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The Particle Size of Natural Rubber Latex Concentrates by Photon Correlation Spectroscopy

T.D. PENDLE* AND P.E. SWINYARD*

Measurement of the particle size of colloidal systems by photon correlation spectroscopy has become quite commonplace in the last decade. This paper describes the application of this technique to natural latex concentrates and provides information on the variation of mean particle size between different batches of latex. Analysis of the scattering data obtained suggests that natural latex concentrates have a bimodal size distribution pattern.

The technique of particle size measurement by photon correlation spectroscopy (PCS) also known as dynamic light scattering (DLS) or quasi-elastic light scattering (QELS), depends upon the measurement of fluctuations in the intensity of scattered light produced by particles in Brownian motion. Detection of the fluctuations requires a rapid-response photomultiplier coupled to a computer to collect and analyse the data. The advantages of this technique are that it is absolute (*i.e.* it requires no calibration), the particles are measured in the suspended state, are not affected by the measurement and the measurement is rapid, usually less than an hour is required. The theory behind the technique has been extensively described by many authors, including Berne and Pecora¹ and Dahneke² and the following is only a very brief outline of the principles involved.

For mono-disperse colloidal system, the intensity fluctuations at the detector, which are more rapid for smaller particles, are characterised by a time base auto-correlation function (G_τ), which is a decaying exponential of the form:

$$G_\tau = Ae^{-\Gamma\tau} + B$$

where A and B are constants dependent upon the sample, experimental geometry and the optical and electronic efficiency of the system

τ is the time interval

Γ is the decay constant, characteristic of the particle size.

It follows therefore that for a poly-disperse system, the auto-correlation function is a summation of the individual functions of the various particle sizes present and may be represented as:

$$G(\tau) = \int_0^\infty F(\Gamma) e^{(-\Gamma\tau)d\Gamma}$$

In this equation, $F(\Gamma)$ which contains details of the size distribution, is obtainable from measurements of $G(\tau)$ by inversion of the equation. Inversion of this integral however, involves numerical analysis with no certainty of a unique solution or of any solution. With poly-disperse latices, therefore, analysis of the data does not necessarily yield an unequivocal answer. The analytical methods available include Pusey's cumulants method³ and the exponential sampling method⁴. The latter is preferred for poly-disperse systems although it has been reported⁵ that it can produce false size distribution peaks in some circumstances.

For this work, the analytical methods used were in the computer programmes (*PCS 14, 15, 24*) supplied with the 'Malvern' instrument, *i.e.* the method of cumulants and the exponential sampling method. It should be noted that the average diameter derived from these calculations is an average 'hydrodynamic' particle diameter which is said to correspond closely to the volume average diameter in many systems. The 'poly-dispersity index' values quoted below are derived from the method of cumulant analysis and represent the second moments of the intensity distribution divided by the square of the average decay constant.

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EXPERIMENTAL

Instrument

The photon correlation spectrometer used in these experiments was a Malvern 4600 multi-angle instrument, with a 632.8 nm wavelength Helium-Neon laser (from Malvern Instruments, Malvern, Worcs., UK). The analysis programmes used were *PCS 15* and *24* (cumulants) and the *PCS 14* (exponential sampling) histogram programme for the data from *PCS 24*.

Materials

The mono-disperse latices used in this work were polystyrene or polyvinyl toluene materials supplied by Dow, Seragen or Coulter. The natural latices were all commercial materials, of the types indicated in the text, and came from many different sources. 60% rubber (weight) concentration natural latices were diluted by a factor of approximately 1200 for use in the instrument. The test samples therefore had a particle concentration of the order of 10^{-10} /ml. The water used for dilution of the test samples was taken from a stock of deionised water pre-filtered four times through 0.4 μ filters. The diluting water was further filtered through a 0.20 μ filter immediately prior to addition to the latex.

Measurements

All measurements were carried out at a scattering angle of 90° and a temperature of 25°C, unless otherwise specified.

RESULTS AND DISCUSSION

Mono-disperse Latices

In common with the results of many previous workers, PCS measurements of particle size on

mono-disperse latices proved to be very close to the nominal values. *Table 1* shows the latices used and the results obtained, using the *PCS 24* programme (method of cumulants). It will be seen that in almost all cases, the average particle diameter by PCS is slightly higher than the nominal value (usually obtained by electron microscopy). The discrepancy tends to be greater with increasing particle diameters. The 'within sample' repeatability in all cases was excellent and the 'between sample' reproducibility was very good, showing a coefficient of variation of $\sim 3\%$.

To assess the ability of this technique to cope with broader distributions of particle sizes, three mixtures of mono-disperse latices were prepared as indicated below:

Latex A: Equal volumes of 624 nm and 1110 nm polystyrene latices.

Latex B: Equal volumes of 94 nm and 2030 nm polystyrene latices.

Latex C: A mixture of equal volumes of 'A' and 'B' above, using dilutions of equal scattering power. (The overall size range of this mix roughly approximates to that found in NR latex concentrate.)

These three mixtures were each examined on the PCS apparatus using all three programmes (*PCS 15*, *24* and *14*) at both 90° and 50° scattering angles. The particle size values and poly-dispersity indices obtained from the *PCS 15* and *24* programmes are shown in *Tables 2* and *3* respectively. It is noticeable that *Mix A* yields essentially the same mean diameter and poly-dispersity index (PDI) regardless of the programme or scattering angle. The PCS technique is unable to separate

TABLE 1. PCS MEASUREMENTS OF MONO-DISPERSE LATICES

Latex type	Source	Nominal size (nm)	Measured size (nm)
Polystyrene	Seragen	91	90
Polystyrene	Dow	624	639
Polystyrene	Coulter	1 110	1 207
Polyvinyl toluene	Coulter	2 030	2 257

TABLE 2. MEAN PARTICLE DIAMETER \pm STANDARD DEVIATION

Programme	Angle	Mean particle diameter \pm SD (nm)		
		Sample A	Sample B	Sample C
PCS 15	90°	616 \pm 17	140 \pm 10	377 \pm 39
PCS 24 Linear	90°	639 \pm 5	223 \pm 145	582 \pm 138
PCS 24 Log	90°	610 \pm 24	239 \pm 56	493 \pm 184
PCS 24 Linear	50°	620 \pm 10	454 \pm 38	802 \pm 10
PCS 24 Log	50°	628 \pm 9	693 \pm 185	924 \pm 37

TABLE 3. POLY-DISPERSITY INDICES \pm STANDARD DEVIATION

Programme	Angle	PDI \pm SD		
		Sample A	Sample B	Sample C
PCS 15	90°	0.08 \pm 0.04	0.32 \pm 0.04	0.55 \pm 0.04
PCS 24 Linear	90°	0.13 \pm 0.03	0.30 \pm 0.08	0.40 \pm 0.02
PCS 24 Log	90°	0.10 \pm 0.03	0.12 \pm 0.04	0.22 \pm 0.02
PCS 24 Linear	90°	0.06 \pm 0.02	0.56 \pm 0.03	0.62 \pm 0.01
PCS 24 Log	90°	0.11 \pm 0.01	0.19 \pm 0.07	0.16 \pm 0.01

the two modes in this mixture as the diameter ratio is <2 and it 'sees' the distribution as mono-modal. With *Latex B*, however, the mean size value obtained does depend on the programme and angle used. The smaller mode appears to dominate the measurements in *PCS 15* and *PCS 24* at 90°. At 50° scattering angle, a more realistic 'mean' size is obtained reflecting a greater contribution from the larger mode.

Latex C containing four modes, only three of which are expected to be resolvable, behaves similarly to *Latex B* but shows much higher mean size values.

The *PCS 14* exponential sampling programme has been used to produce histograms of the particle distributions from the data obtained in the *PCS 24* programme. Selected examples of these are shown in *Figures 1-4*. As expected it was not possible to resolve the two peaks of *Latex A* but the modes in *Latex B* were easily resolved under all the conditions used. The results for *Latex C* tended to

produce a continuous histogram both at angles of 90° and 50°, although at 50° in the linear mode, the 624 nm peak is being detected.

A feature of the use of the *PCS 14* programme is that much better results are obtained if the limits of the distributions are known. The auto-sizing function in the programme often produced entirely different histograms from those shown here. The histograms shown were all obtained by inserting the 'true' values of the largest and smallest peaks into the programme.

Comparing the log and linear modes of operation, the former tends to give higher values of mean size although the *PCS 14* histograms are qualitatively similar (except in the case of *Latex C* at 50°). It seems that although the log mode should be better than the linear for wide distributions of sizes, it is important that a large number of sets of data be accumulated in order to minimise the effects of 'abnormal' results which are often encountered in this mode. The large values of

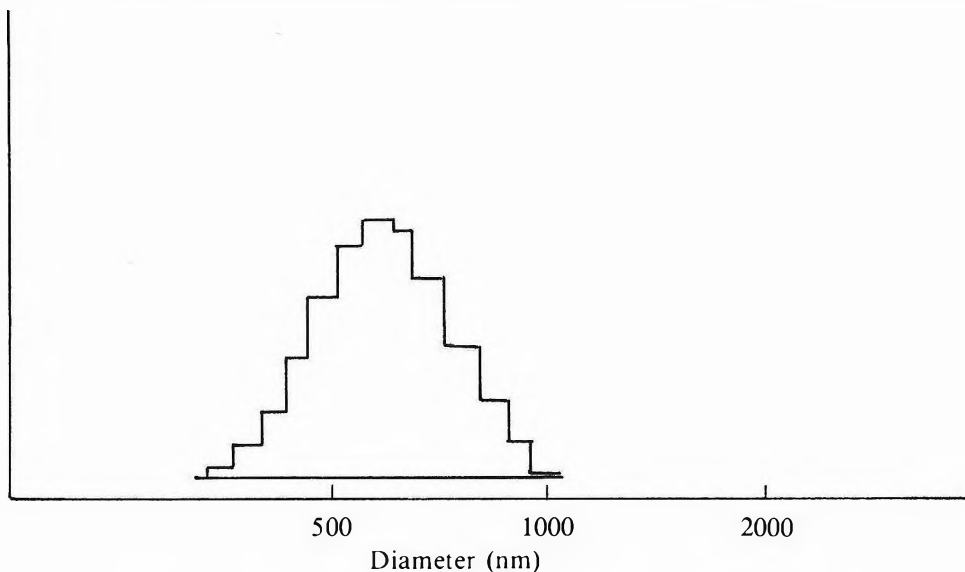


Figure 1. PCS 14 histogram of Sample A (90° angle, log mode).

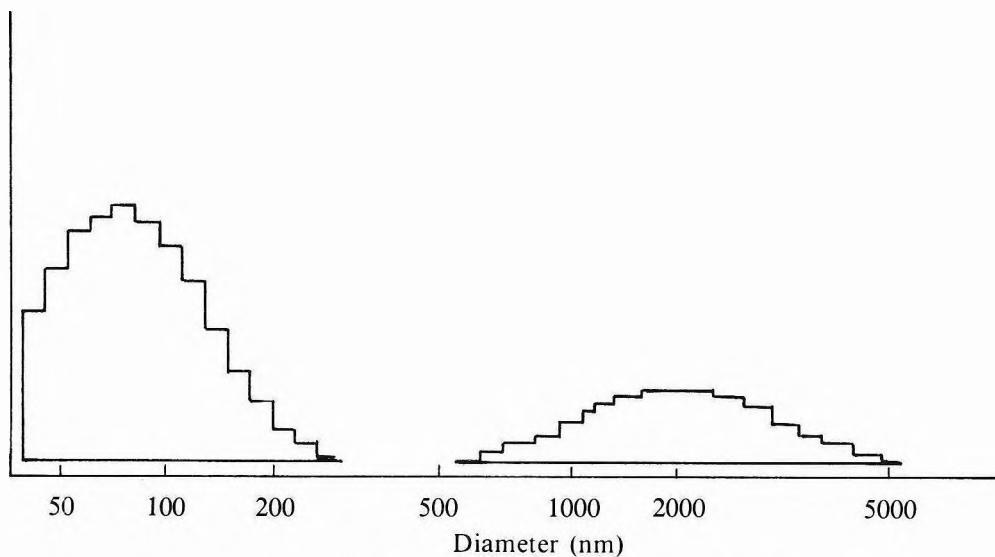


Figure 2. PCS 14 histogram of Sample B (90° angle, log mode).

standard deviations found with some of the log mode measurements (Table 2) probably reflect the influence of these 'abnormal' sets of data.

It is important with systems having a wide range of sizes to choose a sufficiently large 'sample time' (in PCS 24), to obtain consistent

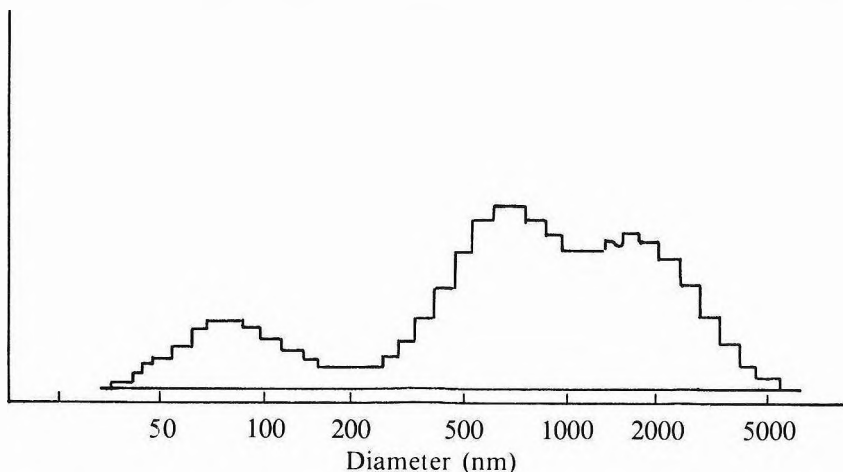


Figure 3. PCS 14 histogram of Sample C (50° angle, linear mode).

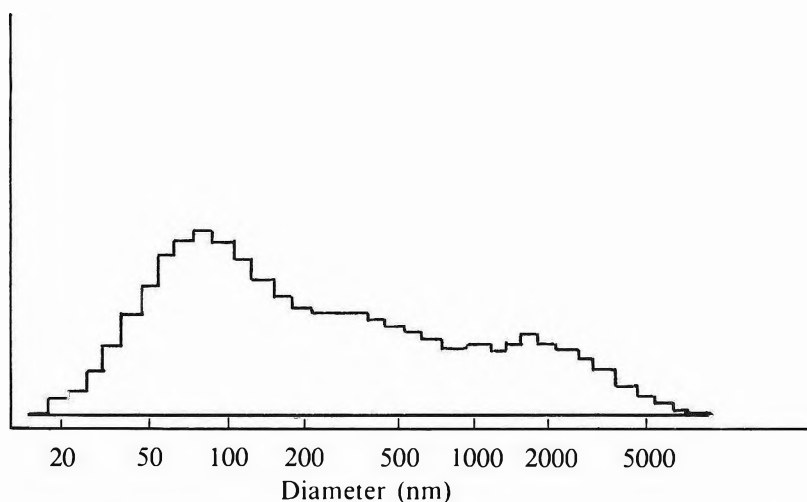


Figure 4. PCS 14 histogram of Sample C (90° angle, log mode).

results. Sample times found adequate in these experiments were 60–100 μ s in the linear mode and 40–80 μ s in the log mode.

These trials established that the *PCS 14* programme can give an approximation to the size distribution of a multi-modal latex and can produce ‘true’ modal diameters provided that the diameter ratios are greater than 2. The trials also established that the histogram obtained from the *PCS* programme depends greatly

on the scattering angle at which the measurements were made — the differences between *Figures 3* and *4* clearly illustrate the expected dependence of scattering power on the diameter and angle.

Natural Rubber Latices

Samples taken from some forty shipments of natural latices into Europe were subjected to particle size measurement by this technique,

using the *PCS 15* programme. This programme is the simplest to use for large numbers of routine measurements and, although it gives little useful information on size distributions, the average diameters derived from it, are not greatly different for NR latex from those given by the more complex *PCS 24* programme. The results of these measurements are shown in *Table 4* for LATZ type latices and in *Table 5* for HA latices. From these results, it is clear that the average diameters are usually in the range 480–550 nm for LATZ latices and in the range 510–600 nm for HA latices, but in both cases, a small number of latices were outside those ranges. Overall, the HA latices showed a higher average diameter than the LATZ latices and a greater variability. Analysis of variance applied to the two sets of data suggests ($p \sim 0.025$) that the apparent difference in size between these two latex types is real and not the result of chance fluctuations. However, a

TABLE 4. AVERAGE DIAMETERS OF LATZ LATICES (PCS 15 PROGRAMME)

Sample	Diameter (nm)	PDI
1	614	0.34
2	510	0.30
3	540	0.34
4	507	0.33
5	512	0.31
6	491	0.31
7	515	0.30
8	493	0.30
9	506	0.28
10	513	0.31
11	522	0.32
12	489	0.30
13	545	0.32
14	493	0.32
15	513	0.27
16	517	0.30
17	521	0.31
18	499	0.30
19	523	0.31
20	611	0.33
21	523	0.31
Overall average (nm)	522	—
Coefficient of variation (%)	6.4	—

TABLE 5. AVERAGE DIAMETERS OF HA LATICES (PCS 15 PROGRAMME)

Sample	Diameter (nm)	PDI
1	587	0.34
2	571	0.33
3	962	0.45
4	548	0.31
5	546	0.33
6	527	0.31
7	558	0.32
8	566	0.32
9	536	0.29
10	569	0.31
11	591	0.31
12	560	0.31
13	515	0.29
14	526	0.30
15	531	0.29
16	521	0.28
17	538	0.30
18	720	0.20
19	651	0.33
Overall average (nm)	585	—
Coefficient of variation (%)	17.7	—

much larger number of latices would need to be tested to confirm this conclusion.

In addition to these measurements, the *PCS 15* programme was used to measure a sample of creamed latex and a sample of ammoniated field latex. The creamed latex gave an average diameter of 494 nm which is at the low end of the centrifuged latex range but the field latex gave the appreciably smaller value of 313 nm.

It was noticeable in all of the above measurements that the poly-dispersity index showed relatively little variation and it therefore seems that the *PCS 15* programme is incapable of revealing useful information about the size distribution in poly-disperse systems.

Particle Size Distribution

It is possible for poly-disperse latices with greatly different particle size distributions to have the same or similar average diameters. In addition, the processing behaviour of a latex

is likely to be much more dependent upon the detailed size distribution than on the calculated average diameter. Indeed, in certain synthetic latices, particle size distribution has been found to have an important effect upon processing characteristics⁵.

To the knowledge of the present authors, the size distributions existing in natural latices have never been adequately investigated and there is no data available to determine whether variability of size or size distribution plays a part in the observed processing behaviour of natural latex. The early work of Lucas⁶ on this subject is probably the best of the published studies but he examined only a small number of latices and they were not typical of modern concentrates. The more recent work of Shuster *et al.*⁷ is also of limited value for reasons discussed elsewhere⁸.

The *PCS 14* programme of the Malvern 4600 instrument provides an opportunity to assess the distribution of particle sizes existing in natural latices by analysis of the data collected by the *PCS 24* programme. In order to use the *PCS 14* programme, the 'bounds' or limits of the distribution must be entered. It should be noted that the limits selected can have a significant effect on the outcome of the analysis and the best results will only be obtained if the 'true' limits are known. The limits can be estimated by means of the 'Auto-sizing' function supplied with the programme but in the present work, we used values obtained independently. For the lower size of the distribution, we used a value of 200 nm which is consistent with the data of Lucas and also the unpublished work of Gorton in 1959. A value of 1500 nm was used for the upper size and this was chosen in accord with unpublished measurements made by Pendle in 1977 using a 'Coulter Counter'. This study showed that although there were many particles present above the 1500 nm limit, even up to 5000 nm, their numbers were insignificantly small, so 1500 nm could safely be taken as the 'effective' upper limit.

The authors have carried out this type of measurement on a large number of natural latex

concentrates and in *Figures 5* and *6* present six histograms, which are considered typical of those obtained in this study. Examination of these six histograms shows that five of them clearly suggest a bimodal size distribution for NR latex. The peak diameters vary somewhat, from 200 nm to 300 nm for the lower peak and from 700 nm to 1500 nm for the higher peak. The sixth latex gave a histogram which was less clearly bimodal but which nonetheless exhibited peaks in the above ranges. Previous studies of *Hevea* latex have not indicated a bimodal distribution. Schoon and Van der Bie⁹ did find multi-modal distributions in a number of monoclonal 'field' latices, but Gomez¹⁰ was unable to find similar distributions in his investigations.

The known uncertainties and difficulties in the mathematical analyses of the light scattering data made the authors cautious about accepting the evidence of the *PCS 14* analysis despite its remarkable consistency over a large number of latices. However, subsequent to the experimental work on photon correlation spectroscopy, we were fortunate to be able to have a few analyses of particle size made using the Sedimentation Field Flow Fractionation (SF³) instrument¹¹ developed by the Dupont Company. The SF³ method combines the effects of centrifugation and flow fractionation to give a complete size distribution analysis of a dispersed system. The Dupont Company carried out analyses on three natural latices for us and in each found a bimodal distribution of particle size with peaks in the regions of 300 nm and 700 nm. The distribution curves obtained by SF³ are shown in *Figure 7*. The latices described in *Figure 7* are two HA concentrates, one twelve years' old and a field latex. The fact that the field latex shows similar bimodality to the concentrates, though with the distribution skewed, to the smaller size, seems highly significant.

The qualitative similarities between Dupont's SF³ analysis and the Malvern *PCS 14* histograms are very striking and form strong evidence for the bimodality of natural latex concentrate particle size.

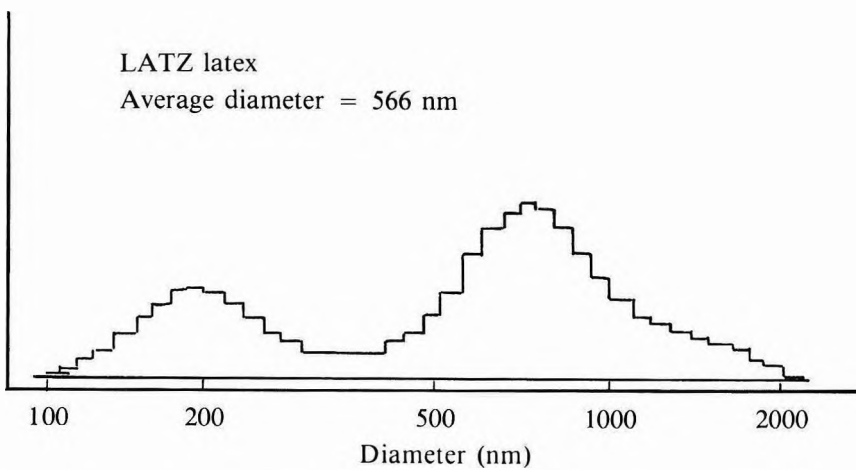
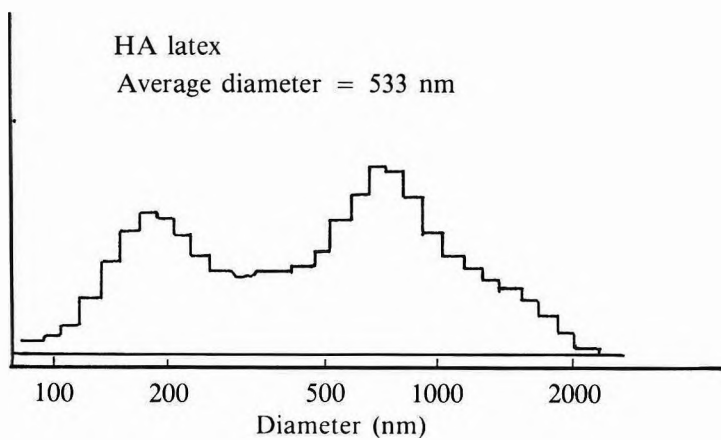
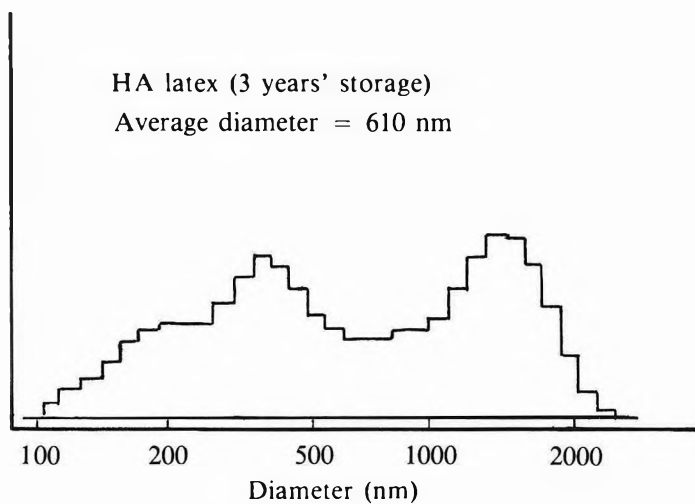


Figure 5. Histograms of latex concentrates obtained from scattering data at 90° angle (PCS 14).

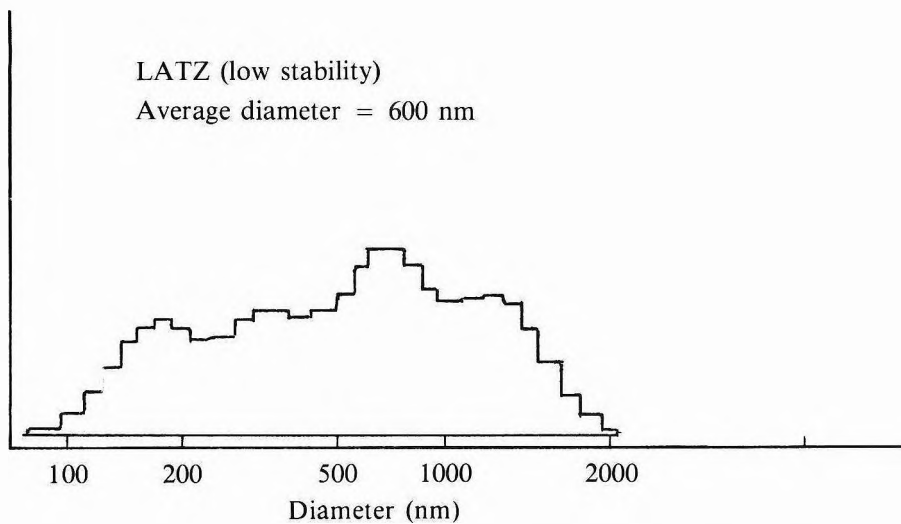
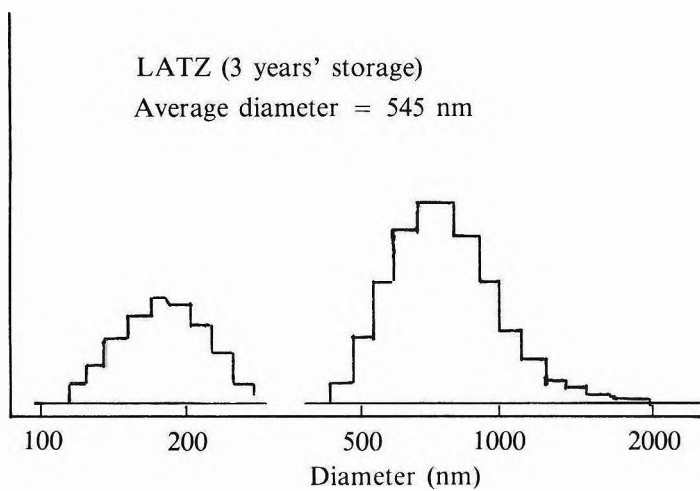
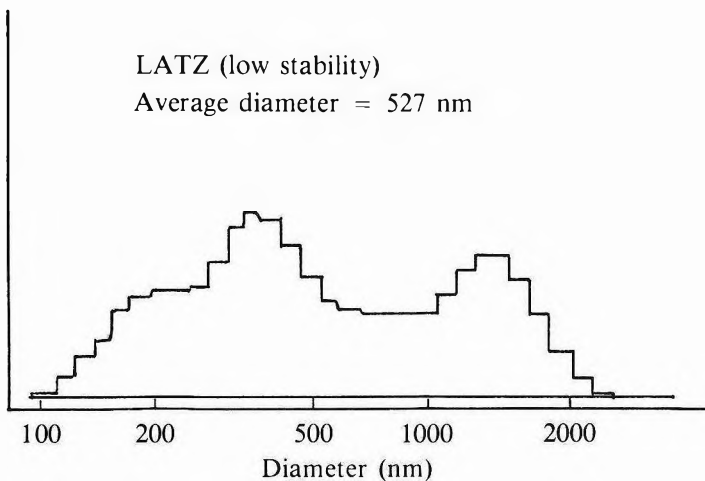


Figure 6. Histograms of latex concentrates obtained from scattering data at 90° angle (PCS 14).

