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Role of Fatty Acids in Autoxidation of Deproteinised Natural Rubber

A.R. ARNOLD* AND P. EVANS*

The effects of stearic, oleic and linoleic acids and their methyl esters on the autoxidation of deproteinised natural rubber (DPNR) have been investigated. The carboxyl group of the free acids was found to be of primary importance in increasing the rate of oxidation and enhancing chain scission. Oleic and linoleic acids exhibited synergistic pro-oxidant activity as a result of their co-oxidation. Chain breaking antioxidants such as butylated hydroxytoluene (BHT) helped protect polyisoprene from fatty acid promoted autoxidation.

The autoxidation of natural rubber (NR) has been studied extensively over the past fifty years due to the realisation that oxidation of the polyisoprene chain leads to a dramatic loss in the physical properties of a vulcanisate^{1,2}. It is therefore important to identify factors which may accelerate the process so that their detrimental effects may be reduced or eliminated. In raw rubber, autoxidation is accelerated by numerous variables such as heat, light and transition metal ions³⁻⁶. Although non-rubbers such as tocotrienols may impart stability to the rubber due to their known antioxidant activity, the role of other non-rubbers such as proteins is less clear⁷. In technological sulphur vulcanisates, autoxidation becomes increasingly more complex due to the presence of different types of sulphur crosslinks, fillers and curative residues such as accelerators, sulphur and zinc oxide^{8,9}.

Recent research by Boon¹⁰ proposed that the acid catalysed decomposition of allylic hydroperoxides (Hock Cleavage) is partly responsible for main-chain scission in NR sulphur vulcanisates. In this study, sodium carbonate and proton sponge were found to reduce the loss in tensile properties of a semi-efficient vulcanisate and to a lesser extent a conventional vulcanisate. In contrast, base was found to have no effect on the tensile properties of a peroxide vulcanisate suggesting that sulphur acids were the source of catalysis for

Hock Cleavage. It was also suggested that Hock Cleavage explains the discrepancies in the classical scission mechanism derived from peroxy radical cyclisation.

There have been other investigations on the role of acidic substances in polymer degradation¹¹⁻¹⁴. Cooray and Scott¹¹ demonstrated the dual action of hydrogen chloride in the degradation of PVC. They found evidence for homolytic and heterolytic decomposition mechanisms. At low ratios of hydroperoxide to hydrogen chloride, a free-radical mechanism predominated but at high ratios, the ionic process was prominent. It has similarly been shown that sulphur dioxide and derived acids, which are thought to be important in the activity of sulphur-containing antioxidants, act through both homolytic and heterolytic mechanisms¹².

Keller *et al.*¹⁵ have examined the oxidative role of fatty acids in Guayule resin. They proposed that the unsaturated acids such as linoleic and linolenic acids were highly susceptible to autoxidation and their oxidation products (hydroperoxides) acted as initiators in polyisoprene oxidation. As NR contains a variety of saturated and unsaturated fatty acids, it was of interest to investigate the effect of these acids in terms of the rate of autoxidation and the amount of chain scission that occurs during oxidation.

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This paper reports the role of stearic, oleic and linoleic acids and their methyl esters in the autoxidation of DPNR.

EXPERIMENTAL

Gas Liquid Chromatography

Fatty acid methyl esters (FAME) were prepared using methanolic boron trifluoride and analysed by GLC using heptadecanoic acid as the internal standard. Experimental procedures were essentially the same as those of Crafts *et al.*¹⁶

Gel Permeation Chromatography

Analyses were carried out on two 60 cm mixed bed columns (Polymer Laboratories Ltd) with THF as the solvent and a flow-rate of 0.5 ml/min at 40°C. UV detection was carried out at 215 nm and the instrument calibrated with polystyrene standards (Polymer Laboratories Ltd).

Purification of Natural Rubber

HA latex was deproteinised according to the procedure of Chong¹⁷ and the DPNR recovered by precipitation in methanol. The rubber was subsequently extracted with cold acetone and the soluble rubber extracted with

re-distilled petroleum ether (bp 30°C – 40°C). The soluble rubber was re-precipitated in methanol, dried, re-dissolved in petrol and precipitated once more. This purification procedure resulted in a soluble rubber with a nitrogen content of less than 0.01 wt%.

Oxygen Uptake Measurements

The purified rubber was cast as a thin film (approx. 0.03 mm) on the inside of a test-tube using a rotary film evaporator. The sample tube was placed in a thermostated oil bath at 80°C and oxidation carried out in oxygen at atmospheric pressure. The apparatus consisted of the sample tube connected *via* capillary tubing to a graduated pipette with glass side-arm (containing low viscosity silicone oil). A number of taps allowed the apparatus to be evacuated and the introduction of oxygen or nitrogen. Errors in following oxygen uptake could be minimised by making allowances for changes in atmospheric temperature and pressure.

RESULTS AND DISCUSSION

Fatty Acid Composition of Bale Rubbers

The free fatty acid compositions of a number of SMR grades are presented in *Table 1*. All

TABLE 1. FATTY ACID COMPOSITION OF VARIOUS SMR GRADES
(RESULTS PRESENTED AS WT% FATTY ACID WRT RUBBER)

| Fatty acid | SMR L | SMR 5 | SMR 10 | SMR 20 | SMR CV | Skim |
|------------|-------|-------|--------|--------|--------|------|
| 12:0 | Trace | Trace | Trace | Trace | Trace | 0.08 |
| 14:0 | Trace | 0.01 | 0.01 | 0.01 | Trace | 0.02 |
| 16:0 | 0.06 | 0.08 | 0.10 | 0.10 | 0.05 | 0.24 |
| 16:1 (n-9) | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.04 |
| 18:0 | 0.14 | 0.22 | 0.18 | 0.16 | 0.12 | 0.44 |
| 18:1 (n-9) | 0.14 | 0.11 | 0.13 | 0.12 | 0.10 | 0.84 |
| 18:2 (n-6) | 0.30 | 0.33 | 0.30 | 0.23 | 0.28 | 0.97 |
| 18:3 (n-3) | 0.02 | 0.03 | 0.03 | 0.02 | 0.03 | 0.07 |
| Furanoic | 0.10 | 0.14 | 0.08 | 0.10 | 0.04 | 0.07 |
| Total | 0.77 | 0.93 | 0.84 | 0.76 | 0.63 | 2.77 |

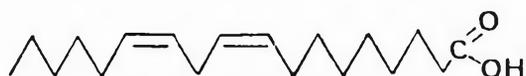
rubbers had fatty acid level of between 0.5 wt% and 1.0 wt% with the exception of skim rubber which contained 2.68 wt%. The major fatty acids were found to be stearic, oleic and linoleic acids (1, 2 and 3)



1. 18:0



2. 18:1 (n-9)



3. 18:2 (n-6)

which accounted for nearly 70% of the total. A furanoid fatty acid which is reported to be a major constituent of field latex was present at relatively low levels¹⁸.

Effects of Fatty Acids on Rate Profile

Soluble deproteinised natural rubber (sol DPNR) was used in all autoxidation experiments to avoid interpretational difficulties from non-

rubbers and to simplify the molecular weight analysis. Measurements were made in the absence of added radical initiators such as AIBN to avoid the possibility of masking subtle effects of the fatty acids on the rate profile. This procedure had the disadvantage of increasing the variability of oxidation rate between nominally identical samples. All comparisons were therefore made between sets of samples prepared together from the same rubber solution.

Effects of Stearic Acid on Rate

The effects of varying concentrations of stearic acid on the oxygen uptake of purified sol DPNR are presented in *Figure 1*. The results showed that as the concentration of stearic acid was increased, an enhancement in the rate of NR autoxidation occurred. This may have resulted from an increase in the number of radicals participating in chain propagation. A heterolytic mechanism such as Hock Cleavage does not produce free radicals and would therefore not have been expected to contribute to the enhanced rate. However, the oxidation of stearic acid itself is recognised as a slow process and is unlikely to have contributed to the observed results. One possible explanation which we are currently investigating is the formation of hydrogen bonded complexes between the fatty acids and rubber-bound hydroperoxides. Privalova and Maizus¹⁹ demonstrated that homolysis of such dimers is a more facile process than unimolecular decomposition of the free hydroperoxide.

Caproic acid was found to increase the rate of oxidation of n-decane and the rate of hydroperoxide decomposition at 140°C. In addition, caproic acid was found to act catalytically and could be recovered quantitatively from the reaction:



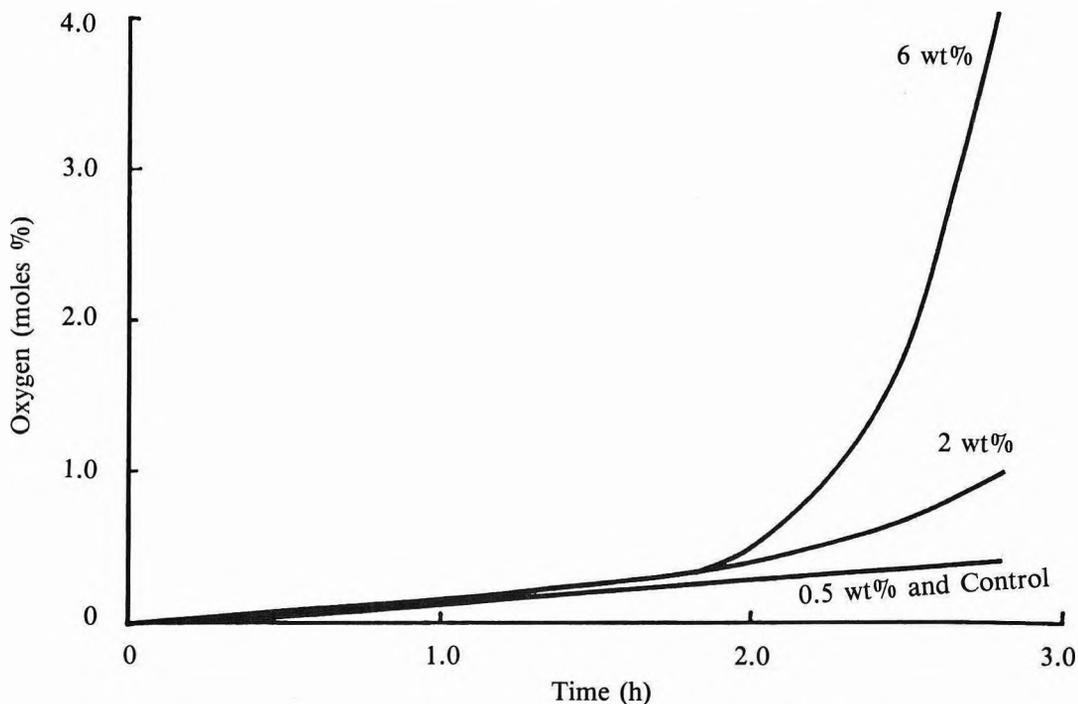


Figure 1. Effect of varying levels of stearic acid on autoxidation of sol DPNR at 80°C.

Although carboxylic acids are susceptible to attack by peroxy radicals, leading to decarboxylation, hydrogen-bonding has been reported to prevent this occurring²⁰. In non-polar solvents, carboxylic acids and hydroperoxides are believed to exist almost entirely as hydrogen-bonded dimers. In NR, added carboxylic acids would be expected to have greater mobility than rubber-bound hydroperoxides which may have resulted in carboxylic acid-hydroperoxide complexes having formed in preference to hydroperoxide dimers. Further research is obviously required to identify the formation of such complexes in NR and on how readily they decompose.

Another possible explanation for the catalytic activity of stearic acid is the reaction of pro-oxidant metals such as copper, cobalt, iron and manganese with fatty acids to produce metal carboxylates. This could have increased the solubility of the metal and imparted a more favourable redox potential. The role of metal

carboxylates and chelating groups in the oxidation of cyclohexane has been extensively studied by Chalk and Smith^{21,22}. They found that metal ion solubility, the presence of chelating groups and concentration were all important factors in predicting the metal's pro-oxidant activity. The actual state of metal ions in DPNR is not known but they might be expected to be co-ordinated to functional groups such as epoxides and carbonyls in addition to residual protein. Addition of a fatty acid may disrupt this association, although it would be extremely difficult to predict the effect on activity of the metals.

Butylated hydroxytoluene (BHT) was found to reduce the catalytic activity of stearic acid (Figure 2) and provide further evidence that rate enhancement did not occur *via* Hock Cleavage. These results suggest that antioxidants indigenous to NR may help protect it from fatty acid promoted oxidation.

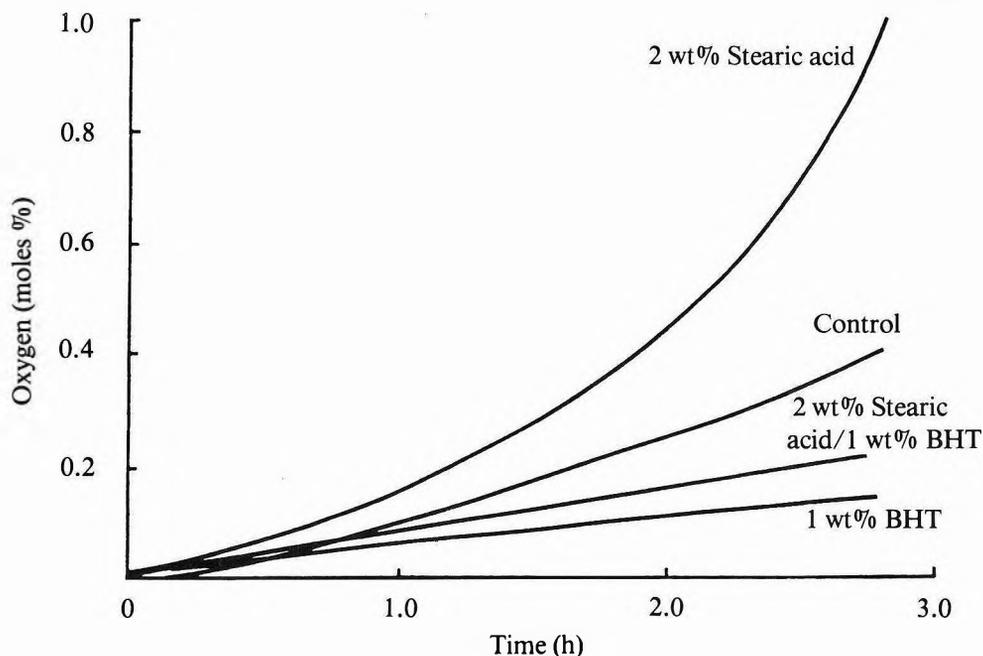


Figure 2. Effect of stearic acid and BHT on autoxidation of sol DPNR at 80°C.

Effect of Oleic and Linoleic Acids on Rate

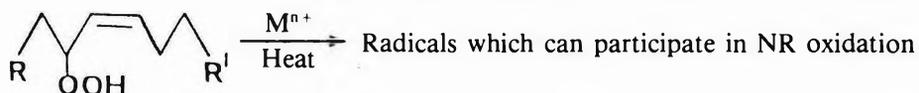
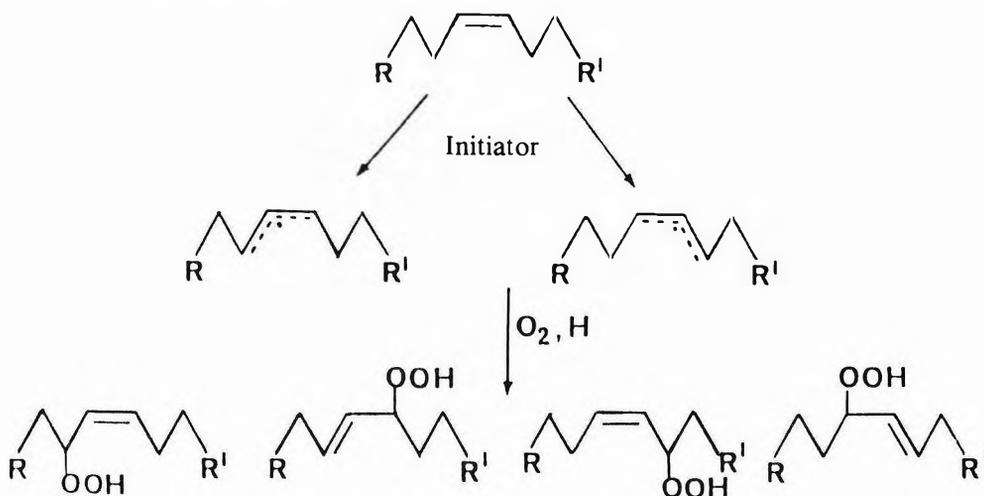
The role of oleic and linoleic acids in promoting NR oxidation was also studied. In addition to the carboxylic group, these acids may themselves oxidise and their oxidation products act as initiators in polyisoprene oxidation. Autoxidation of oleic acid involves hydrogen abstraction from *Position 9* or *12* producing a simple allylic radical that reacts rapidly with oxygen giving a peroxy radical which, after hydrogen abstraction, yields one of four possible allylic hydroperoxides (*Scheme 1*). In linoleic acid, hydrogen abstraction from the doubly allylic CH_2 produces a pentadienyl radical which leads to one of four possible allylic hydroperoxides (*Scheme 2*)²³. The additional delocalisation energy of the pentadienyl radical is proposed to explain the high reactivity of linoleic acid compared to oleic acid. These hydroperoxides would be vulnerable to metal ion catalysed decomposition producing radicals capable of promoting polyisoprene oxidation. A comparison of the differences between stearic, oleic and linoleic

acids in promoting NR oxidation is presented in *Figure 3*. The higher rate of oxidation of NR in the presence of linoleic acid relative to oleic acid is likely in part to have been a consequence of the higher oxidisability of linoleic acid. The horizontal line (*Figure 3*) indicates oxygen uptake to a level equivalent to the concentration of the fatty acid and indicates that oxygen uptake was not just a result of fatty acid oxidation. To differentiate between catalysis by the carboxyl group and that originating from oxidation of the unsaturated centres, the prooxidant activity of the free acids was compared with that of their methyl esters. The results (*Figures 4* and *5*) indicate that the carboxyl group was of key importance in promoting oxidation. However, the greater differences in the catalytic activity of the free acids compared with their methyl esters indicated synergism between the two modes of rate enhancement.

Keller *et al.*¹⁵ demonstrated that the unsaturated fatty acids of Guayule resin enhanced the oxidative deterioration of NR. However, they proposed that the fatty acid

R - Fatty alkyl chain

R' - Fatty acyl chain



Scheme 1

Autoxidation of oleic acid and methyl oleate - the primary products and their decomposition

oxidation products (hydroperoxides) acted as radical chain initiators and were wholly responsible for the enhancement in rate. The results presented here clearly show that the carboxyl group is of primary importance in catalysing NR autoxidation.

Effect on Chain Scission

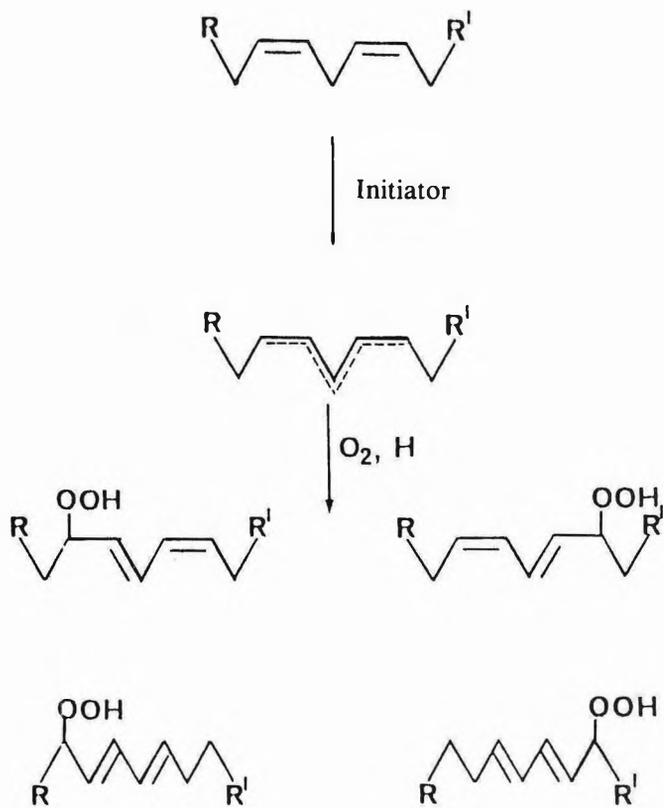
An important consequence of autoxidation is that chain scission of the polymer backbone occurs which ultimately leads to a loss in the

useful elastomeric properties of a vulcanisate. We have studied chain scission by following changes in the molecular weight distribution as determined by GPC. The results are presented as a scission efficiency number (ϵ) which is defined as the number of molecules of oxygen causing one scission event:

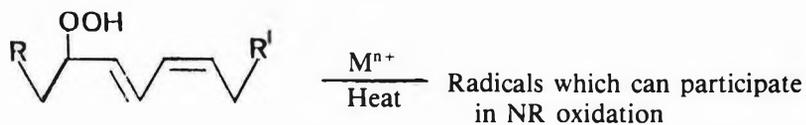
$$\epsilon = \frac{O_2 \text{ uptake mole}\% \cdot Mn}{\left(\frac{Mn_o - Mn}{Mn}\right) \cdot 6800}$$

R - Fatty alkyl chain

R' - Fatty acyl chain



Hydroperoxides susceptible to decomposition



Scheme 2

Autoxidation of linoleic acid and methyl linoleate - the primary products and their decomposition

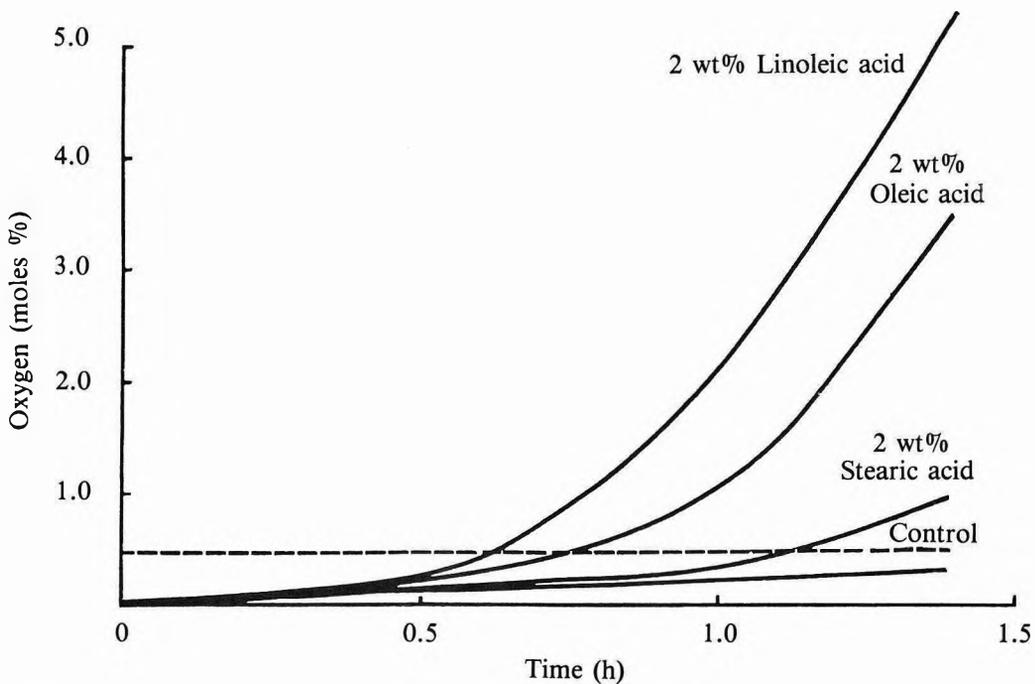


Figure 3. Effect of stearic, oleic and linoleic acids on autoxidation of sol DPNR at 80°C.

