in determining the ease with which a product can be fabricated. In the SMR Scheme, the cure test used to measure cure differences between samples has been, since 1970, the MOD Cure Indicator system[5,42]. This measures the relaxed modulus at 100% extension (MR 100) of the rubber sample, vulcanised at 140°C for 40 min using the ACS 1 mix, giving a single point value which is used to characterise both the rate and state of cure. The measurements are classified as

MOD 5 (slow)	:	0.45-0.55 MPa
MOD 6 (moderate)	:	0.55-0.65 MPa
MOD 7 (fast)	:	0.65-0.75 MPa

Table 8 gives MR100 values of all the forty-three clones tested. It can be seen that while the non-viscosity-stabilised rubbers showed MR100 values varying between 0.53 MPa and 0.70 MPa, the CV-rubbers indicated a narrower range of 0.53 MPa to 0.63 MPa.

In recent years, a rheometric test has been preferred to characterise cure behaviour[42,43]. This test furnishes a rheograph in which the cure behaviour can be comprehensively defined

TABLE 8. CURE CHARACTERISTICS OF FORTY-THREE CLONAL RUBBERS — MR 100 (40 MIN/140°C) AND RHEOMETRIC (160°C) MEASUREMENTS USING ACS 1 MIX

Clone	Non-CV Rubber								CV Rubber							
	MR 100 (MPa)		Torque modulus ΔT (Nm)		Cure rate (t_{90}–t_2) min		Scorch time t_2 (min)		MR 100 (MPa)		Torque modulus ΔT (Nm)		Cure rate (t_{90}–t_2) min		Scorch time t_2 (min)	
	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Class I																
GT 1	0.64	0.03	3.819	0.305	8.3	0.8	1.5	0.2	0.58	0.04	3.571	0.362	9.0	1.2	1.8	0.2
RRIM 600	0.63	0.05	3.786	0.339	8.8	1.9	1.7	0.2	0.57	0.04	3.424	0.170	10.1	1.8	2.0	0.2
RRIM 712	0.65	0.05	3.899	0.294	8.1	1.6	1.5	0.2	0.58	0.02	3.469	0.158	9.7	1.3	1.8	0.2
PR 255	0.61	0.04	3.616	0.136	9.0	1.2	1.7	0.2	0.59	0.05	3.537	0.192	9.2	1.3	1.7	0.2
PR 261	0.65	0.05	3.808	0.305	7.8	1.1	1.6	0.2	0.59	0.02	3.447	0.113	8.9	1.0	1.8	0.2
PB 217	0.53	0.06	3.209	0.475	10.5	2.6	2.0	0.6	0.53	0.08	3.040	0.373	11.9	2.1	2.3	0.5
Class II																
RRIM 623	0.59	0.07	3.627	0.452	8.3	1.2	1.7	0.3	0.57	0.06	3.322	0.142	10.0	1.2	1.9	0.3
RRIM 628	0.57	0.03	3.424	0.226	8.7	0.9	1.8	0.2	0.55	0.03	3.322	0.316	10.5	0.9	1.9	0.3
RRIM 701	0.63	0.03	3.763	0.146	7.9	0.7	1.4	0.1	0.59	0.01	3.503	0.102	8.8	0.5	1.6	0.1
RRIM 703	0.65	0.03	3.865	0.113	7.8	1.0	1.6	0.2	0.59	0.01	3.503	0.170	9.1	1.1	1.8	0.1
RRIM 725	0.65	0.02	3.899	0.305	7.4	0.6	1.4	0.2	0.61	0.02	3.605	0.226	8.1	0.6	1.7	0.2
RRIM 728	0.70	0.04	4.328	0.316	7.0	1.3	1.5	0.2	0.58	0.02	3.548	0.136	9.2	1.0	1.9	0.3
RRIM 729	0.68	0.04	3.955	0.249	6.8	0.7	1.4	0.1	0.59	0.03	3.424	0.158	8.7	0.8	1.8	0.2
RRIM 805	0.62	0.08	3.774	0.497	8.3	2.2	1.5	0.4	0.61	0.07	3.627	0.463	8.4	2.2	1.7	0.5
RRIM 901	0.62	0.01	3.668	0.192	8.0	0.5	1.7	0.1	0.59	0.01	3.503	0.124	8.5	0.8	1.8	0.1
RRIM 905	0.59	0.03	3.616	0.339	8.0	1.6	1.7	0.3	0.61	0.07	3.345	0.090	9.2	1.1	1.9	0.2
PB 28/59	0.59	0.03	3.413	0.226	8.0	0.9	1.6	0.3	0.54	0.02	3.175	0.068	9.1	0.2	1.9	0.5
PB 230	0.61	0.05	3.808	0.350	8.2	1.0	1.5	0.2	0.57	0.05	3.571	0.407	9.1	0.7	1.9	0.3
PB 235	0.60	0.02	3.435	0.237	8.3	1.1	1.6	0.3	0.56	0.01	3.277	0.102	9.4	0.9	1.9	0.1
PB 254	0.57	0.06	3.311	0.271	9.2	1.3	1.9	0.2	0.53	0.04	3.119	0.192	10.0	1.2	2.2	0.9
PB 255	0.60	0.04	3.503	0.215	8.1	1.1	1.7	0.1	0.56	0.04	3.334	0.215	8.9	1.0	1.9	0.2
PB 260	0.65	0.05	3.853	0.396	7.3	0.9	1.4	0.1	0.60	0.06	3.571	0.396	8.3	1.3	1.9	0.3
PB 280	0.64	0.05	3.842	0.429	7.7	0.6	1.5	0.3	0.57	0.03	3.367	0.079	8.9	1.0	1.9	0.2
RRIC 100	0.62	0.05	3.593	0.362	9.5	1.5	1.8	0.3	0.59	0.06	3.413	0.418	9.5	1.5	1.7	0.3
RRIC 110	0.66	0.07	3.989	0.452	8.1	1.4	1.4	0.4	0.62	0.08	3.673	0.463	8.6	1.1	1.6	0.4
IAN 873	0.53	0.02	3.108	0.113	11.0	0.7	2.1	0.2	0.51	0.02	3.017	0.124	11.0	0.8	2.3	0.2
PM 10	0.61	0.08	3.401	0.463	8.7	2.3	1.8	0.5	0.59	0.07	3.334	0.407	9.4	2.2	1.8	0.6
BPM 24	0.64	0.06	3.797	0.327	7.9	0.8	1.4	0.3	0.56	0.04	3.367	0.305	9.8	1.6	1.9	0.1
Nab 17	0.65	0.05	3.940	0.429	8.1	0.9	1.3	0.3	0.58	0.03	3.627	0.373	9.2	0.5	1.6	0.3

