The effect of liquids on the dynamic properties of carbon black filled natural rubber as a function of pre-strain

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Abstract

A free oscillation technique has been adopted to measure the dynamic storage and loss moduli of carbon black filled natural rubber materials. These tests are conducted with small oscillations that are superimposed on a range of tensile pre-strains. In addition, the effect of temperature on the dynamic moduli is measured as well as the effect of swelling the materials to various extents by liquids with a range of viscosity. It is observed that the dynamic storage and loss moduli do not depend strongly on the pre-strain at small pre-strains. At higher pre-strains there is a marked increase in both the storage and the loss moduli. An increase in temperature causes a dramatic reduction in both the storage and loss moduli. The dynamic behaviour of the filled rubbers when swollen can be approximately ascribed to the combined effects of a reduction in the modulus of the rubber matrix (caused by the swelling action) and a reduction in the effective volume fraction of the filler. The liquids used had a range of viscosity of more than a factor of a thousand. Despite this, the loss moduli of the swollen rubbers varied by only about a factor of two. This insensitivity could be understood in terms of a previously developed theory, based on free volume considerations. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The dynamic behaviour of filled rubbers is of key importance in the performance of rubber engineering components. In many cases, and in particular tyres, mineral oils are incorporated into the compound during manufacture. The purpose of this is both to improve the processing behaviour and to influence the final properties of the product.

There appear to have been few scientific studies of the effect of the addition of liquids on the dynamic behaviour of filled rubbers, although there has been work by Davies et al. [1] on the effect for unfilled rubbers. This work covered a range of liquids of widely varying viscosity values, and of rubbers of different crosslink densities. In this work, the liquids were incorporated by swelling them into an already vulcanised material. This contrasts with the procedure used in manufacture where the liquid is mixed into the raw rubber together with the other compounding ingredients. The swelling method has the considerable advantage that the degree of crosslinking can be found from measurements on the unswollen material, using rubber elasticity theory. In contrast, if the material is vulcanised after the incorporation

of the liquid the stress–strain data is less reliably interpretable. Also, the liquid may, and often does, interfere with the chemistry of the crosslinking reactions. Therefore for the present work on the effect of liquids on the dynamic properties of filled rubbers, which may be regarded as an extension of that referred to above, the same swelling procedure is used. It is recognised that the usual manufacturing procedure for 'oil extension' will produce, even for identical crosslink densities, a different molecular chain configuration in the vulcanisate from that when the liquid is introduced after crosslinking. Although it seems unlikely that the change in dynamic properties caused by the presence of the liquid will be much different in the two cases.

The experimental technique used is similar to that described by Davies et al. [1]. A static tensile strain is applied to a strip and a small oscillation superimposed. This has relevance to the various engineering applications where an oscillation is superimposed on a static deflection. It is known that the modulus for this small oscillation is greater than that deduced from the slope of the static force-deflection relation at the appropriate deflection, and the difference is often referred to as the 'dynamic/static ratio'. This and other effects, like the 'Mullins effect' and the related stress-softening phenomenon, are associated with complications in the stress–strain behaviour due to

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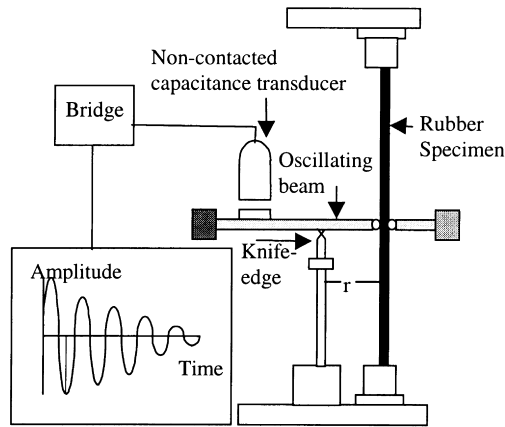 *E-mail address:* j.busfield@qmw.ac.uk (J.J.C. Busfield).

Fig. 1. Apparatus used for dynamic mechanical measurements of strained rubbers in tension.

Table 1
The rubber formulations used in this work

Rubber ingredients	NR0	NR29	NR50	NR59
Natural rubber	100	100	100	100
HAF carbon black (N330)	0	29	50	59
Anti-oxidant	3	2	3	2
Anti-ozonant	0	3	0	3
Accelerator	1.5	2.4	1.5	2.4
Sulphur	1.5	1.0	1.5	2.7

the presence of fillers. Because of this, care has to be taken to avoid any inadvertent pre-stressing of the test piece during the experimentation.