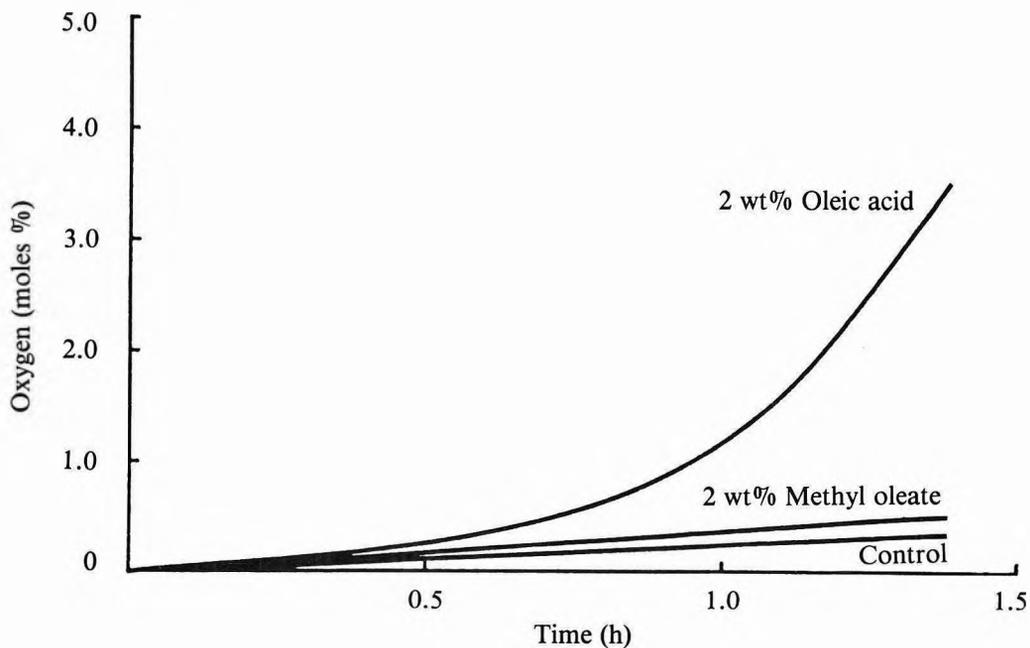


Figure 4. Effect of oleic acid and methyl oleate on autoxidation of sol DPNR at 80°C.

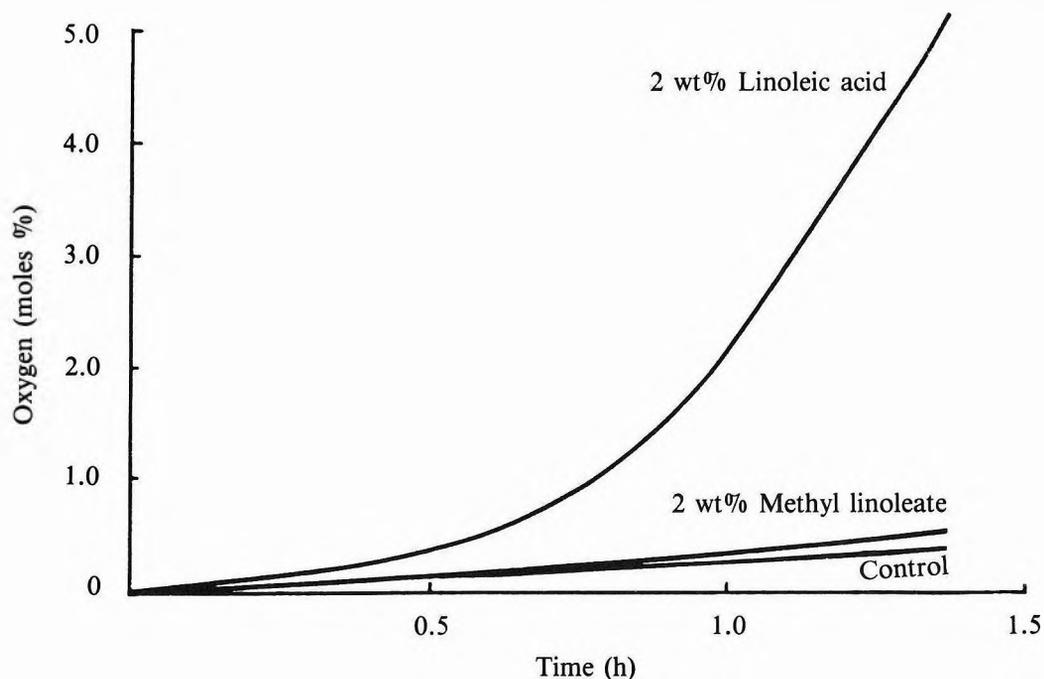


Figure 5. Effect of linoleic acid and methyl linoleate on autoxidation of sol DPNR at 80°C.

Therefore, the lower the number, the more efficient the chain scission. Table 2 presents oxygen uptake and scission efficiency data for a series of rubber samples oxidised with varying levels of stearic acid and in the presence of

BHT. Samples were oxidised for fixed times which resulted in the comparison of rubbers with different oxygen uptake levels. For all samples oxidised with stearic acid, lower scission efficiency values were obtained. Bell²⁴

TABLE 2. EFFECT OF VARYING CONCENTRATIONS OF STEARIC ACID AND BHT ON SCISSION EFFICIENCY (ϵ). SAMPLES WERE OXIDISED FOR 160 MIN AT 80°C

| Additive | O ₂ (mole %) | Mn | ϵ |
|---------------------------------------|-------------------------|-----------|------------|
| Unoxidised Substrate | | 283 850 | |
| Control ^a | 0.41 | 174 350 | 27 |
| 0.5 wt% stearic acid | 0.43 | 115 200 | 12 |
| 2.0 wt% stearic acid | 1.01 | 57 900 | 11 |
| 6.0 wt% stearic acid | 4.09 | 13 000 | 8 |
| 2.0 wt% stearic acid + 1.0 wt% BHT | 0.33 | 234 200 | 45 |
| 1.0 wt% BHT | 0.14 | 2 795 550 | 388 |

^aControl - sol DPNR only

TABLE 3. EFFECT OF STEARIC, OLEIC, LINOLEIC ACIDS, THEIR METHYL ESTERS AND ZINC STEARATE ON SCISSION EFFICIENCY (ϵ). ADDITIVES WERE PRESENT AT CONCENTRATION OF 2 WT% WRT RUBBER AND THE SAMPLES OXIDISED FOR 83 MIN AT 80°C

| Additive | O ₂ (mole %) | Mn | ϵ |
|----------------------|-------------------------|---------|------------|
| Unoxidised Substrate | | 200 500 | |
| Control ^a | 0.38 | 135 450 | 23 |
| Stearic acid | 1.00 | 46 050 | 9 |
| Oleic acid | 3.44 | 17 900 | 10 |
| Linoleic acid | 5.30 | 9 800 | 8 |
| Methyl stearate | 0.24 | 155 500 | 25 |
| Methyl oleate | 0.53 | 857 000 | 12 |
| Methyl linoleate | 0.52 | 84 350 | 12 |
| Zinc stearate | 0.42 | 85 750 | 9 |

^aControl - sol DPNR only

showed that when short kinetic chain lengths are observed (when a catalyst is present) enhanced chain scission occurs. This complication becomes important when considering an autocatalytic rate profile which does not exhibit steady-state kinetics in the early stages. Samples oxidised to varying degrees will have experienced different mean kinetic chain lengths.

Nevertheless, it is important to realise that although there was only a small difference in the level of oxygen uptake between the control and DPNR oxidised in the presence of 0.5% stearic acid, there was a significant difference in scission efficiency. This suggests that the enhanced scission in the presence of the acid cannot entirely be explained by the kinetic chain length effect. BHT appeared to inhibit stearic acid promoted chain scission of DPNR which suggests that scission occurred *via* a homolytic rather than heterolytic (Hock Cleavage) mechanism. This result is at variance with previously published results which found that the scission step is enhanced in the presence of a chain-breaking antioxidant²⁵.

In a separate experiment, the effect of stearic, oleic and linoleic acids, their methyl

esters and zinc stearate on chain scission were investigated (*Table 3*). The scission efficiency of samples oxidised with the free acids were all lower than of the control but very similar considering the large differences in oxygen uptake levels. DPNR oxidised in the presence of methyl stearate exhibited no enhanced chain scission in comparison to the control but both methyl oleate and linoleate caused a lowering in scission efficiency. The precise reason for the enhanced chain scission shown by the esters is difficult to explain. However, if the decomposition of H-bonded dimers (NR hydroperoxide-fatty acid hydroperoxide) was an important process, chain scission may have resulted from β -scission of these alkoxy radicals. Although zinc stearate did not exhibit significant pro-oxidant character, it did appear to reduce the molecular weight of the rubber. Zinc is not recognised as a powerful pro-oxidant due to an unfavourable redox potential but some catalytic activity has been observed previously²¹.

CONCLUSION

In conclusion, free fatty acids were found to be capable of promoting the autoxidation of

DPNR. The pro-oxidant activity of the acids was reduced in the presence of chain-breaking antioxidants such as BHT. It is likely to be diminished in the presence of natural antioxidants such as tocotrienols which are present in NR. Fatty acids esterified as lipids would be expected to show a lower pro-oxidant activity due to the absence of the free carboxyl group. The free fatty acids enhanced chain scission during autoxidation but the parallel effect on autoxidation rate suggests that this enhancement is associated with the free radical autoxidation process rather than Hock Cleavage that has been characterised for stronger acids. Zinc stearate also appeared to enhance chain scission but to a much smaller extent than the free acids.

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Distribution of Crosslinks Between the Phases of Vulcanised ENR 25/cis-BR Blends

P.S. BROWN* AND A.J. TINKER*

The recently developed NMR method of rubber blend analysis^{1,4} has been applied to gum vulcanisate blends of epoxidised natural rubber (ENR) and cis-1,4 polybutadiene (BR). It was observed that the degree of crosslinking in each of the two rubbers of the blend was different from that found in the analogous single polymer vulcanisates, the ENR having increased crosslink levels while the BR had reduced crosslink levels. This difference has been quantified in terms of the curative levels required to give vulcanisates of the individual rubbers the same crosslink density as found in that component in the blends.

In the search for optimum product properties, most rubber goods are manufactured using blends of two or more dissimilar polymers. The physical properties of these blends are determined both by the properties of the individual component rubbers and by the physical structure of the blend. To understand the properties of the blend, the physical structure must be characterised. Recent papers^{1,2} report the first method for directly determining the distribution of crosslinks between the phases of a blend, adding to the other well established techniques of blend characterisation.

This new technique compares the line widths observed in a continuous wave ¹H NMR spectrum of the blend with those of the analogous single polymer vulcanisates. Line width is measured as the proportion of signal strength at a reference position on the side of the peak to that at the peak and denoted H%. H% is observed to increase smoothly with curative level¹, the volume fraction of rubber in the swollen state (*V_r*) in chloroform¹ or the crosslink density^{2,3} of a single polymer vulcanisate.

In this study, blends of an epoxidised natural rubber with a high *cis*-polybutadiene are examined using the NMR technique.

EXPERIMENTAL

The rubbers used in this study were *cis*-1,4 polybutadiene, BR, (Europrene *cis*, 94% *cis*-1,4 polybutadiene, Enichem) and an epoxidised natural rubber, ENR 25 (25 mol% epoxidised natural rubber, Rubber Research Institute of Malaysia). Rubber chemicals were standard commercial-grade materials, solvents of AR grade except for the NMR solvents which were of spectroscopic grade [deuteriochloroform and hexamethyldisiloxane (HMDS) Aldrich Chemical Company].

Compounding (*Table 1*) was performed using a BR-size Banbury internal mixer and/or a two-roll mill, the curatives being added on a two-roll mill. The single polymer vulcanisates were produced from masterbatches mixed in the Banbury. For each polymer, two batches were crossblended on the mill before finalising the blends. The blends were produced either in the Banbury mixer with the curatives added on the two-roll mill or by the crossblending of single polymer masterbatches on the two-roll mill ensuring that the polymers were well blended before the curatives were added. The same cycle was used for all batches mixed in the internal mixer (*Table 2*).

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TABLE 1. MIX FORMULATIONS

| Compound | Formulation | | | | |
|-----------------------|------------------|---------------|---------|---------|---------|
| | ENR 1- ENR 10 | BR 1- BR 8 | Blend 1 | Blend 2 | Blend 3 |
| ENR 25 | 100 | | 50 | 80 | 85.7 |
| Europrene- <i>cis</i> | | 100 | 50 | 20 | 14.3 |
| Zinc oxide | 5 | 5 | 5 | 5 | 5 |
| Stearic acid | 2 | 2 | 2 | 2 | 2 |
| TMQ ^a | 2 | 2 | 2 | 2 | 2 |
| MBS ^{bc} | 0.3-2.3 | 0.4-2.3 | 0.5-2.5 | 0.5-1.9 | 0.5-1.9 |
| Sulphur ^c | 0.3-2.3 | 0.4-2.3 | 0.5-2.5 | 0.5-1.9 | 0.5-1.9 |

^apoly-2,2,4-trimethyl-1,2-dihydroquinoline (e.g. Flectol-H Monsanto)

^b2-morpholinothiobenzothiazole-2-sulphenamide

^cSulphur: MBS ratio = 1:1

TABLE 2. BANBURY MIX CYCLE^a

| Time (s) | Operation |
|----------|----------------------|
| 0 | Add polymer/polymers |
| 30 | Add powders |
| 12 | Sweep |
| 210 | Dump |

^aRotor speed = 116 r.p.m. Water as required to keep the temperature below 130°C

Samples of vulcanisate for NMR analysis were extracted for 4 h with methanol in a hot Soxhlet apparatus and dried to constant weight *in vacuo* in the dark until required. Small slivers ($\sim 15 \times 0.5 \times 1$ mm) were allowed to swell in deuteriochloroform (CDCl_3) in a NMR tube to equilibrium uptake for between 36 h and 60 h in the dark. If necessary, these samples were then trimmed so that they can spin freely in the NMR tube. A small amount of fresh CDCl_3 containing chloroform (CHCl_3) as an internal marker and HMDS as an internal lock were added just before acquisition of the spectrum.

The equilibrium swelling of each vulcanisate in chloroform was determined for specimens swollen at 23°C in the dark. The swollen vulcanisate was dried *in vacuo* and the volume

fraction of rubber in the swollen gel, V_r , was calculated with due allowance for the zinc oxide in the vulcanisate⁴.

The NMR spectra were obtained using a Perkin-Elmer R32 90 MHz continuous wave spectrometer interfaced to a BBC microcomputer for computer accumulation of the transients to improve the signal to noise ratio. The spectrometer was run at an 80 s sweep of 10 p.p.m. width with between forty and eighty transients combined for each spectrum. $\text{H}\%$ was evaluated as described previously¹ using reference positions -0.2 p.p.m. and $+0.2$ p.p.m. from the olefin peak positions of ENR 25 and BR respectively. Duplicate or sometimes triplicate spectra were obtained from freshly swollen samples.

RESULTS AND DISCUSSION

The analysis of a binary polymer blend for the level of crosslinking within each component using the NMR technique¹ is made with reference to the NMR spectra of vulcanisates of the individual polymers in the blend. Thus, two series of single polymer vulcanisates are required to provide the individual $\text{H}\%$ - V_r and $\text{H}\%$ -curative level relationships (*Figures 1 and 2*). Ideally, the cure system used for these single

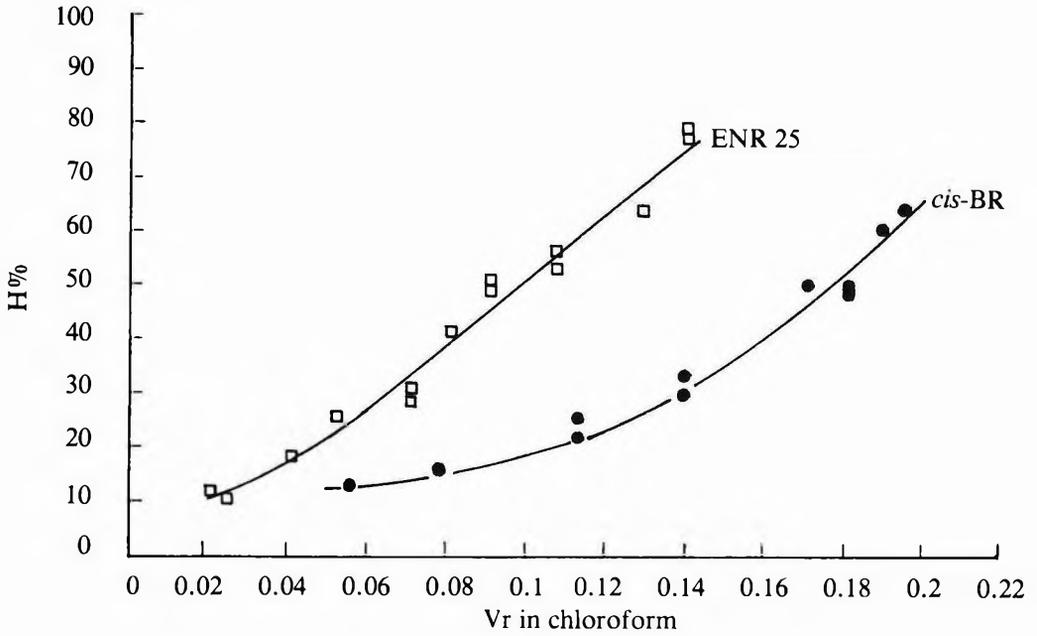


Figure 1. $H\%$ versus V_r in chloroform for single polymer vulcanisates.

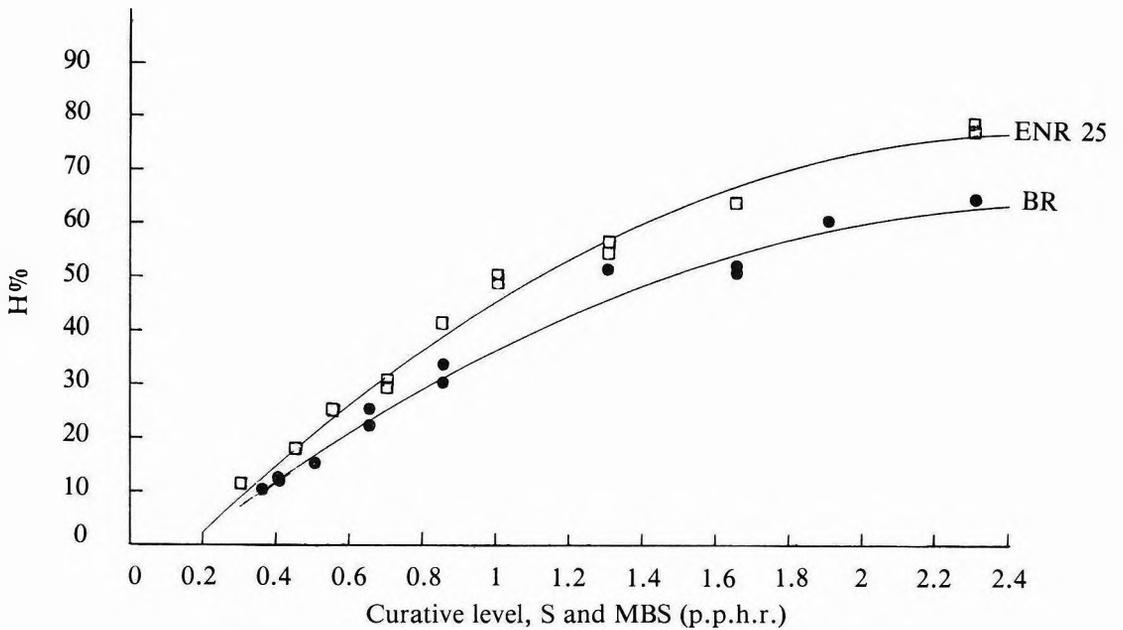


Figure 2. $H\%$ versus curative level for single polymer vulcanisates.

polymer vulcanisates should be that used in the blends of interest, however the potential for diffusion of curatives and, more importantly, crosslinking intermediates, means that the cure systems active in each phase of the blend are likely to differ from that of the compounding. It has previously been shown that $H\%$ is independent of the particular cure system used, at least within a class of cure systems (e.g. accelerated-sulphur)², so that differences in the effective accelerator/sulphur ratio resulting from curative diffusion before and during vulcanisation do not affect the application of the NMR technique. This study used a cure system having a 1:1 ratio of sulphur and N-morpholino-benzothiazole-2-sulphenamide (MBS) compounded at levels ranging from 0.3 p.p.h.r. to 2.3 p.p.h.r. to produce the ten ENR 25, eight BR and twelve blend vulcanisates (Table 1).