TABLE 8. CURE CHARACTERISTICS OF FORTY-THREE CLONAL RUBBERS — MR 100 (40 MIN/140°C) AND RHEOMETRIC (160°C) MEASUREMENTS USING ACS 1 MIX *(CONT'D)*

Clone	Non-CV Rubber								CV Rubber							
	MR 100 (MPa)		Torque modulus ΔT (Nm)		Cure rate (t_{90}–t_2) min		Scorch time t_2 (min)		MR 100 (MPa)		Torque modulus ΔT (Nm)		Cure rate (t_{90}–t_2) min		Scorch time t_2 (min)	
	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Class IIIA																
RRIM 709	0.65	0.09	4.091	0.678	8.1	1.1	1.5	0.4	0.59	0.01	3.729	0.622	9.2	1.5	1.8	0.4
RRIM 710	0.67	0.06	4.147	0.452	7.9	1.0	1.6	0.3	0.63	0.06	3.797	0.463	8.5	1.1	1.8	0.3
RRIM 717	0.69	0.02	4.181	0.181	7.3	0.9	1.4	0.8	0.63	0.02	3.808	0.102	8.0	0.9	1.7	0.1
RRIM 730	0.58	0.03	3.526	0.203	8.8	0.7	1.6	0.2	0.54	0.02	3.356	0.124	9.7	0.6	1.9	0.1
RRIM 803	0.67	0.03	4.034	0.124	7.1	0.8	1.5	0.1	0.60	0.02	3.503	0.124	8.6	0.6	1.8	0.2
RRIM 804	0.64	0.05	3.808	0.215	8.4	1.2	1.6	0.2	0.60	0.03	3.537	0.136	8.7	0.9	1.9	0.1
RRIM 806	0.64	0.09	3.899	0.633	8.4	2.0	1.7	0.5	0.59	0.06	3.548	0.407	9.5	1.8	1.9	0.4
RRIM 809	0.60	0.08	3.593	0.441	8.6	1.4	1.7	0.4	0.57	0.09	3.447	0.520	9.1	2.1	1.8	0.5
PB 242	0.59	0.06	3.695	0.509	8.6	1.2	1.7	0.4	0.55	0.04	3.334	0.203	9.7	0.9	2.0	0.3
PB 274	0.58	0.05	3.379	0.283	8.9	1.2	1.9	0.4	0.54	0.02	3.153	0.079	9.7	0.4	2.2	0.2
PB 312	0.65	0.09	3.808	0.565	8.5	2.1	1.5	0.4	0.62	0.09	3.571	0.565	9.4	2.0	1.8	0.5
PM 8	0.63	0.06	3.831	0.452	8.5	1.8	1.6	0.3	0.58	0.04	3.458	0.294	9.2	1.2	1.9	0.2
RRIC 101	0.63	0.08	3.740	0.644	8.9	1.6	1.6	0.5	0.61	0.08	3.469	0.509	9.4	1.4	1.9	0.6
RRIC 102	0.64	0.06	3.673	0.463	8.3	1.1	1.7	0.5	0.60	0.06	3.514	0.475	8.3	1.2	1.9	0.4
L.S.D.		0.06		0.437		1.5		0.35		0.06		0.370		1.43		0.34
S.D.		0.05		0.384		1.3		0.30		0.05		0.325		1.26		0.30

