The influence of molecular weight distribution and branching on the relaxation behaviour of uncrosslinked natural rubber*

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The sol component of a Hevea natural rubber was fractionated, and each fraction characterized by gel permeation chromatography and intrinsic viscosity. Estimates of the branching were obtained, the values ranging from 1×10^{-6} at molecular weights below 1×10^6 to about 6.4×10^{-6} at a molecular weight of 2.24×10^6. Stress relaxation tests were carried out on the fractions and on polydisperse and near monodisperse synthetic, linear polyisoprenes. Comparison of the data established that the branching was a substantial influence on the behaviour of the natural rubber. The reptation model of Doi–Edwards and a simple, linear blending law provided reasonable predictions of the observed relaxation behaviour of the narrow and, surprisingly, the broad distribution synthetic polyisoprenes.

INTRODUCTION

The rheological properties of uncrosslinked Hevea natural rubber, like any polymer melt, are affected by[1]:

(a) average molecular weight;
(b) molecular weight distribution;
(c) branching of the polymer chains.

In addition to these are factors more particular to natural rubber[2]:

(d) gel;
(e) solvent extractable material, such as fatty acids;
(f) strain crystallization.

The relative importance of these factors in determining the differences in rheological, and hence processing behaviour between the various grades of Hevea natural rubber (NR)[2] and between natural and synthetic *cis*-polyisoprenes remains to be established[3]. This investigation examines the influence of the molecular factors (a), (b) and (c) on the flow behaviour of NR by carrying out stress relaxation measurements on well-characterized material.

The extensive studies of the molecular aspects of polymer melt viscosity have been recently reviewed by Pearson[4]. Much of the molecular theory is developed from the work of Doi and Edwards[5] who based their model on the reptation of chains within a tube of constraints. The original pure reptation theory for monodisperse polymers was confined to the long-time region; it has been refined to take account of faster relaxation processes[6] and the effect of chain contour length fluctuations[7]. The influence of polydispersity can, according to the pure reptation model, be accounted for

by a linear addition of the contributions to the relaxation from weight fractions of each molecular species. This simple approach has been found to fail[8,9], because of the need to consider additional relaxation mechanisms associated with release of the tube constraints[10–13].

The presence of chain branches of a length greater than the entanglement spacing has a marked effect on the rheology of polymer melts[14,15]. In terms of the original tube model relaxation is greatly retarded because the branch point is effectively fixed until the arms have retracted. For a star-branched polymer the longest relaxation time, T^b_{max}, becomes[10,16,17]

$$T^b_{max} = (M_b/M_e) \exp(v' M_b/M_e) \qquad (1)$$

where M_b and M_e are, respectively, the molecular weight of the branches and the entanglement molecular weight, and v' is a constant of the order unity. It is predicted[17] that at long times the stress relaxation does not follow a purely exponential form. Experiments[18] have suggested that the values of T^b_{max} given by equation (1) are reduced by tube-renewal mechanisms[19,20]; these have the effect of lowering the value of v' (ref. 21). The relaxation of H-polymers has been found to be slower than in three- or four-arm stars with the same number of entanglements per branch[22]. The central part of the molecule between branch points is particularly constrained and is likely to control the long-time relaxation process. Theories for H- and other multiply branched polymers have been developed[23,24].

The presence of gel—the proportion remaining undissolved in a solvent—in natural rubber makes a complete molecular characterization of this material uncertain as techniques such as gel permeation chromatography (g.p.c.) and intrinsic viscosity can only be applied to the soluble or 'sol' component. The origin of the gel component appears to involve reactions between non-isoprene groups on the rubber chain and proteinaceous material present in the natural rubber[25–28]. The

reactions ultimately product a network and hence gel, but a precursor to that could be the linking of chains to form molecules with long-chain branches. The presence of such branching in NR has been suggested[29] and its extent more recently measured[30]. Previous work has studied how the gel effects the rheological properties of one grade (SMR L) of NR[31]. By investigating in particular the stress relaxation behaviour, it appeared that the gel component increased the modulus of the rubber but interestingly did not strongly influence the rate at which it relaxed. Thus the slower relaxation of the Hevea in comparison with synthetic polyisoprenes[3] would seem to depend upon the properties of the sol material, and hence the factors (a), (b) and (c) mentioned earlier.

Campbell and Fuller[31] also showed that the solvent extractable non-rubbers had a marked effect on the stress relaxation behaviour. These materials therefore need to be removed before assessing the influence of such factors as molecular weight distribution. In the present investigation crystallization was avoided by appropriate choice of test conditions; its presence would have made the assessment of the factors primarily under study difficult.