The olefin region of the NMR spectra of each of the single polymer vulcanisates was analysed to determine three parameters; $H\%$, $P\%H$ and $R\%H$ ¹. $H\%$, the measure of peak broadening, is the ratio of the peak intensity at a reference

position 0.2 p.p.m. from the peak centre to that at the peak maximum expressed as a percentage, $100Bb/Aa$ (Figure 3) and $P\%H$ and $R\%H$ are the peak overlap terms given by:

$$P\%H = 100 Pp/Aa$$

$$R\%H = 100 Rr/Aa$$

where P and R of Figure 3 are the peak centre and the reference positions of the second polymer to be used in the blend. $P\%H$ and $R\%H$ are found to correlate well with $H\%$ (Figures 4 and 5). In these two figures, the solid curves represent the best fits of the data to first-, second- or third-order polynomial equations in $H\%$ as appropriate. These polynomial equations are used in the analysis of the olefin region in the spectra of blend vulcanisates when calculating the corrections for signal overlap to enable determination of $H\%$ for each polymer in the blend, as described by Loadman and Tinker¹.

There is considerable overlap of the olefin signal from these two polymers (Figure 6), the ENR peak maximum being at 5.08 p.p.m. and

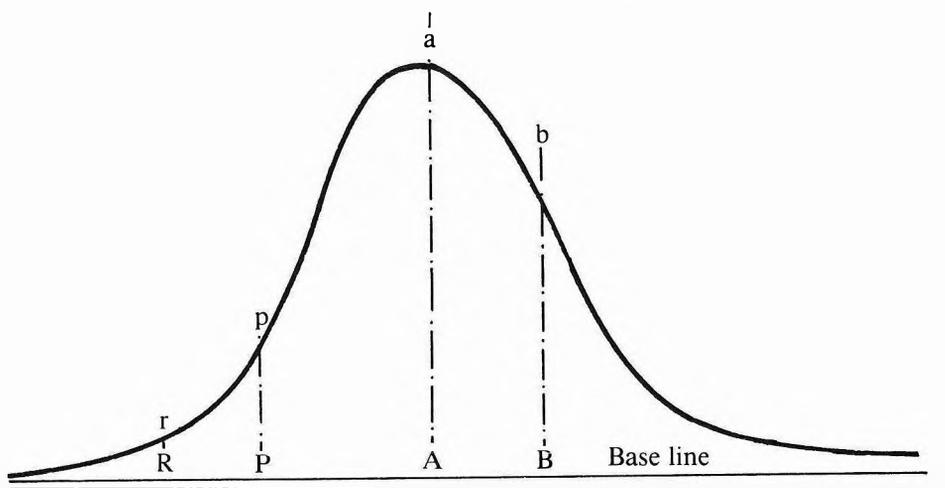


Figure 3. Diagrammatic representation of the determination of $P\%H$, $R\%H$ and $H\%$. A and B are the peak centre and reference positions of the polymer whose NMR spectrum is given, P and R are the peak centre and reference positions of the other polymer in the blend to be studied. Aa , Bb , Pp and Rr represent the NMR intensity at the positions A , B , P and R , respectively. $H\% = Bb/Aa$, $P\%H = Pp/Aa$ and $R\%H = Rr/Aa$, all expressed as percentages.

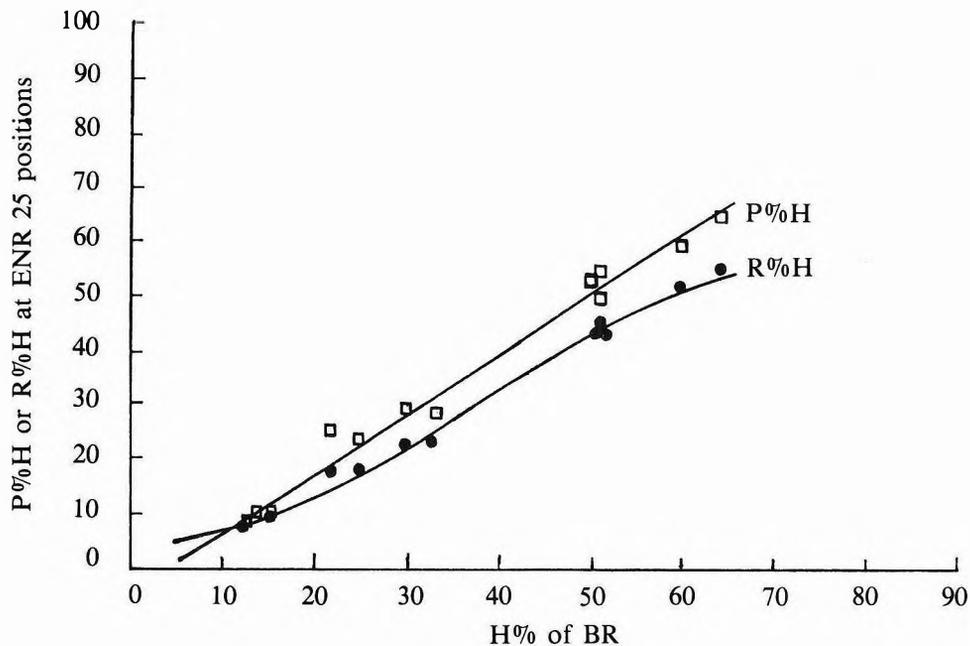


Figure 4. P%H and R%H at the peak and reference positions of ENR 25 in the NMR spectrum of BR versus H% of BR.

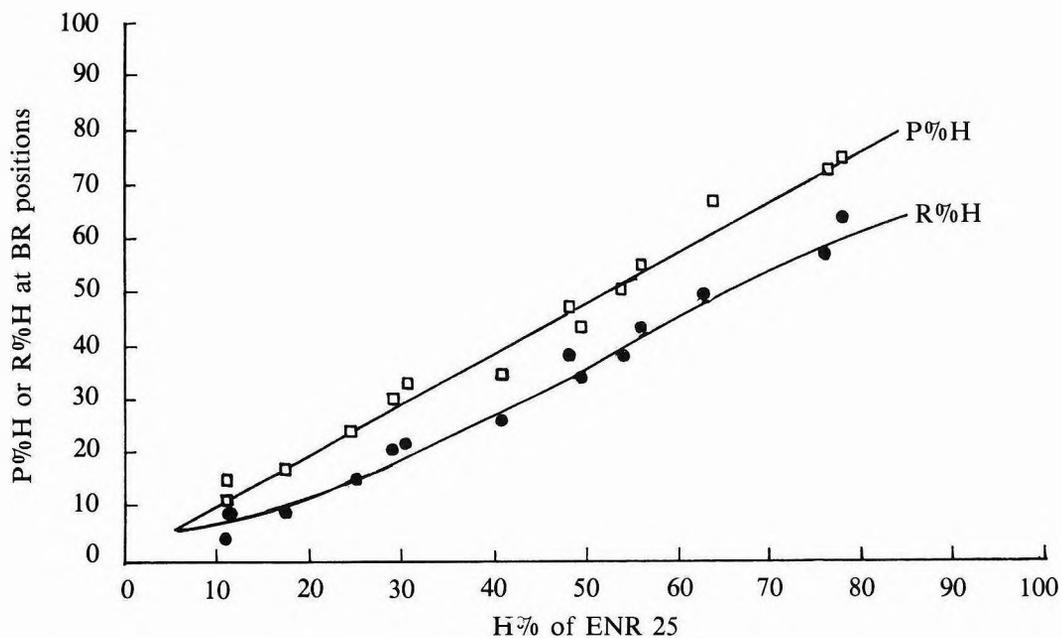


Figure 5. P%H and R%H at the peak and reference positions of BR in the NMR spectrum of ENR 25 versus H% of ENR 25.

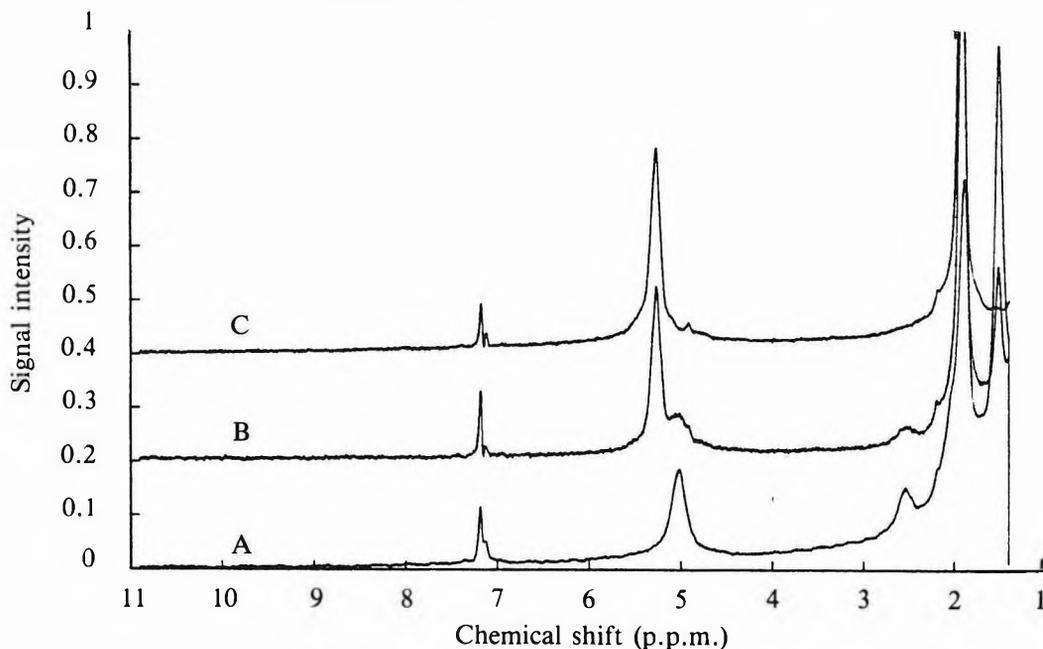


Figure 6. Proton NMR spectra of single polymer vulcanisates of ENR 25 (A) and BR (C) and of a 1:1 (wt/wt) blend (B), all compounded using 0.5 p.p.h.r. sulphur and MBS.

that of BR at 5.34 p.p.m. This close proximity of the peaks in the NMR spectrum of a blend of ENR and BR results in relatively large corrections being applied to the observed intensities to deconvolute these signals. In addition to the problem of peak overlap, the two polymers possess different concentrations of olefinic proton ($3.70 \times 10^{-2} \text{ mol g}^{-1}$ rubber for BR and $1.04 \times 10^{-2} \text{ mol g}^{-1}$ rubber for ENR 25). As a consequence, the olefin region of the NMR spectrum of the blend is dominated by the BR peak for all but the highest ENR concentrations (Table 3, Figure 6) and this in

turn restricts the polymer ratios which may be investigated by the technique using proton NMR spectroscopy.

A qualitative result may be obtained by comparing the NMR spectrum of a blend vulcanisate with the spectra of its single polymer analogues. Figure 6 shows the spectrum of blend 1F (Table 4) together with the spectra of the single polymer ENR and BR vulcanisates also compounded using 0.5 p.p.h.r. sulphur and 0.5 p.p.h.r. accelerator. The ENR olefin signal, chemical shift (δ) 5.05, is obviously broader in the blend vulcanisate (B) than in the homopolymer vulcanisate (A). This indicates that the ENR has a higher crosslink density in the blend than as the single polymer despite nominally equivalent curative loadings. The BR olefin peaks at δ 5.35 are similar in shape (B and C), it is therefore not possible to draw any conclusions regarding the crosslinking of this component of the blend. Quantitative analysis of the NMR spectrum of a blend vulcanisate requires the application of the NMR technique¹.

TABLE 3. OLEFINIC PROTON RATIOS^a

| Blend | Blend ratio (wt/wt) | Proton ratio olefin region |
|-------|---------------------|----------------------------|
| 1 | 1:1 | 1:0.282 |
| 2 | 1:4 | 1:1.126 |
| 3 | 1:6 | 1:1.689 |

^aAll ratios calculated as BR/ENR

TABLE 4. BLEND ANALYSIS RESULTS

| Blend | Polymer ^a ratio | S (p.p.h.r.) | ENR | | BR | | S _{ENR} /S _{BR} |
|-------|-------------------------------|-----------------|------|-------------------------------|------|------------------------------|-----------------------------------|
| | | | H% | S _{ENR} ^b | H% | S _{BR} ^b | |
| 1A | 1:1 | 0.5 | 16.6 | 0.45 | 9.5 | 0.3 | 1.50 |
| 1B | 1:1 | 1.0 | 51.3 | 1.1 | 18.6 | 0.6 | 1.83 |
| 1C | 1:1 | 1.5 | 62.7 | 1.55 | 38.6 | 1.0 | 1.55 |
| 1D | 1:1 | 2.0 | 72.2 | 2.05 | 52.2 | 1.4 | 1.46 |
| 1E | 1:1 | 2.5 | 83.6 | >2.5 | 55.3 | 1.55 | >1.6 |
| 1F | 1:1 | 0.5 | 32.8 | 0.7 | 13.7 | 0.45 | 1.55 |
| 1G | 1:1 | 0.9 | 38.6 | 0.8 | 27.1 | 0.75 | 1.07 |
| 1H | 1:1 | 1.4 | 70.9 | 1.95 | 43.1 | 1.1 | 1.77 |
| 1I | 1:1 | 1.9 | 83.2 | >2.5 | 57.9 | 1.7 | >1.5 |
| 2A | 4:1 | 0.5 | 21.2 | 0.5 | 13.5 | 0.45 | 1.11 |
| 2B | 4:1 | 0.9 | 43.2 | 0.95 | 20.5 | 0.65 | 1.46 |
| 2C | 4:1 | 1.4 | 55.2 | 1.25 | 31.0 | 0.8 | 1.56 |
| 2D | 4:1 | 1.9 | 80.9 | 2.45 | 52.7 | 1.4 | 1.75 |
| 3A | 6:1 | 0.5 | 31.6 | 0.65 | 13.0 | 0.45 | 1.44 |
| 3B | 6:1 | 0.5 | 56.4 | 1.3 | 37.5 | 0.95 | 1.36 |
| 3C | 6:1 | 1.4 | 64.9 | 1.6 | 36.6 | 0.95 | 1.68 |
| 3D | 6:1 | 1.9 | 85.0 | >2.5 | 60.5 | 1.8 | >1.4 |

^aBy weight ENR 25:BR

^bS_{ENR} and S_{BR} determined from the calculated H% values by reference to *Figure 2*. Note the calibration stops at 2.5 p.p.h.r. S which in ENR 25 gives a H% value of 82.

Vulcanisates from the three blend systems (*Table 1*) were analysed using the procedure of Loadman and Tinker¹ to give H% values for the two component polymers. These H% values were translated into equivalent curative levels by reference to *Figure 2* and the data presented as a function of total curative level in the blend in *Figure 7*. These data show that the notional curative levels effective in the blend components are not the same with that in the ENR 25 being higher than that in the BR by approximately 50% (*Table 4*). The degree of scatter in these results is quite large and probably arises from a combination of effects. The proximity of the two signals, as mentioned above, results in relatively large P%H and R%H correction terms being applied to the

observed signal intensities at the two peak and two reference positions. Furthermore, the uneven crosslink density, biased as it is towards the ENR component of the blend, renders the ENR signal considerably broader than and consequently much lower in intensity than the BR olefin peak. The nett effect is to cause relatively large corrections to be applied to the signal at the ENR peak and reference positions during the iterative deconvolution calculations. Thus, any errors in the polynomial fits of the P%H - and R%H - H% relationships are of substantial consequence when the blend spectra are analysed, resulting in the increased scatter observed. When the NMR technique is applied to blends of NR and a butadiene-acrylonitrile copolymer (NBR), for which the olefin

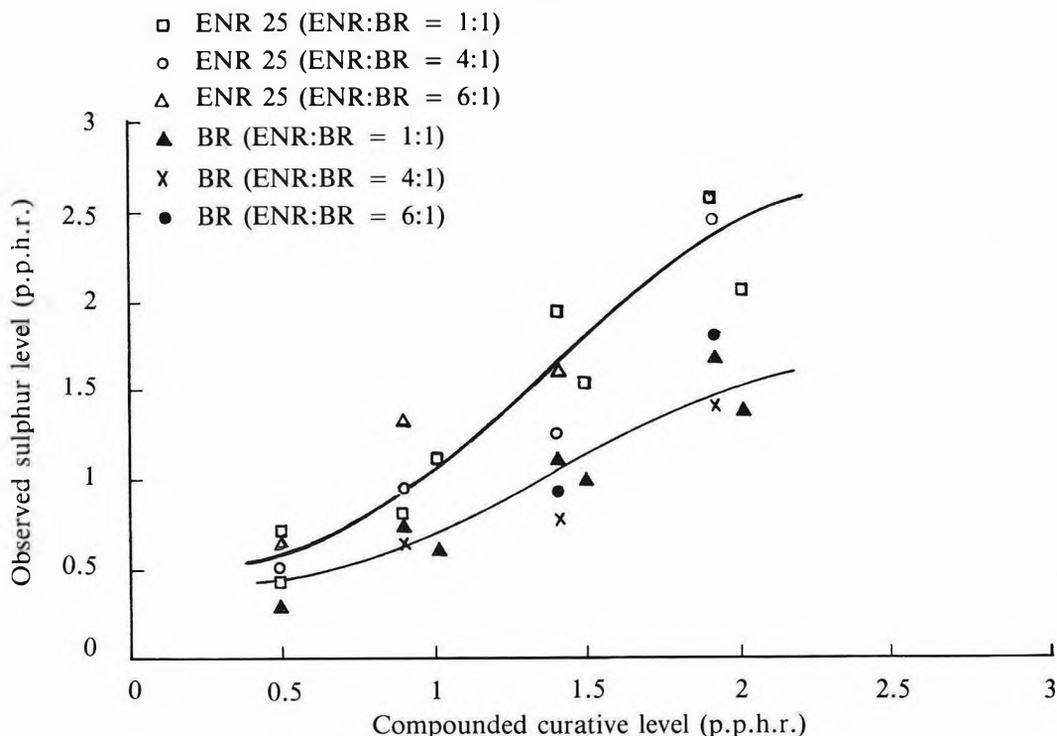


Figure 7. Effective sulphur level observed in each phase versus the compounded sulphur level in the ENR 25/BR blend for blend ratios of 1:1, 4:1 and 6:1 (ENR:BR)

signals are more separated, the H% and derived crosslinking data show much less scatter³.

The uneven curative utilisation indicated by these results probably reflects the partitioning of the actual crosslinking agents between the two polymers in the blend. This partitioning is achieved by the diffusion of crosslinking agents (CLA) from the BR to the ENR phase before and during vulcanisation. Such effects of CLA diffusion have been observed previously in blends of natural rubber (NR) with an ethylene-propylenediene rubber (EPDM)⁵ and in blends of NR with NBR³. In the former blend, the CLA diffusion is driven by the more rapid utilisation of materials by the NR phase because of the higher concentration of olefin group in NR. However in the latter blend, this is not so, the observed crosslink densities show that the CLA diffusion has been away from the polymer of highest olefin concentration. Similarly here,

the ENR has utilised more of the curative during the blend vulcanisation. The presence of the oxirane group in ENR should make this polymer more polar than BR, indeed the solubility parameters of these polymers confirm this thesis [17.09 (MPa)^{1/2} for BR⁶, 17.4 (MPa)^{1/2} for ENR 25⁷]. The compounds involved in vulcanisation chemistry are generally quite polar in nature⁸ and might therefore be expected to have a higher solubility in the ENR phase than in the BR phase of the blend. Consequent partition of the CLA between the rubbers would lead to the observed crosslink distribution. Similar arguments apply to the results obtained by Tinker³.

It must be noted that the chemical nature of the CLA is dependent on the crosslinking system used. The distribution of CLA between the polymers in a blend is therefore dependent not only on the polymers in the blend but also on the vulcanising ingredients in the compound

and possibly on the relative proportions of these ingredients. Thus, the results of the blend analyses reported herein are specific to this particular cure system when used in these two polymers. A change in just one component may, by changing the distribution of the CLA in the blend, alter the distribution of crosslinks between the polymers — a change which would be detected by the application of the NMR technique of polymer blend analysis.

CONCLUSIONS

Blends of ENR 25 with BR having three different polymer ratios have been studied using swollen state NMR spectroscopy¹. The crosslink densities within each component of each blend have been expressed in terms of the curative concentrations required to produce that crosslink density in a single polymer vulcanisate. In all cases, this nominal curative level was higher for the ENR 25 component, typically by as much as 50%. This uneven utilisation of the curatives is caused by the more polar nature of the ENR polymer, containing as it does 25 mol% epoxidation of the olefin groups of NR, resulting in increased concentrations of the crosslinking agents within the ENR phase at the expense of the BR phase.

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Contribution of Storage Hardening to Plasticity Retention Index Test for Natural Rubber

M.D. MORRIS*

Two experiments were designed to investigate the influence of natural or storage hardening on Plasticity Retention Index (PRI) test results. The first experiment involved ageing of PRI test-pieces under vacuum and the second made use of sequential hardening and ageing of the rubber. Results from both experiments showed that storage hardening had a marked effect on PRI test results, even for natural rubber samples which were not freshly prepared. Quantitative estimates of the contribution of hardening to the PRI test were correlated with accelerated storage hardening test results. The correlation indicated that approximately half of the total potential of a rubber sample for storage hardening occurs during the PRI ageing treatment.

The Plasticity Retention Index (PRI) is a measure of the susceptibility of raw rubber to thermal oxidative degradation. It is determined by measuring the Wallace plasticity of a rubber sample before and after ageing for 30 min in an air oven at 140°C. Since its inclusion in the Standard Malaysian Rubber (SMR) specifications, it has become one of the primary indicators of raw rubber quality for Technically Specified Rubbers.

The phenomenon of storage or natural hardening in raw rubber has also been known for many years. It is the slow increase in viscosity of rubber, which occurs during transport and storage and is thought to be due to the linking of oxygen-containing groups on the NR polymer. Most of the reported evidence is consistent with the groups being aldehydic in nature¹⁻³, but the involvement of rubber-bound epoxide groups has also been postulated^{4,6}. The hardening process certainly involves amino-acids which are present in natural rubber^{2,7}, though the mechanism of their involvement has been the subject of some debate^{5,8}. Whatever the nature of the chemical reactions responsible for storage hardening, they can be effectively and economically inhibited by the addition of chemicals such as hydroxylamine to the rubber⁹. However, while a number of viscosity-

stabilised grades of NR are well established, the majority of rubber produced is still not protected against this natural hardening process.