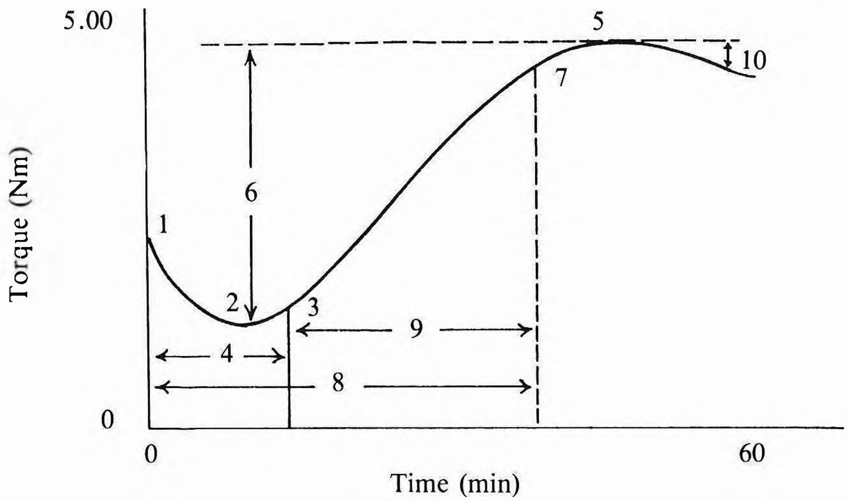

Figure 6. A rheometric cure curve showing the initial viscosity (1), minimum torque, T_{min} (2), induction point (3), induction or scorch time, t_2 (4), maximum torque, T_{max} (5), $\Delta T = (T_{max} - T_{min}$ (6), optimum torque, T_{90} (7), optimum cure time, t_{90} (8), cure rate $(t_{90} - t_2)$ (9), and reversion (10).

(Figure 6). The important cure characteristics include the scorch or induction time (t_2), rate of cure $(t_{90} - t_2)$ (where t_{90} represents the optimum cure time), and the change in torque (ΔT) during vulcanisation, as denoted by $(T_{max} - T_{min})$.

Results of such measurements using the ACS 1 formulation for the forty-three clonal rubbers are also shown in *Table 8.* For the non-viscosity-stabilised rubbers, the mean ΔT was seen to vary between 3.108 Nm and 4.328 Nm, while the mean cure rate ranged from 6.8 min to 11.0 min, and the scorch time from 1.3 min to 2.1 min. Two clones, PB 217 of *Class I* and IAN 873 of *Class II* were observed to show relatively lower curing efficiencies, having mean ΔT values of 3.209 Nm and 3.108 Nm respectively, which were accompanied by slower cure rates of 10.5 min and 11.0 min and longer scorch times of 2.0 min and 2.1 min respectively. Five other clones: RRIM 728 *(Class II),* RRIM 709, RRIM 710, RRIM 717 and RRIM 803 (all of *Class IIIA*), on the other hand, exhibited comparatively faster and better curing behaviour, as reflected in the cure rates of less than 8.1 min and their higher ΔT values of more than 4 Nm. Differences in their scorch times were however not as apparent.

The corresponding viscosity-stabilised clonal rubbers were generally found to be slower and less efficiently cured, as indicated by slower cure rates of 8.0 min to 11.0 min, a lower mean ΔT range of 3.017 Nm to 3.808 Nm, and scorch times which varied between 1.6 min and 2.3 min. These represent a change of 0%-31% in cure rate, 2%-18% in ΔT and 0%-37% in scorch time. These effects are evidently due to the treatment by hydroxylamine neutral sulphate (HNS) in the preparation of the CV rubbers[44]. The mechanism involved is not yet clear.