The technique of using a free oscillation, with measurements of frequency and logarithmic decrement to determine the dynamic properties, was adopted by Davies et al. [1] because it gives a much more accurate means of assessing the loss modulus for low loss materials than most forced oscillation methods. It was retained for similar reasons in the present work. The method has the limitations that the frequency cannot be easily controlled, and the test amplitude is, of necessity, variable. Fortunately, for these materials the frequency dependence of their behaviour is only slight; the possible non-linearity at the small test strains is considered later.
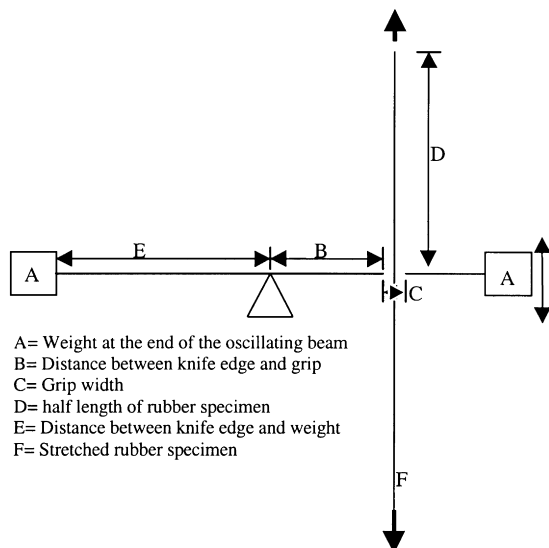
2. Experimental

A plan of the apparatus is given in Fig. 1 and the significant geometry is shown in Fig. 2. The apparatus measures the dynamic visco-elastic properties as a function of pre-strain and temperature. The oscillating beam, with weights of a known independently measured moment of inertia, was supported by the knife-edge. The beam was clamped at the centre of a rubber specimen. The specimen was stretched by moving the position of the end grips and was left to reach equilibrium. The oscillation was activated remotely by switching off an electromagnet. The signal from the capacitance transducer was recorded on a chart recorder and the frequency and logarithmic decrement of the oscillation calculated.

The behaviour of linear visco-elastic materials can be represented by a complex modulus E^* thus:

$$E^* = E' + iE''. \tag{1}$$

Here E' is the storage modulus (elastic component) and E'' is the loss modulus (dissipated energy component). In our case the definitions of E' and E'' are expressed in terms of the deformed geometry. This approach was adopted because Davies et al. [1] showed that for unfilled rubbers the loss modulus expressed in this way was independent of the pre-extension up to quite large pre-strains (about 200%).

With our experimental arrangement E' and E'' are given by

$$E' = \left(\frac{I\omega^2}{2r^2}\right)\left(\frac{l_0}{a_0}\right)\lambda^2 \tag{2}$$

$$E'' = \left(\frac{\Lambda}{\pi}\right)E'. \tag{3}$$

Here I is the moment of inertia of the beam, λ the extension ratio, r the distance from knife edge to the clamped rubber, ω is 2π times the frequency of oscillation, Λ its logarithmic decrement, l_0 and a_0 are the original length and cross-sectional area of the test-piece respectively and λ is its extension ratio. Akutagawa [2] showed that it is important that the width, C, of the grip attaching the strip to the inertia beam is small compared with the knife edge-grip length. This prevents a significant distortion of the geometry on rotation of the beam.

The formulations of the rubber compounds used in the

A= Weight at the end of the oscillating beam
B= Distance between knife edge and grip
C= Grip width
D= half length of rubber specimen
E= Distance between knife edge and weight
F= Stretched rubber specimen

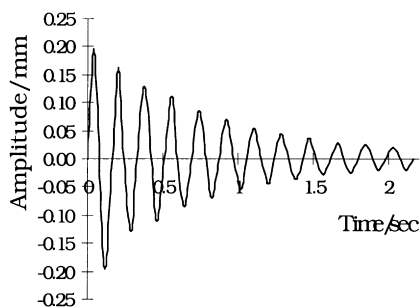Fig. 2. A schematic of the oscillating beam used for this work.