In spite of the fact that storage hardening is known to be accelerated by increased temperature and by conditions which favour removal of water from the rubber¹⁰, the influence of hardening on PRI test results has not been properly assessed. It has been shown that the contribution of storage hardening to oven ageing gives artificially high PRI values for freshly-prepared rubber samples^{3,11,12}. PRI results in excess of 100, indicating a net increase in Wallace plasticity on ageing, have been reported for some of these samples. The SMR specifications for PRI, which are generally 10 units higher for the producers than for the consumers, reflect the general acceptance that storage hardening does influence PRI results in freshly-prepared natural rubber. It is not clear from the literature however, whether the above effect is of significance in commercial samples of NR or rubber that has been stored for some time. In a series of papers on the kinetics of degradation during the PRI test, the contribution of storage hardening was assumed to be negligible without sufficient justification^{11,13}. An attempt is made here to investigate, both qualitatively and quantitatively,

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the influence of storage hardening on PRI test results from various grades of Malaysian natural rubber of various ages.

MATERIALS AND METHODS

Fresh latex rubber was prepared by coagulating fresh field latex with formic acid at pH 4.5, passing the coagulum five times through a creping mill and drying the creped sheet at 100°C until just dry by visual inspection (1.5–2 h). Testing was carried out within 24 h of the latex being collected from the trees. Other samples of natural rubber were taken from stocks which had been stored under various ambient conditions.

All plasticity tests were carried out on one Wallace Rapid Plastimeter for which operating conditions and sample preparation procedures conformed to requirements for SMR testing¹⁴. Three test pellets were used for each test and the result quoted is the median. The pellets were treated in one of the following ways before testing the Wallace plasticity:

- P_O – No treatment
- P_{30} – Aged for 30 min at 140°C in an air oven, then allowed to cool
- P_H – Placed in a vacuum desiccator over phosphorus pentoxide, evacuated for 1 h, stored for 48 h at 60°C under vacuum then cooled over 1 h
- P_{30+H} – Aged as for P_{30} then treated as for P_H
- P_{H+30} – Treated as for P_H then aged as for P_{30}
- P_S – Placed on the base of a preheated vacuum desiccator which was then evacuated for 3 min before sealing and heating at 140°C for 30 min. The desiccator was cooled for 3 min then opened and the rubber pellets removed to cool in air.

RESULTS AND DISCUSSION

Anaerobic Ageing

To probe experimentally the subject of this paper, the most direct approach was considered to be to carry out the ageing process of the PRI test in the absence of air. Unfortunately, this approach was complicated by two matters. Firstly, the experimental inaccuracies were expected to be large because the application of vacuum necessitated the use of a closed container of considerable mass. The temperature – time profile of the rubber samples could not therefore be controlled with the same accuracy as for those aged in an air oven. Secondly, even in the absence of air, thermal oxidative degradation could not be completely eliminated because of dissolved oxygen in the rubber and the contribution of anaerobic thermal degradation. For this reason, the results of the P_S test which is comparable to a P_{30} test in the absence of air (*Table 1*) do not provide a measure of the contribution of hardening to PRI, but rather a combination of hardening and thermal degradation. To obtain realistic estimates of the contribution of hardening, it was necessary to obtain independent information on the degree of thermal degradation for each rubber sample. This was achieved by hardening a sheet of the rubber to its full extent using the accelerated method (P_2O_5 /vacuum/60°C/48 h), then re-testing P_O and P_S .

The overall PRI ageing process can be considered as the sum of three contributions which are assumed to be mutually independent:

- A – the contribution of oxidative degradation
- T – the effect of thermal degradation which is taken to include the contribution from dissolved oxygen
- H – the effect of natural hardening

If A , T and H are defined as the respective changes in plasticity as a percentage of P_O and S is defined as $\frac{P_S - P_O}{P_O} \times 100$ then,

TABLE 1. WALLACE PLASTICITY DATA FOR AEROBIC AND ANAEROBIC AGEING OF VARIOUS NATURAL RUBBER SAMPLES AT 140°C

| Sample | P _O (W.P. units) | P ₃₀ (W.P. units) | P _S (W.P. units) | PRI (% of P _O) | S (% of P _O) |
|--------|--------------------------------|---------------------------------|--------------------------------|-------------------------------|-----------------------------|
| A1 | 38 | 40 | 50 | 107 | + 32 |
| A1Hd | 80 | 52 | 71 | 65 | - 11 |
| A2 | 51 | 46 | 57 | 90 | + 12 |
| A2Hd | 95 | 53 | 63 | 56 | - 34 |
| A3 | 59 | 44 | 65 | 74 | + 9 |
| A3Hd | 86 | 51 | 78 | 60 | - 10 |
| B1 | 45 | 39 | 54 | 86 | + 19 |
| B1Hd | 72 | 46 | 64 | 64 | - 11 |
| B2 | 56 | 28 | 40 | 50 | - 29 |
| B2hd | 68 | 26 | 41 | 39 | - 40 |
| B3 | 50 | 40 | 52 | 79 | + 3 |
| B3Hd | 65 | 47 | 54 | 72 | - 18 |

A1-A3 are fresh latex rubber samples
 B1 is a six-month-old sample of SMR L
 B2 is a six-month-old sample of SMR 10
 B3 is a nine-year-old sample of RSS 1

The postscript Hd refers to samples which were hardened in vacuum over P₂O₅ at 60°C for 48 h before testing.

$$\begin{aligned} \text{PRI}_{\text{raw}} - 100 &= A + T + H \quad \dots 1 \\ \text{and } S_{\text{raw}} &= T + H \quad \dots 2 \\ \text{likewise, PRI}_{\text{hard}} - 100 &= A + T \quad \dots 3 \\ \text{and } S_{\text{hard}} &= T \quad \dots 4 \end{aligned}$$

where the subscript 'raw' denotes raw rubber values and the subscript 'hard' indicates values for the fully hardened samples. It can be seen that estimates of *H* are obtainable both by subtraction of Equation 4 from Equation 2 and of Equation 3 from Equation 1.

$$\text{Thus } H = \text{PRI}_{\text{raw}} - \text{PRI}_{\text{hard}} \quad \dots 5$$

$$\text{and } H = S_{\text{raw}} - S_{\text{hard}} \quad \dots 6$$

There is reasonable agreement between values of *H* obtained from Equations 5 and 6 (Table 2) considering the experimental limitations and the assumptions made. The average value of *H* derived for the various rubber samples ranged from 11 to 42. If these

results are converted to absolute changes in Wallace plasticity, *h*, increases of 6 to 20 units are obtained (Table 2).

Successive Ageing and Hardening

Due to the limitations of the direct approach discussed above, an alternative, indirect probe to the subject of study was considered.

If a certain amount of hardening does occur during the ageing test, then the capacity of a rubber sample for storage hardening would be expected to be lower after ageing than before. Likewise, the softening of the rubber during ageing should be greater for a hardened sample than it was before storage hardening. The tests P_{30+H} and P_{H+30} were designed to examine these differences. For this approach to have quantitative significance, it is necessary for the softening and hardening reactions to be mutually independent. These conditions could not initially be assumed since aldehyde groups are among

TABLE 2. ESTIMATES OF CONTRIBUTION OF STORAGE HARDENING TO PRI AGEING RESULTS

| Sample | H _{eq5} (% of P _O) | H _{eq6} (% of P _O) | Mean H (% of P _O) | h (W.P. units) | ΔP (W.P. units) |
|--------|--|--|----------------------------------|-------------------|--------------------|
| A1 | +42 | +43 | 42.5 | 16 | 42 |
| A2 | +34 | +46 | 40.0 | 20 | 44 |
| A3 | +14 | +19 | 16.5 | 10 | 27 |
| B1 | +22 | +30 | 26.0 | 12 | 26 |
| B2 | +11 | +11 | 11.0 | 6 | 12 |
| B3 | +7 | +21 | 14.0 | 7 | 15 |

the products identified from autoxidation of NR and such groups are almost certainly involved in the storage hardening process^{1,2}. Furthermore, the crosslinks or chemical bonds responsible for the hardening phenomenon could be significantly more or less susceptible to oxidative cleavage than the polymer itself.

Various Wallace plasticity measurements for samples of various grades of natural rubber ranging in age from one day to eleven years were made (Table 3). It can be seen that the reduction in Wallace plasticity of the raw rubber ($P_O \rightarrow P_{30}$) is generally less than that for the hardened samples ($P_H \rightarrow P_{H+30}$) whether these are considered as percentage changes or as absolute changes in plasticity. Also, the hardening of aged samples ($P_{30} \rightarrow P_{30+H}$) is less than that for the unaged samples ($P_O \rightarrow P_H$) except in several of the very old samples in which storage hardening was essentially complete. These results provide qualitative support for the hypothesis that natural hardening occurs during the PRI ageing process.

Considering the results in Table 3 quantitatively, it is observed that there is good agreement between the P_{30+H} values and the corresponding P_{H+30} values. A statistical analysis of the figures reveals that P_{30+H} is greater than P_{H+30} by an average of 0.9 units for the thirty-nine samples while the mean difference between the two measurements is 2.3 units. The actual values of P_{H+30} range from 17 to 58 units with a mean of 40 and standard deviation of 10.2 units. It is

conceivable that the good agreement between P_{30+H} and P_{H+30} is the result of two or more opposing influences of the hardening process on oxidisability and *vice versa*. A more convincing explanation, however, is that the two reactions are in fact occurring independently. Thus, the same final plasticity is reached irrespective of the order in which the ageing and hardening occur.

A further implication of the agreement between P_{30+H} and P_{H+30} for the various natural rubber samples is that plasticity changes due to thermal oxidation must be considered in absolute terms rather than as a percentage of P_O when comparing rubber samples of different initial plasticities. The underlying rate of change of plasticity due to thermal oxidation seems to be independent of the initial plasticity. This deduction is in contrast to published reports in which first-order kinetics have been observed^{11,15} and which presumably led to results¹⁵ of standard PRI tests being expressed as a percentage of P_O . In neither of the earlier studies however, was any attempt made to isolate the effects of storage hardening from the oxidative softening process.

By accepting the above explanation and its implications, two equations can be written to obtain values for h , the absolute change in Wallace plasticity due to storage hardening which occurs during the ageing of each sample:

$$h = (P_H - P_{H+30}) - (P_O - P_{30}) \dots 7$$

$$h = (P_H - P_O) - (P_{30+H} - P_{30}) \dots 8$$

TABLE 3. WALLACE PLASTICITY DATA FOR VARIOUS SAMPLES OF NATURAL RUBBER

| Sample No. | Age | P _O | P ₃₀ | P _H | P _{30+H} | P _{H+30} |
|------------|----------|----------------|-----------------|----------------|-------------------|-------------------|
| L/1 | 1 week | 41 | 37 | 70 | 48 | 56 |
| L/2 | 1 week | 42 | 39 | 76 | 50 | 56 |
| L/3 | 1 week | 43 | 39 | 75 | 51 | 57 |
| L/4 | 1 week | 43 | 39 | 77 | 50 | 51 |
| L/5 | 1 week | 41 | 36 | 68 | 45 | 46 |
| L/6 | 1 day | 52 | 48 | 87 | 64 | 58 |
| L/7 | 1 month | 43 | 37 | 64 | 43 | 45 |
| L/8 | 1 month | 42 | 35 | 61 | 43 | 44 |
| L/9 | 1 month | 45 | 39 | 70 | 50 | 50 |
| L/10 | 1 month | 42 | 35 | 59 | 45 | 45 |
| L/11 | 1 month | 45 | 40 | 74 | 50 | 50 |
| L/12 | 6 months | 45 | 39 | 72 | 45 | 46 |
| L/13 | 2 years | 47 | 39 | 65 | 49 | 48 |
| L/14 | 9 years | 50 | 25 | 67 | 35 | 35 |
| L/15 | 9 years | 49 | 27 | 56 | 36 | 34 |
| L/16 | 9 years | 67 | 40 | 74 | 48 | 46 |
| L/17 | 9 years | 55 | 31 | 67 | 38 | 35 |
| L/18 | 9 years | 63 | 36 | 71 | 46 | 42 |
| 10/1 | 1 week | 47 | 34 | 66 | 41 | 42 |
| 10/2 | 1 week | 45 | 33 | 57 | 40 | 40 |
| 10/3 | 1 week | 42 | 31 | 56 | 39 | 38 |
| 10/4 | 1 week | 43 | 31 | 59 | 38 | 37 |
| 10/5 | 1 week | 46 | 32 | 68 | 44 | 40 |
| 10/6 | 1 week | 50 | 36 | 70 | 44 | 40 |
| 10/7 | 1 week | 47 | 35 | 70 | 45 | 42 |
| 10/8 | 1 week | 45 | 29 | 66 | 38 | 37 |
| 10/9 | 1 week | 45 | 32 | 65 | 37 | 36 |
| 10/10 | 1 week | 39 | 23 | 58 | 31 | 28 |
| 10/11 | 6 months | 56 | 28 | 75 | 38 | 34 |
| 10/12 | 11 years | 38 | 24 | 41 | 28 | 25 |
| 10/13 | 9 years | 41 | 16 | 49 | 21 | 20 |
| 10/14 | 9 years | 38 | 20 | 49 | 25 | 23 |
| 10/15 | 9 years | 47 | 22 | 59 | 30 | 26 |
| 10/16 | 9 years | 42 | 19 | 49 | 28 | 24 |
| 10/17 | 9 years | 44 | 17 | 55 | 19 | 17 |
| CV/1 | 1 day | 45 | 39 | 58 | 47 | 45 |
| CV/2 | 1 day | 45 | 38 | 50 | 43 | 42 |
| 5/1 | 11 years | 42 | 31 | 42 | 34 | 31 |
| RS/1 | 11 years | 50 | 40 | 75 | 50 | 49 |

Age corresponds to approximate time from drying of the raw rubber.

Sample codes L/, 10/, CV/, 5/, and RS/ correspond to SMR L, SMR 10, SMR CV, SMR 5 and RSS 1 grades of natural rubber respectively.

Values of h derived using these two equations (Table 4) range from -2 to $+25$ Wallace plasticity units.

Correlation of Estimates with Measured Values of Storage Hardening

The amount of hardening which occurs during the standard PRI ageing, h , has been found to vary widely (Tables 2 and 4). This variation is not surprising in view of the variety of age and consequent variety in potential for storage hardening of the samples. The capacity of each sample for storage hardening is taken as $P_H - P_O$ and is denoted as ΔP . The values of ΔP for the samples studied ranged from 0 to 44 units (Tables 2 and 4). A plot of h against ΔP (Figure 1) shows the correlation between the estimate of the contribution of hardening to PRI and the measured potential of the rubber for natural hardening. Although the points from the anaerobic ageing experiments tend towards a line of lower gradient compared to the other results, there is reasonable agreement between the two experimental approaches. Taking all of the results together, the value of the linear coefficient which is derived will be influenced more by the greater number of data points from the indirect experimental approach. This weighting reflects the greater confidence in the reliability of results from the latter set of experiments. Linear regression analysis gives the best straight-line fit for the points corresponding to the equation:

$$h = 0.59 \Delta P - 1.1$$

with a correlation coefficient of 0.83. Alternatively, the best straight line passing through the origin for the same set of points gives the equation:

$$h = 0.54 \Delta P$$

with a correlation coefficient of 0.82. This degree of correlation is acceptable, considering the level of accuracy of the measurements. In the absence of a satisfactory explanation of the practical significance of an intercept, the latter relationship between h and ΔP seems to be more appropriate.

The importance of the hardening effect on PRI test results can be judged by considering an example. A typical SMR L tested by the producer could be expected to have a P_O of around 40 and ΔP of 25 units while its PRI could be 90%. According to the relationship derived from this work, the contribution of hardening would be about 0.54×25 or 13.5 Wallace plasticity units, which corresponds to 33% of P_O . Thus, the PRI results would be 33 units lower than the one quoted if the hardening effect was absent. A similar exercise for a typical SMR 10 sample with P_O of 45 and ΔP of 15 provides an estimate of eighteen percentage points as the influence of natural hardening on PRI results.

While the effects illustrated by the above examples are large, they do not invalidate the PRI test as a means of comparing raw rubbers of the same grade, as these would generally have similar potentials for storage hardening. The results do indicate however, that PRI test results may be misleading if they are used to compare the oxidisability of different grades of rubber. The test is particularly unsuitable for comparing the resistance to oxidation of stabilised grades with that of unstabilised grades of NR.

CONCLUSIONS

Results from two different sets of experiments have shown that storage hardening does have a significant influence on the change in plasticity which occurs during ageing for the standard PRI test. This influence is evident in all samples of raw natural rubber except those which have little or no potential for storage hardening, either because of viscosity stabilisation or through old age.

Both sets of experiments gave results which indicated an approximately linear correlation between the extent of hardening occurring during PRI ageing, h and ΔP . The overall relationship of $h = 0.54 \Delta P$ with a correlation coefficient of 0.82 is based on all of the results from both sets of experiments. The relationship between h and the measured value ΔP seems to be independent of the grade of NR and its age,

TABLE 4. CALCULATED VALUES OF ABSOLUTE CHANGES IN WALLACE PLASTICITY AND MEASURED VALUES OF ΔP FOR VARIOUS NATURAL RUBBER SAMPLES

| Sample No. | h(eq 7) | h (eq 8) | Mean h | ΔP |
|------------|---------|----------|--------|------------|
| L/1 | 10 | 18 | 14 | 29 |
| L/2 | 17 | 23 | 20 | 34 |
| L/3 | 14 | 19 | 16.5 | 32 |
| L/4 | 22 | 23 | 22.5 | 34 |
| L/5 | 17 | 18 | 17.5 | 27 |
| L/6 | 25 | 19 | 22 | 35 |
| L/7 | 13 | 15 | 14 | 21 |
| L/8 | 10 | 11 | 10.5 | 19 |
| L/9 | 14 | 14 | 14 | 25 |
| L/10 | 7 | 7 | 7 | 17 |
| L/11 | 19 | 19 | 19 | 29 |
| L/12 | 20 | 21 | 20.5 | 27 |
| L/13 | 9 | 8 | 8.5 | 18 |
| L/14 | 7 | 7 | 7 | 17 |
| L/15 | 0 | - 2 | - 1 | 7 |
| L/16 | 1 | - 1 | 0 | 7 |
| L/17 | 8 | 5 | 6.5 | 12 |
| L/18 | 2 | - 2 | 0 | 8 |
| 10/1 | 11 | 12 | 11.5 | 19 |
| 10/2 | 5 | 5 | 5 | 12 |
| 10/3 | 7 | 6 | 6.5 | 14 |
| 10/4 | 10 | 9 | 9.5 | 16 |
| 10/5 | 14 | 10 | 12 | 22 |
| 10/6 | 16 | 12 | 14 | 20 |
| 10/7 | 16 | 13 | 14.5 | 23 |
| 10/8 | 13 | 12 | 12.5 | 21 |
| 10/9 | 16 | 15 | 15.5 | 20 |
| 10/10 | 14 | 11 | 12.5 | 19 |
| 10/11 | 11 | 7 | 9 | 19 |
| 10/12 | 2 | - 1 | 0.5 | 3 |
| 10/13 | 4 | 3 | 3.5 | 8 |
| 10/14 | 8 | 6 | 7 | 11 |
| 10/15 | 8 | 4 | 6 | 12 |
| 10/16 | 2 | - 2 | 0 | 7 |
| 10/17 | 11 | 9 | 10 | 11 |
| CV/1 | 7 | 5 | 6 | 13 |
| CV/2 | 2 | 1 | 1.5 | 5 |
| 5/1 | 0 | - 3 | - 1.5 | 0 |
| RS/1 | 16 | 15 | 15.5 | 25 |

- Results from anaerobic ageing experiments
- Results from successive ageing and hardening experiments

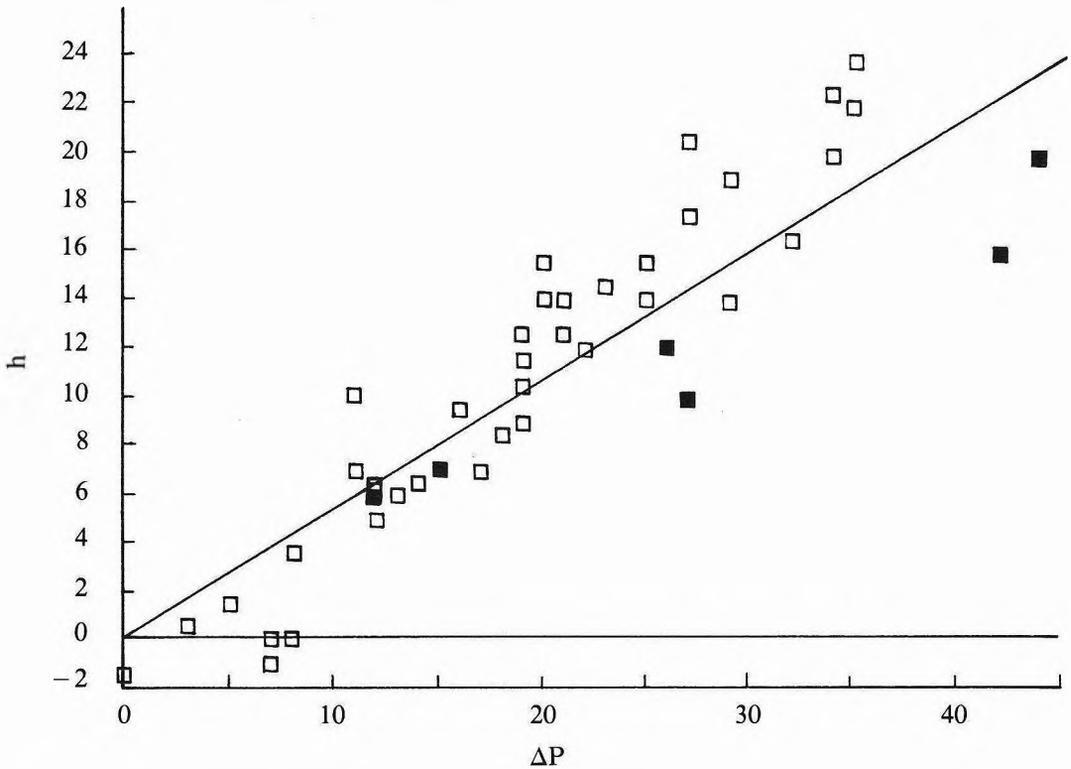


Figure 1. Correlation between values of h derived from two experiments and measured values of ΔP .

so this may be a useful empirical tool for estimating the contribution of hardening to PRI test results.