Few experimental studies of the relation between molecular parameters and rheology appear to have been carried out in the case of natural rubber. Work reported[32,33] has used technological measures of rheology performed on the whole material. As a consequence any influence of gel and soluble non-rubbers was not allowed for, and the mechanical data is less readily interpreted in terms of fundamental parameters. An investigation of the relaxation of linear and star-branched, narrow molecular weight distribution, synthetic cis-polyisoprene has, however, been performed[34].

Here further stress relaxation measurements are carried out on a wider range of near monodisperse, synthetic cis-polyisoprenes and one broad distribution polyisoprene. The ability of the pure reptation theory of Doi–Edwards to fit the data from the monodisperse material is tested, along with the applicability of the simple, linear blending law to the behaviour of the wide distribution polymer. Relaxation measurements are also obtained from fractions of sol, Hevea rubber characterized in terms of molecular weight distribution and degree of branching. In the light of the data from linear polymers, the influence of branching upon the relaxation of the NR is assessed.

EXPERIMENTAL

Materials

The NR was SMR CV grade. The near monodisperse cis-polyisoprenes (96% cis 1,4 content) were molecular weight standards obtained from Polymer Laboratories Ltd, UK, and the wide distribution polyisoprene (92% cis 1,4 content) was Cariflex IR-305 (Shell, UK). The synthetic materials were thought to be free of chain branching.

Sol separation and fractionation of natural rubber

The separation into sol and gel components was carried out by progressive dissolution in dichloromethane (AR). The rubber was cut into small cubes and added to 3 l of solvent in a separating funnel. The rubber swelled and floated on the solvent. A clear solution containing the soluble rubber components was produced and could be readily drained off, leaving the gel phase.

Fresh solvent was carefully introduced into the separating funnel from below and after further dissolution another solution was recovered. This process was repeated several times, using fresh solvent, until approximately 50% of the soluble component had been separated from the bale rubber. The dissolution was carried out in subdued light and under a blanket of nitrogen to reduce photo- and oxidative degradation.

For the fractionation, the extracted solutions were combined and reduced in volume to make a 1% w/v solution, which was placed in a water-jacketted glass reaction vessel kept at 25°C. Methanol (AR) was added dropwise to the stirred solution until the cloud-point was reached. The temperature was raised until the mixture cleared, usually at between 30°C and 40°C, and then it was cooled very slowly, without stirring, back to 25°C. Consequently a rubber fraction came out of solution and collected on the surface. The solution was drained off, separating it from the fraction, which was redissolved in dichloromethane. The fractionation procedure was repeated until a large proportion of the sol rubber had been recovered. The fractions were dried by rotary evaporation and stored in the dark under vacuum.

Viscometry

The solution viscosities of the synthetic polyisoprenes and the NR fractions were measured for a range of concentrations by using a single-bulb Ubbelohde viscometer. The measurements, like the g.p.c. analyses, were carried out at 40°C in tetrahydrofuran (THF), stabilized with 0.05% 2,5-di-tert-butyl-4-methyl-phenol (BHT). The solvent efflux time was 137 s and so kinetic energy corrections were not considered necessary. No corrections were made for the shear rate dependence of the intrinsic viscosity. The NR fractions were filtered through two layers of lens tissue before measurement of flow times. An aliquot of the solutions was dried to constant weight to determine the concentration.

The intrinsic viscosities were determined by extrapolating the data to infinite dilution in two ways, one using the Huggins equation:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

and the other the Kraemer equation:

$$\ln \eta_r/c = [\eta] + k''[\eta]^2 c$$

where η_{sp}/c is the reduced viscosity; $\ln \eta_r/c$ is the inherent viscosity; $[\eta]$, the intrinsic viscosity, is the limiting value of these at infinite dilution; c is the concentration expressed as $g\,dl^{-1}$, and k' and k'' constants. The two procedures gave very similar values of $[\eta]$, the average being taken.

Gel permeation chromatography

The g.p.c. analyses were carried out on a set of two 60-cm mixed bed columns (Polymer Laboratories Ltd) using THF at a flow-rate of 0.5 ml min⁻¹ and a temperature of 40°C; concentrations were kept at about 0.2% w/v in all cases. The detector utilized ultra-violet light at 215 nm. The instrument was calibrated with polystyrene standards (Polymer Laboratories Ltd).