Fig. 3. Oscillation amplitude plotted against time for NR29 material.

work are detailed in Table 1. The compounded rubbers were vulcanised into 1 mm thick sheets at a temperature at 155°C for 10 min. From these sheets test pieces of dimensions $100 \times 5 \times 1$ mm^2 were prepared. The tensile stress–strain tests were conducted on an Instron 1122 at a crosshead speed of 1 mm/min, the load being recorded at extension ratio intervals of 0.1.

The most mobile liquid used was di-butyl adipate, a plasticizer, and the five other liquids being oils of the type used in rubber compounding. Their viscosities, which were determined by the falling ball method, are shown in the figure captions.

The liquids were incorporated by swelling. The volume of liquid absorbed, V_s, was calculated from the weight increase and the density of the liquid. The degree of swelling, denoted by V_r, was referred to the rubber network fraction, and was calculated using the relationship

$$V_r = V_{rn}/(V_{rn} + V_s) \tag{4}$$

where V_{rn} is the volume of rubber network and V_s is the volume of absorbed liquid.

The rubber network refers to the network formed from the rubber hydrocarbon and the curative by the vulcanisation process. V_{rn} can be calculated from the initial weights of the samples and the mix compositions, using the relationship

$$V_{rn} = (M_0 M_{rn})/(M_t \rho_{RH}). \tag{5}$$

where M_{rn} is the weight of rubber network (including the weight of the rubber and the sulphur), M_t is the total weight
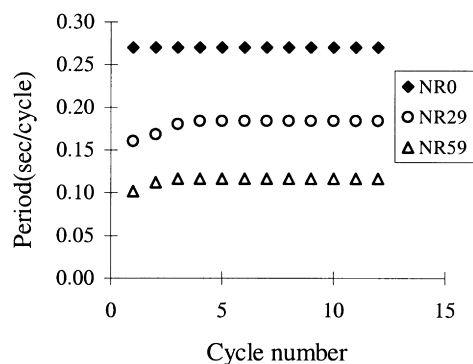

Fig. 4. Period of oscillation versus the number of cycles derived from Fig. 3.
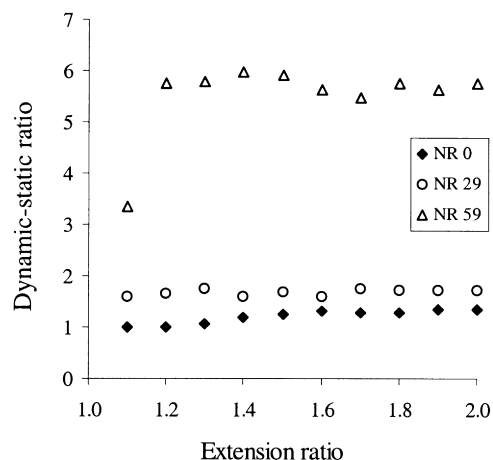

Fig. 5. A comparison between the modulus measured from the tangent of the stress-strain behaviour and E' measured using the oscillating beam.

of mix formulation, M_0 is the weight of the specimen and ρ_{RH} is the density of natural rubber hydrocarbon.

A range of swellings was obtained by immersing the samples for various times, removing them from the liquid and allowing enough time for a uniform distribution to be reached. This uniform distribution time was assumed equivalent to that required for equilibrium swelling in the oil to be reached. The dynamic properties of these swollen samples were then measured as before.

3. Results and discussion

The analysis of the results as storage and loss moduli requires that for the small oscillations used the materials behave in a linearly visco-elastic manner. It is important to check this for filled rubbers as these are known to behave in a non-linear manner at strains of only a few percent. This was done as follows. Having initiated an oscillation, a plot of the deflection versus time was obtained on a chart recorder for each test. A typical result is shown in Fig. 3 for the unswollen compound containing 29 parts of HAF carbon black (N330) filler. From this the period, and hence frequency, of each cycle could be calculated. The results
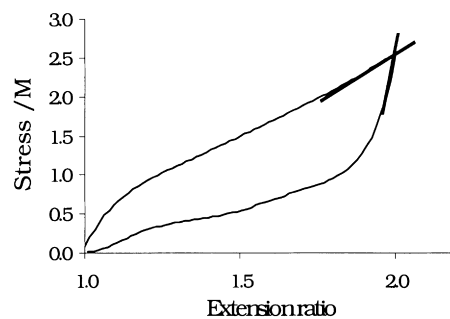