Freshly-produced CV grades of SMR are known to give PRI values comparable to those of unstabilised grades from the same latex. By definition, natural rubber graded as CV has very limited ability for storage hardening ($\Delta P < 7$). In the light of the findings presented here, it seems that by stabilising the viscosity of natural rubber with hydroxylamine, its susceptibility to thermal oxidative degradation is reduced. This effect is the subject of continuing studies in this laboratory.

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Lipids Associated with Rubber Particles and Their Possible Role in Mechanical Stability of Latex Concentrates

H. HASMA*

Lipids, which form one of the major membrane components surrounding the rubber particles (RP) in natural latex, could play a role in the mechanical stability of the latex on storage in ammonia. Results showed that the main lipid components which changed on storage in ammonia were the glycolipids and phospholipids which hydrolysed to free higher fatty acids (HFA). The amount of glycolipids and phospholipids in fresh RP of six Hevea brasiliensis clones did not vary much. Consequently, the amount of HFA generated in each clone was expected to be equal. The mechanical stability time (MST) of the six clonal latices however differed significantly, some giving MST well above 1000 s while some gave MST below 300 s even after three months' storage. This led to the conclusion that the formation of HFA is not the major factor contributing to the increase in MST of high ammoniated (HA) latex concentrates, contrary to what has been reported previously.

Mechanical stability time (MST) which assesses the resistance of natural rubber latex to destabilisation by mechanical forces, is an important property of latex concentrate. Freshly prepared HA latex concentrate normally has a MST of less than 100 s but this can increase to more than 1000 s after three months' storage. The amount of increase depends on the clonal origin of the latex¹. Clones of *H. brasiliensis* stabilised with high ammonia can be broadly divided into two groups: clones with low MST, which register a MST of less than 650 s after three months' storage and clones with high MST, which give higher MST values.

Various factors have been reported to affect the MST of latex concentrate; some are deleterious while some are beneficial. For example, magnesium is the major naturally occurring element associated with the destabilisation of natural rubber latex concentrate² while alkalis and sodium pentachlorophenate have been shown to increase the mechanical stability of the latex³. However, the much discussed substances among the group of compounds found to increase the MST of latex are the natural free

higher fatty acid (HFA) soap formed by hydrolysis of the phospholipids of the latex^{3,4}. Chen and Ng⁴ found a good correlation between the concentration of HFA and the increase in MST of some clones up to a period of three to six weeks after which the HFA concentration remained constant. They however could not ascertain the factors which affect the further rise in MST after the specified period.

Besides the HFA and phospholipids, there are other lipids associated with the membrane surrounding the rubber particle⁵ (RP) which might also have an influence on the MST. This paper aims to demonstrate the role of these lipids on the MST of latex concentrate, focusing on their composition in fresh RP, how it changes on storage in ammonia and their possible contribution to the rise in MST of latices with both high and low MST.

MATERIALS AND METHODS

Materials

Latex was obtained from mature unstimulated trees. The RP were isolated from fresh latex or

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HA latex concentrate by ultracentrifugation of the latex in a Beckman L8-70 ultracentrifuge at 19 500 r.p.m. using rotor 21 for about 1 h. The HA latex concentrates were prepared by centrifuging about 0.5% ammoniated field latex in a De Laval LRH 410-70A centrifugal latex separator. This gave latex concentrates of about 60% dry rubber content, which were further ammoniated to 0.7%.

Extraction, Fractionation and Quantitation of Lipids

Lipids were extracted from the RP by first redispersing the RP in a minimum amount of water and then adding the suspension dropwise to five volumes of a continuously stirred chloroform/methanol (2:1, v/v) mixture. The subsequent procedures for the isolation of lipids, their fractionation and quantitation were as reported⁶.

Determination of MST

The MST values of HA latex concentrates and RP redispersed in water ammoniated to 0.7% were determined at 55% total solids content at 35°C using a Klaxon instrument as specified by the International Standards Organisation⁷. The method of assessing the end point of the test was to observe the first signs of flocculation in a thin film of latex spread on the palm of the hand.

RESULTS AND DISCUSSION

MST of Some Clonal Latex Concentrates

Ultracentrifugation of freshly prepared HA latex concentrate at 19 500 r.p.m. for 1 h gave two fractions: an upper rubber phase and a lower aqueous serum phase with some sediments at the bottom of the centrifuge tube. On redispersing the RP in distilled water and ammoniating to 0.7% the resulting latex showed increasing MST with storage time (*Figure 1*). The RP of both clones with high MST (RRIM 701, RRIM 730 and PB 28/59) and clones with low MST (RRIM 600, RRIM 804 and PR 255) gave MST values of above 1000 s after sixty days of storage. This showed that the increase in the MST of redispersed RP could

be governed mainly by changes in the RP on storage in ammonia.

Although all the clonal RP redispersed in ammoniated water gave high MST on storage, the rate of rise in MST differed. The RP of the two clones with high MST, RRIM 730 and PB 28/59, gave the fastest rise in MST, reaching a value of 1000 s before thirty days of storage while the RP of the remaining clone with high MST, RRIM 701, and the RP of all the three clones with low MST gave a more gradual increase in MST to 1000 s after fifty to sixty days' storage. The fast rise in MST was not confined to the RP of clones with high MST. In this study, it was observed that the RP of a clone with low MST, RRIM 729, also gave a fast rise in MST of 1000 s after twenty days of storage. This difference suggested that the components in the membrane might have an influence on the rise in mechanical stability of the RP and they might differ with clones.

When the RP were dispersed in their own serum, as in the normal preparation of HA latex concentrate, only the RP of clones with high MST gave a MST of over 1000 s while the RP of clones with low MST gave a MST of less than 300 s even though the latex concentrate was stored for more than two months (*Figure 2*). The apparent inhibition of the rise in MST of RP of clones with low MST was not only observed when the RP were dispersed in their own serum but also when they were redispersed in the sera of clones with high MST (*Table 1*). On the contrary, the RP of clones with high MST consistently gave high MST values even when redispersed in the sera of clones with low MST (*Table 1*). The serum constituents thus seemed to preferentially inhibit the rise in MST of RP of clones with low MST but seemed to exhibit no significant effect on the rise in MST of RP of clones with high MST. The results indicate that there is an interaction between the RP of clones with low MST and serum (of both types) and this interaction does not occur with clones with high MST. This also means that there is a factor on the surface of RP from clones with low MST, which is absent on the surface of RP of clones with high MST. The latter difference may be reflected in their

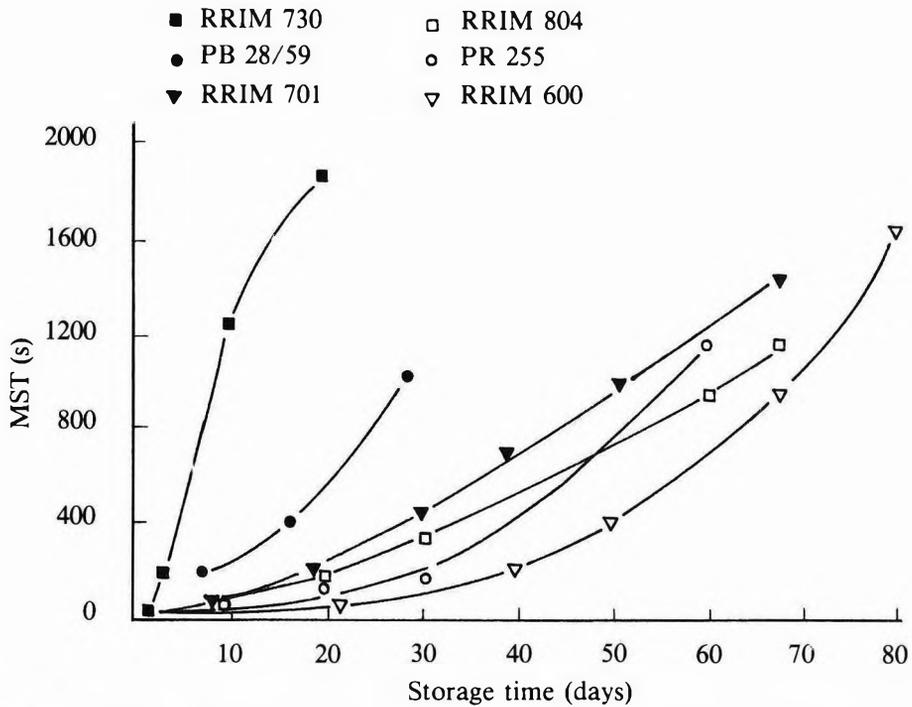


Figure 1. MST of 0.7% ammoniated redispersed RP from six *H. brasiliensis* clones.

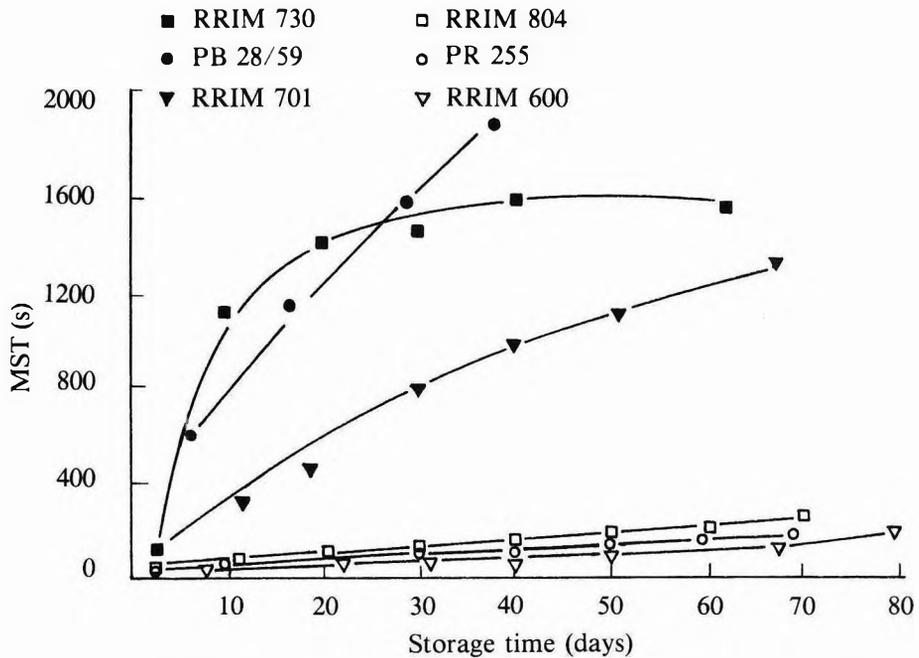


Figure 2. MST of HA latex concentrates from six *H. brasiliensis* clones.

TABLE 1. EFFECTS OF SERUM ON THE MST OF REDISPERSED RUBBER PARTICLES AFTER TWO MONTHS' STORAGE

| Serum | MST (s) | |
|-----------------------|-----------|-------------|
| | PR 255 RP | RRIM 730 RP |
| RRIM 701 ^a | 214 | - |
| RRIM 730 ^a | 150 | 1 200 |
| RRIM 804 ^b | - | 1 370 |
| PR 255 ^b | 125 | 1 055 |

^aClone with high MST^bClone with low MST

lipid composition though differences in the protein components of the membrane may be another possibility.

Lipid Composition of Fresh Rubber Particles

Lipids in fresh *H. brasiliensis* latex have been classified into neutral lipids, glycolipids and phospholipids⁶. The qualitative composition of the neutral lipids, glycolipids and phospholipids in the membrane surrounding fresh RP of the six clones studied here was similar to the lipid composition of fresh RRIM 501 latex⁶. The neutral lipids comprised triglycerides, diglycerides, free fatty acids, free and esterified sterols, free and esterified tocotrienols and fatty alcohols and their acetates (*Figure 3*). The glycolipids consisted mainly of free and esterified steryl glucosides and mono-galactosyl and digalactosyl diglycerides while the phospholipids consisted of phosphatidyl ethanolamine, phosphatidyl choline and phosphatidyl inositol. The amounts of glycolipids and phospholipids varied from 0.2% to 0.5% and 0.3% to 0.6%, respectively (*Table 2*). The neutral lipids showed a greater variation of 0.5% to 2.3%, with the two clones with high MST, RRIM 701 and PB 28/59, showing the highest neutral lipid content. This was however not a characteristic of clones with high MST as RRIM 730 had a lower level of neutral lipids.

The high neutral lipid content of the whole latex was found to be mainly due to the prominently higher level of triglycerides

compared to the other neutral lipid components (*Table 3*). The triglycerides of whole latex of RRIM 701 and RRIM 501 constituted about 1.5% - 1.7% of the rubber compared to the triglycerides of GT 1 and PR 107 which constituted only about 0.15% - 0.18%. This made the neutral lipid content of the former two clones much higher than that of the latter clones. A similar distribution of triglycerides was expected to occur in the neutral lipids of the RP since the latter made up about 70% to 80% of the total neutral lipids of the whole natural rubber latex. *Figure 3* shows the prominent distribution of triglycerides in the neutral lipid composition of the RP. Further analysis on the RP of RRIM 501 revealed that a high proportion, about 48%, of the neutral lipids consisted of triglycerides. The triglyceride content in the neutral lipids of the whole latex of RRIM 501 was 63%.

Lipid Composition of Rubber Particles Stored in Ammonia

The composition of lipids associated with the RP changed on storage in ammonia. The most prominent changes were the decreasing levels of glycolipids and phospholipids (*Figures 4* and *5*) and the increasing level of free HFA in the neutral lipid fraction (*Figure 3*).

The hydrolysis of glycolipids and phospholipids of RP with a high MST, RRIM 730 (*Figure 4*), could be approximately divided into three stages. In *Stage I*, 0 - 12 days' storage, the hydrolysis of the polar lipids was the fastest. During this time, about 68% glycolipids and 81% phospholipids hydrolysed. *Stage II*, of duration 12 - 40 days, has a slower rate of hydrolysis; a further 28% and 15% of the glycolipids and phospholipids, respectively, hydrolysed. In *Stage III*, 40 days onwards, very little hydrolysis of the polar lipids occurred. A similar pattern was observed with the hydrolysis of polar lipids of RP with low MST, RRIM 600 (*Figure 5*). This, in fact, formed a general pattern for the hydrolysis of glycolipids and phospholipids associated with RP of clones with both high and low MST, dispersed in HA serum or water. The three stages marking three different rates of hydrolysis of

A = Fresh rubber particles

B = Rubber particles stored in ammonia for one month

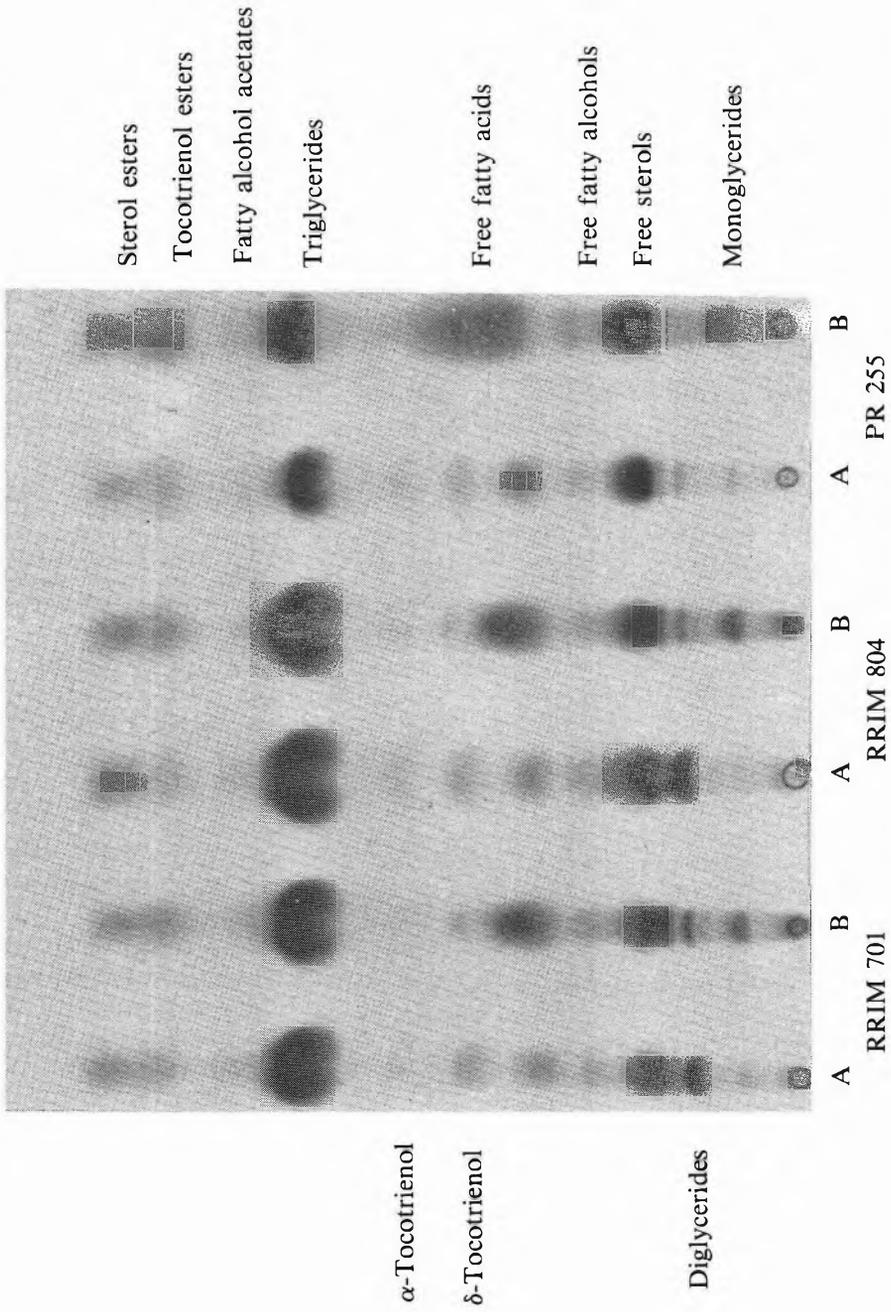


Figure 3. Thin layer chromatogram of neutral lipids associated with the rubber particles from various clonal lattices.

TABLE 2. COMPOSITION OF LIPIDS FROM FRESH RUBBER PARTICLES OF SIX *HEVEA* CLONES

| Clone | Composition (% dry weight of rubber) | | |
|----------|--------------------------------------|-------------|---------------|
| | Neutral lipids | Glycolipids | Phospholipids |
| RRIM 701 | 2.32 | 0.53 | 0.49 |
| RRIM 730 | 0.55 | 0.53 | 0.39 |
| PB 28/59 | 2.34 | 0.45 | 0.57 |
| RRIM 600 | 0.45 | 0.30 | 0.58 |
| PR 255 | 0.64 | 0.28 | 0.37 |
| RRIM 804 | 0.92 | 0.41 | 0.54 |

TABLE 3. COMPOSITION OF NEUTRAL LIPIDS FROM FRESH LATICES OF FOUR *H. BRASILIENSIS* CLONES

| Clone | Composition (% dry weight of rubber) | | | |
|----------|--------------------------------------|--------|---------------|--------------------------|
| | Total neutral lipids | Esters | Triglycerides | Remaining neutral lipids |
| RRIM 701 | 2.77 | 0.53 | 1.55 | 0.69 |
| RRIM 501 | 2.66 | 0.43 | 1.70 | 0.53 |
| GT 1 | 1.48 | 0.77 | 0.15 | 0.56 |
| PR 107 | 1.13 | 0.52 | 0.18 | 0.43 |

the polar lipids corresponded well with the three rates of production of HFA determined by Chen and Ng⁴.

Analysis of the acyl composition of the free HFA fraction in the neutral lipids of RRIM 701 HA latex concentrate showed a high concentration of stearic, oleic and linoleic acids with smaller amounts of palmitic, palmitoleic, linolenic and furanoid fatty acids (*Table 4*). This corresponded to the acyl composition of sterol esters, tocotrienol esters, glycolipids and phospholipids⁶. As the content of the first two acyl lipids did not reduce (*Figure 3*), the HFA must have been derived mainly from the hydrolysis of glycolipids and phospholipids.

An interesting observation was the low concentration of furanoid fatty acid in the HFA fraction of RRIM 701 latex which was

characterised by a high amount of furanoid fatty acid in its triglyceride fraction. This implied that a large proportion of this triglyceride remained unhydrolysed, possibly as a result of the location of the triglyceride deep in the membrane away from the aqueous interface making it inaccessible to the hydrolysing agents. This is not unlikely in view of the hydrophobic character of this triglyceride. The furanoid fatty acid found in the HFA fraction was thus derived mainly from the hydrolysis of glycolipids, the only other acyl lipids containing this acid⁶. The fact that the furanoid fatty acid appeared only after fourteen days of storage showed that the acylglycolipids containing this acid were less readily hydrolysed than the other acyl polar lipids except those containing palmitoleic acid, which also appeared after the same period of storage.

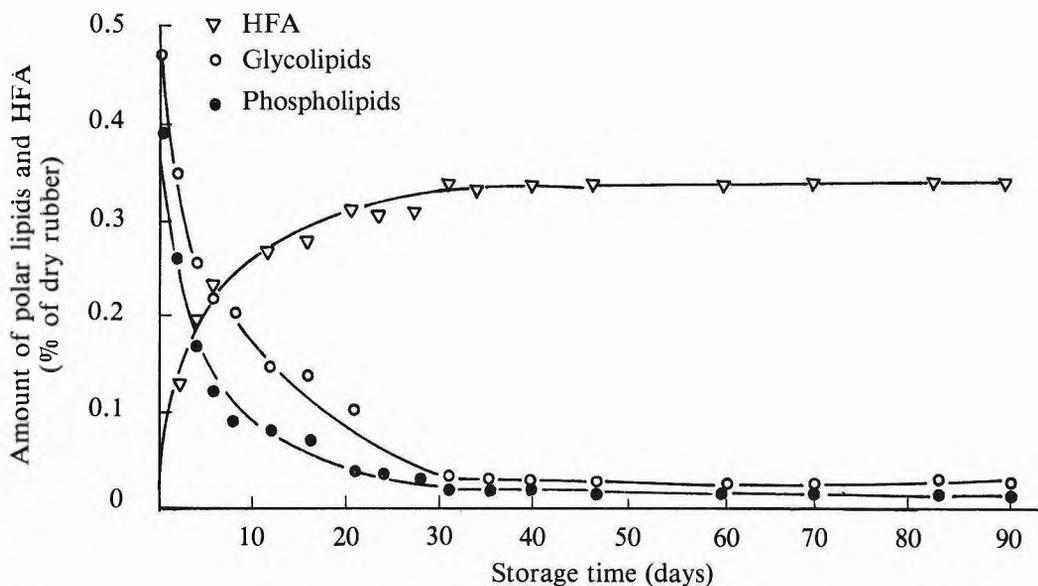


Figure 4. Effect of storage time on the amount of glycolipids, phospholipids and HFA associated with 0.7% ammoniated rubber particles of a clone with high MST, RRIM 730.