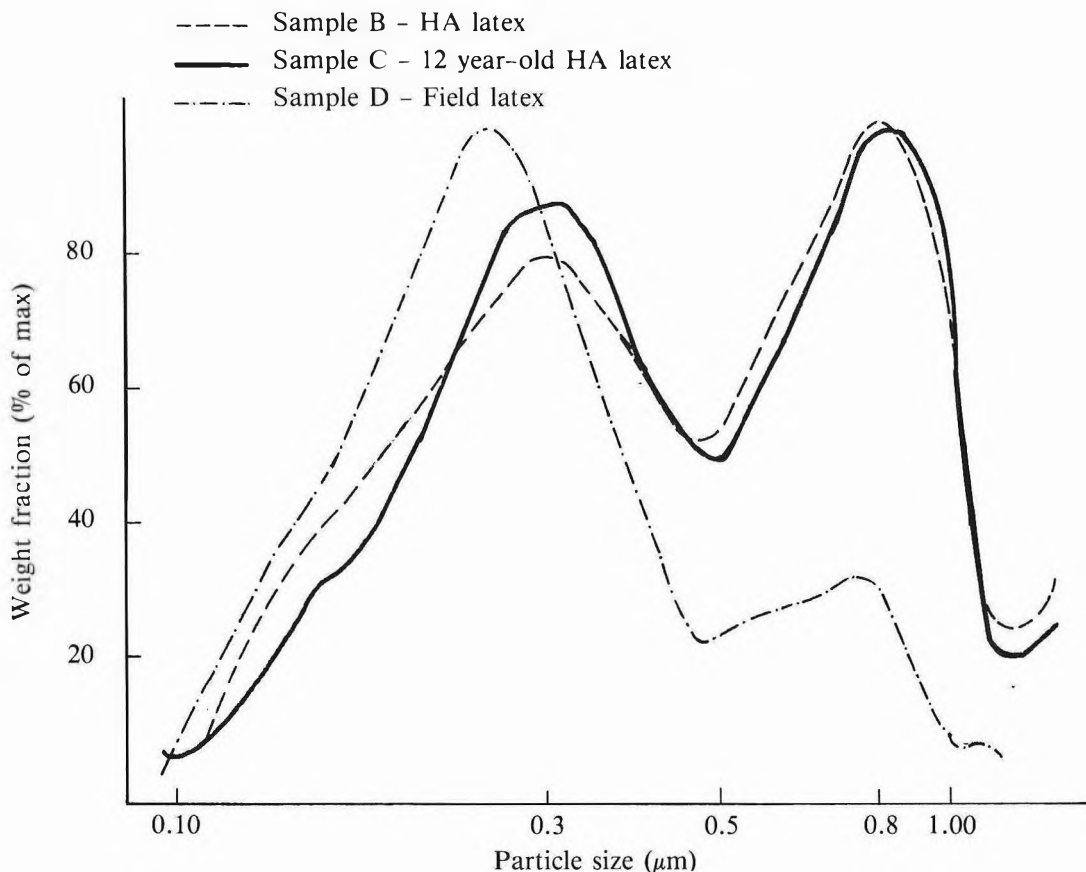


Figure 7. Weight distribution plots by SF^3 (courtesy Dupont).

Lucas¹² suggested that the smaller particles in natural latex agglomerated during storage to form larger ones. According to his results, the coalescing process appeared to be quite rapid but this is not consistent with the small effects of long-term storage on average diameter. *Table 6* shows the measurements of average diameter on a HA and a LA-TZ latex stored for up to four years at 21°C. It can be seen that the LA-TZ latex showed no significant change in particle diameter even after three years' storage. The HA latex was also stable for up to one year but thereafter showed a measurable increase. From these results, therefore, it appears that during normal storage periods, say up to one year, any spontaneous agglomeration of the latex particles, if occurring at all, must be on a negligible scale. However, prolonged storage may permit the effects of spontaneous

TABLE 6. EFFECT OF LONG-TERM STORAGE ON PARTICLE SIZE (STORAGE TEMPERATURE 21°C)

Storage time (years)	Diameter (nm)	
	HA	LA-TZ
0	542	536
0.5	561	544
1	551	550
2	622	509
3	611	539
4	798	—

agglomerations to be seen. It also appears that particle size changes on long-term storage are more likely to occur with HA latices, than with

LATZ latices, but this conclusion is by no means certain and is not supported by the results on *Latex C* in *Figure 7*.

SUMMARY

The average hydrodynamic diameter of HA latex is normally in the range 510–600 nm, but a few batches are significantly larger than this.

The average hydrodynamic diameter of LA latices is normally in the range 480–550 nm but, again, a few batches are outside (larger) this range. The differences between the HA and LA latex particle diameters may possibly be statistically significant but further work is required to confirm this.

The distribution of sizes, for both HA and LATZ latices, appears to be bimodal, with modal peaks at approximately 300 nm and 700 nm.

The PCS size technique appears very suitable for measurement of average particle diameters in natural latices and the exponential sampling procedure appears capable of producing a qualitatively correct simulation of the size distribution.

The authors believe that the work described in this paper adds materially to our knowledge of the particle size variations occurring between various batches of natural latex concentrates and also indicates that a bimodal distribution may be the norm for these materials. Much more work remains to be done on this subject, in particular with reference to the variation of size distributions and to changes occurring during storage of fresh concentrates and to the effects of clones and of trees of different ages.

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Thermally-induced Changes in the Mechanical Stabilities of Natural Rubber Latex Concentrates

R.T. DAVIES* AND T.D. PENDLE*

This paper describes an investigation of the increased mechanical stability obtained by heating latex concentrate at 60°C for limited periods. The present study suggests that this does not result from chemical changes due, for example, to accelerated hydrolysis. The heating process appears to affect only the mechanical stability of the latex and the associated property of zinc oxide mechanical stability. It is tentatively suggested that the increase in stability is the result of a reversible structural change in the adsorbed layers on the rubber particles.

The mechanical stability time (MST) of a natural latex concentrate is known to increase markedly during the first three months after centrifugation and it is also known that the storage temperature during this period is important in determining the stability increase. However, once a latex concentrate is three months old, its MST becomes relatively constant and tends to change very little on prolonged storage. It is surprising, therefore, to observe a significant increase in the MST of mature concentrates after a short period of heating at e.g. 60°C. In the present work, the effect of varying the conditions of heat treatment on MST and the effects of heat treatment on other latex properties were investigated in an attempt to find the cause of the phenomenon.

EXPERIMENTAL

The latex concentrates used in these experiments, with the exception of LATZ.2 (the suffix number indicates the sample used), were samples of commercial concentrates imported into the UK in the period 1987-89 and were not less than three months old. The LATZ.2 latex was specially air-mailed to the UK soon after concentration and was only two weeks old at the time of the test.

Mechanical stability tests were carried out in accordance with the international test method (*ISO 35*) at a temperature of 35°C. The zinc

oxide mechanical stability test (ZST) was the 'German' method¹ and the viscosity increase test (ZAAV) was that described by Gorton and Pendle². The KOH numbers referred to in the paper were obtained by the conductimetric titration method of Gorton and Pendle³ but the VFA numbers, alkalinity values, zinc and nitrogen contents and viscosities were all determined by the appropriate ISO test methods.

Latex particle size measurements were carried out by photon correlation spectroscopy using a Malvern 4600 instrument⁴. Each result quoted is the average of ten measurements. The electrophoresis measurements were carried out using an apparatus similar to that described by Blackley and Charnock⁵. The mobile phase was latex diluted to 10% TSC with de-ionised water and the stationary phase was a glycine/sodium chloride/sodium hydroxide buffer solution at the same specific conductivity and pH as the mobile phase. The measurements were made at 25°C.

Measurements of fatty acids were made using the cold extraction method of Chen and Ng⁶ followed by methylation/gas chromatography using heptanoic acid as the internal standard. Latex serum anions were determined by ion-chromatography as previously described⁷. Measurements of specific surface area were carried out by the method described by Chen⁸.

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Measurements of gelling pH and gelling time were carried out at a fixed temperature (25°C) and fixed d.r.c. value (58.0%) by adding 0.8 weight percent of sodium silicofluoride on the weight of rubber.

Low temperature treatments of latex samples were carried out by placing 200 ml of latex in a sealed, screw top, 250 ml bottle in a refrigerator at 4°C for three days or in a freezer at -23°C for 16 h. In both cases, the sample bottles were allowed to return to room temperature naturally. Latex heating experiments were carried out by placing *ca.* 200 g of latex in a 250 ml screw-top polythene bottle, replacing the bottle cap then standing the bottle in a hot-water bath at the required temperature. After the designated heating time, the bottle was removed from the bath and allowed to cool to room temperature ($\sim 23^\circ\text{C}$) naturally. If not otherwise specified, the term, 'heat treatment' refers to conditions of 60°C for 30 min. (The

temperatures quoted are those of the water bath, refrigerator, *etc.* and only in the longer duration experiments are these the same as the temperature of the latex samples. Under the conditions in use in these experiments, the latex samples reached the temperature of the bath after approximately 30 min immersion.)

RESULTS AND DISCUSSION

When it was found, in the course of our studies of the stability behaviour of natural latex, that a short period of heating at 70°C could significantly increase the mechanical stability of latex, it was decided that this phenomenon merited further investigation. Firstly, it was decided to establish the range of heat treatments that would produce a stability increase. Therefore, the effect on the stability of samples of latex of heating for 15 min at a range of temperatures was investigated. The results of these tests are shown graphically in *Figure 1*.

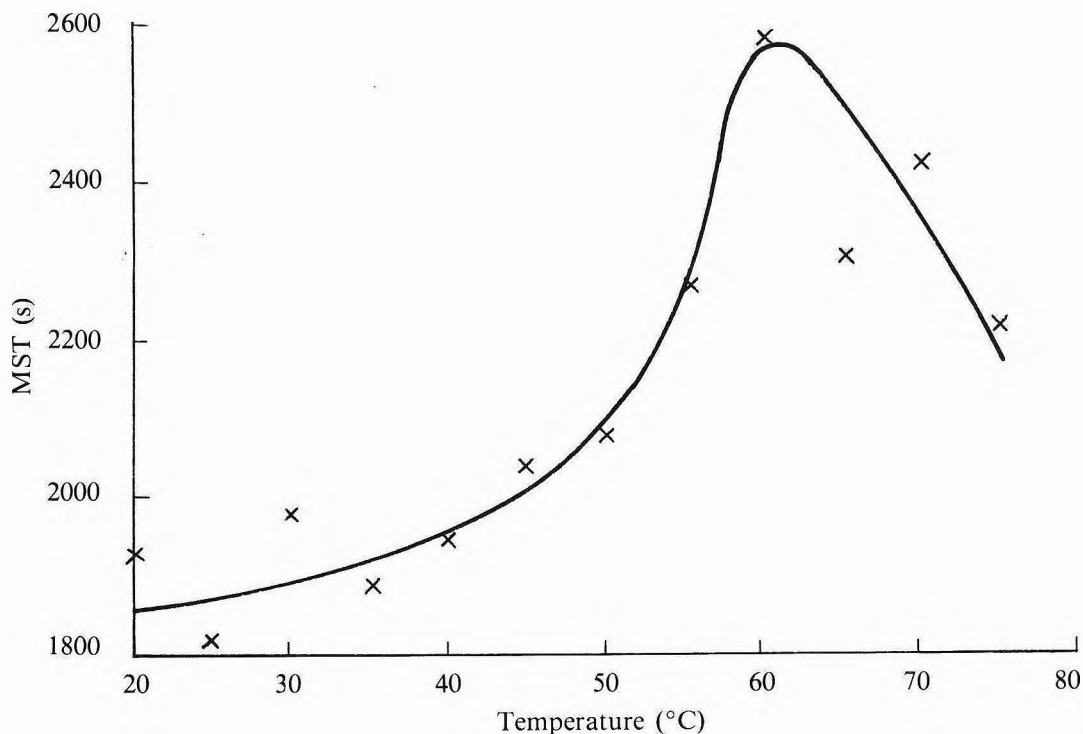


Figure 1. Mechanical stability time of HA. 2 latex as a function of temperature of heat treatment.

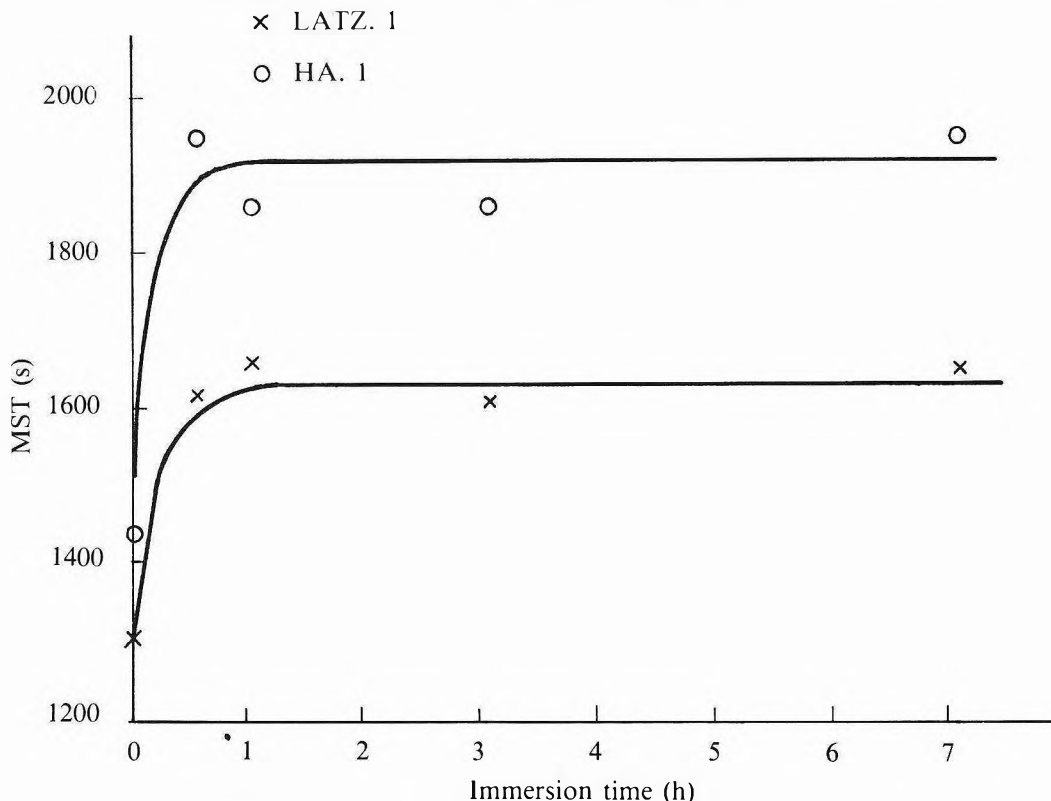


Figure 2. Mechanical stability time of latex as a function of duration of heating.

From these results, it is clear that no increase in mechanical stability is obtained at temperatures below 45°C and that the maximum stability increase occurs at about 60°C. The effect of duration of heating was then examined by heating latices at 60°C for various periods. The results obtained with two latices are shown in Figure 2. From these data, the optimum duration of heating, at 60°C, is 30–60 min and it is clear that prolongation of heating (up to 7 h) has little further effect.

To determine whether the induced stability increase was a permanent effect, two latices that had been heat-treated were stored at room temperature for up to 200 days. Control samples of the same latices were simultaneously stored under the same conditions. At the end of this period, the mechanical stabilities of the heat-treated samples were not greatly different from those of the control samples (Table 1), since the mechanical stabilities of the control samples increased much more during storage.

TABLE 1. MECHANICAL STABILITY CHANGES ON STORAGE IN AIR

Storage time (days)	Mechanical stability changes (ratios to initial control values)			
	HA. 1		LATZ. 1	
	Control	Heated	Control	Heated
0	1.00	1.35	1.00	1.25
200	1.91	1.83	1.62	1.68

The results were essentially the same when the air above the surface of the latex was replaced with nitrogen (*Table 2*), thus suggesting that

the MST increase was not related to the well-known phenomenon of increased stability due to exposure to oxygen⁹. Further evidence of

TABLE 2. MECHANICAL STABILITY CHANGES ON STORAGE UNDER NITROGEN

Storage time (days)	Mechanical stability changes (ratios to initial control values)			
	HA. 1		LATZ. 1	
	Control	Heated	Control	Heated
0	1.00	1.26	1.00	1.22
200	1.85	1.64	1.48	1.52

this was given by the results of experiments in which the air over the latex was replaced by nitrogen during the heat treatment itself (*Table 3*).

This possibility was examined by comparing the effect of heating on two concentrates, one only two weeks old and the other three years old. The results are given in *Table 4* and show that the 'young' concentrate increased in stability much more than the older one. This, again, suggest that the heat treatment is in effect producing an accelerated maturation of the latex.

TABLE 3. INFLUENCE OF AIR AND NITROGEN ON HEAT-TREATMENT EFFECT

Latex sample	Gas over latex sample	MST (s)
HA. 1	Air	2 240
HA. 1	Nitrogen	2 210
LATZ. 1	Air	1 610
LATZ. 1	Nitrogen	1 600

The traditional view of the increase in mechanical stability of a fresh NR latex concentrate on storage is that it arises through hydrolysis of lipids with the consequent production of fatty acid soaps. To investigate whether this short period of heating did produce any detectable change in the fatty acid content of a latex, a comparison was carried out on a HA latex. The results are presented in *Table 5*. It is concluded that no significant difference is detectable between the heated sample and the control. The rise in the mechanical stability of a latex could be due to an increase in the ionic charge on the particles, due to the production of soaps or other ionic species, and this possibility was examined by two independent methods. Electrophoretic mobility measurements were carried out (*Table 6*) and measurements

These results suggest that the heat treatment may simply be accelerating a change that would otherwise have occurred naturally on prolonged storage. If this were the case, some relation to the changes presumed to take place when a fresh latex concentrate matures might be expected. Also, the extent of change in stability on heating would be expected to be greater in a freshly-made concentrate than in an older one.

TABLE 4. INFLUENCE OF AGE OF LATEX ON THE RESULTS OF HEAT TREATMENT

Latex	Age	MST(s)		Relative MST heat treatment
		Normal	Heat-treated	
LATZ. 2	2 weeks	420	840	2.0
LATZ. 3	3 years	1 125	1 245	1.11

TABLE 5. EFFECT OF HEAT TREATMENT ON HIGHER FATTY ACID CONTENT (HA. 6 Latex)

Fatty acid	Concentration (mg/100g latex)	
	Control	Heated
C12	34	35
C14	2	1
C16	32	31
C16:1	2	2
C18	70	72
C18:1	67	69
C18:2	173	183
C18:3	13	14
C20	4	5
Furanoate	9	3
Total	406	415

TABLE 6. EFFECT OF HEAT TREATMENT ON ELECTROPHORETIC MOBILITY

Latex sample	Electrophoretic mobility ($10^{-8} \text{m}^2 \cdot \text{v}^{-1} \cdot \text{s}^{-1}$)	
	Control	Heated
HA. 2	6.3	6.1
LATZ. 4	6.2	6.4
HA. 5	6.4	6.3

TABLE 7. EFFECT OF HEAT TREATMENT ON CONDUCTIMETRIC KOH TITRES (HA. 2 Latex)

Latex/serum	KOH titres (mmoles KOH/100g rubber)	
	Control	Heated
Latex	17.16	17.00
Serum	13.97	13.97
(Latex-serum)	3.19	3.02

TABLE 8. EFFECT OF HEAT TREATMENT ON ZST AND ZAAV VALUES

Latex sample	ZST value(s)		ZST/MST ratio		ZAAV ratio	
	Control	Heated	Control	Heated	Control	Heated
HA. 2	405	455	0.21	0.18	1.2	1.3
LATZ. 4	330	420	0.37	0.36	1.3	1.5

of the total ammonium ion concentrations present in the latex and the serum were also made (*Table 7*). Neither of these methods revealed any significant change due to the heat treatment.

The failure to find evidence of changes in the absorbed surface ions after heat treatment made it necessary to look for alternative explanations. A wider range of latex properties and characteristics was therefore examined for evidence of change due to heat treatment. *Table 8* shows the effects of heat treatment on the zinc stability characteristics of two latices. It can be seen that the zinc oxide mechanical stability values increase, as would be expected, in parallel with the MST values whereas the zinc-ion viscosity stability behaviour (ZAAV value) is essentially unaffected.

The average particle size values of a number of latices were measured before and after heat treatment (*Table 9*) because a change in particle size could conceivably produce a change in mechanical stability. Once again, however, no significant change was detectable.

The concentration and nature of ions in the serum of a latex may play a part in determining its stability and it was therefore decided to analyse the serum anions of a latex before and after the heat treatment. The results of these measurements are given in *Table 10* and indicate no significant change in the total anion concentration or in the concentrations of individual anions. The absence of change in the total anion concentration is consistent with the results obtained by KOH titration of the serum of the same latex (*Table 7*).

Recent work in this laboratory has shown that the quantity of zinc associated with the rubber phase of a latex influences its stability,

TABLE 9. EFFECT OF HEAT TREATMENT ON LATEX PARTICLE SIZE

Latex sample	Z Average diameter (nm)	
	Control	Heated
HA. 3	614	642
HA. 4	553	596
LATZ. 1	533	532
LATZ. 5	527	533
LATZ. 6	536	564

TABLE 10. EFFECT OF HEAT TREATMENT ON SERUM ANION CONCENTRATIONS (HA. 2 Latex)

Anion	Concentration (mmol.dm ⁻³)	
	Control	Heated
Citrate	16.8	17.7
Acetate	15.3	15.9
Malate	13.4	13.3
Succinate	4.83	5.08
α Glycerophosphate	4.44	4.34
β Glycerophosphate	2.32	2.28
Oxalate	1.45	1.34
Formate	1.40	1.53
Phosphate	0.97	0.86
Sulphate	0.95	1.05
Chloride	0.58	0.68
Total	62.54	64.06

this phenomenon will be discussed in a later publication, measurements were therefore made of the distribution of zinc in a LATZ latex

TABLE 11. EFFECT OF HEAT TREATMENT ON THE DISTRIBUTION OF ZINC (LATZ. 1 Latex)

Phase	Zinc content ($\mu\text{g/g}$ latex)	
	Control	Heated
Rubber	121.7	117.1
Serum	82.9	81.0
Sediment	5.9	3.2
Total	210.5	201.3

before and after heat treatment. The results, shown in *Table 11*, indicate no significant change.

With the exception of the MST and ZST values, no other characteristic of the latex has been found to change significantly as a result of heat treatment, including all of the factors likely to affect colloidal stability. To confirm this conclusion, a further range of latex properties were determined before and after heat treatment. The properties measured and the results obtained are shown in *Table 12*. In no case was any effect of heat treatment detected.

The absence of any evidence of chemical or physical changes (other than MST and ZST) after heat treatment suggested that the stability rise could possibly be a consequence of a thermally induced *structural* change in the adsorbed layer at the particle surface. This in turn, suggested that the reverse effect might occur if the latex were cooled. In consequence, experiments were carried out on three latices to

TABLE 12. EFFECT OF HEAT TREATMENT ON VARIOUS LATEX PROPERTIES

Property	Latex	Control	Heated
Viscosity (cP)	HA. 2	95	95
pH of gelation	LATZ. 4	7.38	7.28
Gelling time (s)	LATZ. 4	108	113
Alkalinity (%)	LATZ. 1	0.19	0.21
VFA number	LATZ. 1	0.04	0.04
Surface nitrogen (mg/g latex)	HA. 2	1.69	1.65
Specific surface area (m ² /cc rubber)	LATZ. 1	11.1	11.1

assess whether cooling them would reduce their mechanical stability values. In addition, after cooling to low temperatures and returning to room temperature, samples of the latices were subsequently heat-treated to determine whether an increase in MST could still be obtained. The results of these measurements are given in *Table 13*. It is clear that cooling, even at temperatures well above freezing, does reduce the MST values (measured at 35°C) but that the effect is quite reversible because subsequent heat treatment produces a substantial increase.

Table 14 shows that even the effect of freezing can be partially reversed by subsequent heating although the degree of reversal varies among different latices.

TABLE 13. EFFECT OF COOLING AND HEATING ON THE MECHANICAL STABILITY OF LATICES

Cooling/heating	MST(s)	
	HA. 7	LATZ. 7
Control	1 215	960
Heated	1 470	1 095
Cooled	1 130	900
Cooled then heated	1 405	1 100
Heated then cooled	1 430	1 095

The heat-treatment effect itself is not substantially reversed by subsequent freezing. Again, the degree of reversal depends on the particular latex tested.

TABLE 14. EFFECT OF FREEZING AND HEATING ON THE MECHANICAL STABILITY OF LATICES

Freezing/heating	MST (s)		
	LATZ. 1	HA. 7	LATZ. 7
Control	1 275	1 215	960
Heated	1 600	1 470	1 095
Frozen	980	630	180
Frozen then heated	1 370	880	295
Heated then frozen	1 530	930	310

CONCLUSION

Heating natural latex concentrates, of almost any age, to 60°C produces significant increases in mechanical stability which are not due to changes in the quantity or nature of the adsorbed or serum ions, and are not due to a particle size change. The changes appear to be purely thermally induced and to be at least partially reversible.

It is suggested that the mechanical stability increase may be due to a reversible change in the structural configuration of the adsorbed surface layer, possibly in the adsorbed protein, but there is no direct experimental confirmation of this idea.