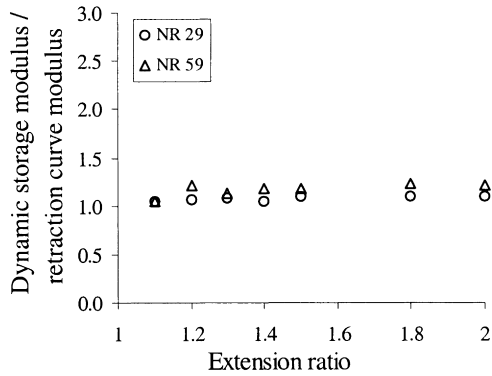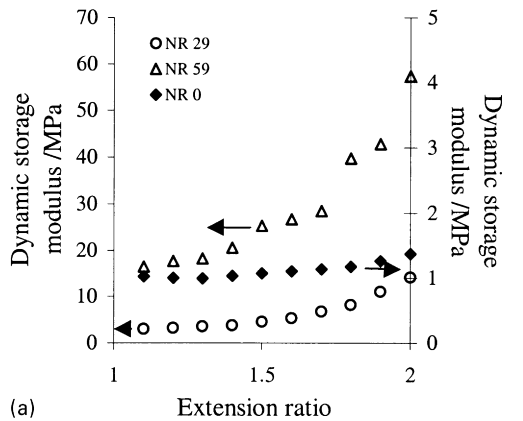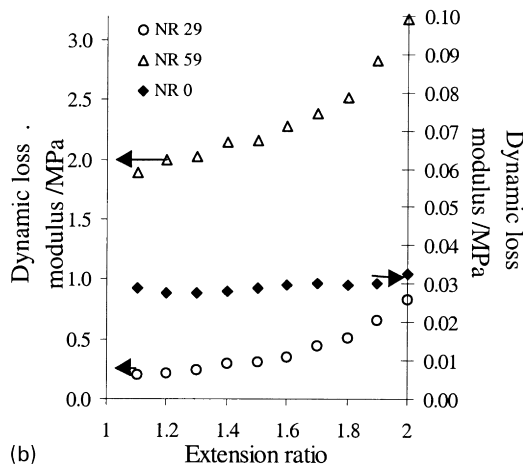Fig. 6. The extension and retraction stress versus strain relationship for the first loading cycle for NR59.

Fig. 7. A comparison between modulus measured from the tangent of the retraction stress-strain behaviour for NR29 and NR59 compared with the dynamic storage modulus, E'.

for each of the unswollen materials are shown in Fig. 4. Apart from the first two cycles, where transient effects associated with the triggering process would be expected, the period is constant despite the continually changing amplitude shown in Fig. 3. This implies that the stiffness is independent of amplitude and thus a linear analysis is valid.