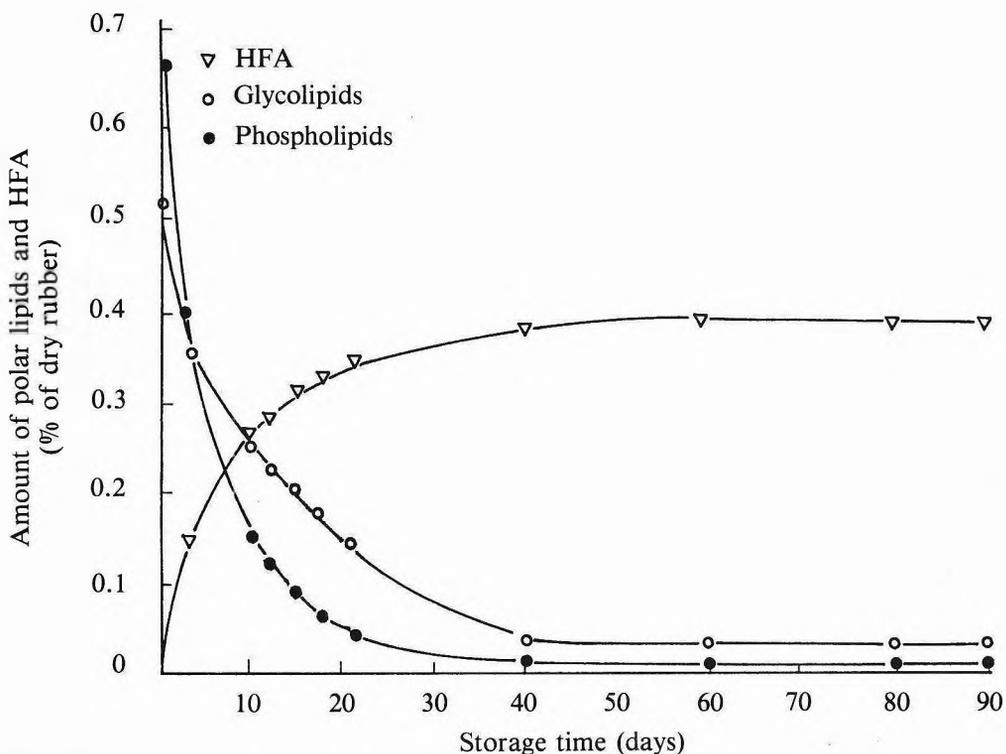


Figure 5. Effect of storage time on the amount of glycolipids, phospholipids and HFA associated with 0.7% ammoniated rubber particles of a clone with low MST, RRIM 600.

TABLE 4. COMPOSITION OF FREE FATTY ACIDS OF HA LATEX CONCENTRATE OF RRIM 701 AFTER DIFFERENT STORAGE TIMES IN AMMONIA

| Days of storage | Relative fatty acid composition (%) | | | | | | |
|-----------------|-------------------------------------|------|------|------|------|------|----------------|
| | 16:0 | 16:1 | 18:0 | 18:1 | 18:2 | 18:3 | F ₂ |
| 0 | 13.2 | - | 25.2 | 29.1 | 22.8 | 9.7 | - |
| 9 | 13.8 | - | 15.4 | 27.6 | 37.6 | 5.5 | - |
| 14 | 6.4 | 3.3 | 18.3 | 23.3 | 29.4 | 5.3 | 14.1 |
| 21 | 7.3 | 2.4 | 20.1 | 21.3 | 31.0 | 5.2 | 12.6 |
| 28 | 3.4 | 2.2 | 10.4 | 23.5 | 31.8 | 9.1 | 19.6 |

F₂ = Furanoid fatty acid

Besides the free HFA content, the other lipid component which appeared only after storage in ammonia was the component more polar than the diglyceride fraction (*Figure 3*). Based on the *R_f* values obtained on thin-layer chromatograms⁸ and the infra-red spectrum of the isolated fraction, the component was deduced to be monoglycerides. The presence of monoglycerides could result from incomplete hydrolysis of glycolipids and phospholipids to free HFA. The production of monoglycerides was confirmed by separate hydrolysis of glycolipids and phospholipids of fresh natural rubber latex in 0.7% ammonia for about a week. This gave monoglycerides as well as HFA and diglycerides at equivalent *R_f* values to those of the neutral lipid components from the ammoniated RP.

Role of Lipids in Mechanical Stability of Latex Concentrate

The membrane surrounding the RP stored in ammonia can be visualised to contain extra negative charge imparted by the hydrolysis products of glycolipids and phospholipids, the free HFA, located at the aqueous interface. The additional charge could render the RP more stable to externally applied mechanical forces. However, from the results presented in this paper, the HFA present in the membrane could be argued to be not the major contributing factor to the rise in MST as widely thought. This could be explained through the rates of production of HFA, calculated from the

hydrolysis of glycolipids and phospholipids as depicted in *Figures 4* and *5* which did not correspond well with the rise in MST of the HA redispersed RP except that of RP of RRIM 730 (*Figure 1*). At the initial period of fast production of HFA, the RP of RRIM 730 gave a fast rise in MST of over 1000 s. The MST of PB 28/59 increased sharply during the second stage of slow production of HFA while the remaining clonal RP showed a fast rise in MST after forty days when the HFA production would presumably have ceased. In fact, after forty days of storage when the latices were expected to contain equal HFA levels as indeed shown by Chen and Ng⁴, the MST values differed significantly. This means that there is no correlation between the rise in MST and increase in HFA.

There are reports that the rise in MST caused by HFA depends on their chain lengths⁹. The present work however does not show the dependence of rise in MST on the fatty acid chain lengths of C₁₄ to C₂₀. The fatty acid composition in the HFA fraction derived from the hydrolysis of phospholipids and glycolipids of four clonal latices (*Table 5*) was about the same, yet the MST of RRIM 701 and GT 1 differed from those of PR 107 and RRIM 600. RRIM 701 and GT 1 are clones with high MST while PR 107 and RRIM 600 are clones with low MST. Besides this, the addition of HFA, normally in the form of ammonium laurate, does not guarantee an equal increase in the MST of all clonal latex concentrates; the MST of some clones remains unaffected¹.

TABLE 5. FREE FATTY ACID COMPOSITION OF FOUR CLONAL LATICES

| Clone | Relative fatty acid composition (%) | | | | | | | | |
|----------|-------------------------------------|------|------|------|------|------|------|------|----------------|
| | 14:0 | 16:0 | 16:1 | 18:0 | 18:1 | 18:2 | 18:3 | 20:0 | F ₂ |
| RRIM 701 | 0.5 | 9.4 | 2.5 | 16.1 | 15.8 | 29.2 | 2.9 | 0.7 | 23.0 |
| GT 1 | 0.5 | 8.6 | 1.6 | 17.7 | 23.6 | 42.5 | 2.2 | - | 3.3 |
| RRIM 600 | 0.4 | 9.0 | 1.4 | 18.0 | 17.9 | 49.7 | 3.2 | - | 0.4 |
| PR 107 | 0.6 | 8.1 | 1.1 | 17.1 | 16.4 | 48.3 | 4.9 | - | 3.5 |

F₂ = Furanoid fatty acid

Free fatty acid content alone cannot be considered as the main factor controlling the rise in MST of NR latex on ammoniation. This can be further deduced from the effects of serum on the MST of HA latex concentrates. As stated earlier, serum did not inhibit the hydrolysis of glycolipids and phospholipids of RP with both high and low MST. Thus, RP of the two groups of clones dispersed in serum fraction would contain comparable amounts of HFA. The fact that the MST of the two groups of RP still differed when the latter were dispersed in serum (*Figure 2*) clearly shows that other factors, and not HFA alone, inherent in the RP are more responsible for the mechanical stability of natural RP.

These studies were carried out using three samples of each clone. Since the composition of NR latex is known to vary greatly with clones it will be necessary to study more clones to confirm the observations described in this paper.

CONCLUSION

This rise in MST of HA natural latex concentrates was controlled mainly by changes in the membrane surrounding the RP. These changes were affected by the serum constituents which were found to inhibit the rise in MST of clonal latex with low MST, but not the rise in MST of clonal latex with high MST. This pointed to possible differences in the composition of the membrane surrounding the two groups of RP. The lipid membrane components do not show the expected

differences. Although on storage in ammonia the glycolipids and phospholipids hydrolysed to HFA, the increasing presence of which had been broadly linked to the rise in MST, the formation of these fatty acids does not explain the different rates of rise in MST of different clones. Other substances present in the membrane must be involved in controlling the rise in MST of natural latex concentrates.

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Latex Preservation in Polybags and Latex Concentrate Production

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Rubber collected in polybags is of poorer quality compared to premium rubbers obtained from similar latex collected by conventional methods. A study on keeping the latex fluid and well-preserved in the polybags for two to four weeks in the field was carried out. This paper describes some improvements to the existing process of collecting latex in polybags. Latices in polybags were successfully kept fluid for up to four weeks by preservative/biocide systems based on TMTD/ZnO, PRBL and PROXEL GXL. Concentrates produced from such latices were also found to store normally and had no adverse technological properties.

Collection of rubber in polybags, a method in which special polybags are left on the trees for several tappings, was first developed and reported by the Rubber Research Institute of Malaysia (RRIM) in the late sixties. With this method, tapping is carried out in the normal way, but the latex is collected in a polybag fixed to the tree. The process is repeated for several tappings over a period of two to four weeks. The bag containing the coagulated rubber is then collected and brought to the factory for it to be processed into bulk rubber.

There are advantages and disadvantages of collecting rubber in polybags. It is known to result in the production of lower quality rubber compared to the premium rubbers obtained from similar latex collected by conventional methods. The loss factor is therefore a major consideration.

A preliminary investigation has been carried out on the feasibility of preserving latex fluid in polybags and producing it into latex concentrate. This paper reports on the methods and biocide systems found effective for the process and the properties of the subsequent concentrates.

Latex collection in polybags minimises tapping and collection costs which form a major portion of the overall production

expenditure. It has also been suggested as a method to extend latex flow-time and for high-yielding trees where the traditional tapping cups have been found to be inadequate. In recent years, the shortage of plantation workers has resulted in some producers resorting to this method of latex collection.

MATERIALS AND METHODS

Latex

Polybag latex trials were carried out at the RRIM Experiment Station, Sungei Buloh, Selangor, for fifteen to thirty days.

The polybag collection set designed by the Tapping Section of the RRIM consists mainly of the polybag, collection bowl and supporting wire.

Chemicals

The chemical biocide systems used were those based on tetramethyl thiuram disulphide/zinc oxide (TMTD/ZnO, 1:1)^{1,2,3} triazine/benzotriazole derivative (PRBL)⁴ and 1,2-benzisothiazolin-3-one (PROXEL GXL)⁵.

Each system was prepared as a dilute dispersion or solution for addition to the latex. In combination with ammonia, they acted as secondary preservatives.

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TABLE 1. PREPARATION OF COMPOSITE PRESERVATION SYSTEMS

| Type | Preservation system | | System A/150 g latex | | System B/150 g latex | |
|--------------------------------|---------------------|--|----------------------|------------|----------------------|------------|
| | Chemical | | % | Weight (g) | % | Weight (g) |
| NH ₃ /TZ | Ammonia | | 0.300 | 0.4500 | 0.500 | 0.7500 |
| | TMTD | | 0.025 | 0.0375 | 0.025 | 0.0375 |
| | ZnO | | 0.025 | 0.0375 | 0.025 | 0.0375 |
| | Water | | 6.317 | 9.4750 | 6.117 | 9.1750 |
| NH ₃ /PRBL | Ammonia | | 0.300 | 0.450 | 0.500 | 0.750 |
| | PRBL | | 0.100 | 0.150 | 0.100 | 0.150 |
| | Water | | 6.267 | 9.400 | 6.067 | 9.100 |
| NH ₃ /PROXEL GXL | Ammonia | | 0.300 | 0.450 | 0.500 | 0.750 |
| | PROXEL | | | | | |
| | GXL | | 0.100 | 0.150 | 0.100 | 0.150 |
| | Water | | 6.267 | 9.400 | 6.067 | 9.100 |

Dosages of Preservatives

The optimum dosages of preservatives were screened and established after a series of initial trials in the field to ensure good latex preservation.

To determine the amount of preservatives to be added to the latex, the average yield of the tree had to be assessed. The yield of a tree varied between 100 g and 300 g during the year under normal tapping conditions and a yield of 150 g of latex per tree per tapping was taken as the average.

Details of the chemical preparation are shown in *Table 1*. In all cases, about 10 ml of prepared solution containing the appropriate amount of preservatives was added. Two modes of addition were used:

- *System A* — preservatives added at every tapping
- *System B* — preservative added once every three tappings

To treat 1000 trees, 10 litres of bulk solution were required for *System A* and 30 litres for *System B*. As an example, the bulk solution for the NH₃/TZ system was prepared as shown in *Table 2*.

Since TMTD and ZnO are powders insoluble in water, care was taken when preparing the bulk solution. Water was slowly added to TMTD/ZnO and mixed to form a paste. When a uniform light dispersion had been achieved, the required amount of ammonia solution was added.

Trial 1

A trial was carried out to assess the effectiveness of preservation of latex in polybags over a period of thirty days. The polybag set was fixed to every tree in place of the normal latex cup one day before tapping. On the first day of tapping, 10 ml or 30 ml of bulk (preservative) solution was added to the polybag 2 h or 3 h after tapping was completed.

TABLE 2. PREPARATION OF BULK SOLUTION OF NH₃/TMTD/ZnO PRESERVATION SYSTEM

| Chemical | System A | | System B | |
|----------|----------|------------|----------|------------|
| | % | Weight (g) | % | Weight (g) |
| Ammonia | 0.300 | 450 | 0.500 | 2 250 |
| TMTD | 0.025 | 37.5 | 0.025 | 112.5 |
| ZnO | 0.025 | 37.5 | 0.025 | 112.5 |
| Water | 6.317 | 9 475 | 6.117 | 27 525 |

TABLE 3. CHEMICAL TREATMENT OF FIELD LATEX

| Reference | Treatment of field latex | Duration on trees (days) |
|----------------|---|--------------------------|
| A | Control (0.7% NH ₃) | — |
| B | 0.5% NH ₃ + 0.05% TZ | 17 |
| C ₁ | 0.5% NH ₃ to 0.05% TZ | 30 |
| C ₂ | 0.5% NH ₃ + 0.10% PRBL | 30 |
| C ₃ | 0.5% NH ₃ + 0.10% PROXEL GXL | 30 |
| D ₁ | 0.5% NH ₃ + 0.05% TZ | 15 |
| D ₂ | 0.5% NH ₃ + 0.10% PRBL | 15 |
| D ₃ | 0.5% NH ₃ + 0.10% PROXEL GXL | 15 |

The preservatives were poured by means of a dispenser into the opening of the polybag by lifting the bowl of the polybag set. The latex was then mixed thoroughly with the preservatives by shaking the polybag. In *System A*, 10 ml of the preservative was added to the polybag on every tapping day, whereas in *System B*, the next addition of preservative was only done on the fourth tapping day. Latex was thus accumulated in the polybag until the quantity was sufficient for collection, normally between fifteen and thirty days.

Trial 2

A second trial on polybag latex preservation was carried out using the preservation systems shown in *Table 3*. The duration of the trial was fifteen to thirty days. Addition of preservative was as in *System B*, *i.e.* once every three tappings with the trees tapped once every three days.

Preparation of Latex Concentrates

After collection, the latex was centrifuged using a commercial Alfa-Laval LRH 410 model centrifuge machine. No over-night maturation was required since the latex had already matured in the polybags.

For bowl or separating efficiency testing, latex in the polybag treated with TMTD/ZnO was compared with HA and LA/TZ controls. Bowl or separating efficiency was calculated using the formula:

$$E = \frac{C(F - S)}{F(C - S)} \times 100$$

where E is the bowl efficiency; C , S and F are the dry rubber content (d.r.c.) values of the concentrate, skim and field latices, respectively.

Concentrates from field latices collected in polybags presented in *Table 3* were subsequently treated as shown in *Table 4*.

TABLE 4. TREATMENT OF LATEX CONCENTRATES

| Reference ^a | Treatment of concentrate |
|------------------------|--|
| A | 0.7% NH ₃ + 0.02% Ammonium laurate |
| B | 0.2% NH ₃ + 0.025% TZ + 0.05% Ammonium laurate |
| C ₁ | 0.2% NH ₃ + 0.025% TZ + 0.05% Ammonium laurate |
| C ₂ | 0.2% NH ₃ + 0.05% PRBL + 0.05% Ammonium laurate |
| C ₃ | 0.2% NH ₃ + 0.05% PROXEL GXL + 0.05% Ammonium laurate |
| D ₁ | 0.2% NH ₃ + 0.025% TZ + 0.05% Ammonium laurate |
| D ₂ | 0.2% NH ₃ + 0.05% PRBL + 0.05% Ammonium laurate |
| D ₃ | 0.2% NH ₃ + 0.05% PROXEL GXL + 0.05% Ammonium laurate |

^aThe formulations are given in *Table 3*.

Technological Evaluations

The latex concentrates were evaluated in terms of latex properties, chemical stability, film properties, latex processibility and vulcanisate properties.

For the control, a high-ammonia latex concentrate prepared from one-day-old field latex from the same source was used.

RESULTS

Trial 1

It is not possible to preserve latex on the tree effectively for a long period of time using ammonia alone, without a secondary preservative. Without secondary preservatives such as TMTD/ZnO, PRBL or PROXEL GXL, the ammonia level had to be more than 0.2% (w/w). Trials were initially carried out in the field to determine the optimum concentrations of ammonia and secondary preservatives necessary to stabilise latex collected in polybags effectively on the tree for at least one month. The optimum levels of preservatives to be added to the polybag at every tapping in order to keep the latex in the polybags stable are shown in *Table 5*.

TABLE 5. PRESERVATION SYSTEMS FOR LATEX COLLECTED IN POLYBAGS

| Preservation system | NH ₃ (%) | Secondary preservative |
|-----------------------------|---------------------|------------------------|
| NH ₃ /TZ | 0.3 | 0.05% TMTD/ZnO |
| NH ₃ /PRBL | 0.3 | 0.10% PRBL |
| NH ₃ /PROXEL GXL | 0.3 | 0.10% PROXEL GXL |

Initially, preservatives were added to the polybag during every tapping. Since addition of preservatives involves more labour and is time consuming, it is an advantage to reduce the frequency of addition. Ideally addition of preservative is once a month on the first day of tapping, but this is not possible due to the volatile nature of ammonia.

After a series of trials, it was found that preservatives could be added effectively once every ten days when the ammonia concentration was increased to 0.5% (w/w). Depending on the frequency of tapping, *i.e.* alternate-day, third-day or fourth-day tapping, the preservatives could be applied as shown in *Table 6* to maintain the stability of latex in the polybag for one month.

Trial 2

Field latex accumulated in polybags was treated with chemical preservatives once in about ten days (three tappings on d/3 tapping frequency) with optimum dosage levels. Collection of the preserved latex in polybags was done after fifteen days and thirty days where samples were taken and tested for bacterial counts and volatile fatty acid production. It was observed that 0.5% NH₃ and 0.5% TMTD/ZnO gave better preservation when compared to PRBL or PROXEL GXL systems. Preservation with 0.5% NH₃ alone failed to stabilise the latex in the polybag due to the escape of ammonia causing reduction in its concentration in the polybag and allowing ammonia-resistant bacteria to proliferate. On the other hand, the incorporation of secondary preservatives kept the volatile fatty acid (VFA)

TABLE 6. PRESERVATION SYSTEMS FOR LATEX IN POLYBAGS AT D/2, D/3 AND D/4 TAPPING FREQUENCIES

| Preservation system | NH ₃ (%) | Secondary preservative | No. of tappings/addition | | |
|-----------------------------|---------------------|------------------------|--------------------------|-----|-----|
| | | | d/2 | d/3 | d/4 |
| NH ₃ /TZ | 0.5 | 0.05% TMTD/ZnO | 4 | 3 | 2 |
| NH ₃ /PRBL | 0.5 | 0.10% PRBL | 4 | 3 | 2 |
| NH ₃ /PROXEL GXL | 0.5 | 0.10% PROXEL GXL | 4 | 3 | 2 |

number at not more than 0.08 and their bacterial populations remained at about 10^5 bacteria per millilitre latex (Table 7). Although the bacterial populations that survived were mainly acid-producing bacteria, they were biochemically inactive. This was indicated by the arrest of VFA build-up in the preserved latex.

Latex Properties

The latex concentrates were prepared using the treatments shown in Table 4. The ammonia

level was adjusted to 0.2% and the concentrates were further treated with 0.05% ammonium laurate to boost the mechanical stability time (MST). A sample of HA concentrate was prepared from the same source of field latex and used as the control. The concentrate samples were tested for their properties after up to six months' storage (Table 8). It was shown that latex collected in polybags gave well-preserved concentrates. Properties such as potassium hydroxide (KOH) number, MST, colour of latex film and alkalinity appeared to be satisfactory.

TABLE 7. BACTERIAL COUNTS AND VOLATILE FATTY ACID NUMBERS OF LATEX AFTER COLLECTION IN POLYBAGS

| Reference ^a | Duration on trees (days) | Residual NH ₃ (%) | pH | VFA No. | Bacterial count (log/ml) |
|-----------------------------|--------------------------|------------------------------|------|---------|--------------------------|
| A | — | — | — | — | — |
| B | 17 | 0.23 | 9.50 | 0.05 | 4 |
| C ₁ | 30 | 0.26 | 9.60 | 0.07 | 4 |
| C ₂ | 30 | 0.24 | 9.60 | 0.08 | 4 |
| C ₃ | 30 | 0.25 | 9.60 | 0.08 | 5 |
| D ₁ | 15 | 0.27 | 9.65 | 0.07 | 4 |
| D ₂ ^b | 15 | 0.20 | 8.55 | 0.20 | 8 |
| D ₃ | 15 | 0.26 | 9.60 | 0.08 | 5 |

^aThe formulations are given in Table 3.

^bRain spoilage, deleted from further testing.