The fact that the thermally induced MST increase appears to be an acceleration of the effect of long-term storage suggests in turn that the MST rise observed as latex concentrates mature may not be solely due to the hydrolysis of lipids. This conclusion has also been reached by Hasma¹⁰ on the basis of other evidence.

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Solubility Parameters of Epoxidised Natural Rubber

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Solubility parameter values have been obtained for a series of epoxidised natural rubbers (ENR) both by calculation and from equilibrium swelling data. A 41 mole% epoxidised synthetic cis-1, 4-polyisoprene was also included in the study; its solubility parameter was determined by the viscosity technique. Solubility parameters increased in a linear manner with the extent of epoxidation. These data can be employed to predict a number of ENR properties e.g. polymer solubility, solvent resistance and compatibility with other polymers. However, any specific solvent/ENR or polymer/ENR interactions such as dipole or hydrogen-bonding forces can lead to erroneous conclusions unless these are also taken into account.

Epoxidised natural rubber (ENR) is produced by the chemical modification of natural rubber latex with peroxycarboxylic acids. One consequence of the modification is that resistance to swelling by hydrocarbon oils and solvents increases. These solubility characteristics should be reflected in various thermodynamic interaction parameters. Solubility parameters of ENR have been calculated and derived from swelling measurements. The solubility parameter of a 41 mole% epoxidised synthetic cis-1,4 polyisoprene has also been determined.

The solubility parameter concept is based on Hildebrand's solution theory¹ and can be related to polymer solvent interaction coefficients and to cohesive energy density, which in turn yields information on intermolecular forces in polymers. This data will be useful in predicting a number of polymer properties, e.g. polymer solubility, compatibility with other polymers and solvent resistance.

The solubility parameter of a low molecular weight liquid can be readily determined from its energy of vapourisation but those of polymers cannot be measured in this way as they cannot be vapourised without decomposition.

The solubility parameters of polymers are determined by studying their interactions with a series of solvents of known solubility parameters

and assigning to the polymer the value of the liquid which appears to be the best solvent². This can be achieved by swelling the crosslinked polymer in a series of solvents or the intrinsic viscosity of the polymer can be determined in a series of solvents. In both cases, the solubility parameter of the polymer is assumed to be that of the solvent in which a maximum in the property measured, swelling or intrinsic viscosity, occurs. The values of solubility parameter determined by the above methods can depend on the type of solvents used. This is particularly noticeable when strong hydrogen-bonding solvents are employed which can interact with functional groups in the polymer. A 'three dimensional' solubility parameter has been described³ to take account of dispersion forces, dipole forces and hydrogen bonding, but in this work a simple approach was taken with care to avoid the use of strong hydrogen-bonding solvents.

Solubility parameter values can also be obtained from a knowledge of the chemical structure and density of the polymer by utilising the concept of molar attraction constants developed by Small⁴.

The above methods have been utilised to determine the solubility parameters of a range of epoxidised natural rubbers.

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EXPERIMENTAL

Materials

The natural rubber (NR) used was a sample of Malaysian SMR L; 26 mole% and 48 mole% epoxidised natural rubbers (ENR 26 and ENR 48) were obtained from the Rubber Research Institute of Malaysia and 71 mole% epoxidised natural rubber (ENR 71) prepared by epoxidation of NR latex employing peroxyacetic acid solution⁵. The 41 mole% epoxidised synthetic *cis*-1,4 polyisoprene was prepared from Cariflex IR305 (Shell) by reaction with peroxyacetic acid in dichloromethane solution.

Samples for the swelling measurements were taken from 2 mm thick sheets which were produced by crosslinking the rubbers with 1.5 p.p.h.r. of dicumyl peroxide.

Oil resistance measurements (*ISO 1817*) were carried out on vulcanisates produced according to the formulations in *Table 1*.

All the solvents used were of laboratory reagent standard with a purity >99%. Their solubility parameters are recorded in *Table 2*.

Prior to swelling, all the rubber vulcanisates were extracted with acetone in a soxhlet apparatus for 24 h under an atmosphere of nitrogen. The extracted samples were dried to constant weight under vacuum.

Equilibrium Swelling Measurements

Samples 30 × 5 × 2 mm of the extracted vulcanisates were weighed accurately and then immersed in a glass vessel containing the solvent (30 cm³) at 23°C. The vessels were stored in the dark and periodically the rubber samples removed, dried of excess surface solvent with lens tissue, and weighed in a closed bottle to prevent evaporation. The sample was replaced in the solvent and the process repeated until a constant weight was obtained. The fraction of solvent swollen in the rubber was determined by drying the sample under vacuum.

Viscosity Measurements

Flow times of solvents of known solubility parameters (*Table 2*) and of solutions of 41 mole% epoxidised *cis*-1,4 polyisoprene in these solvents within the concentration range 0.02 – 0.21 g/dl were measured in an Ubbelohde viscometer at 23°C. Intrinsic viscosities were determined from double plots of η_{sp}/C and $1/\eta_r$ against C ; η_{sp} is specific viscosity, η_r is relative viscosity and C is concentration.

RESULTS AND DISCUSSION

Equilibrium swelling measurements on NR, ENR 26, ENR 48 and ENR 71 gum peroxide vulcanisates were carried out in a range of solvents of known solubility parameters. The results are recorded in *Table 2*. The volume fraction of solvent in the samples, swollen to equilibrium, are plotted against the solubility parameter of the solvent in *Figure 1*. The values of solubility parameter for NR and the ENR estimated by this technique are recorded in *Table 3*. The accuracy of the solubility parameter values determined by this technique depends on the positioning of the curve maximum. In the case of ENR 71 data, it is not possible to determine the maximum with any real accuracy because of a low dependence of swelling on δ for this polymer.

Solubility parameters can also be obtained from swelling data *via* the modified Flory-Rehner equation:

$$-\ln(1-Vr) - Vr - \chi Vr^2 = \rho V_0 (Vr^{1/3} - V_0^{-1/3} Vr) / Mc \dots 1$$

where V_0 = molar volume of solvent
 Vr = volume fraction of rubber in the swollen network
 χ = polymer solvent interaction parameter
 Mc = average molecular weight of rubber chains between crosslinks
 ρ = density of rubber.

From a knowledge of the polymer solvent interaction parameters (χ), solubility parameters (δ) can be calculated from Huggins' equation⁶:

$$\chi = \beta^1 + (V_0)_{RT} (\delta_1 - \delta_2)^2 \dots 2$$

TABLE 1. FORMULATIONS EMPLOYED TO DETERMINE THE OIL RESISTANCE OF POLYMERS

Item	Formulation						
	1	2	3	4	5	6	7
Polymer	NR	ENR 26	ENR 48	NBR ^c	NBR ^f	NBR ^g	Polychloroprene ^h
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
Antioxidant ^a	2	2	2	2	2	2	2
S	1.3	1.22	1.14	0.87	0.67	0.99	0.45
MBS ^b	1.3	1.22	1.14	0.87	0.67	0.99	—
TMTD ^c	0.2	0.19	0.17	0.13	0.1	0.15	0.8
DPG ^d	—	—	—	—	—	—	0.8
Vulcanisates cured to optimum at 150°C							
Modulus at 100% extension (MPa)	0.84	0.80	0.83	0.83	0.82	0.85	0.82
Modulus at 300% extension (MPa)	1.97	1.80	1.80	1.13	1.05	1.23	1.38
Tensile strength (MPa)	20.5	21.3	23.2	3.1	2.7	3.9	16.5
Elongation at break (%)	640	680	710	800	823	675	830
Oil resistance							
Volume swelling (%), 70 h at 100°C							
ASTM No. 1 oil	130	31	4	13	3	2	19
ASTM No. 2 oil	194	104	36	51	16	8	60
ASTM No. 3 oil	276	190	80	98	40	17	141

^a Poly 2,2,4-trimethyl 1,2-dihydroquinoline

^b 2-Morpholinothiobenzothiazole-2-sulphenamide

^c Tetramethylthiuram disulphide

^d Diphenyl guanidine

^e 18% Acrylonitrile NBR

^f 28% Acrylonitrile NBR

^g 34% Acrylonitrile NBR

^h Baypren 110

TABLE 2. EQUILIBRIUM SWELLING OF NR, ENR 26, ENR 48 AND ENR 71 GUM PEROXIDE VULCANISATES AT 23°C

Polymer	Solvent (δ) ^a	V _s	V _r	χ
NR	Pentane [14.4 (MPa) ^{1/2}]	0.623	0.377	0.618
	Hexane [14.9 (MPa) ^{1/2}]	0.671	0.329	0.559
	Octane [15.6 (MPa) ^{1/2}]	0.691	0.309	0.513
	Decane [15.9 (MPa) ^{1/2}]	0.678	0.322	0.510
	Cyclohexane [16.8 (MPa) ^{1/2}]	0.792	0.210	0.433
	Butyl acetate [17.4 (MPa) ^{1/2}]	0.642	0.358	0.589
	Methyl propyl ketone [17.8 (MPa) ^{1/2}]	0.505	0.495	0.736
ENR 26	Decane [15.8 (MPa) ^{1/2}]	0.444	0.556	0.782
	Cyclohexane [16.8 (MPa) ^{1/2}]	0.717	0.283	0.526
	Methyl isobutyl ketone [17.2 (MPa) ^{1/2}]	0.737	0.263	0.487
	Butyl acetate [17.4 (MPa) ^{1/2}]	0.763	0.237	0.440
	Methyl propyl ketone [17.8 (MPa) ^{1/2}]	0.667	0.333	0.581
ENR 48	Cyclohexane [16.8 (MPa) ^{1/2}]	0.525	0.475	0.715
	Methyl isobutyl ketone [17.2 (MPa) ^{1/2}]	0.788	0.212	0.448
	Butyl acetate [17.4 (MPa) ^{1/2}]	0.789	0.211	0.422
	Toluene [18.2 (MPa) ^{1/2}]	0.830	0.170	0.376
	Ethyl acetate [18.6 (MPa) ^{1/2}]	0.753	0.247	0.498
	Methyl ethyl ketone [19.0 (MPa) ^{1/2}]	0.770	0.230	0.513
ENR 71	Butyl acetate [17.4 (MPa) ^{1/2}]	0.815	0.185	0.424
	Methyl propyl ketone [17.8 (MPa) ^{1/2}]	0.824	0.176	0.435
	Methyl propionate [18.2 (MPa) ^{1/2}]	0.806	0.194	0.477
	Methyl ethyl ketone [19.0 (MPa) ^{1/2}]	0.808	0.192	0.480
	Acetone [20.3 (MPa) ^{1/2}]	0.746	0.254	0.560
	Methyl formate [20.8 (MPa) ^{1/2}]	0.755	0.245	0.558

V_s = Volume fraction of solvent

V_r = Volume fraction of rubber

χ = Solvent polymer interaction parameter

^aSolubility parameter of solvent²

In order to determine the interaction parameter, the number average molecular weight of rubber chains between crosslinks in the vulcanisate has to be established. These can be obtained from C₁ values:

$$C_1 = \rho RT_{/2Mc} \quad \dots 3$$

C₁ values (Table 4) were obtained by the standard procedure from stress strain measurements on the unswollen vulcanisates⁷. Bristow and Porter have shown that comparable C₁ values are obtained from swollen

vulcanisates⁷. The values for χ presented in Table 4 were calculated using Equations 1 and 3.

Assuming that Equation 2 represents a valid means of determining solubility parameters, rearrangement gives:

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_0} = [2\delta_2/RT]\delta_1 - \frac{\delta_2^2}{RT} - \beta^1_{/V_0}$$

The slope of the plot of $\delta_1^2/RT - \chi/V_0$ against δ_1 thus yields the solubility parameter of the polymer. Good straight-line plots (Figure 2)

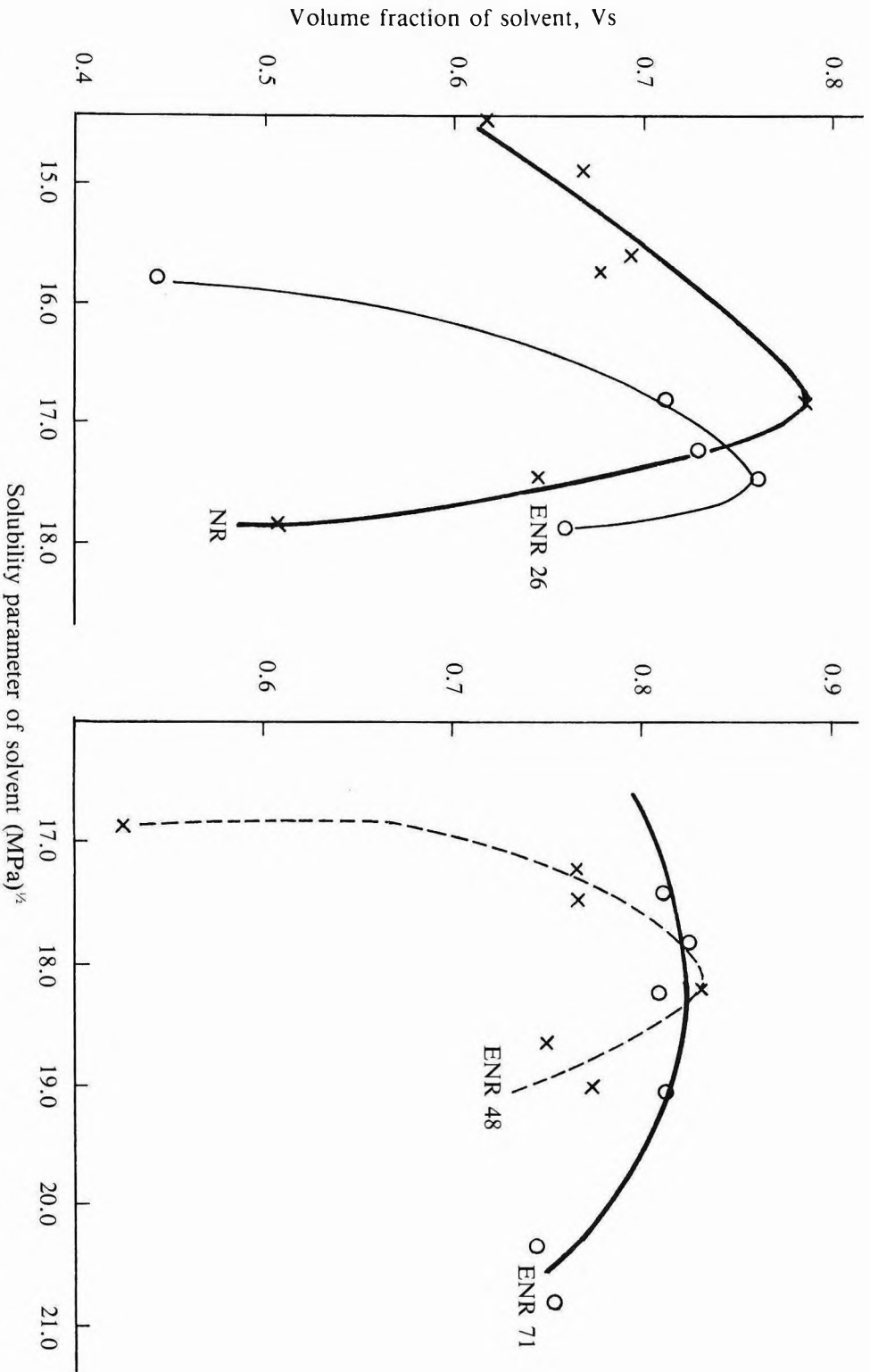


Figure 1. Equilibrium swelling of gum peroxide vulcanisates of NR, ENR 26, ENR 48 and ENR 71 at 23°C in a range of solvents of known solubility parameters.

TABLE 3. SOLUBILITY PARAMETERS OF NR AND ENR

Polymer	Solubility parameter (MPa) ^{1/2}			
	A	B	C	D
NR	16.8	16.9	17.0	—
ENR 26	17.4	17.4	17.6	—
ENR 48	18.1	18.2	18.2	—
ENR 71	18.4	18.7	18.6	—
ENR 41 ^a	—	—	17.9	17.8

A - Values determined from equilibrium swelling plots

B - Values determined *via* modified Flory-Rehner equation⁴

C - Calculated by Small's method using Hoy's constants

D - Value determined from viscosity measurements

^a41 mole% epoxidised Cariflex IR305

TABLE 4. ELASTIC PARAMETER, C₁ OF THE EXTRACTED PEROXIDE CROSSLINKED RUBBERS USED IN THE SWELLING MEASUREMENTS

Vulcanisate	C ₁ (MPa)
NR	0.174
ENR 26	0.165
ENR 48	0.137
ENR 71	0.101

were obtained employing the data recorded in *Table 2*. The solubility parameters of NR and the ENR obtained are recorded in *Table 3*.

Solubility parameters of polymers can also be estimated from 'molar attraction constants', a technique which was developed by Small⁴. He assumed that the geometric mean rule holds and thus the contributions of the different groups in the polymer are additive, *i.e.*

$$\delta = \frac{(\Sigma F)}{V}$$

F = molar attraction constant, V = molar volume of a polymeric repeat unit which contains all the different groups.

The solubility parameters of the ENR studied in this paper were calculated employing the molar attraction constants established by Hoy⁸ and the results are recorded in *Table 3*.

The solubility parameter of a 41 mole% epoxidised synthetic *cis*-1,4 polyisoprene was also determined, in this case, the viscosity technique⁴ was employed. The intrinsic viscosities of the polymer are plotted in *Figure 3*. The solubility parameter of the polymer was assigned as that at which the maximum intrinsic viscosity was observed (*Table 3*).

All the results are collected together in *Figure 4* which plots solubility parameter against the extent of epoxidation of the rubber. A linear relationship is observed with the solubility parameter increasing with the level of epoxidation.

The resistance of rubbers to hydrocarbon oils is normally measured by determining their volume swell in standard ASTM oils. It is possible to estimate the oil resistance of a rubber from its solubility parameter. This is illustrated in *Figure 5*, where the oil resistance of a series of rubber vulcanisates of similar modulus (*Table 1*) are plotted against their solubility parameters. During this work, it was noted that the literature solubility parameter values^{4,9} of polychloroprene cover a wide range, 16.6 (MPa)^{1/2} to 19.2 (MPa)^{1/2}. Data obtained from the swelling of polychloroprene, ENR and NBR in ASTM No. 1, 2 and 3 oils (*Table 1*) would indicate a solubility parameter for chloroprene of 17.6 (MPa)^{1/2} to 17.7 (MPa)^{1/2} (*Figure 5*). The solubility parameter values for NBR were taken from the *Polymer Handbook*¹⁰.

Ply adhesion values between ENR and other polymers have been published¹¹. The adhesive strength between NR and a series of ENR can be related to the solubility parameters, as the difference in the polymer-polymer interaction parameters increases, the adhesive strength decreases.

A number of ENR properties can be predicted from solubility parameter values, but this approach needs to be treated with care. For example, the adhesive strength between poly vinyl chloride (PVC) and ENR 50 is high and the two components have been shown to be completely compatible¹¹, only one glass transition temperature is observed intermediate

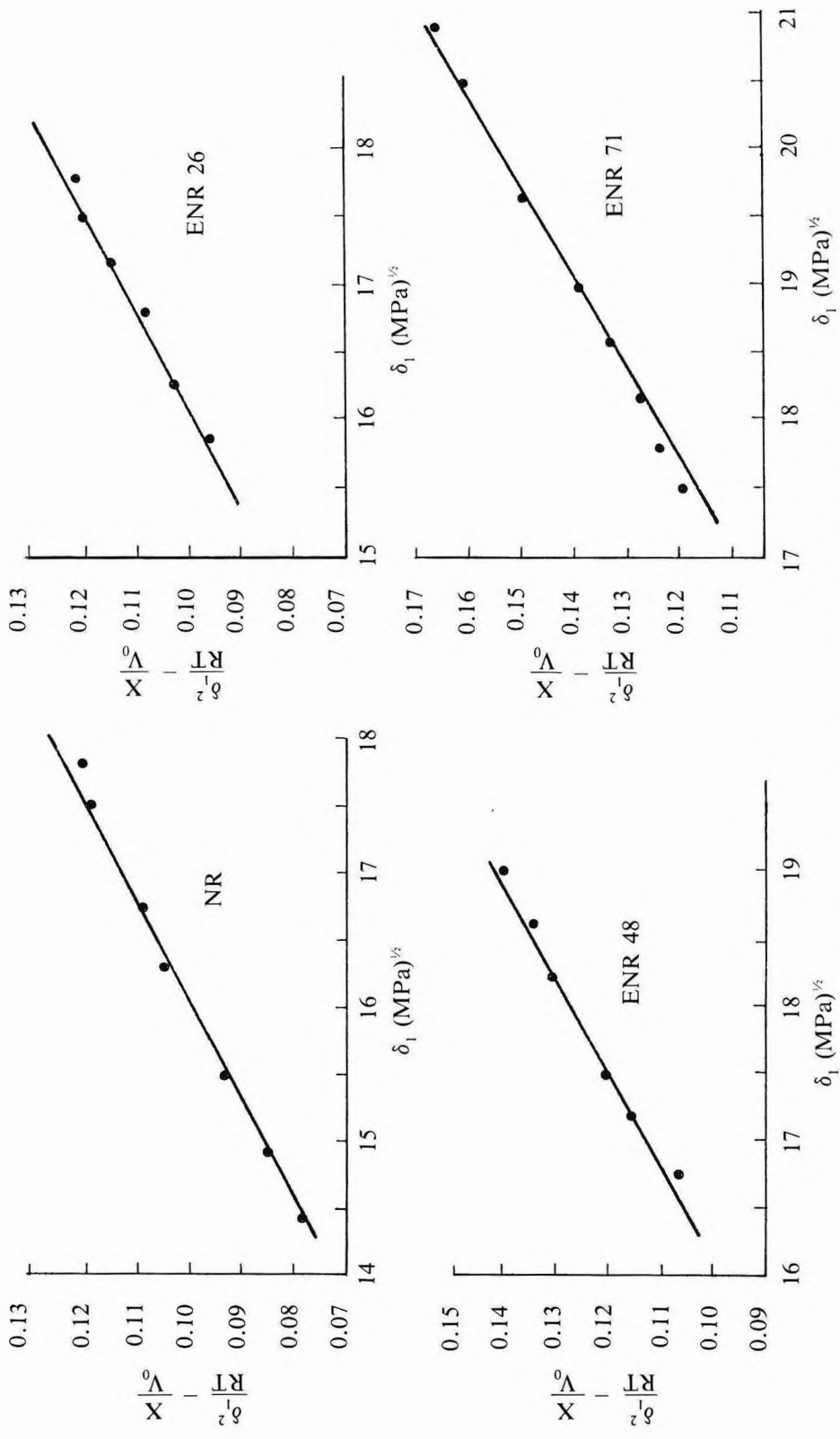


Figure 2. Modified Flory-Rehner plots of volume swelling data for NR, ENR 26, ENR 48 and ENR 71 to determine solubility parameters.

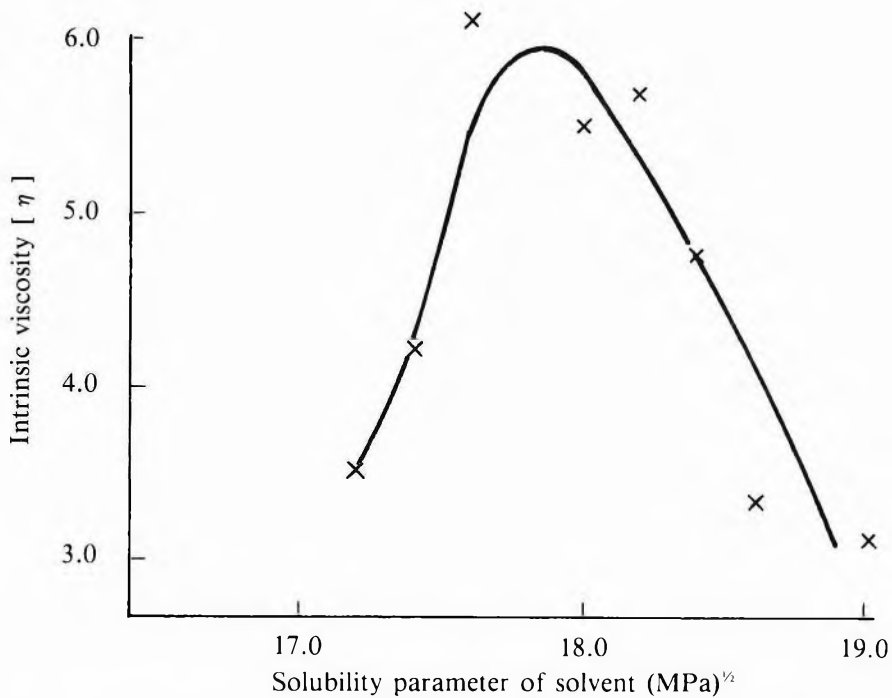


Figure 3. Plot of intrinsic viscosity of 41 mole% epoxidised Cariflex IR305 in a range of solvents of known solubility parameters.

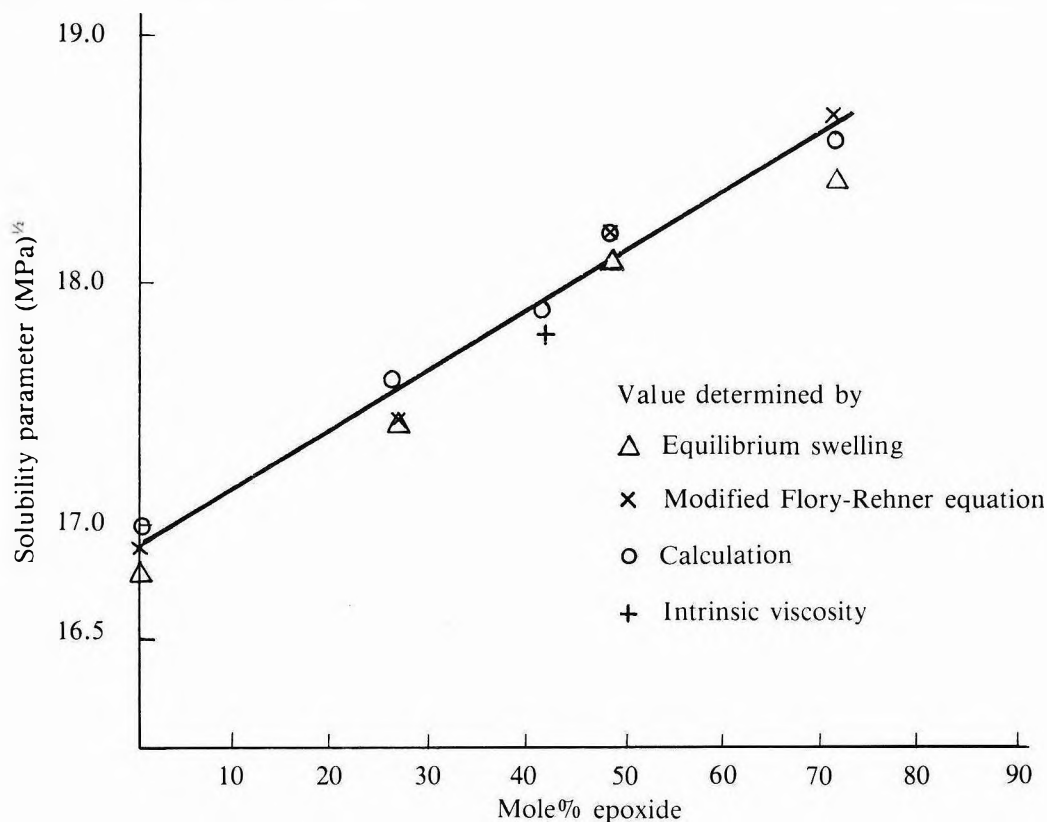


Figure 4. Dependence of solubility parameters of ENR on epoxide content.