The associations of lower ΔT values with slower cure rates and longer scorch times, and *vice-versa,* suggested the existence of certain relationships between these characteristics. Statistical analysis subsequently carried out revealed that ΔT is negatively correlated with both cure rate and scorch time *(Figures 7* and *8),* while the cure rate is positively correlated with scorch time *(Figure 9).*

For a given vulcanisation formulation — the ACS 1 in this case — differences in vulcanising behaviour between NR samples can be ascribed to the presence of various naturally occurring

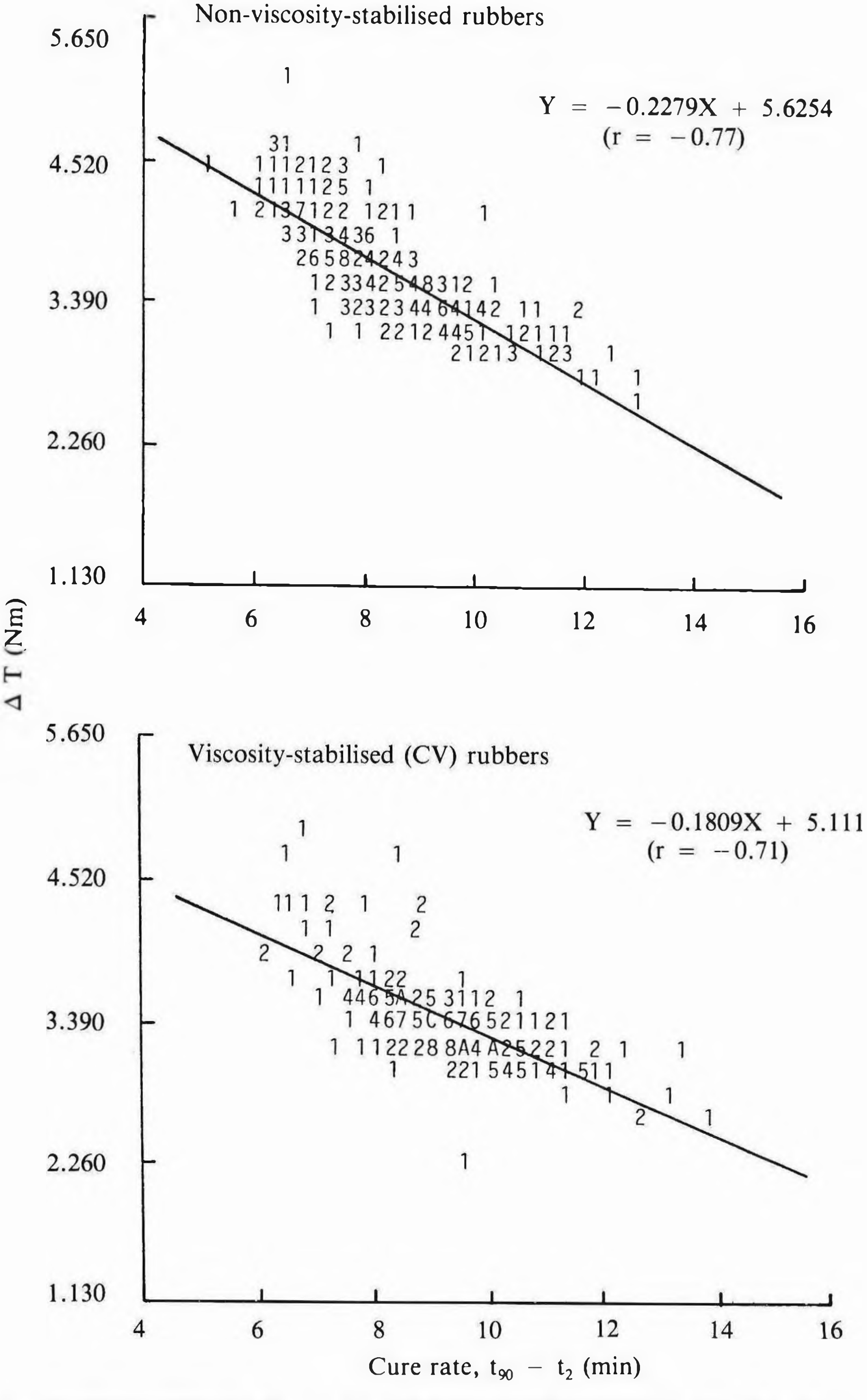

Figure 7. ΔT versus cure rate (t_{90} − t_2) for non-viscosity-stabilised and the corresponding viscosity-stabilised rubbers of forty-three clones vulcanised at 160°C using ACS 1 mix. The numbers 1–9 stated in the graph denote the number of points plotted in a given position. Similarly the alphabets A, B, C .... L represent 10, 11, 12 .... 16 points respectively.