Fabrication of testpieces

Cast films of each of the synthetic polyisoprenes and the NR fractions were prepared from a fairly viscous

toluene solution (2% w/v) poured onto a flat sheet of cellophane that had been stretched over a form. The cast film was dried in a cabinet purged with nitrogen. The process was repeated to build up a film of reasonable thickness. When dry, the film was peeled away from the cellophane, and cut into strips approximately 30 mm long, 3 mm wide and 1 mm thick. The residual stresses formed in the strips during the drying procedure were allowed to decay for several days. The testpieces were stored in the dark, under vacuum prior to mechanical testing.

Stress relaxation

The stress relaxation tests were performed on the strips deformed in tension, using a purpose-built jig that enabled the testpieces to be rapidly strained in about 50 ms. The subsequent decay of the load whilst the extension was held fixed was followed, using a strain-gauged cantilever load cell, over the period $0.3-10^4$ s after straining. The tests were performed in a nitrogen atmosphere at a temperature of 27°C. The sample was stuck to the grips with cyanoacrylate glue and a small 'prestrain' applied to ensure that the strip was not buckled. The preload developed was allowed to decay either to a constant value or at least for a period of time comparable with the duration of the relaxation test. Hence any change after the application of the test extension could be assumed to be zero or to occur at a constant rate, and thus the preload value at any given time throughout the experiment determined by extrapolation. The preload was subtracted from the observed load to give the relaxation load. Consistent with the subtraction of the preload the extension was measured with respect to the prestrained length. The cross-sectional area was calculated from the weight of each strip and the density of the rubber; the area was corrected to take account of the prestrain.

The range of extensions covered in the tests was 20-80%; these should have been sufficiently low for the NR results not to be affected by strain crystallization. The extensions were measured by observing fiducial marks on the strips with a cathetometer; two sets of marks were used in order to check the uniformity of applied strain.

Estimation of branching

The determination of branch content is generally based on the relative size of branched and linear polymers in solution[35]. The hydrodynamic volume of a branched polymer molecule is smaller than that of a linear polymer of the same molecular weight, the reduction being expressed in terms of the branching index, g'. For a polydisperse material the average branching index g'_{M_w} is defined as:

$$g'_{M_w} = [\eta]_b/[\eta]_1 \qquad (2)$$

where $[\eta]_1$ is the intrinsic viscosity of a linear polymer of the same molecular weight distribution as the branched polymer of intrinsic viscosity, $[\eta]_b$, measured in the same solvent and at the same temperature. The assumption is made here that the solvent expansion factor is not significantly affected by branching[36].

The calculation of the branching index of a polydisperse polymer can be found from a combination of g.p.c. and intrinsic viscosity measurements, using the

fact that the hydrodynamic radius is a unique function of the product $[\eta]M$ for both branched and linear molecules, where M is the molar mass[37]. Thus by analogy, the average branching index g'_{M_w} can be expressed as[35]:

$$g'_{M_w} = g'_{\eta,M_w} = ([\eta]_b/[\eta]^*)^{a+1} \qquad (3)$$

where $[\eta]^*$ is the intrinsic viscosity of a linear polymer having the same elution curve as the branched material and a is the index in the Mark–Houwink equation. This apparent intrinsic viscosity is calculated from the apparent molecular weight distribution of the branched material using the equation:

$$[\eta]^* = K \sum w_i M_i^{*a} \qquad (4)$$

where w_i is the mass fraction of each species M_i^* within the distribution, and K and a are the Mark–Houwink constants determined for the linear polymer.

For a given functionality of the branch points, the number of branches per molecule, N can be calculated from the parameter g, which is the ratio of the mean square radius of gyration of the branched and linear molecules[38]. Some allowance for polydispersity in the branched material is made by using expressions for the weight average number of branches per molecule, N_w derived by Zimm and Stockmayer[38] for the case of the most probable distribution of branched polymers. The relationship between g and g'_{M_w} is often expressed as:

$$g^x = g'_{M_w} \qquad (5)$$

where x depends on the type and extent of branching. It has been proposed that x equals 0.5 for star-like polymers, and for very low degrees of long-chain branching; as the degree of branching increases the value of x has been found to rise towards 1.5 (ref. 39). The branch density, $\tilde{\lambda}$ is calculated from the relation:

$$\tilde{\lambda} = N_w/M_w \qquad (6)$$

where M_w is the weight average molecular weight.

RESULTS AND DISCUSSION

Intrinsic viscosity and g.p.c.