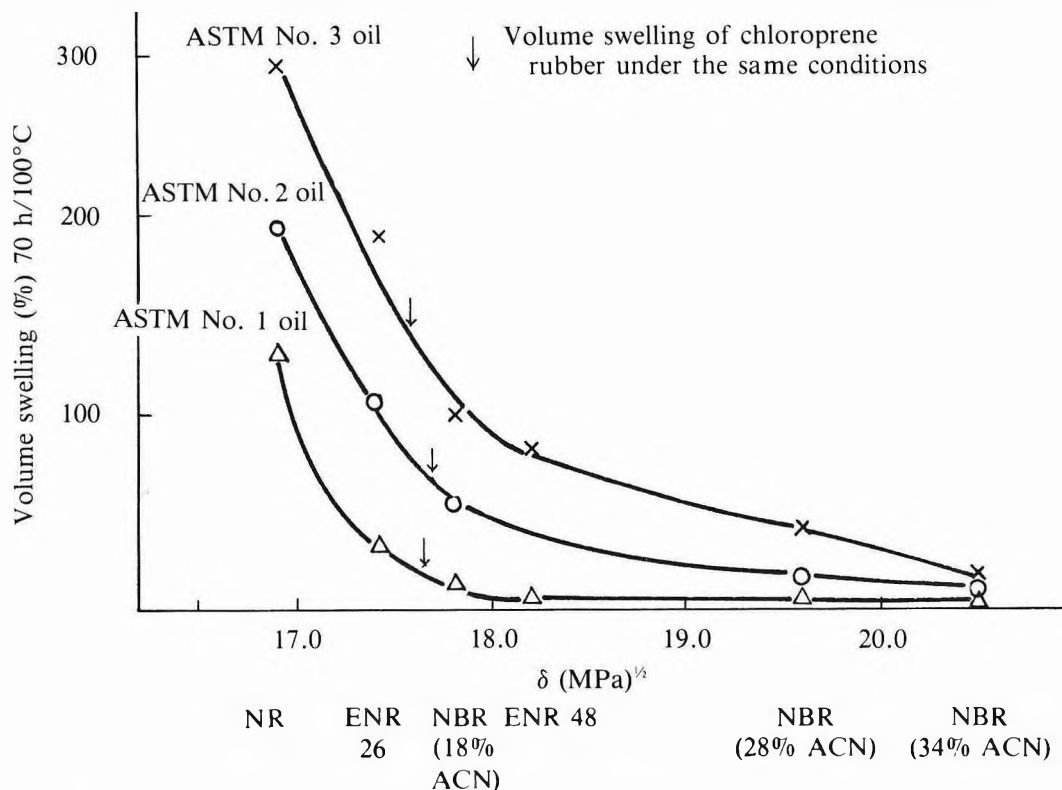


Figure 5. Volume swelling of a series of ENR and NBR of known solubility parameters in ASTM oils.

between that of ENR 50 and PVC. The difference in solubility parameters of these materials is $1.3 \text{ (MPa)}^{1/2}$. However, the solubility parameters of ENR 25 and ENR 50 differ by only $0.7 \text{ (MPa)}^{1/2}$, yet the adhesive strength between these two materials is only moderate¹¹ and they are not compatible, the two individual glass transition temperatures are observed by differential scanning calorimetry.

The unexpected high degree of compatibility between ENR and PVC can be ascribed to polar/polar and/or donor-acceptor interactions between the acidic α hydrogen of PVC and the epoxide groups¹².

Chloroprene rubber and ENR 50 are also completely compatible¹³, in this case the difference in solubility parameter is $0.5 \text{ (MPa)}^{1/2}$ but it is known¹⁴ that ENR with a solubility parameter difference of only $0.3 \text{ (MPa)}^{1/2}$ are

not compatible and hence specific interactions also probably contribute to the miscibility of chloroprene and ENR 50.

When using solubility parameters of ENR to predict interactions with solvents or other polymers, consideration must be given to the possible involvement of dipole and hydrogen-bonding forces.

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Exudation of Plasticiser from Vulcanised Rubbers

K. MUNIANDY* AND A.G. THOMAS**

A rather intriguing exudation process, termed sweating is described. This process which does not appear to be due to supersaturation effects, seems at first sight to contradict the thermodynamics of equilibrium swelling. Conditions and factors which affect this process in natural and synthetic rubber vulcanisates, previously swollen to equilibrium in dioctylphthalate, are discussed. It is suggested that the process could be due to surface tension effects caused by the presence of impurities or imperfections on the swollen rubber surface or simply contact of the swollen rubber with foreign substrates.

Rubber compounds contain a variety of ingredients which in some instances can include oils and plasticisers. These are usually incorporated into the rubber at moderately high temperatures because they then become more soluble in the polymer. When the compounded and subsequently vulcanised rubber is cooled to ambient temperatures, the solubility of some of the ingredients in the rubber becomes much reduced and they move to the rubber surface. This supersaturation model is applicable if the material does not precipitate out in the bulk of the rubber. If precipitation does occur, then a different mechanism which involves elastic stresses acting around the precipitates, provides the necessary driving force for the movement of the material to the rubber surface. Such is the case for wax blooming in rubber vulcanisates¹.

However, it has been found that such conditions are not always necessary. If a sheet of rubber, swollen to equilibrium in a high swelling non-volatile liquid at a particular temperature, is taken out of the liquid, its surfaces cleaned and left otherwise undisturbed at the same temperature, droplets of the liquid somewhat similar in character to beads of sweat, form on the surface of the rubber after some time. This phenomenon of 'sweating' is not unique to any type of liquid and many liquids which swell the rubber appreciably (e.g. plasticisers) show this behaviour. Nah² carried

out some studies on this phenomenon. He found that sweating occurred in both unextracted and acetone-extracted natural rubber (NR) vulcanisates and that the liquid which sweated to the rubber surface was virtually identical to the liquid in which the rubber was previously swollen except for minute traces of unidentified materials. Nah also observed that when a sample which had sweated for some time was re-immersed in the liquid, re-swelling occurred and the equilibrium swelling attained was virtually identical to the original².

The phenomenon is puzzling from the thermodynamic point of view. During the sweating process, the rubber is apparently in equilibrium with the liquid droplets on its surface, but this equilibrium is not the same as that found when the rubber is completely immersed in the liquid. The reason for this is not immediately obvious, and this paper reports and discusses investigations aimed at clarifying the mechanism.

MATERIALS AND METHODS

The liquid used for these investigations was dioctylphthalate (DOP) because it is sufficiently non-volatile and exhibits considerable sweating². Acetone-extracted peroxide-cured natural and synthetic rubber vulcanisates were used. Such a cure system eliminates

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complications in the interpretation of results caused by vulcanisation ingredients and residues. The rubber formulations for the various rubbers used are given in *Table 1*.

TABLE 1. RUBBER FORMULATIONS

Vulcanisate	Amount (parts by weight)
NR	
NR (SMR L)	100.0
Dicumyl peroxide	2.0
BR	
BR (Europrene)	100.0
Dicumyl peroxide	0.6
IR	
IR (Cariflex IR 305)	100.0
Dicumyl peroxide	1.0
EPM	
EPM (Vistalon 404)	100.0
Dicumyl peroxide	2.5

All four rubber samples were vulcanised for 10 min at 100°C followed by 60 min at 160°C

Test samples, usually 50 mm square and about 0.6 mm thick were used. These were immersed in DOP and their weight regularly monitored until equilibrium swelling was reached. Once this was attained, the samples were cleaned with filter paper to remove the excess liquid on the rubber surface and then allowed to sweat under various experimental conditions. The amount of sweating was monitored by weighing the sample periodically after cleaning, using an analytical balance.

RESULTS AND DISCUSSION

Figure 1 shows typical swelling and sweating curves of the NR vulcanisate at $(30 \pm 0.2)^\circ\text{C}$ and serves to illustrate the essential features of the sweating phenomenon. For this particular case, the swollen rubber was wrapped up in aluminium foil and allowed to sweat. The mass uptake (swelling) or loss (sweating) of plasticiser

per unit area, M_p , has been corrected for lateral increase in the dimensions of the testpiece, which usually occurs as a result of swelling. This is done by multiplying the weight change by $(v_r^{2/3}/A_0)$, where v_r is the volume fraction of rubber and A_0 the total unswollen area of the sample.

The swelling curve (*Curve A*) in *Figure 1* has the general features of a diffusion-controlled process from which an average diffusion coefficient can be calculated. Since the rubber swells considerably, the mutual diffusion coefficient³, D^* , is probably more appropriate although it is realised that this quantity, appropriate for diffusion in one dimension only, is not strictly applicable to isotropic swelling. For this NR vulcanisate which had a shear modulus, G , of 0.5 MPa, the weight uptake of DOP at 30°C was 120% and its mutual diffusion coefficient $1.5 \times 10^{-12} \text{ m}^2\text{s}^{-1}$.

Curve B in *Figure 1*, the sweating curve, shows an initial linear relationship between M_p and \sqrt{t} where t is the time for which the sample has been allowed to sweat. This coupled with the fact that the sweating rate was independent of the sample thickness² suggest that the process is diffusion-controlled. However, at longer times, this curve tends to become convex to the \sqrt{t} axis probably due to oxidation of the highly swollen rubber and its removal during the cleaning process prior to weighing. The initial sweating rate was $4.1 \times 10^{-6} \text{ kg m}^{-2}\text{s}^{-1/2}$ while the swelling rate was $9.2 \times 10^{-5} \text{ kg m}^{-2}\text{s}^{-1/2}$. This suggests a much lower diffusion coefficient (D) of the DOP during the sweating process. The low D during sweating is however, not due to concentration effects on D since the asymptotic D of the plasticiser, near equilibrium swelling, was similar to that calculated from the initial slope of the swelling curve, both being about $2 \times 10^{-12} \text{ m}^2\text{s}^{-1}$. It should be noted that after twenty-seven days, the amount of material that had exuded to the surface of the rubber was only about 3% of the equilibrium plasticiser uptake and the process persisted even after three months by which time the rubber sample had also become quite sticky.

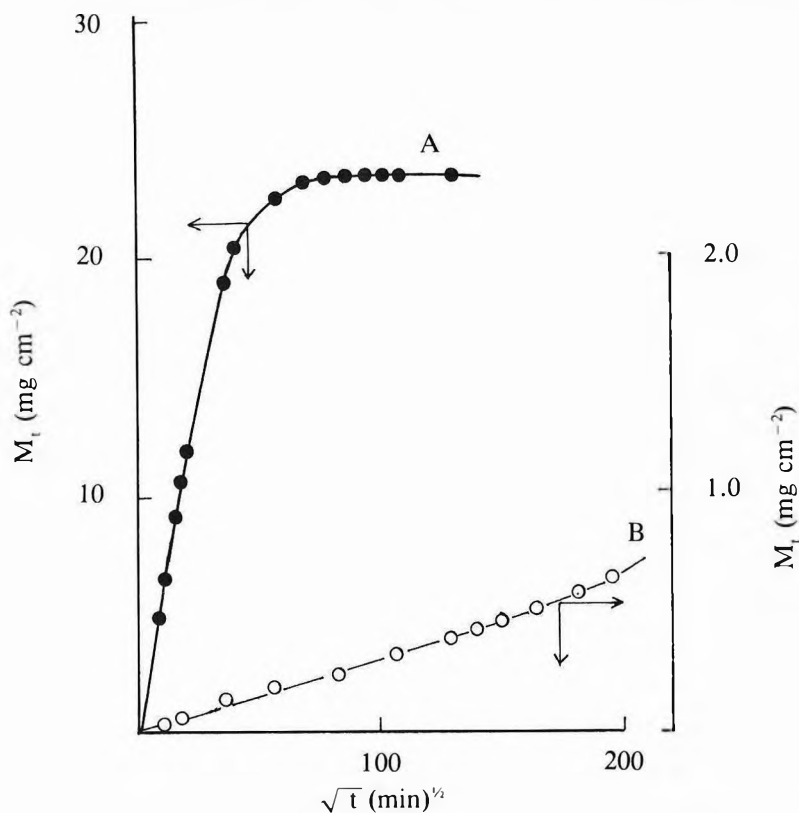


Figure 1. Swelling A and sweating B curves of dioctylphthalate in vulcanised natural rubber (2.0 p.p.h.r. DCP) at 30°C.

Effect of Materials in Contact with the Swollen Rubber

Samples of the NR vulcanisate, swollen to equilibrium in DOP at $(30 \pm 0.2)^\circ\text{C}$, were allowed to sweat at the same temperature under the following conditions: a) wrapped up in aluminium foil; b) sandwiched between two Whatman Qualitative No. 1 filter papers; c) dusted with ballotini No. 15 (*i.e.* glass beads whose diameters were between $60 \mu\text{m}$ and $95 \mu\text{m}$) and then wrapped up with aluminium foil; and d) ballotini-treated as in c) but the sample was sandwiched between two of the same filter papers as above. After weighing, all the rubber samples were either wrapped up with clean aluminium foil or sandwiched between clean filter papers, as necessary, before being returned to the oven at $(30 \pm 0.2)^\circ\text{C}$. For

samples treated with ballotini, fresh ballotini was dusted onto the rubber surfaces before the samples were re-wrapped. Figure 2 shows the results of this experiment.

For low sweating rates (*Curves C and D*), the initial linear region extends for a long time, up to about twenty-five days while for high sweating rates (*Curves A and B*), the linear regions extend either for a short time or are virtually non-existent. The amount of sweating is greater when the swollen rubber is in contact with filter paper than with aluminium foil, especially at longer times. Figure 2 also shows that dusting the samples with ballotini effectively reduces the amount of sweating.

If it is assumed that the mechanism of sweating is due to surface tension forces at

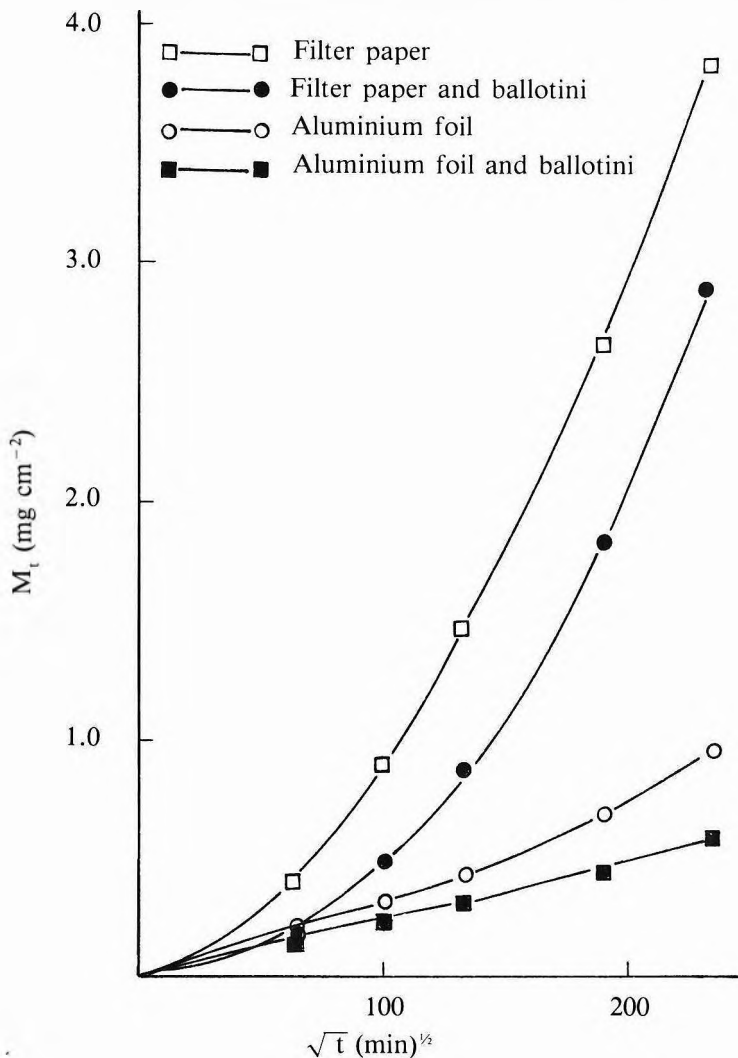


Figure 2. Effect of surface contact conditions on the sweating rate of DOP from a NR vulcanisate (2.0 p.p.h.r. DCP) at 30°C.

points of contact between the rubber and any foreign material such as dust, filter paper debris, filter paper or aluminium foil, then the above results imply that these points of contact are fewer when the swollen sample is wrapped up with aluminium foil than with filter paper. However, the surface tension hypothesis does not provide an explanation why the process continues over such long periods even after the amount of liquid exuded is more than sufficient to saturate the foreign material⁴.

The higher sweating rate observed with filter paper could be due to it being absorbent but this effect cannot be large since droplets of DOP were still seen on the rubber surface. This suggests that intimate contact was lacking between paper and rubber and placing a light load on the paper did indeed increase the sweating rate and there were many fewer discrete DOP droplets seen on the rubber surface. This increased sweating over the 'no-load' condition is shown in Figure 3, where

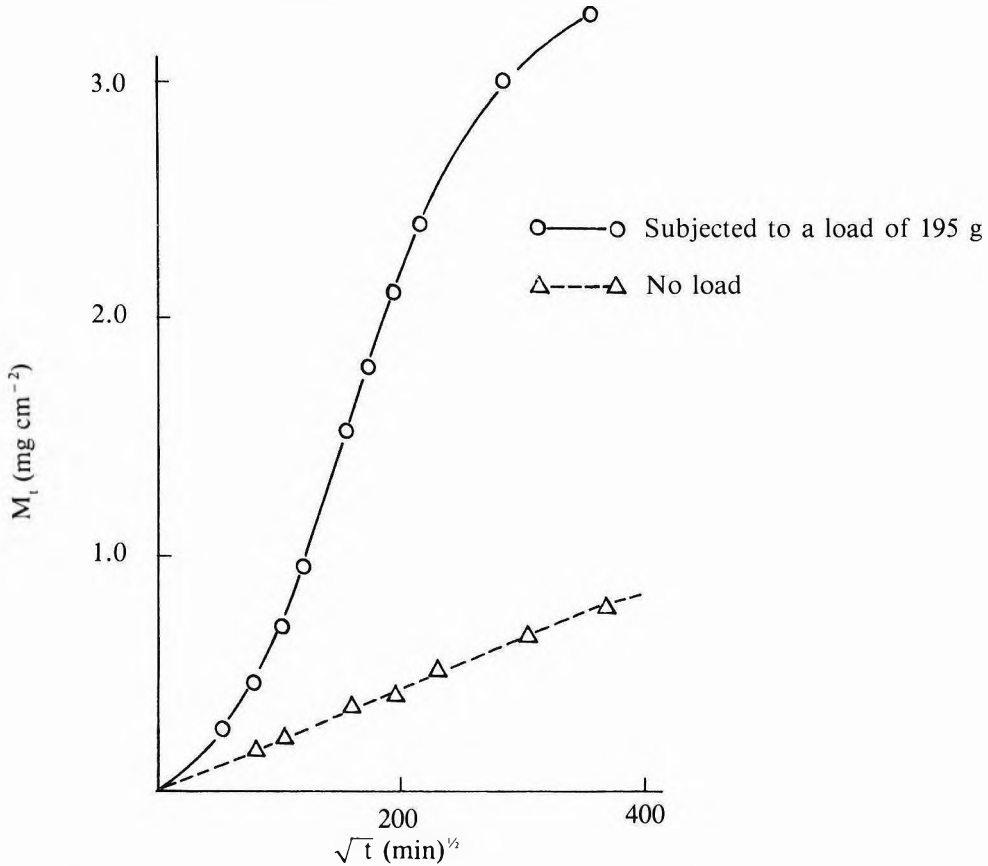


Figure 3. Sweating of DOP from swollen NR vulcanisate (1.6 p.p.h.r. DCP). Rubber sandwiched between two Whatman No. 42 filter papers.

a load of 195 g was evenly applied to the filter paper/rubber sandwich. The hydrostatic pressure required to change the equilibrium swelling in the rubber by the amount of DOP that had sweated out from these rubbers after three months was calculated from the Flory-Huggins equation⁵ and was found to be 0.09 MPa. This value is one hundred times higher than the pressure acting on the sample due to a load of 195 g. Thus, the increased sweating must be associated with a more intimate contact between the fibres in the filter paper and the swollen rubber. This would give rise to more points of contact between the two which, according to the surface tension hypothesis, would result in more sweating.

The effect of ballotini on the sweating rate, shown in Figure 2, is a little puzzling. It is possible that the presence of the glass beads causes a net reduction in the surface tension forces acting on the liquid in the rubber since these beads will generally be larger than dust particles. However, why there should be a difference in sweating rates of ballotini-dusted samples that were wrapped up in aluminium foil and those sandwiched between filter papers is not entirely clear. Since it was observed that in the latter case the bottom filter paper always tended to have more DOP stains than the top one, it is suggested that the sweated liquid runs down the spaces between the glass beads and is subsequently absorbed by the bottom filter

paper giving rise to the observed higher sweating.

This investigation shows that the sweating rate can be altered by changing the physical conditions at the surface of the swollen rubber suggesting that the phenomenon is merely due to surface effects. It is therefore in accord with the hypothesis suggested above, which is that the driving force for the phenomenon is derived from surface tension effects acting on the liquid near the surface of the rubber caused by the presence of foreign contacts on the swollen rubber surfaces.

Sweating in Other Rubber Vulcanisates

So far, the discussion of sweating has been limited to NR. However, this phenomenon

is also observed in other rubber vulcanisates and results are presented for synthetic *cis*-polyisoprene (IR), *cis*-polybutadiene rubber (BR) and ethylene propylene copolymer (EPM). These polymers were chosen because of the specific differences over NR. IR is a synthetic analogue of NR but has a much lower impurity content. BR affords a higher mobility to DOP while EPM is relatively more resistant to oxidation than NR.

Acetone-extracted samples of the synthetic vulcanisates, 0.5 mm thick and 5 mm square, were swollen to equilibrium in DOP at 21°C and then allowed to sweat wrapped up in aluminium foil at the same temperature. The swelling curves for the three vulcanisates are shown in *Figure 4*. From such curves,

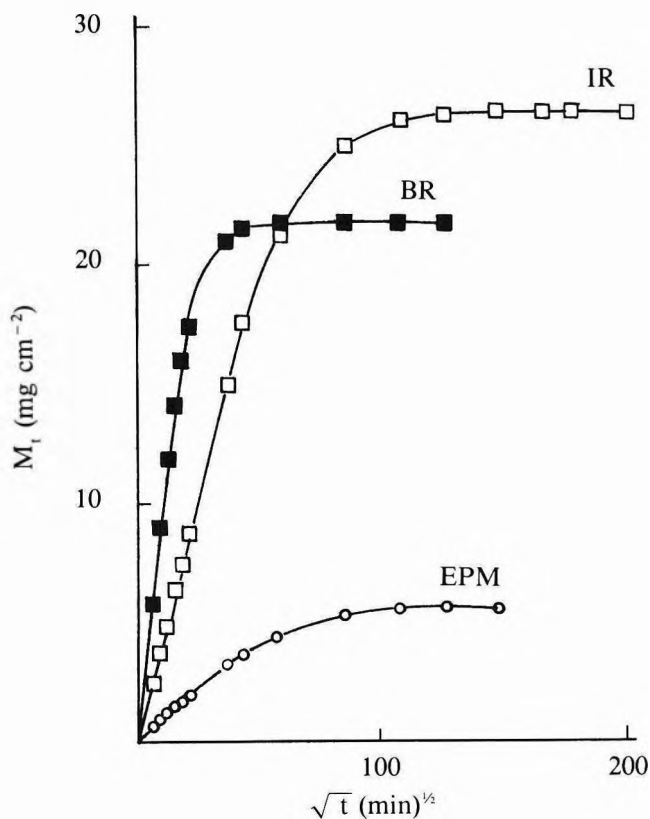


Figure 4. Swelling of some synthetic rubbers in DOP at 21°C.

TABLE 2. SWELLING PARAMETERS OF VARIOUS RUBBER VULCANISATES IN DIOCTYLPHTHALATE AT 21°C

Rubber	Shear Modulus G (MPa)	Equilibrium uptake (%)	v_r	X	$D^v \times 10^{12}$ ($m^2 S^{-1}$)
BR	0.46	135	0.446	0.44	4.6
IR	0.29	146	0.428	0.52	0.8
EPM	0.28	23	0.835	1.33	0.4
NR ^a	0.30	119	0.411	0.47	1.2

^a Refers to data calculated from Nah's results² for a NR vulcanisate cured with 1.0 parts of DCP per 100 parts of rubber.

v_r is the volume fraction of rubber at equilibrium DOP uptake. G is the shear modulus of the unswollen vulcanisate and X the rubber/DOP interaction parameter.

the mutual diffusion coefficient, D^v , was calculated. These, together with the interaction parameter X , equilibrium uptake and shear modulus G , are presented in *Table 2*. As expected, the diffusion coefficient of DOP in BR was significantly greater than in the other two vulcanisates. At equilibrium, EPM absorbed less than 20% of the DOP uptake in the other rubbers.

The sweating curves of the vulcanisates when the swollen samples were wrapped up in aluminium foil are shown in *Figure 5 (a)*. The sweating curves are initially linear and this linearity extends over much longer times for BR and IR than it does for EPM. Although IR absorbed more DOP at equilibrium than BR, the sweating rate in the latter is higher, perhaps due to the higher diffusion coefficient of DOP in BR. However, the difference is not as large as would be expected from the diffusion coefficients of DOP in these two rubbers (*Table 2*) and could be attributed to a dissimilar increase in the size or number of contact regions between the rubbers and the aluminium foil due to the difference in their moduli. The amounts of DOP sweated out after 120 days in BR, IR and EPM were 8%, 6% and 1.1% by weight respectively, which are small relative to their equilibrium DOP uptake.