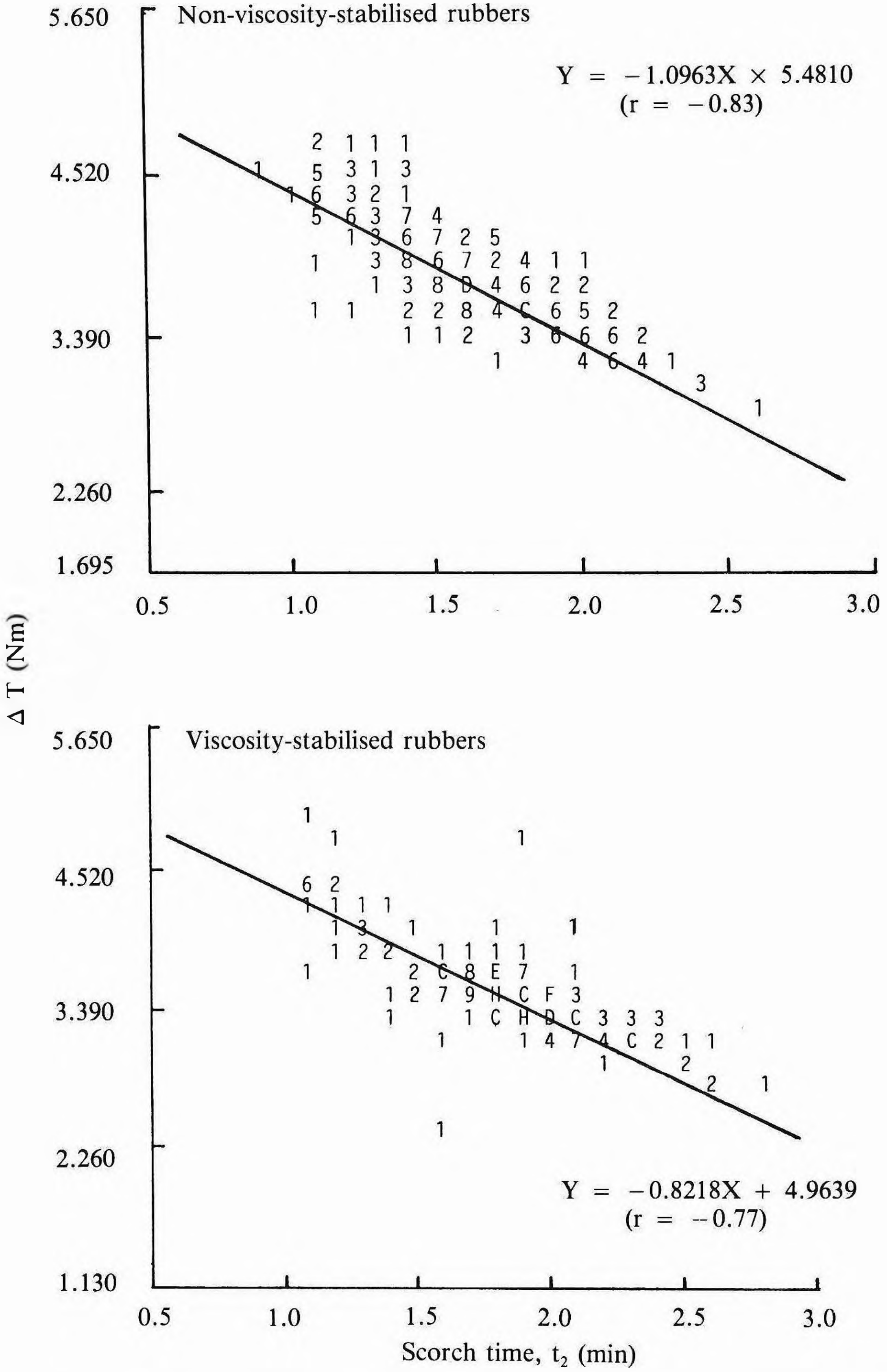

Figure 8. ΔT versus scorch time (t_2) for non-viscosity-stabilised rubbers and the corresponding viscosity-stabilised rubbers cured at 160°C using the ACS 1 mix, for forty-three clones. The numbers 1-9 stated in the graph denote the number of points plotted in a given position. Similarly the alphabets A, B, C .... L represent 10, 11, 12 .... 16 points respectively.