Figures 1 and *2* show the respective gel permeation chromatograms obtained from the original bale SMR CV rubber and four of the subsequent fractions. Although the molecular weight distributions of the fractionated rubber are much narrower than the original bale rubber they are still broad when compared with the polyisoprene standards $(M_w/M_n = 1.03-1.15)$. The breadth partly re-
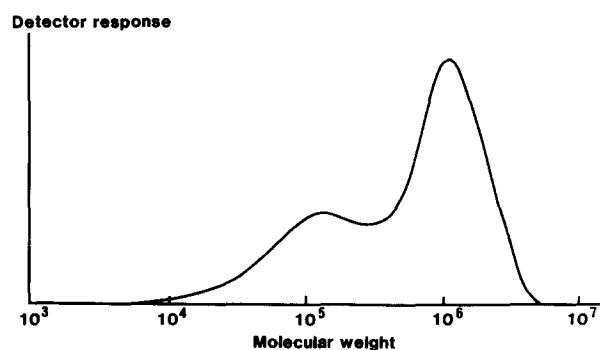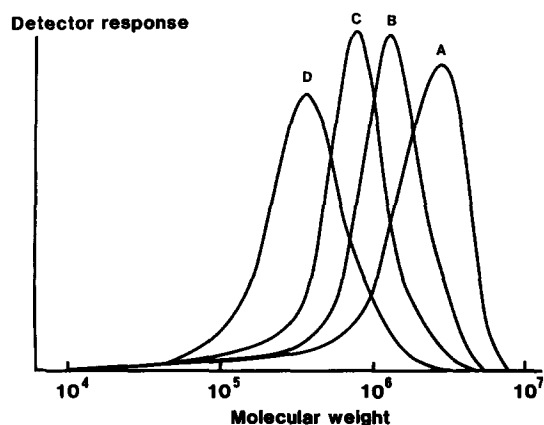

Figure 1 Molecular weight distribution of SMR CV, Hevea natural rubber

Table 1 Molecular characterization and branch content of natural rubber fractions and IR-305

Rubber	$M_w{}^a$ $(\times 10^{-6})$	$M_w/M_n{}^a$	$[\eta]$ $(dl\,g^{-1})$	$[\eta]^{*b}$	g'	N_w	$\tilde{\lambda}$ $(\times 10^6)$
NRF1	2.24	2.39	6.76	9.50	0.558	6.4	2.9
NRF2	1.38	2.89	5.82	6.63	0.800	1.3	1.0
NRF3	0.83	2.14	4.05	4.43	0.858	0.8	1.0
NRF4	0.42	1.70	2.36	2.54	0.882	0.6	1.4
IR-305	1.48	2.45	7.69	6.05	–	–	–

^{a} Obtained by g.p.c.
^{b} $[\eta]^*$ is the apparent intrinsic viscosity calculated from equation (4)

Figure 2 Molecular weight distributions of four natural rubber fractions: A, NRF1; B, NRF2; C, NRF3; D, NRF4

sulted from the need for each fraction to contain enough material for the stress relaxation measurements.

Polyisoprene is susceptible to degradation in the g.p.c. column by several mechanisms, one of which is shear degradation induced by the flowing solution. McIntyre *et al.*[40] subjected several polyisoprenes to a range of flow times and column configurations to show the extent of such degradation. In the present work preliminary investigations suggest that the g.p.c. flow conditions used could result in some shear degradation above a molecular weight of 1×10^6, the severity increasing as the molecular weight rose. The presence of degradation is implied from a comparison of the calculated and measured intrinsic viscosities of the IR-305 (*Table 1*). The value calculated from equation (4) is 20% less than that measured and thus the distributions for the fractions NRF1 and NRF2 as well as the IR-305 are probably distorted at the higher molecular weights.

The intrinsic viscosities of the polyisoprene standards (*Table 2*) gave, from a least squares fit to the data, the following values of the Mark–Houwink constants: $K = 2.802 \times 10^{-4}$ and $a = 0.71$, where $[\eta]$ is in $dl\,g^{-1}$ and M in $g\,mol^{-1}$. These can be compared with values for K of 1.09×10^{-4} and for a of 0.79 obtained by Subramaniam for *cis*-1,4 polyisoprene[41].