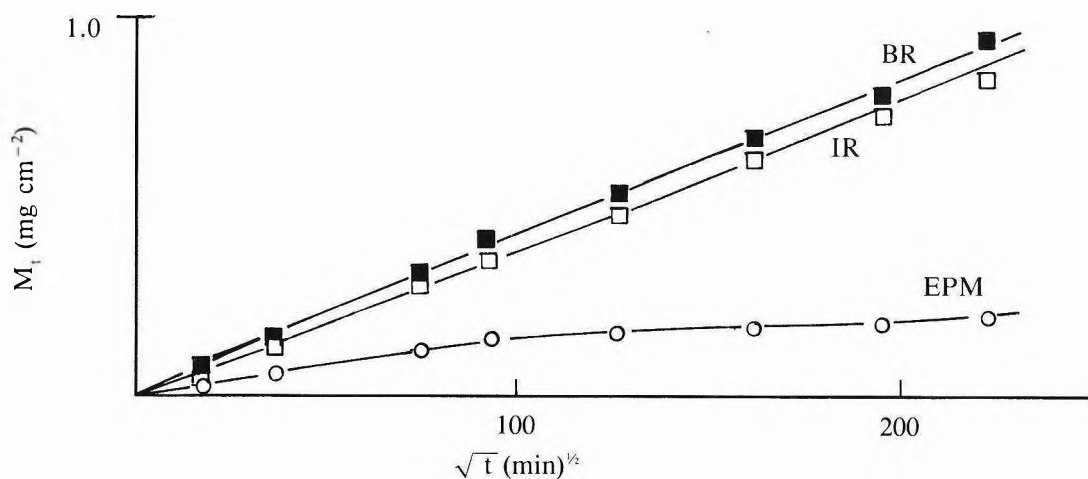
Figure 5 (b) shows the sweating curves when the swollen rubbers were sandwiched between filter papers (Whatman Paper No. 42) and a

load of 195 g evenly applied to the assembly. It shows that the amount of sweating was greatly increased, by between 1.5 and 5 times the sweating rate when the samples were in contact with aluminium foil. It is interesting to note that in *Figure 5 (b)*, the curves for BR and IR are non-linear while that of EPM remains linear even beyond \sqrt{t} of 200 $min^{1/2}$.

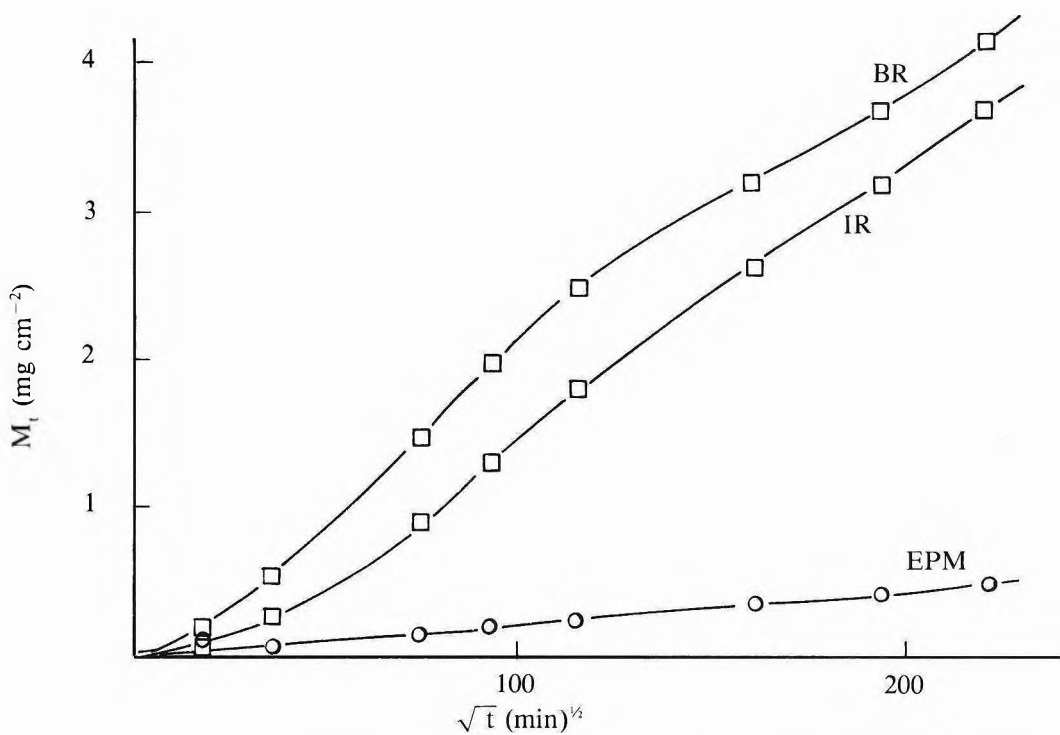
This investigation shows that IR, BR and EPM also exhibit the sweating phenomenon. That the process occurs in acetone-extracted IR suggests that sweating in NR vulcanisates is not due to its non-rubber impurities since IR is a much cleaner rubber containing very low non-rubber constituents. Furthermore, infra-red analysis of the sweated liquid from the IR vulcanisate showed that it was virtually identical to the original DOP used to swell the rubbers except for a small amount of unidentifiable 'dirt' which was detected mainly between 300 cm^{-1} and 350 cm^{-1} . Oxidation could not be the cause of sweating since this is also observed in the EPM which has a high resistance to oxidation.

CONCLUSIONS

A variety of rubber vulcanisates, previously swollen to equilibrium in a plasticiser such as dioctylphthalate, exhibit a rather puzzling exudation phenomenon. This process, called sweating, is not due to supersaturation effects caused by temperature variation or impurities



(a) Wrapped up in aluminium foil.



(b) Sandwiched between two Whatman No. 2 filter papers No. 42 and subjected to a compressive load of 159 g.

Figure 5. Sweating of DOP from synthetic rubbers at 21°C.

present in the rubber. It is also known that when a sample, after it has sweated for some time, is re-immersed in the liquid at the same temperature, it re-swells to approximately the same equilibrium value. These observations are rather difficult to reconcile with the thermodynamics of equilibrium swelling.

It has been shown that the amount of sweating can be significantly altered by varying the physical conditions at the surface of the rubber. Furthermore, the intimacy of contact at the swollen rubber surface is an important feature and strongly influences the kinetics of the sweating process. These observations suggest that the process is primarily due to surface effects.

It is postulated that sweating in a highly swollen rubber is caused by surface tension effects due to the presence on the rubber surface of extraneous debris (e.g. dust) or microscopic surface irregularities or simply due to contact with other substrates. Surface tension forces will cause the liquid near the rubber surface to move to the surface forming droplets in regions where such forces exist. If

the process can be modelled along the lines where dust particles or imperfections at the rubber surface act as small isolated sinks for the plasticiser, then it is possible to explain, at least qualitatively, the slow rate of migration of the liquid during sweating and the observed effects of perfection of contact at the swollen rubber surface.

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Synthesis of Photo-crosslinkable Elastomers by Chemical Modification of Liquid Natural Rubber

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Photo-crosslinkable elastomers were synthesised by addition of photo-sensitive alcohols to the alkylsuccinic ring of liquid natural rubber (LNR) and synthetic liquid 1,4-polyisoprene (LIR) was modified for the first time by reaction with maleic anhydride. Two reagents were used: 2-hydroxyethyl cinnamate (HEC) and 2-hydroxyethyl acrylate (HEA). The fixation proceeded by succinic ring opening by the action of the alcohol function of the photo-reactive molecule and led to a hemi-ester adduct. At moderate temperature (about 70°C), the reaction on succinic anhydride functions of maleinised LIR was fast and quantitative when it was catalysed by pyridine and led to polymers which were completely soluble in organic solvents. On the other hand, under the same conditions, yields of HEC addition on succinic rings of maleinised LNR were less significant (~ 60%) than on maleinised LIR, and in the case of the acrylate reagent, the reaction was affected by the formation of gel structures. The relationship between the polymer structure and its photo-sensitivity is presented. The effects of photo-reactive group contents on the photo-crosslinking kinetics were investigated for each category of prepared polymers. Flexible films with good adherence on metal were prepared by using formulations including LIR or LNR carrying cinnamate groups.

The constant search for more sensitive resins that can photo-polymerise instantly under UV radiation has led to the development of highly reactive functional liquid polymers. As a consequence, UV curable systems have found widespread applications in various industrial sectors¹, mainly as photo-resists for the production of printing plates and integrated circuits and as fast-drying resins for varnishes, printing inks, adhesives and composites.

In an attempt to further improve their photo-reactivity, the performances of new photo-sensitive elastomers with polyisoprene backbone were examined. The aim was to prepare new photo-reactive polymers able to lead, after photo-crosslinking, to flexible and damping materials having the properties of polydienes, *i.e.* elasticity and good adherence to metals.

A new material is produced with the development of a patented process^{2,3} of depolymerisation of natural rubber. It is prepared by controlled degradation of natural rubber in the latex phase according to a redox reaction using the phenylhydrazine/oxygen system². By controlling the reaction conditions, it is possible to obtain liquid compounds called liquid natural rubber (LNR) with low viscosity and the structure of *cis*-1,4-polyisoprene. The feasibility of industrial production of LNR has been demonstrated with the establishment of a semi-industrial pilot plant at the IRCA (Institut de Recherche sur le Caoutchouc) Bimbresso Station in the Ivory Coast.

If LNR can be compared to synthetic liquid 1,4-polyisoprene and used in the same field of applications, it may be useful as a starting

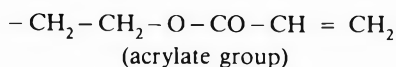
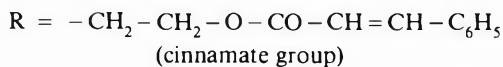
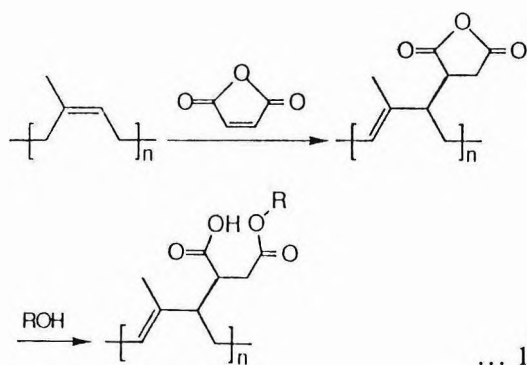
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EXPERIMENTAL

product for the preparation of specific polymers for highly technical applications through judicious chemical modification of its structure. In this way, its transformation into a photo-sensitive product similar to synthetic 1,4-polyisoprene (LIR) was carried out by a two-step process. In the first step, maleic anhydride was added to polyisoprene units to obtain functionalised intermediate polydiene with pendent succinic anhydride functions. The second step of the chemical modification was the introduction of the photo-sensitive graft, using the known reactivity of the succinic rings towards alcohol functions, by reaction of the succinic anhydride groups with photo-reactive alcohols, such as 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl cinnamate (HEC) (Equation 1):



This paper describes the synthesis of the photo-sensitive polydienes derived from LIR and LNR, and compares their photo-reactivity. The photo-reactivities of the different prepared polymers were evaluated by comparison of the kinetics of photo-crosslinking reactions. Some orientation tests were also carried out on the use of modified LNR or LIR in UV formulations of industrial character to obtain flexible and damping films.

Purification of Solvents and Reagents

Solvents were commercial products. Benzene and toluene (99.5% purity) were used as received. Hexane was distilled on LiAlH_4 and kept on a 3 Å molecular sieve. Pyridine was distilled on potassium hydroxide before it was used. Chloroform was distilled on phosphoric anhydride. Methanol was dried by distillation on $\text{Mg}(\text{OMe})_2$ prepared *in situ*. Ethanol was dried on activated lime for several days, distilled and kept on a 3 Å molecular sieve. Methyl ethyl ketone (MEC) was distilled.

Maleic anhydride was recrystallised from benzene. 0.5 N solution of tetrabutylammonium hydroxide in methanol was supplied by Janssen. Ethylene glycol (Janssen) was further dried by azeotropic distillation of benzene. Cinnamoyl chloride (Janssen, 97% purity) was used as received. HEA (Aldrich product) was distilled at low pressure immediately before it was used.

HEC was synthesised in pyridine by reaction⁴ between molten cinnamoyl chloride and ethylene glycol at a temperature below 25°C. The ester was used after purification by distillation. Its purity was verified by $^1\text{H NMR}$.

Synthetic liquid *cis*-1,4-polyisoprene (LIR 30) was supplied by the Japan Kuraray Company. It was purified by re-precipitation from toluene into methanol and dried *in vacuo*. The average molecular weights of LIR were: $\bar{M}_n = 12\,400$, $\bar{M}_v = 12\,700$, $\bar{M}_w = 27\,600$. It consists of 92% of -1,4 and 8% of -3,4 structures.

LNR is a derivative of natural rubber obtained by depolymerisation in the latex phase by a chemical method using the phenylhydrazine/oxygen system^{2,3}. It was supplied by the Institute of Applied Research on Polymers of Le Mans. The average molecular weights of LNR were: $\bar{M}_n = 7700$, $\bar{M}_v = 8900$, $\bar{M}_w = 26\,100$. It consists of 100% *cis*-1,4 structure.

Reaction of Maleic Anhydride to Polyisoprene Structures

Addition of maleic anhydride to polyisoprene structures was carried out by using thermal initiation. Polyisoprene in toluene solution (200 g of polyisoprene for 1 litre of toluene), maleic anhydride and cupric acetylacetonate (0.1 g for 100 g of polyisoprene) used as anti-gel additive, were introduced under nitrogen atmosphere in a 30 ml stainless steel Mecabar autoclave. The reaction mixture was heated to 200°C in a metallic bath (wood alloy). After 24 h, the reaction was stopped. The resulting mixture was poured into excess cold ethanol. The precipitated product which was the maleinised polyisoprene, was immediately recovered and purified by re-precipitation from toluene into hexane. It was stored in toluene solution.

Reaction of Maleinised Polyisoprenes with Photo-sensitive Hydroxyethyl Structures

Addition of 2-hydroxyethyl cinnamate. The addition of 2-hydroxyethyl cinnamate to maleinised polyisoprene was carried out in toluene solution, in the presence of pyridine as a catalyst. 10 g portion of a maleinised polyisoprene free of maleic anhydride⁵ in 100 ml of toluene and 2-hydroxyethyl cinnamate in the molar ratio [2-hydroxyethyl cinnamate]/[succinic anhydride function] = 2.3 and pyridine in [pyridine]/[succinic anhydride function] = 0.5 were placed in a round-bottomed flask fitted with a reflux condenser carrying a calcium chloride guard tube. The mixture was heated while being stirred to 75°C in a thermostated oil bath for 24 h. At the end of the reaction which was controlled by infra-red spectroscopy, by following the disappearance of the succinic bands at 1780 and 1860 cm⁻¹, the resulting mixture was poured into excess methanol (or hexane when the degree of modification by maleic anhydride was too high) and the precipitate was obtained as the product. The product was collected, purified by re-precipitation from chloroform into methanol and stored in chloroform solution under nitrogen atmosphere and sheltered from light.

Addition of 2-hydroxyethyl acrylate. The reaction was conducted in the same manner as for HEC. Maleinised polyisoprene concentration was fixed at 7.5 g portion of polymer in 100 ml of toluene. The reaction was carried out in the presence of hydroquinone (0.3 g for 100 g of maleinised polyisoprene), as the polymerisation inhibitor.

Photo-crosslinking of Photo-sensitive LNR and LIR

Photo-crosslinking kinetics. Photo-sensitive elastomers were dissolved in chloroform at a concentration of 150 g/litre. Film specimens for UV irradiation were prepared by casting the chloroform solution on quartz cell for UV analysis, with a 6 µm Conway bar. After removing solvent under reduced pressure, the film thickness was estimated to be about 1 µm. The UV irradiation was carried out at ambient temperature at a distance of 9 cm from an ultra-high pressure mercury lamp (PCG 9G-1 model from Ultraviolet Products Inc.; 2.5 watts). The principal beams of the used UV lamp are 253.7 (80% of the energy), 312.5 and 365 nm, the others being visible. The photo-crosslinking rate of the synthesised photo-sensitive rubbers was determined by the intensity change of the UV absorption at $\lambda = 278$ nm due to the carbon-carbon double bond of cinnamate groups for polyisoprene modified with HEC and at $\lambda = 200$ nm due to the carbon-carbon double bond of acrylate groups for polyisoprene modified with HEA.

Photo-crosslinking of UV formulations. The selected UV formulation for the present study has been perfected by the Institute of Applied Research on Polymers of Le Mans to obtain a film having properties of adherence on painted steel (used in the car industry), flexibility and good resistance to solvents and shocks. The formulations used were:

- Approximately 50% by weight of photo-sensitive polyisoprene (LIR-HEC or LNR-HEC)
- Mono-functional monomers:
 - glycidyl methacrylate
 - urethane derivative (M 200, Rahn)

- Multi-functional monomers:
 - 1,6-hexanediol diacrylate
 - triacrylate derivative (OTA 480, Union Chimique Belge)
- Photo-initiator: 651 Irgacure (2,2-dimethoxy-2-phenyl acetophenone) (Ciba Geigy)

The mixture was dissolved in chloroform and the films were prepared by casting the chloroform solution on metallic plates. After removing the solvent under reduced pressure, the film was exposed under UV irradiation supplied by a high powerful medium pressure mercury lamp (Aric 8200; 80 watts/cm) from Aric Company, for short periods (3-5 s). The crosslinking test was carried out to control the solubility of the film in chloroform. Qualitative adherence tests were conducted as follows: squaring of the film with a cutter, then estimation of the adherence by peeling with adhesive tape.

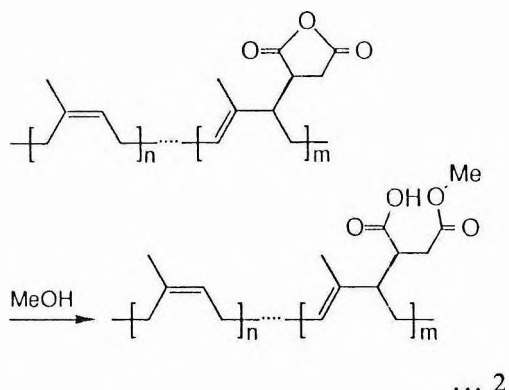
Characterisation of Products

The products were characterised by infra-red, UV and NMR spectroscopy. UV spectra were recorded on a UV/visible Varian DMS 100 spectrometer. Infra-red analyses were carried out on film samples of the polymers on NaCl cells, using a Fourier transform Perkin-Elmer 1750 spectrometer ^{13}C NMR and ^1H NMR measurements were carried out on deuterated chloroform solutions containing tetramethylsilane as the internal standard by using respectively Varian FT 80A (20 MHz) and Varian EM 90 spectrometers.

Molecular weights were determined by gel permeation chromatography (GPC) in THF on a Waters 1500 instrument fitted with 5 μ Styragel columns (0.7×120 cm) of different pore sizes (100, 3×500 and 1000 \AA), calibrated with polystyrene standards.

After maleinisation, the contents of succinic groups in the polyisoprenes were determined by titration using a Metrohm potentiometer (Impulsomat 614; Dosigraph 625; pH-meter 632, Dosimat 655) as described earlier⁵. It consists of titrating the carboxylic acid functions

formed after opening of the succinic rings obtained by reaction of an alcohol with a known quantity of maleinised polymer (Equation 2):



After maleinisation, a portion of the toluene polymer solution was refluxed in the presence of pure MeOH (2 mol for one polymer constitutive unit) for a few hours. The reaction was stopped after complete disappearance of the infra-red bands at 1780 and 1860 cm^{-1} , characteristic of the succinic ring. The esterified product was poured into excess methanol to eliminate the residual reagents and the polymer precipitate obtained was dissolved in toluene and stored in this form.

The contents of photo-sensitive groups in the prepared polymers were estimated according to a previous paper⁴. For the photo-sensitive polymers derived from LIR, it was admitted that the photo-reactive group content was equal to the initial succinic anhydride content. In the case of photo-crosslinkable elastomers prepared from LNR, the usual method cannot be applied because, at the start of the addition of photo-reactive alcohol, some succinic functions were opened by secondary processes which occurred during maleinisation. The amount of incorporated cinnamoyl substrates on maleinised LNR was determined from high performance liquid chromatography (HPLC) by using the standard calibration procedure. The method is based on the measurement of the quantity of residual 2-hydroxyethyl cinnamate contained in the solution⁴.

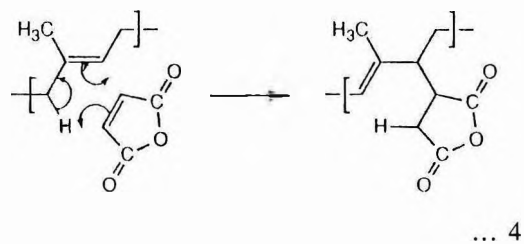
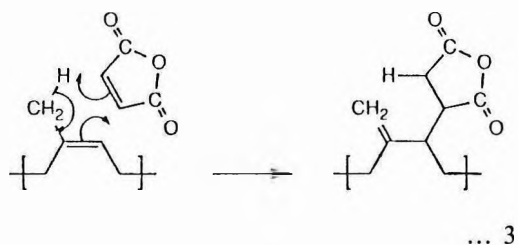
RESULTS AND DISCUSSION

Two products from different origins: a synthetic, 1,4-polyisoprene (92% of 1,4-units; 8% of 3,4-units) (LIR 30) with $\overline{M}_n = 12\,400$ and a liquid natural rubber (100% of *cis* 1,4-units) (LNR) with $\overline{M}_n = 7700$ were studied.

The aim was to study the partial modification of 1,4-polyisoprene structures because only a small proportion of photo-reactive functions is sufficient to permit a good crosslinking reaction. For these reasons, it was decided to limit the modification yield to a maximum of 20% ($[\text{maleic anhydride}]/[\text{polyisoprene units}] < 0.2 \text{ mol. mol}^{-1}$).

Fixation of Maleic Anhydride on LIR and LNR

The addition of maleic anhydride^{5,6} to 1,4-polyisoprene can be carried out by heating to moderate temperature in the presence of free-radical catalysts, or in the absence of catalysts by heating to significantly higher temperatures of 180°C to 230°C. The latter was achieved by thermal processes in the presence of cupric acetylacetonate as the anti-gel additive to prevent the polydiene crosslinking. The thermal reaction which requires high activation temperatures (of about 200°C), proceeds by an electronic 'ene' mechanism as shown in *Equations 3 and 4*:



According to the 'ene' synthesis, five polyisoprenes containing respectively 3%, 7%, 10%, 11% and 15% maleinised units were prepared from LIR, and three with 5%, 9% and 15% maleinised units from LNR (*Table 1*). After maleinisation, each prepared maleinised polymer was systematically controlled under infra-red spectroscopy to verify the eventual existence of some ring opening secondary reactions. With LIR, the yields from the maleinisation reaction were about 70% and the maleinised units were totally in the succinic anhydride form. With LNR, it was necessary to keep the maleinised LNR in solution because they are non-soluble after drying, which can be explained by the existence of hydrogen bond interactions between the chains. The differences in the results obtained with LIR are probably due to the presence of some acid or basic compounds in the initial liquid rubber, which result in the ring opening reaction.

Structural characterisation of maleinised polyisoprenes. The maleinised polyisoprenes derived from LIR or LNR have the same characteristics in ¹H NMR and infra-red spectroscopy.

In ¹H NMR, fixation of maleic anhydride is characterised by a chemical shift at $\delta_H = 2.3 - 2.8$ p.p.m characteristic of the protons on the succinic rings. The presence of two isomer structures, has also been reported⁵. Analysis of polymers derived from LNR which are only composed of 1,4-units, reveals the presence of another signal at $\delta_H = 4.8$ p.p.m. characteristic of protons on 'exo' methylenic carbon-carbon double bonds.

In infra-red spectroscopy, the succinic anhydride function is readily identified by means of two strong absorption bands at 1780 and 1860 cm^{-1} . Products derived from LNR were also present on another absorption band of weak intensity at 1700 cm^{-1} , which characterises the partial succinic ring opening with formation of carboxylic acid functions. As they did not occur during the chemical modification of LIR, it is probable that they are induced by the non-rubber constituents initially present in the LNR which can initiate

TABLE 1. CHARACTERISTICS OF THE PHOTO-REACTIVE POLYISOPRENES OBTAINED AFTER CHEMICAL MODIFICATION OF LIR AND LNR, BY MALEINISATION WITH MALEIC ANHYDRIDE FOLLOWED BY ESTERIFICATION OF THE FORMED SUCCINIC ANHYDRIDE FUNCTIONS BY SELECTED PHOTO-SENSITIVE ALCOHOLS HEC AND HEA

Sample from HEC	Sample from HEA	Modification yield	
		After maleinisation (% of maleinised units)	After addition of the photo-reactive alcohol (% of photo-reactive units)
LIR-HEC-3		3 ^a	3 ^b
LIR-HEC-7		7 ^a	7 ^b
LIR-HEC-10		10 ^a	10 ^b
LIR-HEC-11		11 ^a	10 ^c
LIR-HEC-15		15 ^a	15 ^b
	LIR-HEA-15	15 ^a	15 ^b
LNR-HEC-5		10 ^a	5 ^c
LNR-HEC-9		15 ^a	9 ^c
LNR-HEC-15		27 ^a	15 ^c

^a Determinated by titration

^b Equal to the modification yield by maleic anhydride

^c Determinated from HPLC measurement of the residual HEC

decarboxylation or esterification of some succinic rings.

Addition of Photo-polymerisable Alcohols on Maleinised LIR and LNR

Photo-polymerisable alcohols were added to maleinised LIR or LNR in the presence of pyridine as the catalyst⁴. The studies were conducted in toluene (10 g of maleinised polymer in 100 ml of toluene) at 75°C. A slight excess of photo-reactive alcohol compared with succinic anhydride functions was used: [photo-reactive alcohol]/[succinic anhydride group] = 2.3 mol.mol⁻¹.

The progress of the succinic anhydride chemical modification reaction was controlled by following the disappearance of the infra-red absorption bands at 1780 cm⁻¹ and 1860 cm⁻¹ characteristic of the succinic anhydride function.

Addition of 2-hydroxyethyl cinnamate.
Addition of HEC to the previously prepared

maleinised LIR and LNR was quantitative at moderated temperature after only 24 h of reaction when it was conducted in the presence of pyridine⁴. No side-reaction occurred during maleinisation of LIR, therefore, starting with LIR, the percentages of constitutive units having the cinnamate group were identical (*Table 1*). Alternatively, for the photo-sensitive polyisoprene derived from maleinised LNR, such extrapolation was not possible owing to the partial succinic ring opening noted during maleinisation of LNR and, in this case, it was necessary to find a solution to the problem of determination of the percentage of photo-sensitive units. It was achieved by using the HPLC technique which permits the monitoring each time of the quantity of residual HEC. The results summarised in *Table 1* show that, for all the maleinised LNR, the proportion of maleinised constitutive units really modified by HEC corresponds to about half of the initial one, which by ignoring the ring openings noted during maleinisation, placed the esterification yield at about 60%. This value is

in fact the minimum since the calculation was based on the maleinisation yield which includes all the maleic anhydride modified constitutive units without making a distinction between the closed succinic rings and the opened ones.

Structural characterisation of the cinnamate photo-sensitive polyisoprenes. In GPC, no significant change was noted between the chromatogram of the initial LIR or LNR and those of the correspondent modified products.

The chemical structures of the modified polymers were characterised by ^1H NMR, infra-red and UV spectroscopy. In infra-red spectroscopy, the absorption bands characteristic of the cinnamic ester function appeared at 1713 cm^{-1} (C=O ester and carboxylic acid, stretching), 1638 cm^{-1} and 893 cm^{-1} (C=C cinnamate, stretching). In ^1H NMR, the 2-hydroxyethyl cinnamate addition to maleinised 1,4-polyisoprene structures was verified by a singlet at $\delta_{\text{H}} = 4.4$ p.p.m. characteristic of the methylenic protons -O-CH₂-CH₂-O-. In UV spectroscopy, the two important absorption bands noted at $\lambda = 278$ nm and $\lambda = 200$ nm characterised respectively the cinnamate functions and the polyisoprene carbon-carbon double bonds.