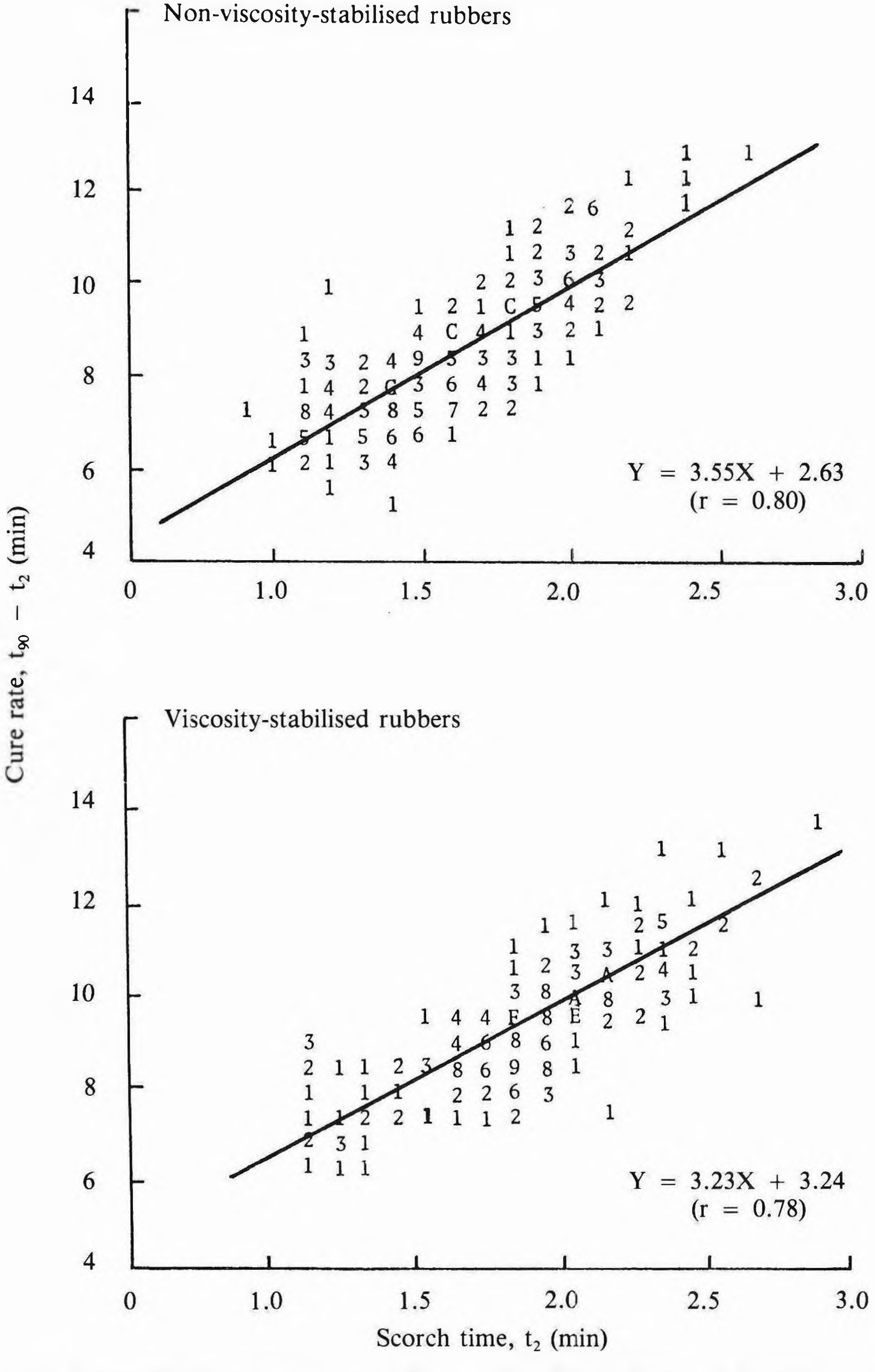

Figure 9. Relationship between cure rate, (t_{90} – t_2) and scorch time (t_2), of non-viscosity-stabilised and viscosity-stabilised rubbers vulcanised at 160°C using ACS 1 mix, for forty-three clones. The numbers 1-9 stated in the graph denote the number of points plotted in a given position. Similarly the alphabets A, B, C .... L represent 10, 11, 12 .... 16 points respectively.