The values for the measured intrinsic viscosities of the NR fractions are listed in *Table 1* together with the corresponding apparent intrinsic viscosities $[\eta]^*$ calculated from equation (4) and the respective branching parameters. It was assumed that the rubber molecules had tetra-functional branch points. The index, x, was assigned a value of 0.5 in equation (5). Any shear degradation, within the g.p.c. column leads to an error in the apparent intrinsic viscosity of the higher molecular weight fractions (NRF1, NRF2) because $[\eta]^*$ is calculated

Table 2 Molecular characterization of polyisoprene standards

$M_w{}^a$	$M_w/M_n{}^a$	$[\eta]$ $(dl\,g^{-1})$
3.42×10^4	1.04	0.42
1.37×10^5	1.04	1.21
2.92×10^5	1.04	2.08
4.53×10^5	1.06	2.89
1.21×10^6	1.03	5.58
1.60×10^6	1.08	6.06
2.50×10^6	1.15	9.32

^{a} Data supplied by Polymer Laboratories UK
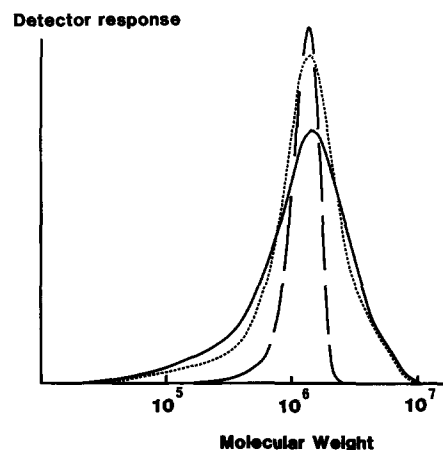
Figure 3 Molecular weight distributions of NRF2 (——), IR-305 (– – – –), and a polyisoprene standard (— —)

from the observed molecular weight distribution. The result is an underestimation of the branch content of the fractions.

Table 1 reveals that the highest molecular weight fraction (NRF1) has the largest branch density. The density decreases with decreasing molecular weight, but tends to a constant value, (1×10^{-6}) below a molecular weight of 1×10^6. Interestingly the rubbers IR-305 and NRF2 have the same peak molecular weight and similar molecular weight distributions (*Figure 3*), and so the ratio of their measured intrinsic viscosities gives an alternative, more direct assessment of branching. Calculations using the measured intrinsic viscosities gave $N_w = 3.8$ and $\tilde{\lambda} = 2.8 \times 10^{-6}$, a three-fold increase of the values calculated from $[\eta]^*$ (*Table 1*). Although the values assigned to $\tilde{\lambda}$ must be treated with caution, the presence of branching is firmly established by the data, in agreement with the work of Angulo-Sanchez and Caballero-Mata[30]. Their calculations used the Zimm and Stockmayer equations for monodisperse material, despite the gel permeation chromatograms revealing polydisperse NR fractions,

with the result that higher degrees of branching were obtained for a given value of g'. Their data indicate that g' is fairly constant with molecular weight, contrary to our findings.

The estimation of the number of branches depends upon assumptions, such as the functionality of the branch points and the relationship between g and g'. If the suggested mechanisms for storage hardening[25-28], by which chains are linked by reactions involving non-isoprene groups distributed along the rubber molecule, are also involved in the formation of long-chain branches, the assumption of tetra-functional branch points is justified. At present, however, there is no direct evidence to indicate the functionality. An assumption of tri-functional branch points would increase the value of $\tilde{\lambda}$ in *Table 1* (for NRF1, $\tilde{\lambda}$ would become 8×10^{-6}), but not alter the ranking of the fractions. Similarly changing the relationship between g' and g would affect the magnitudes of $\tilde{\lambda}$ but not the ranking. The choice of $x = 0.5$ in equation (5) results in upper limits to the value of $\tilde{\lambda}$.

Stress relaxation

The relaxation behaviour is presented in the form of a double logarithmic plot of modulus *versus* time, t. The modulus, $G(t)$, is an apparent shear modulus calculated, assuming the statistical theory of rubber elasticity, from:

$$G(t) = \sigma(t)/(\lambda - \lambda^{-2}) \tag{7}$$

where $\sigma(t)$ is the force per unit original cross-section at time t after the application of the strain, and λ is the extension ratio. The time-dependence of the relaxation, given by the form of the $\log G(t) - \log t$ plots, did not vary significantly with the size of the applied strain for any of the materials investigated.

Representative curves for the five polyisoprene standards are shown in *Figure 4*. At short times they all tend to a plateau modulus, G_N^0, of 0.4 MPa, a figure which agrees well with that given by Pearson *et al.*[34]. G_N^0 is determined by the density of entanglements within a transient network and can be related to the molecular weight between entanglements, M_e, by the equation[42]:

$$M_e = \rho RT / G_N^0 \tag{8}$$

where ρ is the density, R the gas constant and T the absolute temperature. A value of 5700 for M_e is obtained.