Addition of 2-hydroxyethyl acrylate. Contrary to HEC, the addition of HEA to maleinised LIR or LNR was carried out in the presence of hydroquinone to prevent all risks of polymerisation by the intermediate acrylic groups, very sensitive towards heat. The reaction on 15% maleinised LIR went to completion, *i.e.* complete disappearance of the infra-red absorption bands characteristic of the succinic anhydride functions was observed after 9 h of reaction and no gel formation was noted in the medium. It was not possible to fractionate HEA from hydroquinone by HPLC and so, to measure HEA residual quantity each time⁴, it was assumed that the percentage of photo-sensitive acrylate units was, as in the case of the study with HEC, identical to that of maleinisation, *i.e.* with the 15% maleinised LIR (Table 1). With maleinised LNR, the addition of HEA was disturbed by gel formation after only 4 h of reaction, *i.e.* before complete

transformation of the succinic rings by HEA, which was verified in infra-red spectroscopy by the presence of absorption bands at 1860 cm^{-1} and 1780 cm^{-1} .

Structural characterisation of the acrylate photo-sensitive polyisoprenes. The fixation of acrylate groups is confirmed in ^1H NMR by the presence of a singlet at $\delta_{\text{H}} = 4.4$ p.p.m. due to the -O-CH₂-CH₂-O- protons. In infra-red spectroscopy, the principal absorption bands are noted at 1734 cm^{-1} (C=O ester, stretching), 1713 cm^{-1} (C=O acid, stretching), 1666 cm^{-1} (C=C polyisoprene, stretching), 810 cm^{-1} and 1640 cm^{-1} (C=C acrylate, stretching). The UV spectrum presents two adsorption bands at $\lambda = 200$ nm and $\lambda = 250$ nm which characterise respectively the polyisoprene carbon-carbon double bonds and the acrylate groups.

Photo-crosslinking

Polymers bearing cinnamate groups are well known for their ability to be photo-crosslinked *via* 2 + 2 cyclo-addition involving the carbon-carbon double bond of the cinnamate function, resulting in the formation of a cyclobutane ring⁷. However, the photo-chemistry of these polymers cannot be explained by the only cyclobutane structure formation. Nakumura and Kikuchi⁸ have proposed, according to ESR data, the intervention of two different kinds of radical intermediates, one of them being produced by hydrogen abstraction from the main chain of the polymer. It is possible that these radical forms can occur in the cross-linking process. Reiser⁹ analysed the products obtained after UV irradiation of poly(vinyl cinnamate) in the solid state and concluded that at least 65% of the total of the formed structures are cyclobutane dimers, the others being derivatives resulting from combinations between radical species generated along the chain during the irradiation. We have tried to photo-crosslink a film of 15% maleinised LIR and established that photo-crosslinking can occur in the absence of photo-polymerisable graft (Figure 1), which seems to prove that the thesis of a propagation *via* radical species is credible. The time decrease of the UV

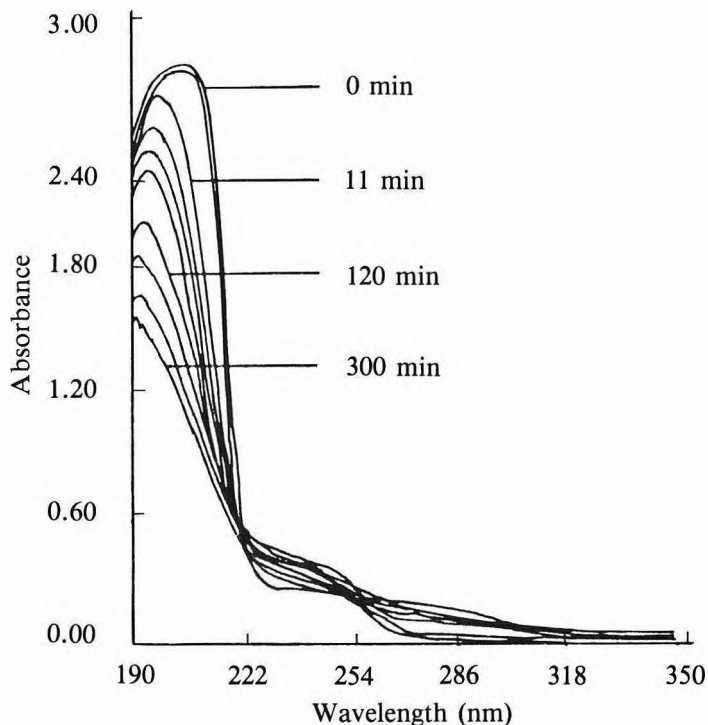


Figure 1. Changes in UV spectrum of 15% maleinised LIR in terms of UV irradiation time.

absorption bands characteristic of the polyisoprene carbon-carbon double bonds at $\lambda = 200$ nm and the gradual insolubilisation of the sample prove the intervention of the polyisoprene unsaturations in the photo-crosslinking process. It is not rejected that the succinic anhydride groups present along the chain can also act as a photo-initiator. Under UV irradiation, radicals can be generated by homolytic cleavage of the bonds in the α position from carbonyl group and initiated propagation involving polyisoprene unsaturations.

For polymers containing the photo-reactive acrylate or methacrylate groups, photo-dimerisation is not expected to play a role in crosslinking. The photo-crosslinking mechanism is essentially a radical chain propagation.

Photo-crosslinking kinetics of the photo-sensitive LIR and LNR. During all the studies

on photo-reactivity of the prepared polymers, the tests were carried out in the solid state and the thickness of the films were measured as the same for each sample (around $1 \mu\text{m}$ after drying).

The UV irradiation tests on the prepared photo-reactive polyisoprenes were carried out on samples prepared according to the method described above.

Kinetic studies of the photo-crosslinking of polyisoprenes bearing pendent cinnamate groups derived from LIR and LNR. In the case of polyisoprene carrying cinnamate groups, Figure 2 shows a slight decrease of intensity of the absorption band around $\lambda = 200 - 210$ nm which corresponds to the polyisoprene carbon-carbon double bond, compared to the absorption band shown in Figure 1 at the same irradiation time. But a significant change in the intensity of the cinnamate absorption band

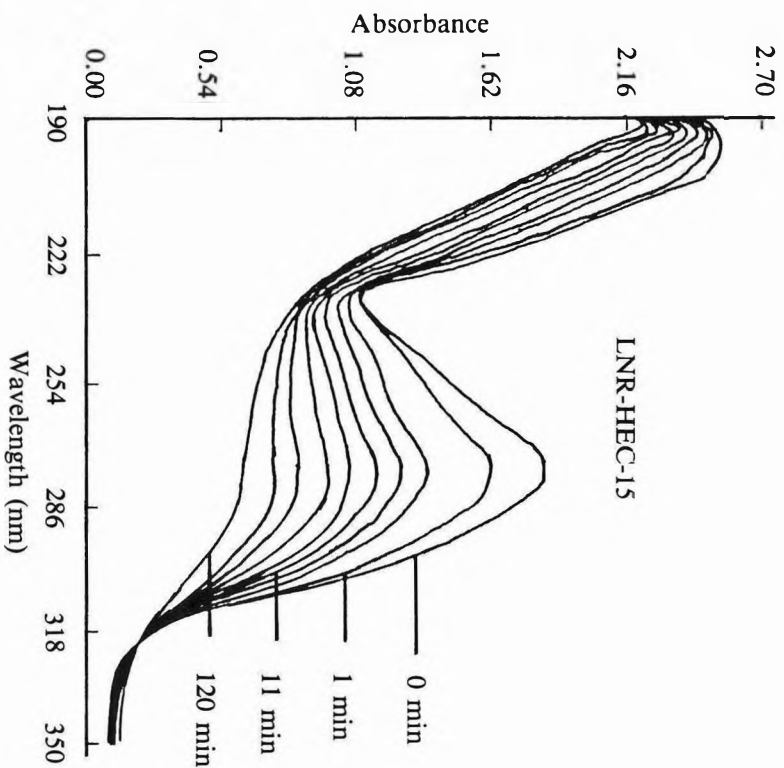
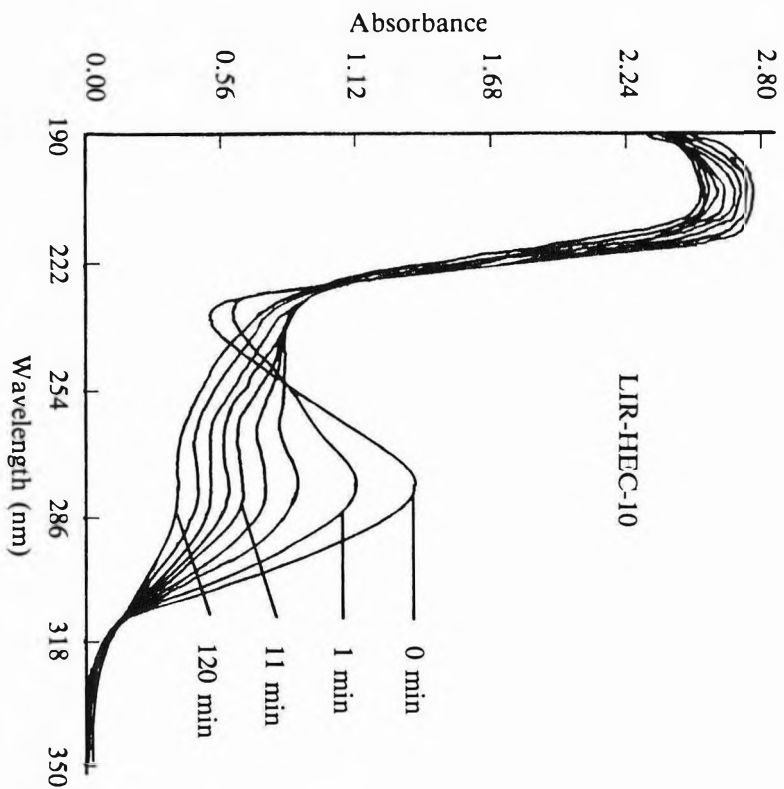


Figure 2. Changes in UV spectra of LIR-HEC-10 and LNR-HEC-15 in terms of UV irradiation time.

at $\lambda = 278$ nm is observed, especially at irradiation time of less than 11 min. Therefore, the photo-sensitivity of the polyisoprene carrying cinnamate groups can be considered principally as a reaction of photo-dimerisation of the cinnamate group as shown earlier.

There are detailed reports by Azuma *et al.*^{10,11} on the photo-dimerisation of cinnamate groups in polydienes or polypentenamers with pendent cinnamoyl ester groups, in which the kinetic equations of the reaction have been expressed.

By considering that the photo-dimerisation of cinnamate groups is finally summarised by four basic reaction paths (Figure 3) according to the previous work of Tsuda¹², and by assuming the steady state of the excited species and the isomerisation of the cinnamate groups does not take place in a solid film, the photo-dimerisation rate is expressed by Azuma *et al.* as follows:

$$-\frac{d[C]}{dt} = 2 \frac{d[C - C]}{dt} = 2\alpha l_{abs} k_2 [C]/lk_4$$

where l and l_{abs} denote film thickness of a specimen and light intensity absorbed by the sample, and α denoted the reciprocal of Einstein:

$$\alpha = (6.023 \times 10^{23} h \nu)^{-1}$$

This expression is formulated in two forms depending on the conditions of the absorbed light intensity:

- In the case where the absorbed light is less than the incident light intensity ($l_{abs} < l_0$), the photo-dimerisation rate is represented as a second-order reaction rate equation based on the concentration of the cinnamate groups and independent of the film thickness, as follows:

$$\frac{1}{[C]} - \frac{1}{[C_0]} = k_{obs}t \quad \dots 5$$

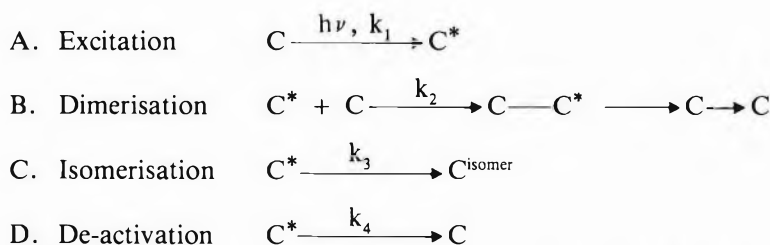
- If the absorbed light is nearly equal to the incident light intensity ($l_{abs} \sim l_0$), the photo-dimerisation rate is represented as a pseudo first-order reaction rate equation and the film thickness term is included in the observed rate constant, as follows:

$$\text{Ln} \frac{[C_0]}{[C]} = k_{obs}t \quad \dots 6$$

In our study, we have verified that the photo-crosslinking rate depends on the film thickness. Consequently, the second expression was retained to express the photo-polymerisation rates.

When a film specimen of polyisoprene carrying pendent cinnamate groups is irradiated with UV light, the absorption intensity of the UV spectrum due to the cinnamate group at $\lambda = 278$ nm decreases.

The consumption of the cinnamate groups was estimated by using the UV spectral change



C and C* denote the cinnamate groups at the ground singlet state and the lowest excited state consisting of the singlet or triplet state, respectively.

Figure 3. Basic reaction paths in photo-lysis of cinnamate groups.

at $\lambda = 278$ nm which is an effective wavelength for the dimerisation of cinnamate groups.

Since measurements were always made on films of the same thickness (about 1 μm), Equation 6 can be written, according to Beer-Lambert's equation, as follows:

$$\text{Ln} \frac{[C_o]}{[C_t]} = \text{Ln} \frac{[A_o]}{[A_t]} = k_{obs}t \quad \dots 7$$

where $[A_o]$ and $[A_t]$ are respectively light intensity absorbed by the film sample at the times t_o and t .

Conversion of cinnamate groups can be expressed as follows:

$$\text{Conversion (\%)} = \frac{[C_o] - [C_t]}{[C_o]} 100 \quad \dots 8$$

According to Beer-Lambert's law, Equation 8 can be written as follows:

$$\text{Conversion (\%)} = \frac{[A_o] - [A_t]}{[A_o]} 100 \quad \dots 9$$

There is little difference between the photo-crosslinking kinetics of photo-sensitive LIR and LNR, as shown in Figures 4 and 5 which represent the time conversions of the cinnamate groups in the different cinnamate polyisoprenes prepared respectively from LIR and LNR and the pseudo first-order kinetics. In all the cases, the rate of conversion was observed to decrease with increasing reaction time, and crosslinking yields after 120 min of irradiation time were generally about 60%. This result is easily explained by the decrease of mobility of the chains, due to the three dimensional network formation which reduces the probability of meeting between the cinnamate groups and/or can probably enhance the intervention of the polyisoprene unsaturations in the photo-crosslinking process. Figure 2 shows, at long periods of irradiation, an increasingly comparable change of intensity of absorption band at $\lambda = 278$ nm and $\lambda = 200 - 210$ nm. This information again supports the fact that at the initial irradiation time, the photo-

crosslinking reaction occurs almost exclusively from cinnamate groups. Furthermore, the rate conversion is not influenced by the content of cinnamate groups on the polyisoprene when it is lower than 10%. The observed rate constants obtained as the initial slope of the pseudo first-order kinetics, owing to the fact that the slopes decrease with reaction duration, are identical when the considered cinnamate polyisoprene result from the same initial polyisoprene (LIR or LNR) (Table 2). At equal cinnamate contents, the observed rate constant is always slightly lower with the LNR derivative than with the LIR derivative. On the other hand, it is surprising that the rate conversion slows down when the cinnamate content exceeds 10%. A possible explanation for this phenomenon is that increasing the carboxylic acid group concentration on the backbone polyisoprene can induce an initial increase of the medium viscosity owing to hydrogen bond interactions, which will increase with the cinnamate proportion.

Because the photo-crosslinking rate of cinnamate derivatives is significantly increased in the presence of photo-initiator compounds¹³, a series of tests of photo-crosslinking of polyisoprenes carrying pendent cinnamate groups was carried out with 2,2-dimethyl-2-hydroxy acetophenone (Darocur 1173), as the photo-initiator. The results obtained with LIR HEC 7 and LNR HEC 9 mixed with a portion of 4 g for 100 g of photo-sensitive polymer were compared with those obtained without photo-initiator. No notable photo-crosslinking rate increase was noted. This may be due to incompatibility between the chemical nature of the two ingredients of the mixture.

Kinetic study of the photo-crosslinking of polyisoprenes bearing pendent acrylate groups derived from LIR. The study was carried out with only one sample: 15% acrylate modified LIR (LIR-HEA-15). Two tests were carried out, with and without photo-initiator (Darocur 1173).

Figure 6 shows the changes in UV spectrum of LIR-HEA-15 in terms of UV irradiation time. Contrary to photo-crosslinking of polyisoprenes carrying cinnamate groups

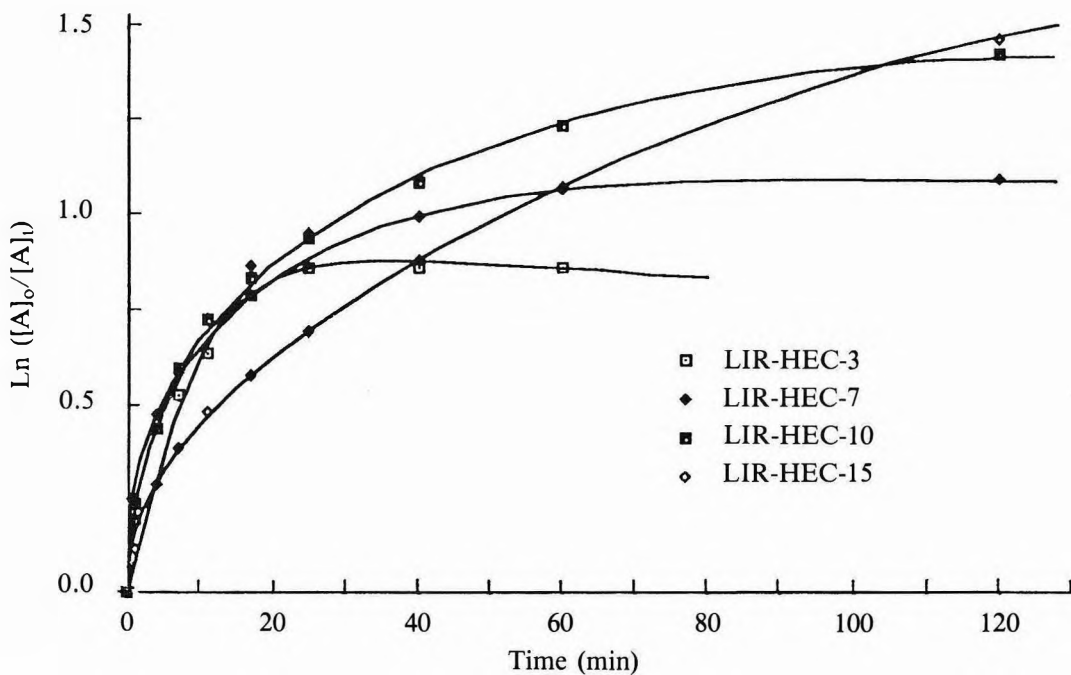
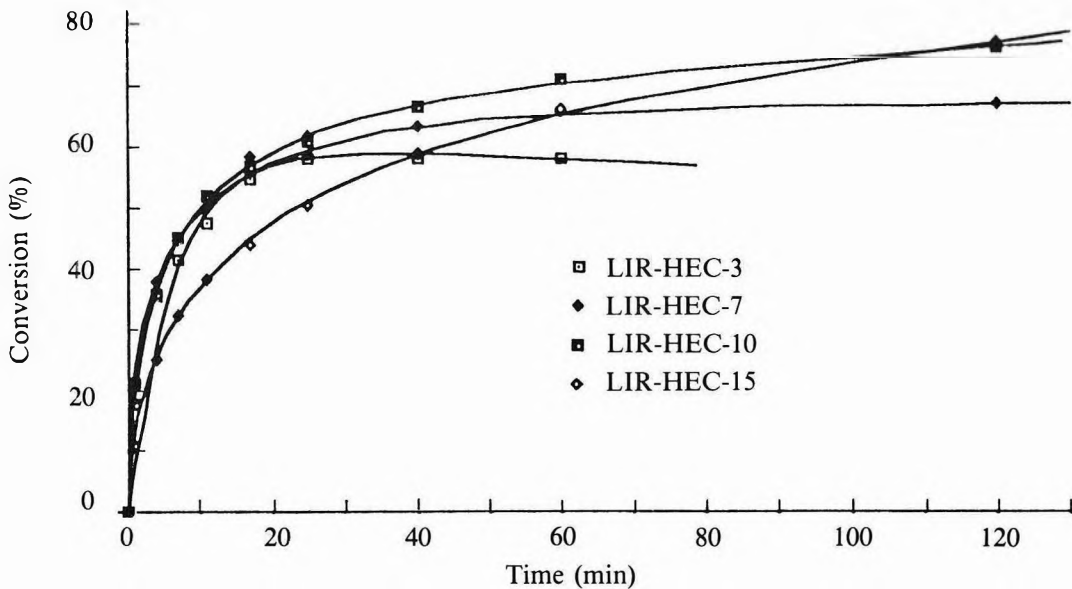


Figure 4. Conversion of cinnamate groups in LIR-HEC in terms of UV irradiation time and the relationship between $\text{Ln} ([A]_0/[A]_t)$ and UV irradiation time.

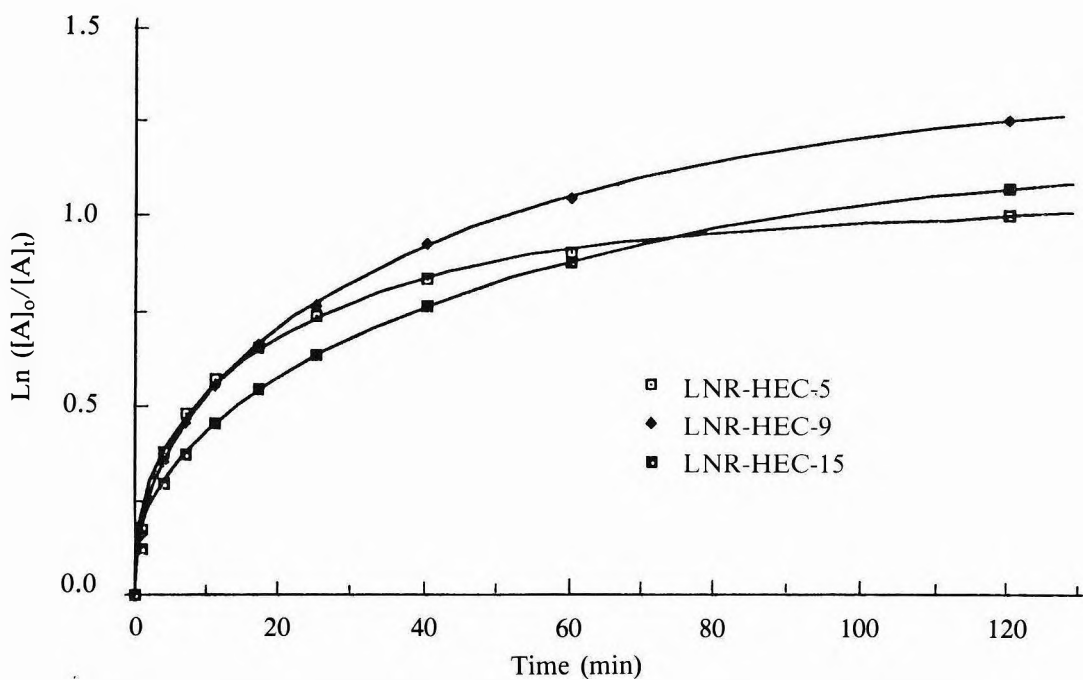
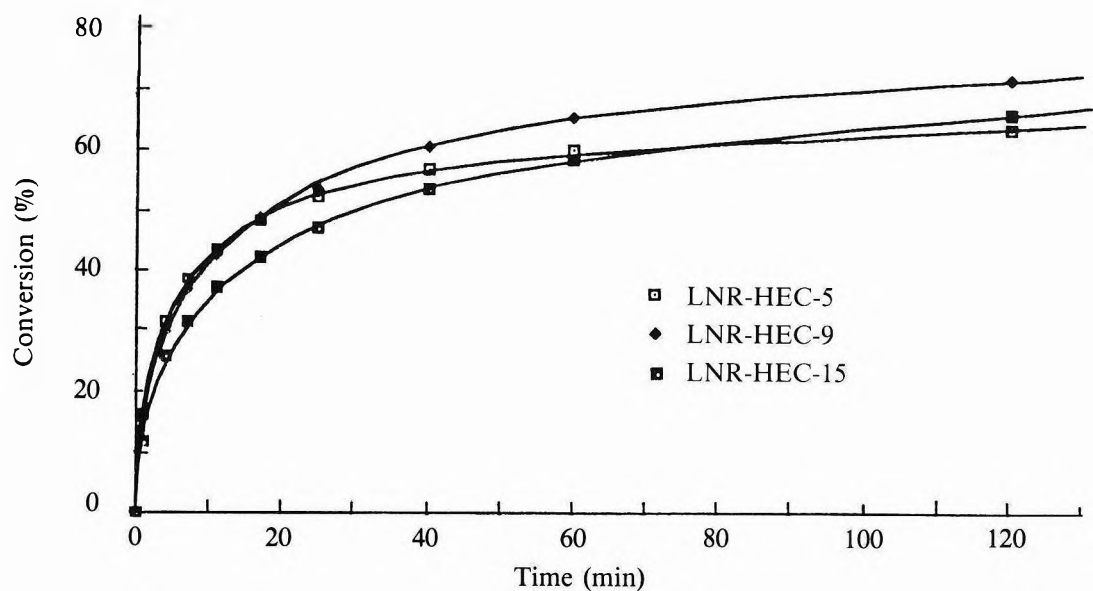


Figure 5. Conversion of cinnamate groups in LNR-HEC in terms of UV irradiation time and the relationship between $\text{Ln} ([A]_0/[A]_t)$ and UV irradiation time.

TABLE 2. PHOTO-CROSSLINKING OF LIR AND LNR CARRYING CINNAMATE GROUPS: OBSERVED RATE CONSTANTS, k_{obs} , OBTAINED AS THE INITIAL SLOPE OF THE PSEUDO FIRST-ORDER KINETICS

Sample	k_{obs}
LIR-HEC-3	0.25
LIR-HEC-7	0.25
LIR-HEC-10	0.25
LIR-HEC-15	0.11
LNR-HEC-5	0.18
LNR-HEC-9	0.18
LNR-HEC-15	0.09

(Figure 2) but in agreement with those of 15% maleinised polyisoprene (Figure 1), a large decrease of the intensity of the polyisoprene unsaturation absorption band at $\lambda = 200$ nm which apparently denotes a simultaneous consumption of polyisoprene carbon-carbon

double bonds and acrylate groups, was noted. However, this decrease was more rapid than for the 15% maleinised polyisoprene. These observations confirm a mechanism different from that observed in the case of the polyisoprene carrying cinnamate groups.