non-rubbers, the qualitative and quantitative compositions of which not only vary between clones but are also influenced by the procedures used in the coagulation process; for example, the pH of coagulation, type of coagulant, degree of dilution of latex prior to coagulation, time of maturation of coagulation and subsequent washing of the rubber. In the present study, in which all the rubber samples tested were prepared using the same processing procedure, the differences observed should be due only to clonal variation in their non-rubber contents. Hydrolysis products of lipids, such as the free fatty acids and amines, and certain nitrogenous substances present in latex are known to affect cure[38-41,45]. Correlations between the nitrogen contents of the clonal rubbers and their corresponding cure parameters have however been found to be insignificant. This is not unexpected since not all the naturally occurring nitrogenous materials exert an influence. Furthermore, while amines like ethanolamine and choline, which are hydrolysis products of phospholipids, and arginine[45] (a basic amino acid) accelerate cure, other amino acids such as cystine, tyrosine, glutamic acid and alanine give rise to slower cure rates[40].

Correlation between vulcanisate modulus and rheometer torque measurements. Analyses of the two sets of cure data showed the following correlations between MR100 and ΔT, where the relaxed modulus values had been corrected to those corresponding to Mooney viscosity 40 of the unvulcanised compounds[5], and $\Delta T = T_{max} - T_{min}$ (in Nm) *(Figure 10)*.

For non-CV rubbers,

$$\text{MR100 (corrected)} = 0.1324\,\Delta T + 0.1299 \quad (r = 0.91)$$

For CV rubbers,

$$\text{MR100 (corrected)} = 0.1389\,\Delta T + 0.0998 \quad (r = 0.87)$$

These findings confirm that a relationship exists between ΔT and MR100, as reported earlier by Bristow[46] who showed a correlation between these two properties obtained from different grades of SMR rubbers as well as rubbers prepared by different processes. His equation is however not strictly comparable to the ones shown above, since the condition for his ΔT measurements were somewhat different although a temperature of 160°C was used in both cases: a change in torque at 10 min as compared to minimum torque, *i.e.* $\Delta T = T_{10} - T_{min}$ (in inch lb) was adopted in that study instead of the difference between maximum and minimum torques.

As indicated earlier, MR100 values may be predicted from the torque measurements or *vice-versa* using these relationships, provided the conditions of measurements are the same as those employed to produce the correlations.

CONCLUSION

Various important technical properties which relate to the qualities of latex concentrate and bulk rubber have been studied for forty-three clones of *Hevea brasiliensis*. The findings reported should provide useful guidelines to the characteristics of each of the clones, even though there may be some variations if the same clones were to be grown in different sites, due to the influence of soil and environmental conditions.

The study has shown that there are clonal differences in almost all the properties examined. Determination of the dry rubber content of fresh latex indicated that except for *Class IIIA* clones, RRIM 710 and PB 274 which gave relatively low d.r.c., all the other clones yielded latices with average to high rubber contents. Provided excessive dilution by water during the latex collection process does not cause the d.r.c. to drop below 25%, all the clonal latices can be processed *via* centrifugation to give latex concentrates.

In the form of high ammonia concentrates, eighteen clones exhibited poor inherent stabilities as reflected in low MST values. Addition of an anionic surfactant at 0.02% to improve these values effected different responses by different clones. While a large number of the unstable clones responded well showing an elevated MST of higher than the specification limit of 650 s after three months' storage, the