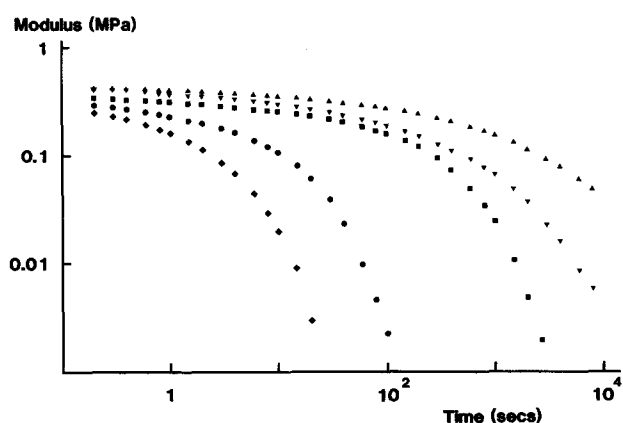The width of the plateau region increases with increasing

Modulus (MPa)

Figure 4 Stress relaxation curves for monodisperse polyisoprenes: ▲, $M_w = 2.50 \times 10^6$; ▼, $M_w = 1.60 \times 10^6$; ■, $M_w = 1.21 \times 10^6$; ●, $M_w = 4.53 \times 10^5$; ◆, $M_w = 2.92 \times 10^5$
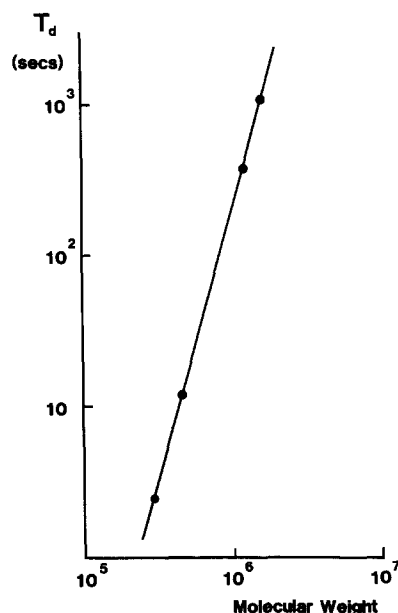
Figure 5 Dependence of T_d on molecular weight for linear, monodisperse polyisoprene

molecular weight. Beyond it these monodisperse standards exhibit a well-defined terminal relaxation region, in which the curve steepens rapidly. Ultimately the longest relaxation time, which corresponds to the tube disengagement time, T_d, in the Doi–Edwards reptation model[5], should dominate and the relaxation modulus, $G(t)$, be expressed as:

$$G(t) \sim \exp - (t/T_d) \tag{9}$$

A value for the tube disengagement time has been abstracted from each curve by plotting $\ln G(t)$ against t; the slope at long times should equal $-1/T_d$. The plot of $\log T_d$ *versus* $\log M_w$ (*Figure 5*) confirmed a power dependence of the tube disengagement time upon the molecular weight:

$$T_d = 1.03 \times 10^{-19} M^{3.6} \tag{10}$$

The value of the index agrees with other experimental observations[43] but not with the M^3 dependence predicted from the Doi–Edwards model[5]. The discrepancy has been explained by the additional relaxation due to chain contour length fluctuations[7].

Relaxation curves for two of the polyisoprene standards ($M_w = 4.53 \times 10^5$ and 1.21×10^6) have been generated from the Doi–Edwards equation modelling pure reptation[5]:

$$G(t) = G_N^0 \frac{8}{\pi^2} \sum_{p \, odd} \frac{1}{p^2} \exp\left(\frac{-tp^2}{T_d}\right) \tag{11}$$

using the T_d values derived above.