TABLE 8. LATEX CONCENTRATE PROPERTIES AFTER SIX MONTHS' STORAGE

| Reference ^a | D.r.c. (%) | TSC (%) | NH ₃ (%) | VFA No. | MST (s) | pH | KOH No. | Latex colour | Film colour |
|------------------------|------------|---------|---------------------|---------|---------|-------|---------|--------------|-------------|
| A | 63.70 | 65.06 | 0.74 | 0.01 | 1 475 | 10.55 | 0.57 | White | Normal |
| B | 62.70 | 64.20 | 0.23 | 0.03 | 1 902 | 9.70 | 0.69 | White | Normal |
| C ₁ | 62.94 | 64.24 | 0.27 | 0.02 | 1 610 | 9.92 | 0.53 | White | Normal |
| C ₂ | 62.53 | 63.81 | 0.25 | 0.03 | >2 400 | 9.87 | 0.60 | White | Normal |
| C ₃ | 62.53 | 63.82 | 0.27 | 0.03 | >2 400 | 9.90 | 0.63 | White | Normal |
| D ₁ | 63.38 | 64.61 | 0.23 | 0.02 | >2 400 | 9.80 | 0.55 | White | Normal |
| D ₃ | 63.64 | 64.87 | 0.23 | 0.04 | >2 400 | 9.80 | 0.61 | White | Normal |

^aThe formulations are given in Table 3.

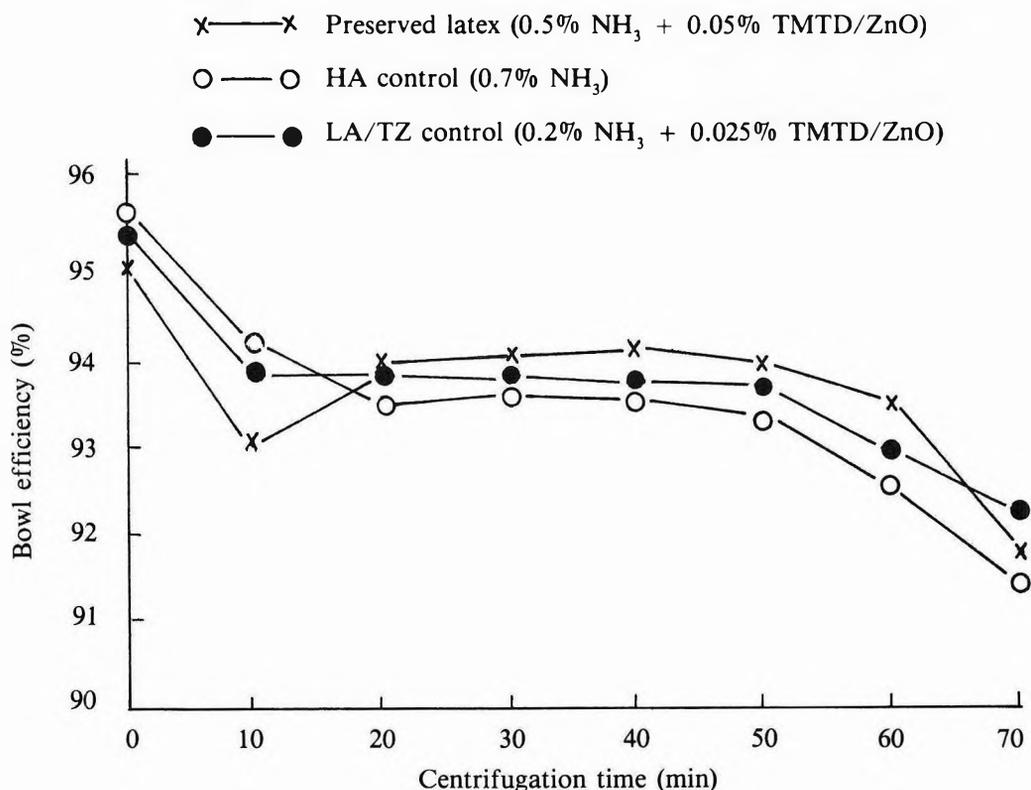


Figure 1. Bowl efficiency of preserved latex in polybags.

Bowl Efficiency

The bowl efficiency of preserved latex in polybags was monitored and found to be comparable to those of HA and LA/TZ controls (Figure 1). Visual inspection of the bowls after running showed no undue accumulation of sludge or other residual materials on the plates.

Chemical Stability

The zinc stability time (ZST) and zinc oxide viscosity (ZOV) values of the various concentrates are given in Table 9. The ZST and ZOV of low ammonia concentrates (B, C₁, C₂, C₃, D₁, D₃) were similar. The fifteen-day concentrates *i.e.* D₁ and D₃ appeared to show higher chemical stability than the thirty-day concentrates (C₁ and C₃) in the polybags.

TABLE 9. CHEMICAL STABILITY OF LATEX CONCENTRATES IN POLYBAGS

| Reference ^a | ZST (s) | ZOV (cps) | |
|------------------------|---------|-----------|---------|
| | | 5 min | 60 min |
| A | 227 | 766 | 3 800 |
| B | 455 | 117 | 381 |
| C ₁ | 535 | 142 | 748 |
| C ₂ | 573 | 211 | Gelling |
| C ₃ | 710 | 75 | 1 880 |
| D ₁ | 710 | 75 | 205 |
| D ₃ | 650 | 87 | 250 |

^aThe formulations are given in Table 3.

Film Properties

Cast films from the latex concentrates in polybags were examined to find out whether the

TABLE 10. FILM PROPERTIES OF LATEX CONCENTRATES IN POLYBAGS

| Reference ^a | Lovibond units | Zinc (p.p.m.) | Mg (p.p.m.) | Fe (p.p.m.) | Mn (p.p.m.) | Cu (p.p.m.) | Ash (%) | P (%) | N (%) | AE (%) | K (%) |
|------------------------|----------------|---------------|-------------|-------------|-------------|-------------|---------|-------|-------|--------|-------|
| A | 3.5 | 14 | 5 | 10 | <1 | 1 | 0.39 | 0.05 | 0.28 | 2.56 | 0.16 |
| B | 5.0 | 315 | 6 | 6 | <1 | 2 | 0.50 | 0.05 | 0.34 | 2.74 | 0.18 |
| C ₁ | 5.0 | 590 | 11 | 7 | <1 | 2 | 0.42 | 0.05 | 0.29 | 2.55 | 0.14 |
| C ₂ | 6.0 | 30 | 11 | 9 | <1 | <1 | 0.37 | 0.05 | 0.30 | 2.79 | 0.16 |
| C ₃ | 5.0 | 16 | 7 | 12 | <1 | <1 | 0.40 | 0.05 | 0.29 | 2.59 | 0.15 |
| D ₁ | 5.0 | 314 | 30 | 7 | <1 | 2 | 0.42 | 0.06 | 0.30 | 2.56 | 0.17 |
| D ₃ | 5.0 | 11 | 6 | 7 | <1 | <1 | 0.42 | 0.06 | 0.30 | 2.56 | 0.17 |

P = Phosphorus ; AE = Acetone extract; Zn = Zinc

N = Nitrogen ; K = Potassium

Mg = Magnesium ; Fe = Iron

^aThe formulations are given in Table 3.

prolonged storage of the field latex had an adverse effect on the raw rubber properties. *Samples B, C₁ and D₁* had higher zinc content (because of the zinc oxide component); *Sample C₁* appeared to have a higher zinc concentration than *Sample B* and *D₁* (*Table 10*).

The concentrates in polybags gave slightly darker films. Other properties such as nitrogen, phosphorous, potassium, magnesium contents and acetone extract values appeared to be normal.

Latex Compound Stability

Latex concentrates are invariably used in a variety of compounding applications. An important general requirement is that the latex does not behave adversely, for example, showing high zinc oxide sensitivity (leading to thickening).

To assess compound stability, the viscosity stabilities of zinc diethyldithiocarbamate (ZDC) and zinc dibutyldithiocarbamate (ZBUD) accelerated compounds, based on five different compositions, were examined (*Tables 11-14*).

The ZDC stability of latex concentrate in polybags (as in other LA concentrates) was generally poorer than that of the HA control, especially at low KOH concentrations. This is expected as low-ammonia concentrates are generally more prone to thickening than HA latex. Of interest is the comparison of various low-ammonia concentrates. The fifteen-day concentrates were marginally more stable than the thirty-day concentrates. Stability systems containing ZBUD showed a higher sensitivity to thickening. A combination of stabilisers was required to stabilise the latex compound.

Vulcanisate Properties

A S/ZDC/ZnO (1:1:1) formulation was used. The latex compounds, stabilised with 0.5% KOH and 0.15% potassium caseinate, were allowed to mature for four days at 28°C - 30°C. Dipped films were prepared using a coagulant of 20% calcium nitrate in industrial methylated spirit (IMS). The wet gels were then leached for 15 min at 50°C and vulcanised for 15 min at 100°C. The vulcanisate properties appeared to be satisfactory. The data in *Table 15* indicate that vulcanisation behaviour was not affected.

TABLE 11. FORMULATION FOR ZDC COMPOUND STABILITY

| Item | Dry weights of Formulations 1-5 | | | | |
|-------------------------|---------------------------------|-----|-----|-----|------|
| | 1 | 2 | 3 | 4 | 5 |
| Latex | 100 | 100 | 100 | 100 | 100 |
| 10% KOH | — | 0.3 | 0.5 | 0.5 | 0.5 |
| 10% Potassium laurate | — | — | — | 0.5 | — |
| 10% Potassium caseinate | — | — | — | — | 0.15 |
| 50% Sulphur | 1 | 1 | 1 | 1 | 1 |
| 50% ZDC | 1 | 1 | 1 | 1 | 1 |
| 50% Zinc oxide | 1 | 1 | 1 | 1 | 1 |
| Water | (to 55% TSC) | | | | |

TABLE 12. ZDC COMPOUND VISCOSITY

| Sample | Formulation ^a | | | | |
|----------------|--------------------------|-------|-----|----|----|
| | 1 | 2 | 3 | 4 | 5 |
| A | | | | | |
| Initial | 44 | 30 | 28 | 30 | 31 |
| 1 day | 44 | 30 | 30 | 32 | 32 |
| 3 days | 46 | 29 | 28 | 32 | 31 |
| 6 days | 46 | 30 | 29 | 32 | 32 |
| B | | | | | |
| Initial | 44 | 46 | 46 | 44 | 49 |
| 1 day | 47 | 45 | 46 | 42 | 50 |
| 3 days | 240 | 143 | 68 | 57 | 58 |
| 6 days | 3 100 | 716 | 137 | 57 | 58 |
| C ₁ | | | | | |
| Initial | 31 | 41 | 37 | 40 | 44 |
| 1 day | 32 | 41 | 39 | 39 | 42 |
| 3 days | 338 | 194 | 69 | 56 | 48 |
| 6 days | 8 350 | 2 140 | 201 | 92 | 57 |
| C ₂ | | | | | |
| Initial | 37 | 38 | 38 | 40 | 42 |
| 1 day | 38 | 39 | 38 | 39 | 40 |
| 3 days | 312 | 64 | 38 | 39 | 41 |
| 6 days | Gelled | 840 | 59 | 46 | 43 |
| C ₃ | | | | | |
| Initial | 36 | 36 | 35 | 38 | 37 |
| 1 day | 35 | 34 | 32 | 33 | 36 |
| 3 days | 141 | 64 | 37 | 36 | 38 |
| 6 days | Gelled | 584 | 54 | 42 | 40 |
| D ₁ | | | | | |
| Initial | 36 | 34 | 33 | 54 | 36 |
| 1 day | 32 | 32 | 31 | 31 | 33 |
| 3 days | 318 | 68 | 47 | 46 | 39 |
| 6 days | Gelled | 650 | 105 | 76 | 46 |
| D ₃ | | | | | |
| Initial | 35 | 33 | 35 | 34 | 34 |
| 1 day | 34 | 31 | 38 | 33 | 35 |
| 3 days | 256 | 62 | 37 | 36 | 36 |
| 6 days | 8 910 | 696 | 80 | 64 | 44 |

^aThe formulations are given in *Table 3*.

TABLE 13. FORMULATIONS FOR ZBUD COMPOUND STABILITY

| Item | Dry weights of Formulations 6-10 | | | | |
|-------------------------|----------------------------------|-----|-----|-----|------|
| | 6 | 7 | 8 | 9 | 10 |
| Latex | 100 | 100 | 100 | 100 | 100 |
| 10% KOH | — | 0.3 | 0.5 | 0.5 | 0.5 |
| 10% Potassium laurate | — | — | — | 0.5 | — |
| 10% Potassium caseinate | — | — | — | — | 0.15 |
| 50% Sulphur | 1 | 1 | 1 | 1 | 1 |
| 50% ZBUD | 1 | 1 | 1 | 1 | 1 |
| 50% Zinc oxide | 1 | 1 | 1 | 1 | 1 |
| Water | (to 55% TSC) | | | | |

TABLE 14. ZBUD COMPOUND VISCOSITY

| Sample | Formulation ^a | | | | |
|----------------|--------------------------|--------|-------|-----|-----|
| | 6 | 7 | 8 | 9 | 10 |
| A | | | | | |
| Initial | 33 | 30 | 29 | 32 | 32 |
| 1 day | 34 | 34 | 30 | 38 | 34 |
| 2 days | 34 | 34 | 31 | 38 | 33 |
| 3 days | 34 | 34 | 31 | 38 | 32 |
| B | | | | | |
| Initial | 46 | 43 | 46 | 44 | 54 |
| 1 day | 4 700 | 862 | 232 | 70 | 68 |
| 2 days | Gelled | Gelled | 1 730 | 84 | 72 |
| 3 days | — | — | 3 460 | 107 | 74 |
| C ₁ | | | | | |
| Initial | 38 | 40 | 40 | 42 | 46 |
| 1 day | Gelled | 2 080 | 316 | 94 | 64 |
| 2 days | — | Gelled | 2 430 | 180 | 73 |
| 3 days | — | — | 3 250 | 69 | 51 |
| C ₃ | | | | | |
| Initial | 34 | 34 | 34 | 37 | 38 |
| 1 day | 8 200 | 916 | 66 | 44 | 41 |
| 2 days | Gelled | Gelled | 402 | 52 | 49 |
| 3 days | — | — | 609 | 69 | 51 |
| D ₁ | | | | | |
| Initial | 32 | 33 | 32 | 34 | 38 |
| 1 day | 6 450 | 528 | 67 | 63 | 46 |
| 2 days | Gelled | Gelled | 552 | 113 | 50 |
| 3 days | — | — | 2 010 | 169 | 51 |
| D ₃ | | | | | |
| Initial | 34 | 34 | 34 | 34 | 38 |
| 1 day | 5 020 | 670 | 71 | 67 | 48 |
| 2 days | Gelled | Gelled | 1 170 | 288 | 112 |
| 3 days | — | — | 3 420 | 469 | 194 |

^aThe formulations are given in Table 3.

TABLE 15. VULCANISATE PROPERTIES OF LATEX CONCENTRATES IN POLYBAGS

| Property | Sample ^a | | | | | | |
|-------------------------|---------------------|------|----------------|----------------|----------------|----------------|----------------|
| | A | B | C ₁ | C ₂ | C ₃ | D ₁ | D ₃ |
| Tensile strength (MPa) | 36.0 | 37.1 | 34.8 | 33.2 | 33.6 | 35.3 | 35.2 |
| EB (%) | 960 | 970 | 970 | 970 | 950 | 990 | 960 |
| Relaxed modules (MR100) | 0.64 | 0.59 | 0.58 | 0.61 | 0.60 | 0.60 | 0.60 |
| Modules at 500% (MPa) | 2.38 | 2.58 | 2.45 | 2.32 | 2.45 | 2.27 | 2.52 |
| Aged 14 days at 70°C | | | | | | | |
| Tensile strength (MPa) | 21.6 | 20.2 | 17.7 | 17.3 | 16.0 | 15.9 | 19.8 |
| EB (%) | 850 | 870 | 890 | 920 | 890 | 850 | 900 |
| Relaxed modules (MR100) | 0.50 | 0.52 | 0.47 | 0.42 | 0.43 | 0.44 | 0.47 |
| Modules at 500% (MPa) | 2.31 | 2.32 | 1.99 | 1.89 | 1.99 | 1.98 | 2.09 |

^aThe formulations are given in *Table 3*.

DISCUSSION AND CONCLUSION

The collection of rubber in polybags in which a special polybag apparatus is left on the tree to accumulate coagula from several tappings over a period of two to four weeks has its advantages and drawbacks.

Collection in polybags may increase the effectiveness of the tapper, overcome the problem of labour shortage by reducing collection frequency, improve cleanliness of the coagulum and provide a larger reservoir for higher yielding trees where traditional tapping cups may be inadequate. The possible drawbacks include loss due to theft, higher cost of bags in the long run and of more importance is the production of a lower quality rubber.

The present study indicates that preserving latex in a fluid stage in polybags in the field for up to thirty-days is a technical possibility.

The concept of latex preservation in polybags is meant to arrest bacterial growth while the bacterial population is still low. With the LA/TZ field latex treatment, control of VFA was excellent in all trials. Field latex was kept stable for up to thirty days and the resulting concentrates had good storage properties and processing characteristics.

The trials also showed that preservation systems using ammonia/PRBL and ammonia/PROXEL GXL were effective for latex preservation in polybags, although requiring higher dosages.

Concentrates derived from latex collection in polybags have shown no abnormal properties. The respective concentrates showed good preservation as indicated by the data on storage. The VFA numbers were low (<0.05) and mechanical stability time exceeded 1500 s. Properties of the rubber films obtained from these concentrates were quite similar to those of the control and the vulcanisation behaviour was considered to be normal and satisfactory.

In conclusion, latex preservation in polybags offers an alternative method for rubber tapping and collection. It combines the advantages of collection of latex in polybags with the realisation that the latex can be processed into a premium latex concentrate.

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Determination of Specific Surface Areas of Clay Fractions of Soils under Rubber by Adsorption of Cetyl Pyridinium Bromide

LAU CHEE HENG* AND CHEN SEONG FONG**

Clay fractions from five contrasting soils under rubber cultivation were separated and their specific surface areas determined by adsorption of cetyl pyridinium bromide from solution. Results obtained showed that the specific surface areas of inland soils determined by the cetyl pyridinium bromide technique were comparable with those determined by adsorption of methylene blue at optimum flocculation. The specific surface areas of the clay were related to the release and adsorption of magnesium and aluminium by the soils. The cetyl pyridinium bromide technique can be used as an alternative method for the rapid determination of the specific surface areas of inland soils which contain predominantly non-expanding clay minerals.

Of the three major fractions in the soil, viz. clay, silt and sand, the clay fraction is the most reactive. The relative reactivity of the clay is determined not only by their mineralogy but also by their specific surface areas. Specific surface areas of the clay fractions of some Malaysian soils determined from the amount of methylene blue adsorbed on the clay to produce optimum flocculation were found to relate to the cation-exchange capacities of the clay¹. These clay fractions which had different specific surface areas had different preferences for H⁺, Na⁺, K⁺, Ca²⁺, Al³⁺ and PO₄³⁻ ions. Lau² also showed that total specific surface areas of soils played an important role in the exchange behaviour of K⁺ and Mg²⁺ ions and their release characteristics.

Besides methylene blue, other polar molecules like ethylene glycol, O-phenanthroline and cetyl pyridinium bromide (CPB) have been used to determine the specific surface areas of soils and clay^{3,4}. Comparing the surface areas of a range of soils and clay determined by the adsorption of CPB from solution and nitrogen, Greenland and Quirk^{5,6} found that there was very good agreement in the results when no expanding lattice material was present. In this

paper, the CPB technique is used to determine the specific surface areas of clay obtained from five contrasting soils under rubber. The results obtained are compared with the values measured by the methylene blue method reported earlier¹. In connection with this study, the relationships between the specific surface areas of clay and the rates of release of potassium, magnesium and aluminium from the clay are also discussed.

EXPERIMENTAL

Surface-soils (0-15cm depth) of contrasting physical and chemical properties were collected from five major areas under *Hevea* cultivation in Peninsular Malaysia. Details of the soils are given in *Table 1*. The soils sampled in bulk from either the unmanured plots or in between tree-rows where no fertilisers were applied, were dried in an air-oven at 45°C and passed through a 2 mm roller-sieve.

Separation and Treatment of Clay Fractions

To remove organic matter 20 g soil (< 2 mm) were repeatedly treated with 15 ml 10% H₂O₂. When the oxidation process was completed, the

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TABLE 1. DESCRIPTION OF THE SOILS

| No. | Soil series | Soil order | Parent material | Mechanical composition (% on oven-dried soil, 105°C) | | | | Clay minerals ^a | | | | | | |
|-----|-------------|------------|------------------------------------|---|-----------|------|------|----------------------------|-------|------|------|-------|--------|--------|
| | | | | Coarse sand | Fine sand | Silt | Clay | Kaol. | Mont. | Ill. | Mica | Gibb. | Goeth. | Quartz |
| 1 | Durian | Ultisol | Siliceous shale | 9.9 | 13.7 | 31.6 | 44.8 | D | nd | X | X | nd | nd | X |
| 2 | Kuantan | Oxisol | Basalt | 5.6 | 7.3 | 27.1 | 60.0 | D | nd | nd | nd | X | X | t |
| 3 | Munchong | Oxisol | Shale | 6.4 | 14.7 | 29.0 | 49.9 | D | nd | nd | nd | X | X | t |
| 4 | Rengam | Ultisol | Granite | 38.2 | 9.5 | 9.8 | 42.5 | D | nd | nd | t | t | t | nd |
| 5 | Selangor | Inceptisol | Mixed marine deposits/ alluvium | 0.8 | 9.6 | 41.1 | 48.5 | D | X | X | t | nd | nd | t |

^aAfter Singh⁸ and Noordijn⁹: Kaol. = kaolinite; Mont. = montmorillonite;

Ill. = illite; Gibb. = gibbsite; Goeth. = goethite

D = dominant (>50%); X = significant (>5%); t = trace (<5%); nd = not determined

clay fraction was separated by the sedimentation and pipette method of Piper⁷. After obtaining sufficient material, the combined clay samples of each soil were made homo-ionic with respect to sodium by washing with successive 50 ml portions of 0.5 M sodium chloride solution until the chloride in the wash solution was unchanged. The homo-ionic clay washed till chloride-free with distilled water (silver nitrate test) was dried at 45°C and kept for determination of specific surface areas.