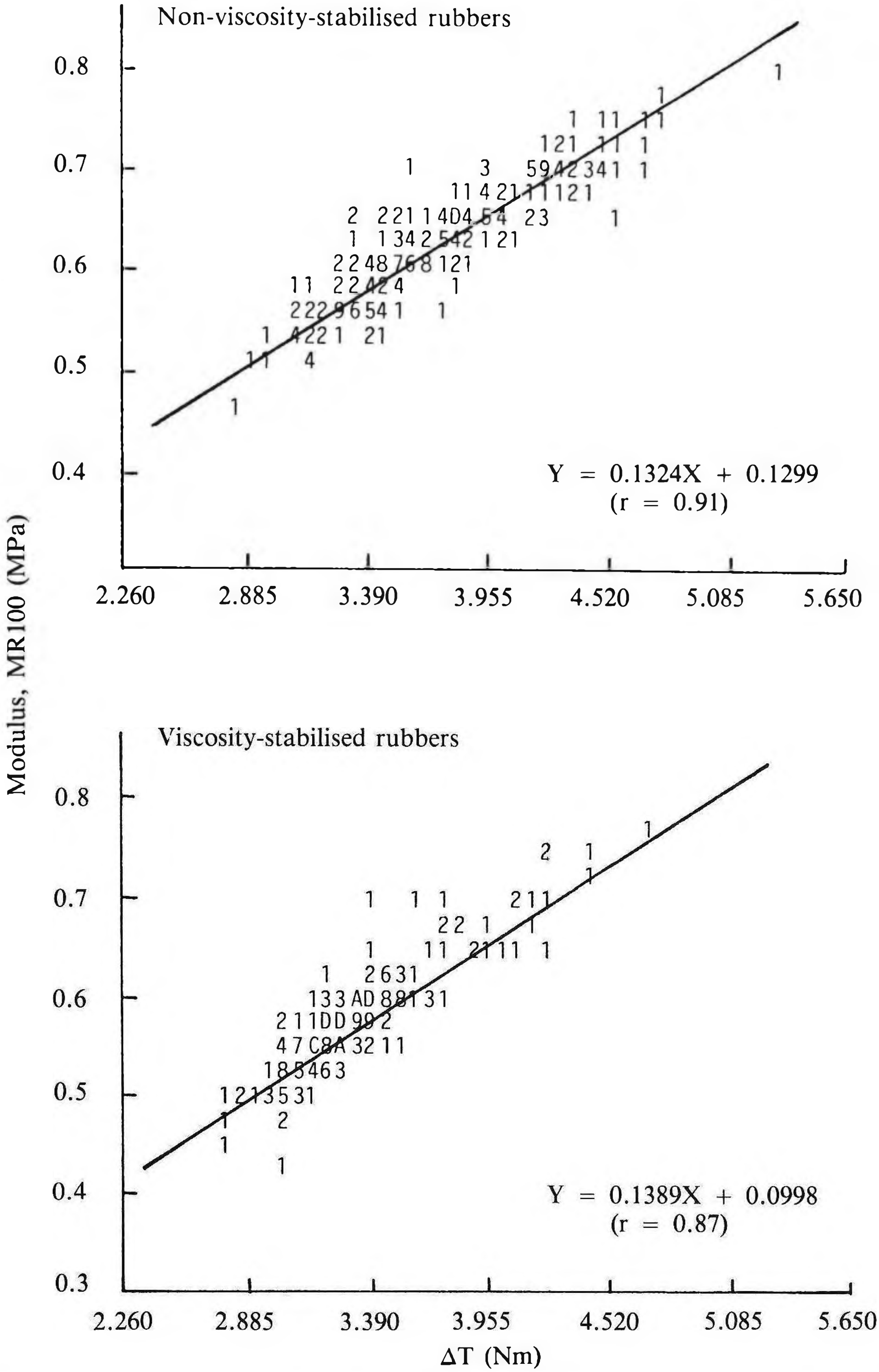

Figure 10. Correlation between MR100 of non-viscosity-stabilised and viscosity-stabilised rubbers vulcanised at 140°C for 40 min and ΔT of the same rubber cured at 160°C, both using the ACS 1 formulation, for forty-three clones. The numbers 1-9 stated in the graph denote the number of points plotted in a given position. Similarly the alphabets A, B, C .... L represent 10, 11, 12 .... 16 points respectively.

MST values of a few other clones remained low. The cause of this is believed to be related to differences in the surface properties of the rubber particles between clones. Apart from the MST measurements, all properties satisfied the specifications set out in *ISO 2004*.

Unstable latex concentrates are often associated with high VFA numbers and hence high KOH numbers. Significant correlation was however not observed between MST and KOH for these clonal latices.

When processed as SMR WF, though not on a large factory scale, the findings have indicated that most of the modern clones produce medium to hard rubbers, and few yield soft rubber. In addition, rubbers from the RRIM clones generally have low to medium viscosities, while those from the PB clones tend to have relatively high viscosity. As all the dry rubber properties tested met the specification requirements for SMR production, non-viscosity-stabilised rubber grades can be prepared from latices of all these clones, twenty-five of which consistently yielded light-coloured rubbers. On the other hand, only fifteen clones were found to be suitable for the production of the viscosity-stabilised grade, SMR CV 60. However, the other clones could also be converted into CV grades by blending with rubbers of appropriate high or low viscosity.

Good correlations were obtained between Mooney viscosity and initial Wallace plasticity of the clonal rubbers for both non-CV and CV rubbers. Their cure characteristics, expressed in terms of ΔT and MR100, were also significantly correlated.

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