A comparison between the experimental and calculated relaxation curves (*Figure 6*) reveals a difference of shape and displacement of the predicted curve along the time axis. Examination of the two polyisoprene standards by g.p.c. revealed a narrow, but significant distribution of molecular weight species, to each of which a relaxation time, T_{d_i}, could be assigned. The theoretical stress relaxation behaviour was recalculated using a simple blending law and equation (11) to give:

$$G(t) = G_N^0 \frac{8}{\pi^2} \sum_{p \, odd} w_i \frac{1}{p^2} \exp\left(\frac{-tp^2}{T_{d_i}}\right) \tag{12}$$
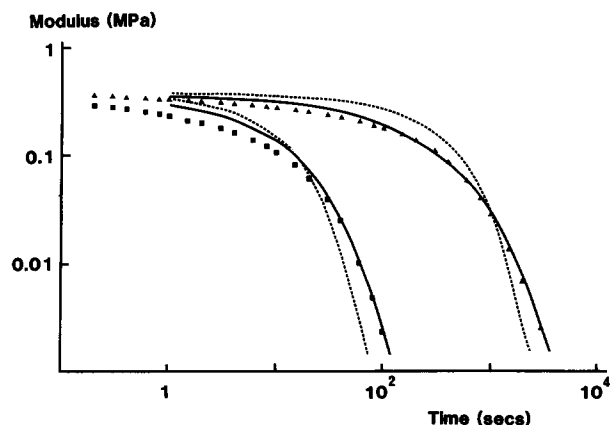
Figure 6 A comparison of experimental ($\blacktriangle$, $M_w = 1.21 \times 10^6$, $\blacksquare$, $M_w = 4.53 \times 10^5$) and calculated stress relaxation for linear monodisperse polyisoprene. ——, Curves calculated from equations (10) and (11); - - - -, curves calculated from equations (10) and (12), and shifted along the time axis (see text)

where w_i was the weight fraction with a tube disengagement time of T_{d_i}. In order to obtain the best fit to the experimental data the two calculated curves had to be shifted along the time axis. The shift required was the same in each case, and the process was equivalent to adjusting the value of the multiplying constant in equation (10) which had been used to evaluate each T_{d_i}, so that T_d is now given by:

$$T_d = 3.83 \times 10^{-20} M^{3.6} \tag{13}$$

It would appear that the simple procedure for estimating T_d gave values systematically too large. Although taking the polydispersity into account and revising the values for T_d gave a good fit to the experimental data at times of the order of, or greater than, T_d, the behaviour at short times is less well predicted particularly for the lower molecular weight material. The discrepancy may be attributed to an additional relaxation mechanism that operates before the chain reptation modelled by equation (11). The process is due to rapid fluctuations of the chain ends brought about by Rouse-like motion, and is more significant for shorter chains[6].

The marked effect of polydispersity upon the relaxation behaviour of a linear polymer is seen (*Figure 7*) from the data obtained from the industrial polyisoprene IR-305 which had a broad molecular weight distribution (*Figure 3*). The allowance for polydispersity was extended to this material using the simple blending law of equation (12) and the disengagement times given by equation (13). Although the absolute values of the moduli were different, attributable in part to the fact that the observed moduli depend upon the applied strain, the shape of the calculated relaxation curve closely followed the experimental data (*Figure 7*). The summation applied in equation (12) assumes that linear additivity of the stress relaxation from each molecular weight species is valid and that there is no interactive effect, such as constraint release. Though such a crude allowance for polydispersity predicts the extent of relaxation behaviour in the time span of this experiment, it is expected that at longer times the interactive effects would cause an increasing discrepancy between experimental and calculated curves.

Figure 8 shows the stress relaxation data obtained from the four NR fractions. The plateau region broadens with increasing molecular weight but the curves do not, even

for the lowest molecular weight NR fraction, exhibit the distinct terminal relaxation time seen with the mono-disperse linear polyisoprene. The fractions have broad molecular weight distributions (*Figure 2*) and contain branched molecules. Both of these factors would be expected to influence the relaxation behaviour, and any attempt to determine how the branched material affects the stress relaxation of NR requires the influence of polydispersity to be taken into account.