Determination of Specific Surface Areas

Samples of clay weighing between 0.5 g and 1.0 g were shaken with 50 ml portions of CPB solutions of concentrations ranging from 0.01 g to 0.20 g CPB per 100 ml solution at room temperature for 16 h. The clay suspension was centrifuged and the concentration of CPB in the supernatant liquid determined by comparing the ultra-violet adsorption of the solution with those of CPB standard solutions at 259 m μ using a Hilger-Watts 'Uvispek'. From the initial and final CPB concentrations, the adsorption of CPB by the clay fraction was calculated⁶.

Adsorption isotherms for CPB adsorbed from aqueous solutions on the various clay fractions were plotted (*Figure 1*). Following this, the specific surface area of each clay sample was determined from the maximum CPB adsorption which corresponds to the 'plateau' of the isotherm and the mean area covered by each adsorbed cetyl pyridinium ion. Assuming that no inter-lamellar adsorption occurs and the external surface coverage is 0.27 nm² per cetyl pyridinium ion, the apparent surface area is related to the amount of CPB adsorbed by the equation,

$$S = 162a \quad \dots 1$$

where S is the apparent specific surface area in square metres per gramme clay and a , the maximum amount of CPB adsorbed in milliequivalent per gramme clay.

The CPB in this study was re-crystallised five times with dried re-distilled acetone before it was left in a vacuum desiccator to dry over sulphuric acid. A plot of surface tension against

concentration of CPB showed that the sample was of about 98% purity.

RESULTS AND DISCUSSION

The soils selected for this study were derived from different parent materials (*Table 1*). The combined clay and silt contents of the soils varied from 89.6% in the Selangor series to 52.3% in the Rengam series. The total amount of coarse and fine sand in the soils ranged from 47.7% in the Rengam series to 12.9% and 10.4% in the Kuantan and Selangor series, respectively. Based on the clay mineralogical data obtained by Singh⁸ and Noordin⁹, the common clay minerals in the soils were kaolinite, goethite, gibbsite, illite and quartz; the lesser ones were mica, chlorite, vermiculite and montmorillonite. The clay fraction of the Durian series soil contained a significant amount of illite and mica while that of the Selangor series contained montmorillonite, illite and a trace amount of mica. In contrast to these two soils, the clay fractions of Kuantan and Munchong series contained appreciable amounts of goethite and gibbsite and that of Rengam series was dominated by kaolinite.

Adsorption of Cetyl Pyridinium Bromide

CPB adsorption isotherms for the clay fractions are shown in *Figure 1*. It is apparent that the adsorption isotherms for different clay fractions were different and in all cases, the maximum adsorption was reached after the concentration of the equilibrium CPB solutions was in the range 0.02–0.05 g/100 ml. The maximum CPB adsorption which corresponds to the 'plateau' of the isotherm varies with the clay fractions and increases in the order: Kuantan < Rengam < Munchong < Durian < Selangor.

Specific Surface Areas of Soil Clays

Based on the assumption that no inter-lamellar adsorption occurs and the external surface coverage is 0.27 nm² per cetyl pyridinium ion, the apparent specific surface area of each soil clay was determined from *Equation 1*. The specific surface areas of the

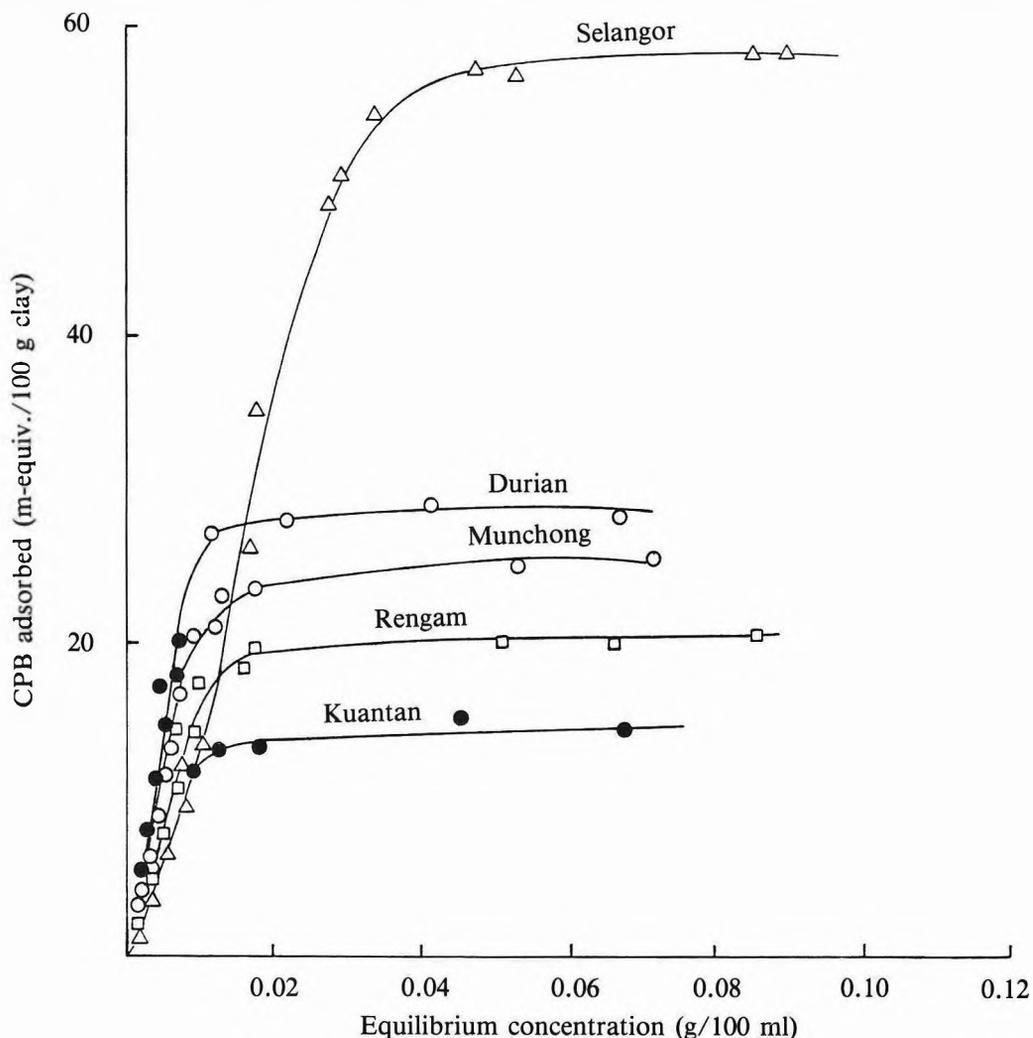


Figure 1. Cetyl pyridinium bromide adsorption isotherms for clay fractions.

soil clays are given in Table 2. Clay from Selangor series soil has the highest value while that from Kuantan series soil has the least value. The variations observed in the specific surface areas indicate that the materials obtained from different soils have contrasting surface properties. Indeed, Selangor series soil which contains a significant amount of 2:1 minerals, especially montmorillonite, and a high cation-exchange capacity shows complete dissimilarity in surface areas when compared with the other soils which are dominated by 1:1 minerals.

In addition, scanning electron micrographs of the Na-saturated clay taken at a magnification of 4000 times showed that the various soil clay had different textural properties and shapes². Clay from Durian series soil is made up of flake-like and crystal-shape materials which are identified as mica and kaolinite by transmission electron microscopy and X-ray diffractograms. On the other hand, clay from Selangor series soil consists of particles and fragmented microstructures of various sizes and shapes. The fragmented micro-structures are associated

TABLE 2. SURFACE AREAS OF CLAY FRACTIONS DETERMINED BY CPB ADSORPTION

| No. | Soil series | Maximum CPB adsorption (m-equiv./100 g clay) | CEC ^a (m-equiv./100 g clay) | Apparent surface area (m ² /g) | Surface area by methylene blue adsorption ^b (m ² /g) | Area (nm ²) per charge based on CPB area |
|-----|-------------|--|--|---|--|--|
| 1 | Durian | 28.76 | 19.2 | 46.6 | 48.4 | 0.40 |
| 2 | Kuantan | 14.76 | 13.5 | 23.9 | 26.2 | 0.29 |
| 3 | Munchong | 25.26 | 14.6 | 40.9 | 46.7 | 0.47 |
| 4 | Rengam | 20.02 | 11.3 | 32.4 | 34.0 | 0.48 |
| 5 | Selangor | 58.26 | 34.4 | 94.4 | 136.4 | 0.46 |

^aCation-exchange capacity of clay fraction by 1N NH₄OAc at pH 7.0

^bLau and Chen¹

with biorelicts from shells of molluscs and chinoderms and plant remains, while the particles are kaolinite and 2:1 minerals. The clay of Munchong and Kuantan series soil are composed of very fine particles which are mainly kaolinite, gibbsite, goethite and some quartz.

Although there appeared to be differences in specific surface areas, particularly in the clay of Durian, Munchong, Rengam and Selangor series soils, the area per unit charge in each clay is fairly constant and falls within a narrow range of 0.40 – 0.48 nm² per unit charge. It is of interest to note that clay from Selangor series soil which has the largest specific surface area has area per unit charge similar to those of Durian, Munchong and Rengam series soils. On the other extreme, clay from Kuantan series soil has low surface area per unit charge. Under humid tropical conditions, clay which are dominated by kaolinite, hydrous aluminium and iron oxides have 'variable charges' which depend on the properties of the surrounding soil solution^{10,11}. It is therefore difficult to determine the relationship between surface charges and specific surface areas of clay fractions in this study. Finally, there is ample evidence that the conventional method of using neutral IM ammonium acetate to determine the cation-exchange capacity and hence surface charges is not suitable¹².

Comparison of Specific Surface Areas Determined by the Methylene Blue Absorption Technique

The specific surface areas determined by the CPB method were generally lower than those obtained by the methylene blue absorption technique (Table 2). With the exception of clay from Selangor series soil, agreement between the two sets of values was found to be satisfactory and the maximum variation of about 12% was observed in clay from Munchong series soil. Under aqueous condition, the adsorption of CPB and methylene blue molecules is subjected to the interaction of the polar molecules with the soil surface and between themselves. Consequently, the calculation of specific surface areas would depend on the mean coverage per molecule or ion on the surfaces of the clay lattice. At maximum CPB adsorption, X-ray work by Greenland and Quirk¹³ showed that the hydrophobic cetyl chain projecting outwards at right angles from the clay surface and the mean coverage per CPB ion on a non-expanding clay lattice was 0.27 nm². In a similar study on methylene blue absorption, Pham and Brindley¹⁴ showed that the methylene blue molecules were lying flat on the clay mineral surfaces when optimum flocculation was reached. The effective area covered per methylene blue molecule under this condition was 1.30 nm². Despite the different orientations of the CPB ions and methylene blue

molecules on the clay surfaces, the specific surface areas of the various clay fractions determined by the two methods were almost similar. All indications are that these methods could be used for rapid measurement of specific areas of clay of Malaysian soils which consist predominantly of non-expanding lattices. Perhaps, the results of the procedures could be further clarified if parallel measurements of surface areas by the Brunauer, Emmett and Teller (B.E.T.) gas adsorption technique were made. In this instance, it is probable that the higher specific surface area of clay from Selangor series soil could be explained by the presence of both internal and external surfaces which could not be discriminately determined by the CPB and methylene blue absorption techniques alone. Therefore, for clay like that from Selangor series soil and the marine alluvial clay, the methylene blue and CPB techniques are not appropriate. For these categories of clay, the B.E.T. gas adsorption measurements will form the main core of future studies.

Correlation of Release and Adsorption of Cations in Soils

In earlier work, Lau² showed that the rates of release of potassium, magnesium and aluminium by five contrasting soils to a strong cation-exchange resin followed the ‘first-order’ rate law and the rates of adsorption of the same

cations from solution followed the ‘parabolic’ rate law. In this study, it was found that the rate constants for the release and adsorption of magnesium and aluminium were significantly correlated with the specific surface areas of the soils. The correlation coefficients and the regression equations are shown in *Table 3*. The good correlations between the rate constants for magnesium or aluminium release and surface areas suggested that the release is associated with the extent of the surface area of the soil for acid attack by the hydrogen ions from the cation-exchange resin. This observation agreed with the work of Ross¹⁵ who showed that acid dissolution of chlorites was influenced by the extent of the exposed surfaces of the clay mineral. Since aluminium and magnesium ions are strongly hydrated, the adsorption of these cations from solution would be strongly governed by the magnitude of the charges of the soil particles and total area of the exchange surface.

The higher specific surface areas of the Selangor and Durian clays allow for better retention of plant nutrients in the soils. However, advances in the agronomy research of rubber have shown that there were no correlations between uptake and yield of rubber and the nutrient retention capacity of the Selangor and Durian series soils as the overriding factor in these two soils are their serious

TABLE 3. LINEAR CORRELATIONS BETWEEN RATE CONSTANTS AND SPECIFIC SURFACE AREAS OF THE SOILS

| Rate constant | Regression equation | Correlation coefficient (r) |
|----------------------------|------------------------------|-----------------------------|
| First-order rate constants | $k_K = 2.046 + 0.003S$ | 0.053 ^{NS} |
| | $k_{Mg} = 0.445 + 0.014S$ | 0.743 ^{P<0.01} |
| | $k_{Al} = 8.453 + 0.062S$ | 0.600 ^{P<0.02} |
| Parabolic rate constants | $k_{K(p)} = 4.826 + 0.016S$ | 0.210 ^{NS} |
| | $k_{Mg(p)} = 2.872 + 0.018S$ | 0.852 ^{P<0.001} |
| | $k_{Al(p)} = 2.778 + 0.024S$ | 0.823 ^{P<0.001} |

NS = Not significant

S = Specific surface area

k_K, k_{Mg}, k_{Al} are first-order rate constants;

$k_{K(p)}, k_{Mg(p)}, k_{Al(p)}$ are parabolic rate constants for K, Mg and Al respectively

soil physical limitations¹⁶. Rubber grown on Kuantan, Muchong and Rengam series soils generally have higher yield as the soils are better structured and root growth is not hampered. Conclusively, specific surface area measurement alone is insufficient and its influence on crop performance has to be considered together with other soil parameters.

CONCLUSION

The cetyl pyridinium bromide technique provides an alternate means for the rapid determination of specific surface areas of the highly leached and weathered inland soils of Malaysia. However, for marine alluvial soils which contain appreciable amounts of 2:1 expanding lattice minerals and organic matter, further clarification is required and parallel determination of specific surface areas using the B.E.T. gas adsorption method is necessary. The specific surface areas determined by the cetyl pyridinium bromide are comparable with those obtained from the amount of methylene blue absorbed by the soil from solution. The physico-chemical properties of the soils are influenced by the effective area of the exchanger.

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SHORT COMMUNICATION

Characterisation of Natural Rubber from Manicoba (Manihot glaziovii): Microstructure and Average Molecular Weight

JUDITH F. RODRIGUES*, ANGELO S. RODRIGUES* AND ANDRÉ L. H. CARDOSO*

The microstructure and average molecular weight of Manihot glaziovii rubber, are presented. This natural rubber constitutes mainly of cis-1,4-polyisoprene units and shows \bar{M}_v values ranging between 1.0×10^6 and 1.5×10^6 . \bar{M}_n and \bar{M}_w were found to be 1.1×10^6 and 2.0×10^6 , respectively, with a polydispersity of 1.3. The structural determination was based on infra-red (ir), ^1H and ^{13}C NMR. The average molecular weights were obtained from viscosity experiments and GPC.

There is great interest in developing alternative sources of natural rubber (NR). NR can be obtained from about 2000 different vegetal species; however only about a dozen of these plants have been commercially exploited. *Manihot glaziovii*, popularly known in Brazil as manicoba, is a tree of 8-12 m, well adapted to dry climates and found in north-eastern Brazil. It belongs to the Euphorbiaceae family and could be an alternative source of NR, the chemical composition of which, has been determined¹⁻⁶. In 1985, Bastos *et al.*⁷ reported their results on manicoba from agricultural and technological experiments. In 1988, Serier⁸ discussed its history, biology, cultivation and economic aspects. No further study has been carried out to confirm the polymer microstructure and the average molecular weight, which is the objective of this report. The possibility of industrial application was examined using mechanical properties of vulcanised rubber⁷ in addition to the results of this study.

MATERIALS AND METHODS

Samples of rubber were collected in Maranguape and Pacatuba Counties, State of

Ceará, north-east of Brazil. They were purified by dissolution in benzene or chloroform (25 g/litre) and coagulated in methanol in the absence of light.

Films for ir were made by vapourisation of benzene solution over NaCl windows. A Perkin Elmer spectrophotometer, Model 293-B was used. The ^1H NMR spectrum was recorded in CDCl_3 solution, using a Bruker spectrometer (80 MHz) and the chemical shifts were related to TMS, used as the internal standard. The ^{13}C NMR spectrum was acquired on a Varian VXR-300 spectrometer (75 MHz).

Ostwald viscometers with t_0 of 95 s and 117 s were used for determination of the flow time. The system was thermostated by immersion in a water bath with a 0.1°C accuracy. For gel permeation chromatography, a Waters Associates Model 200 with styragel columns and toluene as solvent was used.

RESULTS AND DISCUSSION

The ir spectrum of *Manihot glaziovii* rubber is characteristic of polyisoprene. Selection of the 1,4 structure was based on the absence of

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intense bands at 888–889 cm^{-1} and 909 cm^{-1} , characteristic of 3,4 and 1,2 structures, respectively⁹⁻¹². In addition, there is a band at 835 cm^{-1} due to the 1,4 linkage in polyisoprene^{9,11,13}. The spectrum also exhibits bands at 1130 cm^{-1} and 1378 cm^{-1} , all comparable to the values for *cis*-1,4-polyisoprene found by Binder and Ransaw¹⁰, as well as Tanaka *et al.*¹¹. The absence of bands at 1152 cm^{-1} and 1385 cm^{-1} confirms the suggestion of the *cis* configuration.

¹H NMR spectrum shows absorption at 1.68 p.p.m. (*cis* CH₃–C=), 2.02 p.p.m. and 2.06 p.p.m. (–CH₂–C=) and 5.13 p.p.m. (=C–H), typical values for *cis*-polyisoprene¹⁴ in CDCl₃. The proportion between the areas under the peaks at 1.68 p.p.m., 2.02–2.06 p.p.m. and 5.13 p.p.m. is 3:4:1 which is comparable to the relation of methyl, methylene and olefinic protons of the structure [–CH₂C(CH₃)=CHCH₂–]_n. No signals at 1.36 p.p.m. and 4.75 p.p.m. eliminate the possibility of the 3,4 isomer. The characteristic signal of *trans*-1,4 isomer at 1.61 p.p.m. was also not detected¹⁵. The ¹³C chemical shift at 135.2, 125.0, 32.2, 26.4 and 23.4 p.p.m. attributed to carbon α , β , γ , δ and ϵ of the monomeric unit, are also in agreement with a *cis*-1,4 structure¹⁶. Thus, *Manihot glaziovii* rubber is constituted predominantly of *cis*-1,4-polyisoprene.

To obtain more representative \bar{M}_v values, five determinations under different conditions were made: NR origin, purification process, viscometer type and solvent-temperature system (Table 1). Intrinsic viscosity values were obtained from plots of η_{sp}/c versus c . These data, plotted in linear graphs, yielded correlation coefficients between 0.983 and 0.998, calculated using the least squares method. For the calculation of \bar{M}_v the Mark-Houwink-Sakurada equations: $[\eta] = 1.90 \times 10^{-4} \bar{M}_v^{0.745}$ for toluene solution¹⁷ at 30.0°C and $[\eta] = 1.77 \times 10^{-4} \bar{M}_v^{0.735}$ for THF solution¹⁸ at 20.0°C were used. From the data, we can conclude that the \bar{M}_v values of *Manihot glaziovii* rubber range between 1.0×10^6 and 1.5×10^6 , with a mean value of 1.2×10^6 .

Using GPC and polystyrene as a reference, we have calculated \bar{M}_n and \bar{M}_w of Pacatuba NR. The values found were 1.1×10^6 and 2.0×10^6 , respectively, with a polydispersity of 1.3. This \bar{M}_w value falls within the typical range for non-masticated *Hevea brasiliensis* NR (1.6×10^6 to 2.3×10^6). However, the \bar{M}_n value is higher, the typical values are between 2.0×10^5 and 5.0×10^5 . Therefore, the molecular weight polydispersity is much lower than *Hevea* rubber \bar{M}_w/\bar{M}_n , which ranges from 2.8 to 10, according to Tanaka¹⁵.

TABLE 1. VARIABLES IN THE DETERMINATION OF $[\eta]$ AND \bar{M}_v OF *MANIHOT GLAZIOVII* RUBBER

| Origin | Purification process | | Viscometer type | $[\eta]$ (d litre/g) | \bar{M}_v |
|------------|-------------------------------|-------------------|-----------------|-------------------------|-------------|
| | Solvent | Repetition number | | | |
| Maranguape | C ₆ H ₆ | 1 | I | 5.45 ^a | 960 000 |
| Maranguape | C ₆ H ₆ | 1 | II | 5.60 ^a | 1 000 000 |
| Pacatuba | C ₆ H ₆ | 1 | II | 7.20 ^a | 1 370 000 |
| Pacatuba | C ₆ H ₆ | 3 | II | 5.50 ^a | 1 090 000 |
| Pacatuba | CHCl ₃ | 2 | I | 6.20 ^b | 1 530 000 |

I – capillary diameter and length, 0.5 mm and 16 cm respectively

II – capillary diameter and length, 0.6 mm and 15 cm respectively

^aToluene solution at 30.0°C

^bTHF solution at 20.0°C

The possibility of industrial application of manicoba rubber was reported by Bastos *et al.*⁷ Mechanical properties of pure-gum vulcanised rubber were compared with those of *Hevea* vulcanised rubber in the same formulation: Shore A hardness was 44 and 35; elongation at break, 784% and 860%; tensile strength, 16.8 MPa and 17.7 MPa; and, modulus at 300%, 3.58 MPa and 2.21 MPa, respectively.

Hevea NR and *Manihot* NR have the same structure, slightly different molecular weights^{5,19} and close hydrocarbon contents 87.9–94.5 and 84.1%, respectively). Production of *Hevea* NR was 468 kg/ha/year and of *Manihot* NR 414 kg/ha/year. These data and those of mechanical properties indicate the possibility of manicoba rubber as an economically viable raw material, especially in dry climatic regions. Agricultural, technological, chemical and economical aspects have to be studied to obtain a more definitive conclusion.

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