The time conversion of the acrylate groups in LIR-HEA-15 is shown in Figure 7. The positive action of the photo-initiator appeared only after 15 min of exposure. A gradual rate acceleration in function of the duration was then noted.

Photo-crosslinking of a few UV formulations for industrial applications. For industrial applications, the direct use of photo-sensitive polymers without other ingredients cannot be contemplated because its high viscosity sets some problems for its processing. So, for these reasons, they are always incorporated in formulations which are generally composed of different diluent reactive monomers of varied chemical nature, associated to a photo-initiator.

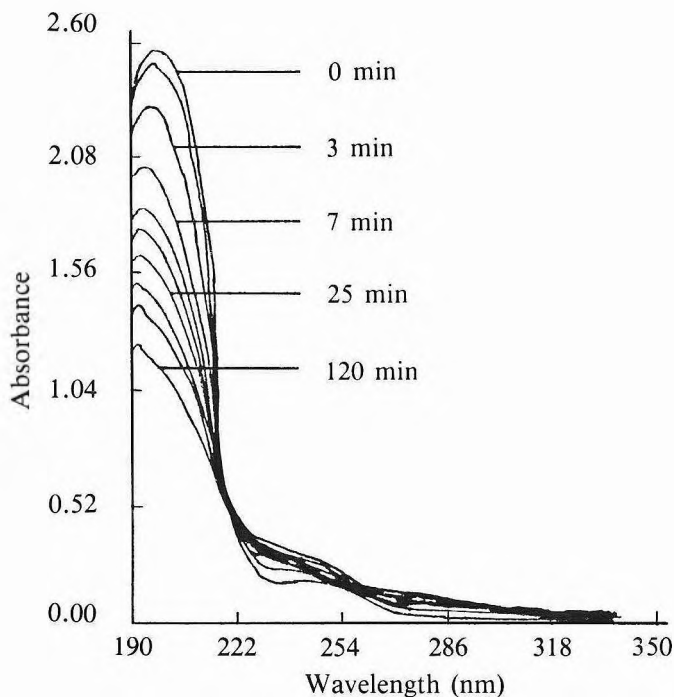


Figure 6. Changes in UV spectrum of LIR-HEA-15 in terms of UV irradiation time.

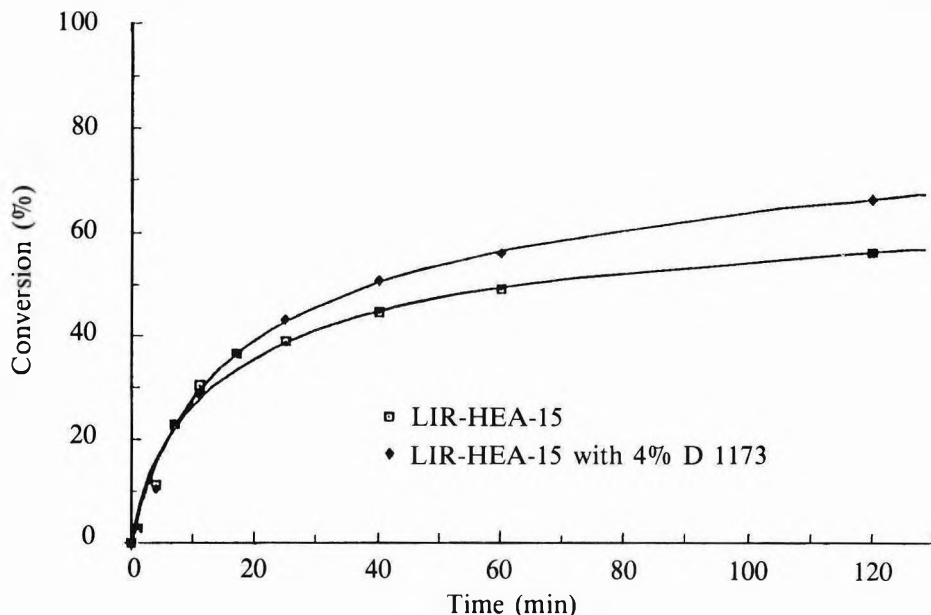


Figure 7. Conversion of acrylate groups in LIR-HEA in terms of UV irradiation time.

Three of the synthesised photo-sensitive polyisoprenes were selected to verify the possibility of obtaining flexible films by their incorporation into formulations: LIR-HEC-7, LIR-HEC-15 and LNR-HEC-9. It was noted that without diluent, after 5 s of irradiation, the polyisoprene carrying cinnamate groups led to partially crosslinked films (the swelling test in chloroform showed swelling with some deterioration of it in the solvent). On the other hand, in the presence of a photo-initiator, no damage of the films was observed after 5 s of irradiation; only its swelling in the chloroform was noted. Contrary to the former results obtained with the PCG 9G-1 UV lamp, these results demonstrate the positive influence of the photo-initiator on photo-crosslinking.

In complete UV formulations prepared with the HEC modified polyisoprenes, films having the mechanical and chemical properties with no swelling in chloroform, a good adherence on the support and a good flexibility were obtained after 3 s of irradiation.

CONCLUSION

The aim of the present study was to synthesise photo-sensitive elastomers from liquid natural rubber (LNR) obtained by depolymerisation of natural rubber in the latex phase with the phenylhydrazine/oxygen system. It was demonstrated that LNR, in the same manner as low molecular weight synthetic 1,4-polyisoprene (LIR), can be used as the starting product in the two-step chemical modification to obtain a photo-sensitive elastomer with the ability to rapidly crosslink under UV irradiation. For the first time, the LNR (or LIR) was maleinised by thermal 'ene' addition of maleic anhydride on polyisoprene unsaturations, and the resulting maleinised elastomer was transformed into the photo-sensitive polymer by reaction of photo-polymerisable alcohols, such as 2-hydroxyethyl cinnamate and 2-hydroxyethyl acrylate, on the succinic anhydride functions.

It was noted that polyisoprenes carrying cinnamate groups were more stable than those bearing acrylate pendent groups which can easily crosslink during the synthetic process.

The former are easily prepared from LNR according to the selected process and are quite soluble in most of the organic solvents, whereas preparation of the latter presented some problems because, generally, gel formation occurred rapidly during the esterification step. The photo-crosslinking studies have shown that in the case of polyisoprene carrying cinnamate groups, the maximum efficiency of the photo-crosslinking rate is obtained with a polymer having less than 10% of photo-sensitive units. Polyisoprene bearing cinnamate grafts are principally photo-crosslinked *via* 2 + 2 cyclo-addition involving the carbon-carbon double bond of the cinnamate functions with formation of cyclobutane rings, which explains the retention of elastic properties of the initial polydiene.

The difficulties encountered during the synthesis of LNR bearing pendent acrylate groups have prevented a study with this family of polymers. A single polymer derived from LIR was tested. It was shown that, with this acrylate LIR category, the polyisoprene carbon-carbon double bonds are involved in the photo-crosslinking process.

The study of formulations including LNR (or LIR) among the different ingredients has shown that these photo-sensitive elastomers can be used to prepare flexible films with good adherence on metal and good resistance to solvent action.

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Agrobacterium-mediated Transformation of Hevea Cells Derived from In Vitro and In Vivo Seedling Cultures

P. AROKIARAJ* AND WAN ABDUL RAHAMAN W.Y.*

Tumour tissue was produced on stems of in vitro and in vivo propagated rubber (Hevea brasiliensis) seedlings of PB 5/51, infected with a strain of Agrobacterium tumefaciens 541 (isolated by the Rubber Research Institute of Malaysia in 1971). The tumour tissues exhibited phytohormone-independent growth in tissue culture and produced octopine. In contrast, controls inoculated with distilled water on seedlings did not produce crown gall. Octopine-utilising Agrobacterium strain 541 was distinguished from non-utilisers on a solid medium containing octopine as the only added nitrogen source with bromothymolblue (BTB) as the pH indicator. On blue BTB plates, this strain formed orange-yellow colonies, while those formed by non-utilisers were translucent. This process of cell transformation may facilitate the transfer of genes of economic importance to rubber.

Crown gall is a neoplastic disease produced in most dicotyledonous plants by infection of the plant with the Gram-negative soil bacterium *Agrobacterium tumefaciens*. The virulent trait of *A. tumefaciens* is carried on diverse tumour-inducing (*Ti*) plasmids^{1,2} which range in size from about 200 kb to 250 kb. In the course of infection, a portion of the *Ti* plasmid, the T-DNA is stably transferred to the plant³ and causes two fundamental changes in the physiology of the plant cells. First, the cells become transformed. Whereas normal plant tissue grows in callus culture only when auxin and cytokinin are added to the medium, the growth of crown gall tissue is characteristically phytohormone-independent⁴. Second, crown gall tissues characteristically synthesise opines, primarily octopine or nopaline, which are not synthesised by normal plant tissues. The particular opine produced is coded by the *Ti* plasmid⁵. Thus, the *A. tumefaciens* - plant interaction is one in which a prokaryote 'genetically engineers' a eukaryote to synthesise a compound which can be used as a carbon, nitrogen and energy source by the bacterium.

Hevea brasiliensis Muell-Arg is a perennial cross-pollinating tree and hybridisation between

good inbred lines will bring about heterotic vigour. Due to the long generation required for *Hevea* in selection, some important techniques effective in crop improvement could be applied to *Hevea*, thus, considerably shortening the process of selection for the desired characters. Genetic transformation would be greatly facilitated by the development of gene transfer systems (with selective markers and reporter gene) which may be adapted to allow genes to be introduced into cells using the tissue culture regeneration systems currently available for *Hevea*. The regeneration of plants from the transformed cells, facilitates the rapid improvement of commercially important cultivars. Engineered genes integrated stably into plant chromosomes can serve as powerful tools for studying the effects of new genetic material on plant development. To exploit the above potential for *Hevea*, of fundamental importance is the stable transformation of *Hevea* plants with the development of the *Agrobacterium* tumour-inducing plasmid (*Ti*) system.

Simple methods for gene transfer have been devised involving leaf disc transformation procedure with *A. tumefaciens*. In this report,

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strain 541/71 of *A. tumefaciens*, was used for the induction and *in vitro* culture of crown gall tumours of *Hevea brasiliensis*.

EXPERIMENTAL AND MATERIALS AND METHODS

Bacterial Strain and Culture Medium

A. tumefaciens strain 541/71 was isolated by the Rubber Research Institute of Malaysia (RRIM) in 1971. This strain of *Agrobacterium* was grown in tubes containing 2 ml of sterile medium composed of 5 g/litre tryptone, 3 g/litre yeast extract and adjusted to pH 7.0 before autoclaving. The tubes were placed on an orbital shaker rotating at 110 rev/min and incubated in the dark at 28°C for 36–48 h until the bacteria reached late log phase ($> 10^9$ bacteria/ml).

Bromothymolblue indicator medium⁶ (BTB) containing: K_2HPO_4 , 0.09 g/litre; NaCl, 0.15 g/litre; $MgSO_4 \cdot 7H_2O$, 0.50 g/litre; $CaCl_2 \cdot 6H_2O$, 0.1 g/litre; glucose, 2.0 g/litre, BTB 0.15 g/litre, and octopine, 0.1 g/litre (as the nitrogen source), unless otherwise stated. The pH was adjusted with NaOH to 7.5. The medium was solidified with 1.8% (w/v) Difco bacto-agar.

Plant Materials

Seeds of *Hevea brasiliensis* PB 5/51 were surface-sterilised with 20% (v/v) chlorox (sodium hypochlorite; a.i. 5.25%) containing two drops of Teepol/100 ml for 20 min and washed several times in sterile distilled water. They were then germinated on Murashige and Skoog⁷ (M&S) hormone-free medium, solidified with 0.7% Difco-bacto agar and incubated at $26^\circ C \pm 1^\circ C$, with a 12 h photoperiod of $30\mu E$ (micro Einstein) $m^{-2}s^{-1}$ irradiance provided by fluorescent light.

Non-sterile plants were grown by sowing the seeds in polybags containing sand and soil (1:1 mixture) and incubated in the glasshouse.

Crown Gall Induction

The bacterial suspension was applied by scratching/injecting the stems of two-week

old *in vitro* seedlings with a hypodermic needle containing a thick bacterial suspension. Inoculation was with small (5–10 ml) droplets. A control was set up to measure the wounding response by injecting the plants with sterile distilled water. One-month-old seedlings of PB 5/51 grown *in vivo* in the glasshouse were used for infection with *A. tumefaciens*. The stems of the seedlings were first swabbed with ethanol (to remove foreign contaminants) in a laminar flow chamber. After injection of the bacterial suspension on the stems, (as described for the *in vitro* plants) the infected areas were wrapped with sterile non-absorbent cotton wool before removal, three days later.

In Vitro Culture of Tumours

After three weeks, the tumours were excised from the *in vitro* infected seedlings and transferred to M&S basal medium (without phytohormones) but containing an inhibitory concentration of Ampicillin (1 mg/ml) to free the isolated tumours of the infected bacteria. The tissue was transferred to fresh medium weekly. After a series of passages, with a reduction in the concentration of Ampicillin with every transfer of the tumour tissue, the tissue was usually free of bacteria and was further maintained on an antibiotic-free M&S basal medium under the same conditions.

After six weeks, the tumours isolated from the *in vivo* grown seedlings were surface sterilised by immersion in 10% (v/v) chlorox solution containing two drops of Teepol/100 ml for 15 min and rinsed with sterile water. The tumour tissues were then subjected to *in vitro* culture as described earlier.

Detection of Opines in Tumour Tissue

The method of Christon *et al.*⁸ was used to analyse the opines synthesised in the transformed tissue. About 100 mg fresh weight of tumour tissue was incubated overnight in M&S basal liquid medium containing 5mM L-arginine to enhance octopine production. Tissues were macerated in a sterile Eppendorf tube. After centrifugation for 10 min in a Beckman microfuge 11 at 13 000 rev/min

(10 000 g), 5 μ l of the supernatants, 2 μ l of octopine 0.02% (w/v), nopaline 0.02% (w/v) and 5 mM of L-arginine were spotted on Whatman k-5 silica gel plates. The plates were developed in 50 ml of TLC buffer containing methanol: 2-butanol: 0.1 M sodium acetate, at pH 4.6 (15:1:4). After 2 h, the plates were removed, dried and sprayed with a 1:1 fresh mixture of 10% NaOH (w/v) in 60% ethanol: 0.04% (w/v) phenanthrenequinone (Sigma Chemical Co.) in absolute ethanol and immediately visualised under UV light (254 nm) and photographed through a UV filter.

RESULTS AND DISCUSSION

Development of Tumours

Two weeks after inoculation, tumour formation was readily obtained from infected areas of *in vitro* propagated rubber plantlets. Four weeks after infection, the whitish yellow tumours on the infected areas reached a diameter of 1.5 cm (Figure 1b). Tumour formation was observed after three weeks in the wounded areas on *in vivo* plants. Though they were slow-growing, the brownish galls measured a diameter of 2 cm upon continued growth after eight weeks (Figure 1c).

Growth of *In Vitro* Cultured Tumour Tissues

Tumour tissues cultured *in vitro* grew independently in M&S basal medium lacking phytohormone, even at one-tenth concentration M&S basal medium, they showed prolific growth (Figure 1d). Attempts were made to differentiate the cells but they remained as fast-growing, undifferentiated cells.

Based on experiments, the strain 541 of *A. tumefaciens* is an octopine-utilising *agrobacterium*. When 10⁹ bacteria (strain 541) were plated on BTB plates, this strain formed orange-yellow colonies indicating the octopine-degrading bacteria, while those of non-utilisers of octopine were translucent. Octopine as a nitrogen source acidified the medium whenever a strain could utilise the nitrogen source present. Strains were tested

for utilisation of nopaline by substituting for octopine in the same medium (Table 1).

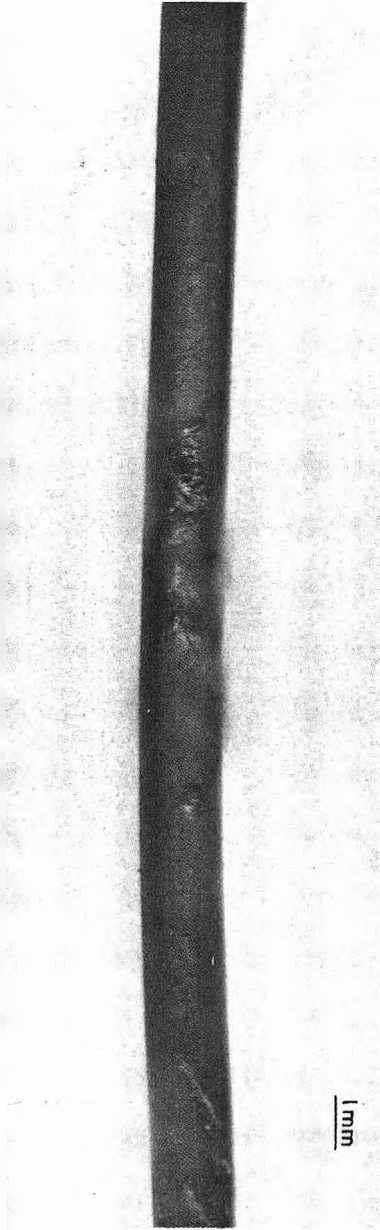
Octopine Synthesis in Tumour Tissue

All tumours except those from control tissue were octopine-positive (Figure 2).

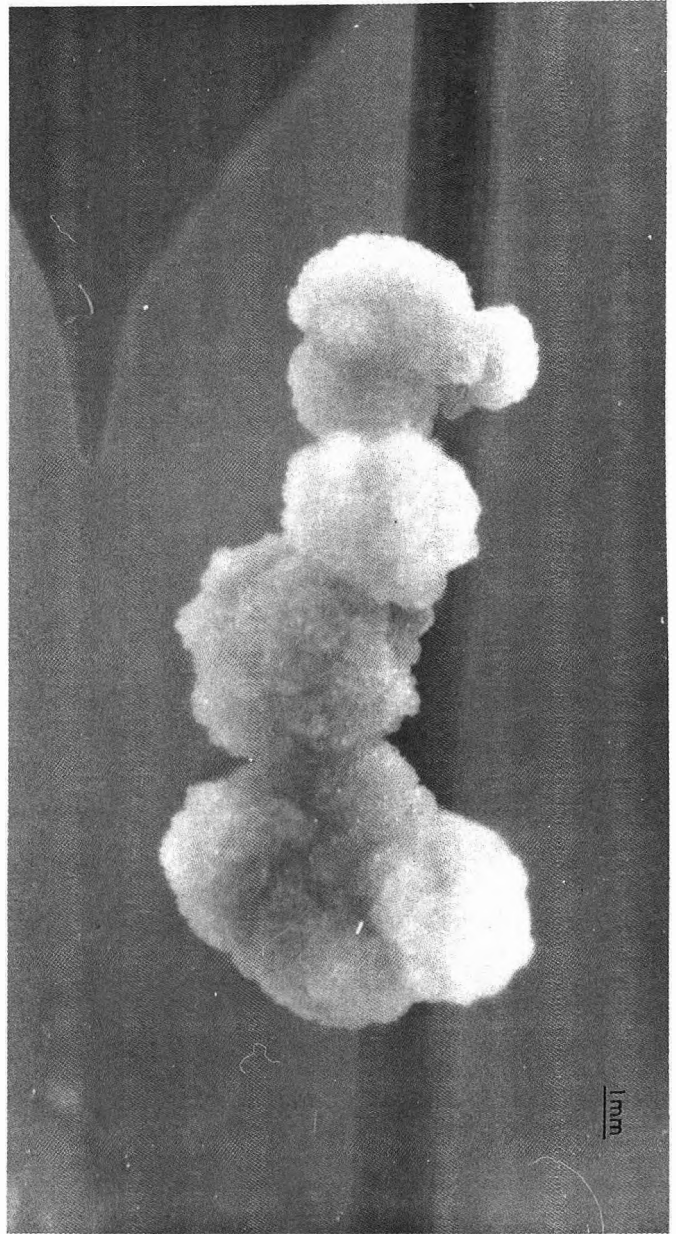
Crown gall formation normally occurs at wound sites. Wounding may have three contributions: 1) to provide access for the bacteria to a cell surface recognition site; 2) to stimulate wound-associated cell divisions which make plant cells competent for transformation; and, 3) to stimulate the production of wound-associated compounds such as acetosyringone which both attract *Agrobacterium* and induce the *vir* genes required for T-DNA transfer⁹. Thus, *Agrobacteria* do not penetrate the healthy plant cells but transform them into tumour cells by transferring a piece of DNA (T-DNA) into them¹⁰. The T-DNA carry genes coding the formation of specific metabolites, the opines as well as those involved in auxin and cytokinin biosynthesis¹¹.

Crown gall tumour cell induced by *A. tumefaciens* strain 541 in rubber seedlings remained small on the plant but can easily produce sterile (bacteria-free cultures), fast-growing callus in culture medium lacking phytohormones because of the constitutive expression of the genes in the T-DNA that encodes for auxin and cytokinin. Normal plant cells required in addition the presence of plant hormones for growth in such a culture medium. As the T-DNA genes also code for the production of opines, the sterile tumour tissue was shown to contain octopine (TLC detection) induced by the octopine-utilising strain.

Agrobacterium strains carrying mutated *Ti* plasmids induce crown galls with an altered hormone balance and in some species, this result in the generation of a 'shooty' mutant tumour¹² (if the genes for the *tms1*-tumour morphology shoot region 1, or *tms2* are inactivated). These properties have been exploited in some laboratories, to regenerate shoot from semi-oncogenic 'shooty mutant' tissue.

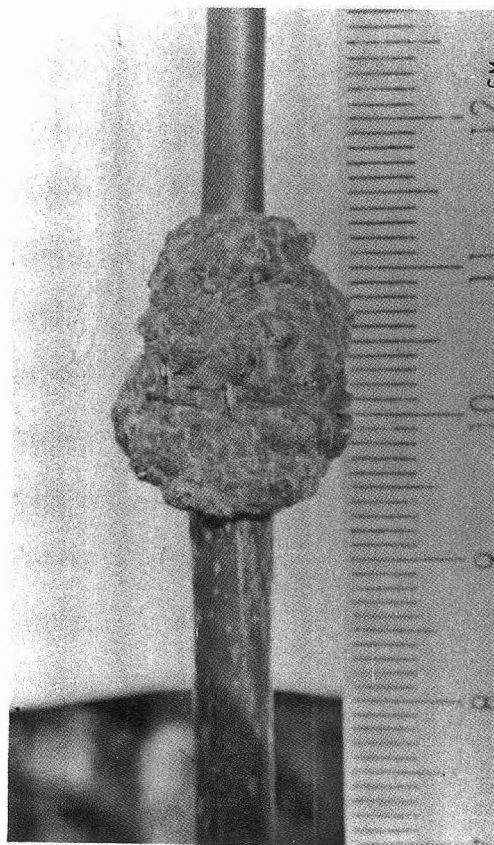


a) Seedling inoculated with sterile distilled water did not develop tumours (Control)

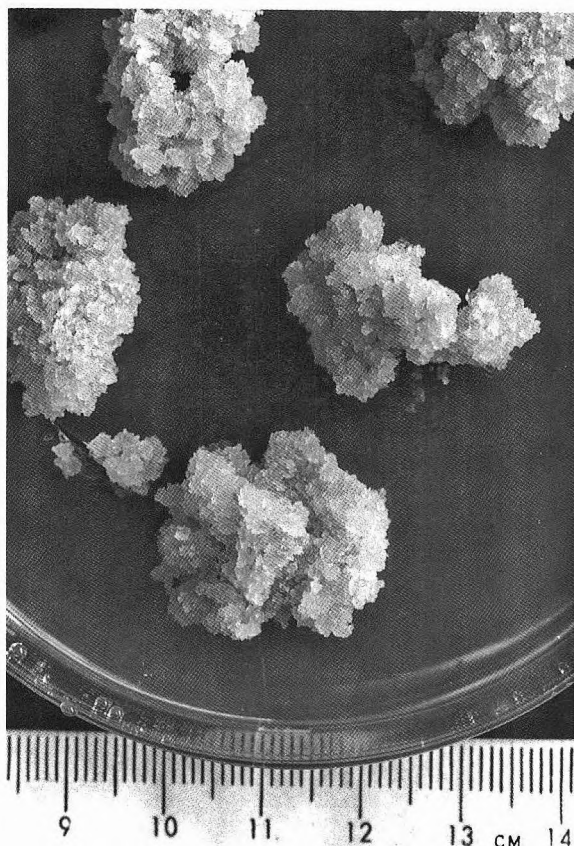


b) Tumours induced by tumourigenic Agrobacterium strain 541 on stem of in vitro propagated rubber seedling.

Figure 1. Development of tumours.



c) Presence of crown gall on stem of in vivo grown rubber seedling, infected with *A. tumefaciens* 541.



d) Phytohormone-independent growth of tumour tissue.

Figure 1. Development of tumours (contd.).