An interesting comparison can be made between the stress relaxation behaviour observed for three poly-isoprenes of virtually identical peak molecular weights (1.25×10^6)—one of the linear monodisperse standards, the linear polydisperse polyisoprene (IR-305) and a NR fraction (NRF2). *Figure 3* shows the molecular weight distributions of these three polyisoprenes; fortuitously, the IR-305 has a similar distribution to the NRF2 fraction. The differences in stress relaxation behaviour (*Figure 9*) are strikingly apparent. Contrasting the polydisperse IR-305 and the monodisperse polymer shows that the low molecular weight material in the former resulted in more relaxation at shorter times, whilst the high molecular weight component shifted any terminal relaxation time beyond the time-scale of the test. Despite the IR-305 and NRF2 fraction having very similar molecular weight distributions, the NR material relaxes at a distinctly slower rate than the IR-305. The slow relaxation would therefore seem to be due to chain
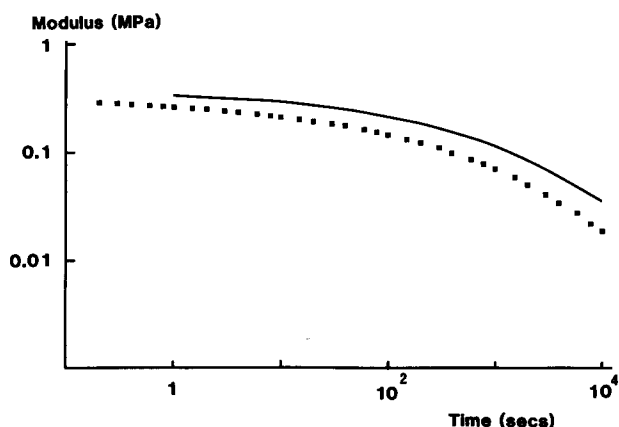

Figure 7 Comparison of experimental ($\blacksquare$) and calculated (——) stress relaxation for polydisperse IR-305. Calculations used equations (12) and (13)
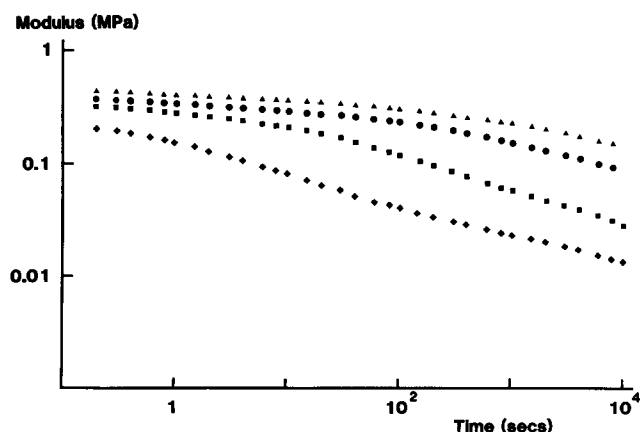

Figure 8 Stress relaxation data for fractionated natural rubber: $\blacktriangle$, NRF1; $\bullet$, NRF2; $\blacksquare$, NRF3; $\blacklozenge$, NRF4
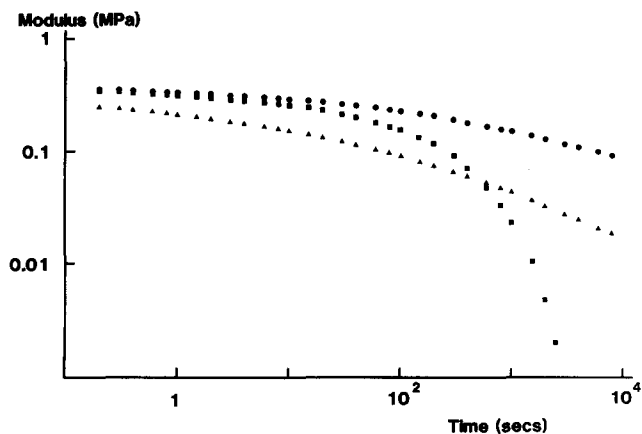
Modulus (MPa)

Figure 9 A comparison of the stress relaxation behaviour of NRF2 (●), linear wide distribution polyisoprene IR-305 (▲) and a linear, monodisperse polyisoprene (■)

branching, the presence of which has been established in the NR by the molecular characterization.

The strong influence of long-chain branching in retarding relaxation has been observed with synthetic polyisoprene[34] and other systems[15], and the mechanism analysed for various regularly branched molecules in terms of the tube model[16,23,24]. However, precise modelling of the behaviour of even fractionated NR appears to be too difficult to attempt at this stage. The branches are probably randomly spaced and their functionality is not definitely established. Moreover, fractionated NR is likely to retain a substantial degree of polydispersity.

CONCLUSIONS

The presence of long-chain branching in sol NR has been confirmed by a combination of intrinsic viscosity and g.p.c. measurements. Comparison of the stress relaxation behaviour of fractionated, sol NR and linear, synthetic polyisoprene has shown the branching to have a substantial influence on the rheology of NR.

The relaxation behaviour of linear polyisoprene in the terminal region has been found to follow predictions of the pure reptation model of Doi–Edwards, when combined with a simple, linear blending law to take account of the slight amount of polydispersity. Surprisingly, a similar analysis provided a reasonable fit to the relaxation of a broad distribution polyisoprene over four decades of time.

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