TABLE I. APPEARANCE OF COLONIES ON BTB MEDIUM CONTAINING OCTOPINE AND NOPALINE AS NITROGEN SOURCES

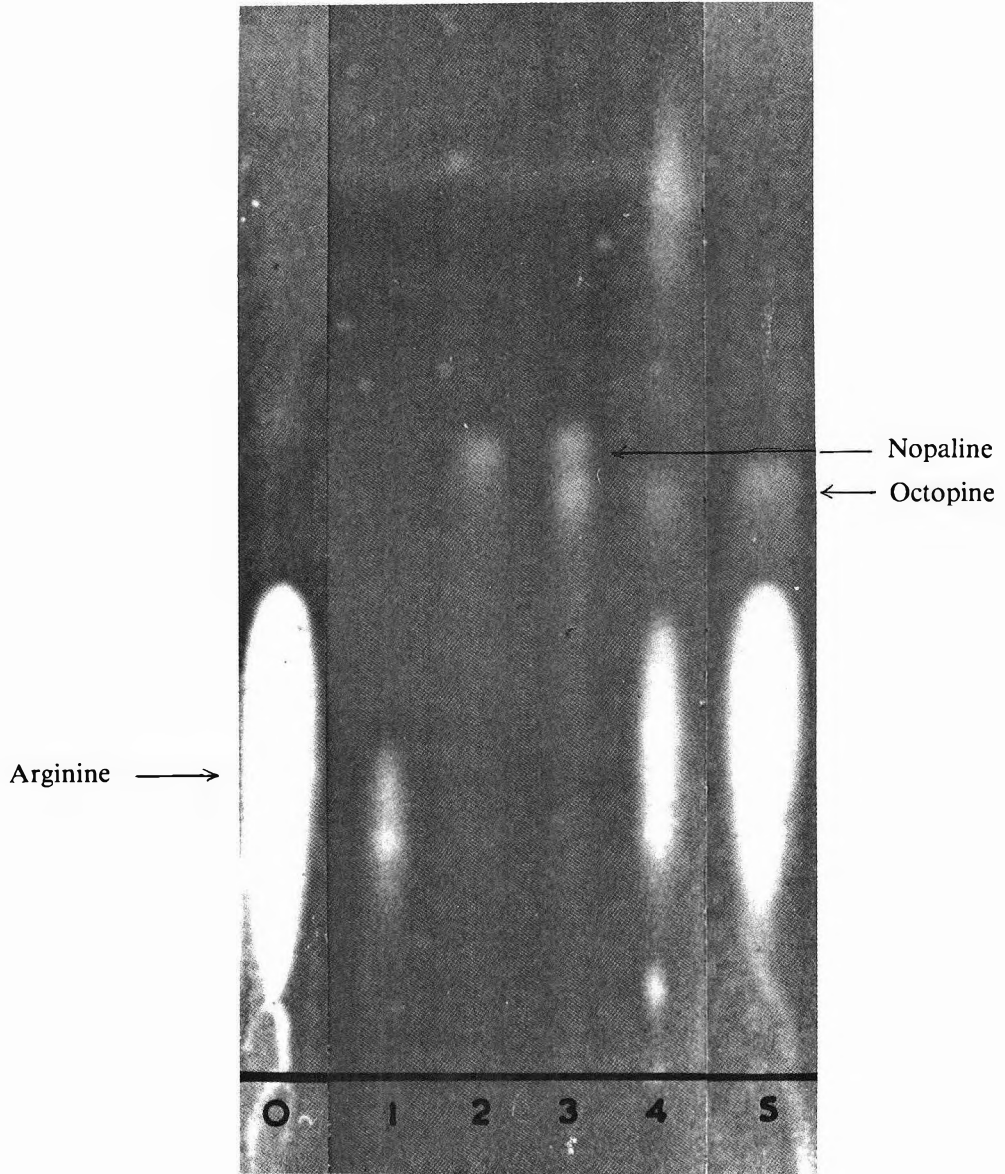
Nitrogen source	Strain ^a		
	C58	T37	541
Octopine	Translucent ^b	Translucent	Orange-yellow
Nopaline	Orange-yellow	Orange-yellow	Translucent

^aStrains C58 and T37 utilise nopaline, 541 utilises octopine

^bOrange-yellow colonies of spontaneous octopine-utilising mutants appeared

Since plasmid transfer is involved in the formation of crown galls, the system is amenable to manipulation for gene transfer in

Hevea. Transformed tissues from *Hevea* could facilitate rapid improvement of commercially important clones.



- Lane 0: Arginine*
Lane 1: Untransformed tissue (Control)
Lane 2: Nopaline standard
Lane 3: A mixture of octopine and nopaline standards
Lane 4: Transformed calli from in vitro propagated PB 5/51 seedlings
Lane 5: Transformed calli from in vivo germinated PB 5/51 seedlings

Figure 2. TLC octopine detection in tumour tissue produced on stem of Hevea plants.

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Influence of Soil Conditions on Growth of Hevea: Glasshouse Evaluations

F.K. YEW* AND E. PUSHPARAJAH**

The influence of soil conditions using the 'least-disturbed soil' sample technique on growth of rubber was studied. Tjir 1 seedlings grown on friable, clayey soils with good physical properties produced the highest dry matter. The Oxisols (Kuantan, Munchong, Segamat, Malacca and Holyrood series) produced more dry matter than the Ultisols (Serdang, Rengam, Chat, Durian and Harimau series). The Entisols (Linau and Briah series) when drained were average in dry matter productivity. The Entisol associated with a high water-table (Linau under flooded conditions) yielded very poorly. The least productive soil was the Histosol (peat), irrespective of whether it was well-drained or flooded.

Soils could be grouped according to texture, favourability of soil conditions for growth and fertility. A higher dry matter production was obtained on clayey soils than on sandier soils. The over-riding importance of a good soil physical condition over that of a high soil fertility status in encouraging dry matter production was demonstrated.

Rubber was shown to be tolerant of loose lateritic clayey soil conditions. Rubber was very sensitive to flooded soil conditions and to peat with resultant very low dry matter yields. It also responded positively to fertiliser applications and yielded poorer at lower sub-surface soil horizons.

Hevea trees have been shown to be more productive on some soils than on others. These variations can be attributed to the different physical and/or chemical properties of the soils¹.

Unfavourable soil conditions include poor soil drainage and a high water-table. Rubber performs poorly under such conditions², as shown when deepening of field drains led to increased yields for clone PB 86. Other poorer soil conditions, viz. less clay and silt contents, shallower soil depths and steeper slopes also decreased growth and yield of rubber in the field³.

Within the genus *Hevea*, certain species have shown variable tolerances to unfavourable soil conditions. For example, Wright⁴ mentioned that in the natural habitat, *Hevea spruceana* occurred on the muddy soils of the islands and river banks of the Amazon river system, which

were subjected to periodic deep inundation. By comparison, *Hevea comorum* occurred on dry savannah land.

Wright⁴ mentioned that *Hevea brasiliensis*, in its natural habitat, occurred on drained sites in the Amazon Basin, Brazil. Occasionally, it was present on sites subjected to brief or slight inundations. This is the sole species on which the Malaysian rubber industry is based.

Soils are spatially distributed, some may occur in distinct localities in the country. In order to study the influence of soil conditions on growth of *Hevea*, a glasshouse trial was set up. The more widespread soils present in Peninsular Malaysia were used in the study.

EXPERIMENTAL

Thirteen soils (*Table 1*) or a combination of these as other treatments, were used for the experiments. Three glasshouse experiments,

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TABLE 1. SOILS USED FOR THE EXPERIMENT

Soil	Parent material	Soil taxonomy (sub-group level)	Soil classification (FAO system)
Linau	Marine alluvium	Typic Sulfaquent	Thionic Fluvisol - saline phase
Briah	Mixed riverine/ marine alluvium	Typic Fluvaquent	Dystric Fluvisol
Chat	Argillaceous shale	Typic Kanhapludult	Ferric Acrisol
Durian	Argillaceous shale	Typic Kanhapludult	Ferric Acrisol
Serdang	Sandstone	Typic Kandiuult	Dystric Nitosol
Rengam	Granite	Typic Kandiuult	Dystric Nitosol
Harimau	Older alluvium	Typic Kandiuult	Dystric Nitosol
Kuantan	Basalt	Typic Hapludox	Orthic Ferralsol
Munchong	Argillaceous shale	Typic Hapludox	Xanthic Ferralsol
Segamat	Andesite	Rhodic Hapludox	Rhodic Ferralsol
Malacca	Argillaceous shale	Petroferric Hapludox	Xanthic Ferralsol - petric phase
Holyrood	Riverine alluvium	Xanthic Hapludox	Xanthic Ferralsol
Peat	Organic material	Hydric Troposaprist	Dystric Histosol

Experiments 1, 2 and 3, were conducted. The experimental design was a randomised complete block design, with treatments replicated thrice in all the experiments.

Tjir 1 selfed seedlings were used as the indicator crop, at the rate of three seedlings per pot. 'Least disturbed soil samples' were collected in 20 cm diameter by 24 cm high, PVC cylindrical pots. The soil samples were collected 10 cm from the soil surface by driving the PVC pipes into the ground with a metal block and retrieving the pipes containing the soil by excavation.

In *Experiment 1*, no fertilisers or nutrient solutions were given to the seedlings during the trial. Twenty-two-day-old seedlings were used. The plants were harvested ninety-three days after transplanting when general nitrogen deficiency was beginning to appear.

In *Experiment 2*, thirty-five-day-old seedlings were used and the experiment was terminated 135 days after transplanting. During the course of the experiment, 200 ml of a complete nutrient solution⁵ which contained 11.2 mg N,

3.1 mg P, 11.8 mg K, 8.0 mg Ca and 6.2 mg Mg were applied to each pot once a week. Thereafter, from the 105th day after transplanting, the same amount of nutrient solution was applied once every fourth day until the end of the experiment.

As the area where the Briah soil was collected was replanted, it was not possible to use this soil in *Experiments 2 and 3*. Additional treatments in *Experiment 2* included collecting samples of Holyrood series at different depths, 7 cm and 25 cm from the soil surface.

In *Experiment 3*, thirty-three-day-old seedlings were used and the experiment was terminated 126 days after transplanting. A granular fertiliser equivalent to Mag.Y (11% N, 10% P₂O₅, 7% K₂O, 2% MgO) was used for all the soils, except for Linau series where Mix.Y (12% N, 11% P₂O₅, 8% K₂O) considered to be more suitable was used. Ammonium sulphate, Christmas Island rock phosphate, muriate of potash and kieserite formed the constituents of the compound fertiliser treatments. In addition, two control treatments, where Munchong and Holyrood soils did not receive any fertilisers at

all were included here. In the first month, 7 g of fertilisers were applied and twice this rate was used every subsequent month. The first fertiliser dosage was applied fourteen days after transplanting. For the sandier soil, like Holyrood, Harimau and Serdang series, the fertilisers were split-applied in two applications per month.

The flooded soil condition in the experiments was achieved by keeping the PVC pots in big earthen-ware pots and adding enough rain-water to maintain a water-level which was 7 cm from the soil surface. The breeding of mosquitoes was minimised by changing the water every week.

The plants in all the trials were watered sufficiently, in the morning and evening. At the end of each experiment, the whole plants, composed of all the leaves, leaf litter, stems and roots, were harvested and the dry weights determined.

At the start of the experiment, some soil samples were collected, air dried and analysed for various physico-chemical properties according to the methods outlined by Norhayati and Singh⁶. Separate samples, five for each soil, were collected from the field for oven-dry bulk density measurements.

The soil surfaces of the 'least disturbed soil' samples in the pots were measured for soil resistance by the use of a pocket soil-test penetrometer. Five measurements were taken for each pot in *Experiment 3*.

RESULTS

Soil Properties

The average volume of the soil occupied by a single 'least-disturbed' core was 7800 ml. The average air-dry weights and bulk densities of the soils used are shown in *Table 2*; Serdang soil being the heaviest and peat, the lightest. Disregarding the organic soil, Linau series was the least dense.

Four Oxisols (Munchong, Segamat, Malacca, Kuantan), three Ultisols (Rengam, Durian,

TABLE 2. AVERAGE AIR-DRY WEIGHTS AND BULK DENSITIES OF THE SOILS

Soil	Weight (kg/pot)	Air-dry bulk density (g cm ⁻²)
Kuantan	7.62	0.98
Munchong	9.61	1.23
Segamat	8.43	1.08
Malacca	11.41	1.46
Holyrood	10.27	1.32
Serdang	12.31	1.58
Harimau	10.93	1.40
Rengam	11.35	1.46
Durian	11.38	1.46
Chat	7.90	1.01
Briah	9.44	1.21
Linau	6.33	0.81
Peat	1.54	0.20
Mean	9.12	1.17

Chat) and two Entisols (Briah, Linau) were considered to be heavy clay-textured according to the ISSS system (*Table 3*). An Oxisol (Holyrood) and an Ultisol (Harimau) were sandy clay-textured. The texture of the Ultisol (Serdang) was sandy clay loam. Malacca series contained 40% of unconsolidated lateritic gravels on a soil weight basis.

Most of the soils studied had a low to very low soil fertility level (*Table 3*) according to an established soil fertility classification system⁷. Malacca, Munchong, Segamat, Holyrood, Serdang, Harimau and Rengam series were classified as very low in fertility while Chat, Durian and Kuantan series were classified as low in fertility. Linau series had a very high fertility status with Briah series having a high fertility status.

The main soil structural properties and moist consistencies of the soils used for the study are given in *Table 4*. All the non-lateritic mineral soils were friable but Durian, Chat, Briah, Rengam (top 8 cm only) and Linau series when drained had a firm consistency. The friable soils also had weak to moderate medium sub-angular blocky structures.

TABLE 3. PARTICLE SIZE DISTRIBUTION, BULK DENSITY AND CHEMICAL CHARACTERISTICS OF THE SOILS

Soil	Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)	Coarse fragments (>2 mm) wt. % of whole soil	Oven-dry bulk density (g cm ⁻³)
Kuantan	2.2	16.8	26.4	54.6	—	0.93
Munchong	13.2	7.5	19.5	59.8	—	1.10
Segamat	1.5	2.5	19.9	79.1	—	0.90
Malacca	2.8	4.9	24.9	67.4	40	1.16
Holyrood	45.6	24.7	8.1	21.6	—	1.21
Serdang	47.7	35.2	2.7	14.4	—	1.17
Harimau	42.5	25.2	3.6	28.7	—	1.16
Rengam	41.6	12.1	4.6	41.7	—	1.31
Durian	6.7	12.6	34.8	45.9	—	1.29
Chat	3.6	13.3	22.6	60.5	—	1.01
Briah	0.2	2.4	34.6	62.8	—	0.99
Linau	2.4	5.6	47.8	44.2	—	1.21
Peat	—	—	—	—	—	0.2

— Not determined

TABLE 3. PARTICLE SIZE DISTRIBUTION, BULK DENSITY AND CHEMICAL CHARACTERISTICS OF THE SOILS (Contd.)

Soil	H ₂ O	pH 1 KCl	Org.C (%)	Total N (%)	Total available P(p.p.m)	Acid extractable			
						K (M-equiv./100 g soil)	Ca	Mg	
Kuantan	4.3	4.2	1.33	0.106	2 029	7	0.51	0.16	2.99
Munchong	4.5	4.2	1.15	0.098	599	4	0.24	0.27	0.51
Segamat	4.5	4.2	0.74	0.087	1 266	5	0.58	0.59	1.19
Malacca	4.4	4.0	1.60	0.149	492	6	0.50	0.21	1.23
Holyrood	4.8	4.4	0.66	0.070	147	4	0.49	0.09	0.72
Serdang	4.3	3.8	0.37	0.054	63	5	1.48	0.14	1.69
Harimau	4.4	4.2	0.50	0.054	53	3	0.16	0.14	0.42
Rengam	4.6	3.9	0.60	0.062	40	5	0.17	0.16	0.38
Durian	4.2	3.5	0.37	0.058	25	7	4.83	0.19	1.88
Chat	4.2	3.6	1.06	0.149	247	4	11.50	0.24	8.00
Briah	4.1	3.4	0.79	0.123	186	7	6.68	0.20	22.75
Linau	3.8	3.2	6.61	0.342	675	28	6.19	1.05	18.38
Peat	3.0	2.2	53.49	1.057	123	20	0.27	6.51	9.85

TABLE 3. PARTICLE SIZE DISTRIBUTION, BULK DENSITY AND CHEMICAL CHARACTERISTICS OF THE SOILS (Contd.)

Soil	K	Exchangeable Ca (M-equiv/100 g soil)	Mg (M-equiv/100 g soil)	Na	Base saturation (%)	CEC NH_4OAc 100 g soil
Kuantan	0.07	0.09	0.03	0.03	2.17	10.13
Munchong	0.07	0.13	0.06	0.04	4.32	6.95
Segamat	0.06	0.36	0.07	0.03	6.86	7.58
Malacca	0.09	0.19	0.09	0.03	4.04	9.90
Holyrood	0.03	0.02	0.01	0.02	2.50	3.20
Serdang	0.04	0.09	0.02	0.02	6.34	2.68
Harimau	0.03	0.08	0.01	0.03	5.81	2.58
Rengam	0.03	0.09	0.02	0.02	4.54	3.52
Durian	0.12	0.05	0.03	0.03	3.63	13.83
Chat	0.11	0.11	0.06	0.03	3.04	10.18
Briah	0.34	0.18	7.17	0.07	33.75	22.99
Linau	0.44	0.92	0.12	1.00	5.60	44.24
Peat	0.27	1.65	4.88	0.85	6.17	123.91

TABLE 4. MAIN STRUCTURAL PROPERTIES AND CONSISTENCIES OF THE SOILS

Soil	Moist consistency	Main soil structure
Kuantan	Friable	Moderate medium sub-angular blocky
Munchong	Friable	Moderate medium sub-angular blocky
Segamat	Friable	Weak medium sub-angular blocky
Malacca	Matrix with 50% loosely-packed laterites on a soil volume basis	
Holyrood	Friable	Moderate weak coarse sub-angular blocky
Serdang	Very friable	Moderate to weak medium sub-angular blocky
Harimau	Friable	Moderate medium sub-angular blocky
Rengam	Top 8 cm firm; bottom friable	Moderate strong coarse sub-angular blocky
Durian	Firm	Strong, very coarse sub-angular blocky
Chat	Firm	Moderate strong coarse sub-angular blocky
Briah	Firm	Very strong, coarse angular blocky
Linau	Sticky ^a	Moderate coarse and medium sub-angular blocky
Peat	—	Moderate fine crumbs

^aWet consistency but when drained, moist consistency was firm

The structure of the other soils with firm consistency ranged from moderately strong to very strong sub-angular blocky and angular blocky. The only organic soil, peat, had a moderate fine crumbly structure.

The soils with firm consistency and a coarser structure e.g. Durian, Rengam, Linau (non-flooded) and Chat soils also had a high resistance to penetration by a penetrometer. Values of resistance to penetration for these soils exceeded 1.0 (Table 5). The other soils had low penetrometer readings, with values of less than 1.0. Peat showed almost no resistance to penetration. The penetrability of Linau series kept with a high water-table was very low.

Total Dry Matter Production

The soils differed in their abilities to support dry matter production by plants, irrespective

of whether they were fertilised or not (Table 6) and the differences were statistically significant (Table 7). Hereafter, the dry matter yield is inferred to relate to for 'soil productivity'.

In *Experiment 1*, where plants were unfertilised, the best growth was obtained on Munchong series and the three soils with poorest growth were Linau (flooded), peat (flooded) and peat. All the plants in this experiment showed general nitrogen deficiency at about 93 days after transplanting.

When fertilisers were applied (*Experiments 2 and 3*), the plants grew for a longer period without suffering from nutrient deficiencies. In *Experiment 2*, three of the Oxisols (Kuantan, Munchong and Malacca series) continued to support high dry matter production. Peat and Linau (flooded) produced the lowest dry matter.

TABLE 5. SOIL RESISTANCE TO PENETROMETER

Soil	Penetrometer reading ^a
Kuantan	0.49
Munchong	0.35
Segamat	0.49
Malacca	Not taken
Holyrood	0.76
Serdang	0.59
Harimau	0.81
Rengam	1.38
Durian	1.54
Chat	1.07
Linau	1.14
Linau (flooded)	0.29
Peat	0
Mean	0.74

^aUncalibrated strength values

The other soils maintained intermediate positions in the ranking.

A lower dry matter production was obtained on Holyrood soil of depth 25–49 cm than at 7–31 cm, indicating that the lower soil horizons had poorer productivity.

In *Experiment 3*, Kuantan and Munchong soils continued to support high dry matter production while Linau series (flooded) and peat produced the lowest yields.

Fertiliser usage increased dry matter production by 44% on the clayey Munchong series and by 49% on the sandier Holyrood series.

The reductions in dry matter caused by the presence of a high water-table and by peat were more severe than that caused by low soil chemical fertility. This is evident from *Table 6*, where both Munchong (no fertiliser) and Holyrood (no fertiliser) ranked higher than Linau (flooded) and peat.

The sum of the total dry matter production for *Experiments 1, 2, and 3* would provide the best overall picture of soil productivity since the

results were based on three croppings. *Table 6* shows that the Oxisols (Kuantan, Munchong, Segamat, Malacca and Holyrood) produced more dry matter than the Ultisols (Serdang, Rengam, Chat, Durian and Harimau). Linau series (Entisol), if not flooded, ranked fourth. When it was associated with a high water-table, its productivity was the lowest among the mineral soils. Peat had the lowest productivity when both mineral and organic soils were considered.

DISCUSSION AND CONCLUSION

The results showed that there were significant yield differences between the soils which could be explained by variations in soil properties. Soil productivity is mainly influenced by four inherent soil properties *viz.* soil texture, favourable soil physical conditions for growth, chemical fertility level and soil depth. The last property was not studied in these experiments.

Figure 1 denotes the clayey soils as *C* and the sandier soils as *S*. Most of the soils were heavy clay while the sandier soils (*S*) were Holyrood, Harimau and Serdang series. Only Linau and Briah series were of high fertility (*F*) while the rest were infertile (*I*) being either low or very low in chemical fertility.

The criterion of soil structure/consistency would reflect the favourability of the soil physical conditions for growth. Soils could be grouped as poor (*P*) or unfavourable or as arable (*A*) or good. Penetrometer resistance could be used to obtain an index of tilth⁸ and reflected the penetrability or compactness of a soil⁹. Based on soil profile descriptions⁷, structural properties and soil consistencies (*Table 4*) supported by penetrometer readings from *Table 5*, soils with favourable soil physical conditions (*A*) were Kuantan, Munchong, Segamat, Malacca, Holyrood, Serdang, Harimau and Linau (flooded). All these soils had penetrometer readings of less than 1.0. Penetrometer readings were not taken for the lateritic soil, Malacca series, but the loose laterites within the clayey soil would infer an easy medium for root proliferation. Relatively, the other soils had poorer soil conditions for growth (*P*).

TABLE 6. DUNCAN'S MULTIPLE RANGE TEST (5% PROTECTION LEVEL) FOR TOTAL DRY MATTER PRODUCTION (MEAN OF MEANS)

Experiment 1		Experiment 2		Experiment 3		Sum of Expt. 1, 2 and 3	
Soil	Total dry matter production (g/plant)	Soil	Total dry matter production (g/plant)	Soil	Total dry matter production (g/plant)	Soil	Total dry matter production (g/plant)
Munchong	9.00	Segamat	18.15	Linau	15.78	Kuantan	40.15
Kuantan	8.79	Kuantan	17.04	Kuantan	14.32	Munchong	37.95
Malacca	7.86	Munchong	15.98	Rengam	12.63	Segamat	36.48
Briah (flooded)	7.85	Malacca	14.84	Munchong	12.61	Linau	35.27
Durian	7.81	Holyrood (7 cm)	14.57	Chat	12.38	Malacca	34.72
Briah	7.80	Holyrood (25 cm)	14.11	Malacca	12.03	Holyrood	33.57
Segamat	7.53	Serdang	13.42	Holyrood	11.73	Serdang	32.09
Serdang	7.52	Rengam	12.40	Durian	11.22	Rengam	31.98
Harimau	7.48	Linau	12.18	Serdang	11.16	Chat	29.95
Linau	7.30	Harimau	10.96	Segamat	10.80	Durian	29.89
Holyrood	7.27	Durian	10.86	Harimau	10.03	Harimau	28.47
Chat	7.11	Chat	10.46	Munchong (unfertilised)	8.74	Linau (flooded)	21.20
Rengam	6.95	Peat	10.25	Holyrood (unfertilised)	7.87	Peat (flooded)	16.45
Linau (flooded)	6.67	Linau (flooded)	8.00	Linau (flooded)	6.53		
Peat (flooded)	4.14			Peat	2.28		
Peat	3.92						

TABLE 7. CONDENSED ANOVA TABLE FOR THE TOTAL DRY MATTER PRODUCTION OF THE VARIOUS EXPERIMENTS

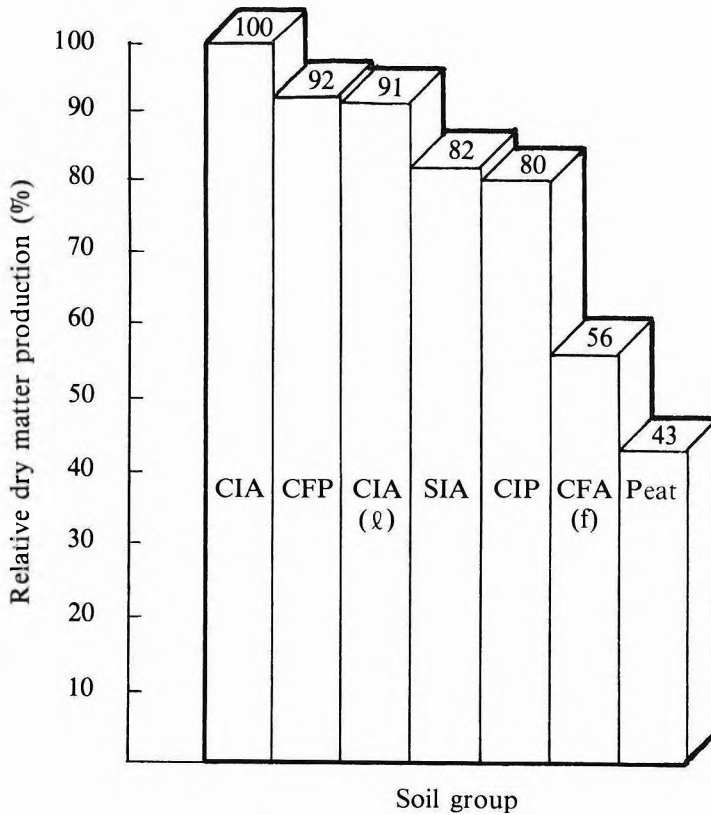
Source	df	Experiment 1 MS	F	df	Experiment 2 MS	F	df	Experiment 3 MS	F	Sum of Expt. 1, 2 and 3 df	MS	F
Replicate	2	0.64	0.48 ns	2	17.07	0.98 ns	2	10.30	1.23 ns	2	18.75	1.29 ns
Soils	15	5.61	4.24***	13	74.58	4.28***	14	32.90	3.91**	12	129.34	8.89***
Error	30	1.33		26	17.42		28	8.38		24	14.56	
Mean (g/plant)			7.19		13.08			10.67				31.40
SD			1.15		2.41			2.90				3.82
CV (%)			16.02		18.41			27.13				12.15

ns = not significant

** = significant P < 0.01

*** = significant P < 0.001

- C - Clayey
- S - Sandy
- F - Fertile
- I - Infertile
- A - Favourable soil physical conditions
- P - Unfavourable soil physical conditions
- f - Flooded
- ℓ - Lateritic



Soils in various groups

- CIA - Kuantan, Munchong, Segamat
- CFP - Linau
- CIA(ℓ) - Malacca
- SIA - Holyrood, Serdang, Harimau
- CIP - Rengam, Chat, Durian
- CFA(f) - Linau (flooded)

Figure 1. Relative dry matter production of Tjir 1 on various soil groups.

Figure 1 shows that soils with high clay contents were more productive than those with low clay contents; supporting similar reported field observations².

When soils of different favourability of soil physical conditions, but of similar textures and chemical fertilities (*CIA* and *CIP*) were compared, the poorer soil structure/firmer consistencies resulted in a 20% reduction in dry matter production. In fact, poorer soil structure or very firm to hard soil consistencies were more important than even a low soil chemical fertility in crop reduction, as seen when *CIA* was compared to *CFP*.

Generally, rubber responded positively to a high soil nutrient status, other conditions being equal as seen when *CFP* was compared to *CIP*. Rubber was also shown to respond to fertiliser usage and to perform poorer at sub-surface horizons. Rubber also grew well on loose lateritic (40% by weight) clayey soil.

The flooding of a soil excluded oxygen from it, while carbon dioxide, hydrogen sulphide and organic acids increased to levels which were toxic to most plants^{10,11}. Rubber was shown to be very sensitive to flooding, the treatment reducing dry matter production by 44%.

Rubber performed poorest on peat when dry matter production was lowered by 57%, compared to the inorganic soils. The very low productivity on peat is attributed to the combined properties such as lack of structure, higher acidity and nutrient imbalances leading to poor root development and subsequent imbalance and poorer uptake of nutrients.

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