With a free oscillation method as used here it is not easy to cover a wide range of frequency and it was not intended to
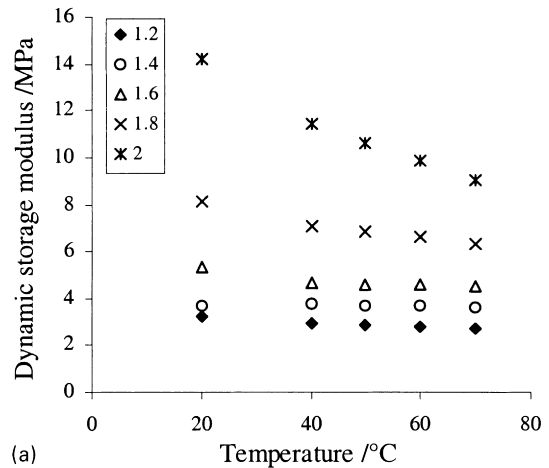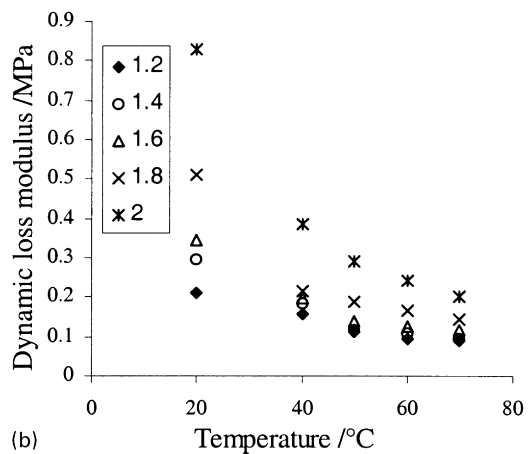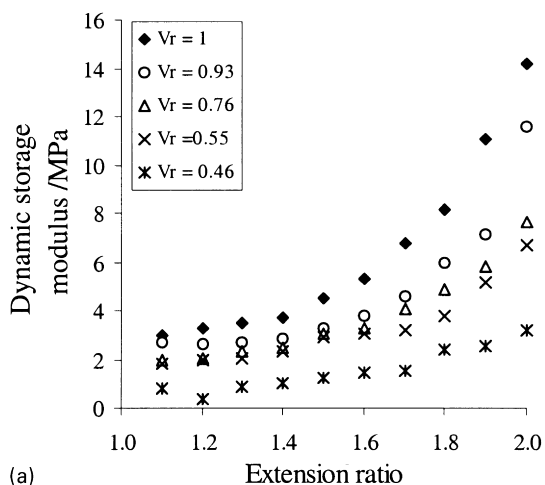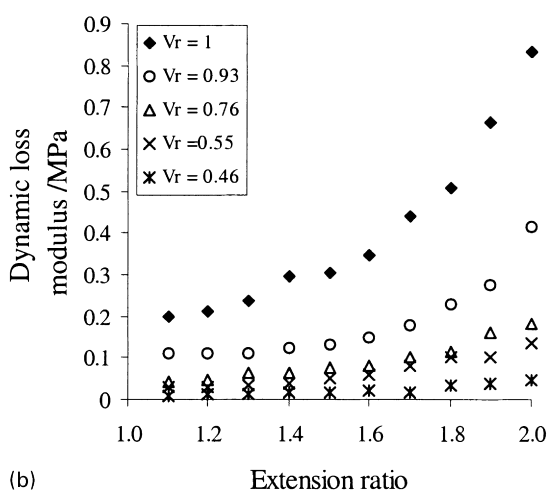

Fig. 9. The dynamic storage (a) and loss (b) moduli of NR29 plotted as a function of temperature. The different series represent the different pre-extension ratios.

investigate frequency dependence in any detail in this work. It is difficult to maintain a precisely fixed frequency as the various variables are changed, and a range of about 4–15 Hz was encountered. Some experiments were therefore done in which the frequency was intentionally changed, with the result that a frequency effect of less than about 5% in the loss modulus, was found for NR29 over this range. This is not unexpected in the light of published data on rubber visco-elastic behaviour, including those due to Davies et al. [1], and accordingly this slight effect, being comparable to the experimental precision, was ignored.

For a perfectly elastic material the slope of the extension stress–strain curve would be equal to the dynamic, incremental, modulus as measured in the present experiments. For imperfectly elastic materials this would of course no longer be the case although for unfilled natural rubber vulcanizates, being highly resilient, Medalia [3] showed that the slope and the dynamic modulus are very similar. However, Fig. 5 shows that for a filled rubber the dynamic modulus is typically several times greater than the slope of the extension stress–strain curve. In engineering applications this effect is well known, and is usually referred to as the
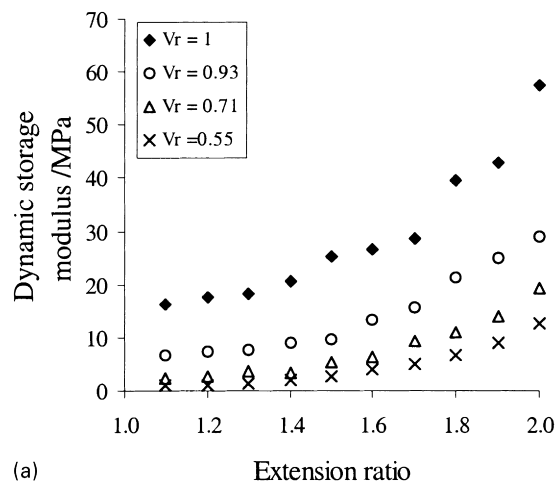

Fig. 8. The dynamic storage (a) and loss (b) moduli of NR0, NR29 and NR59 plotted as a function of pre-strain.

Fig. 10. The dynamic storage (a) and loss (b) moduli of NR29, swollen in DBA to different volume fractions as a function of strain.

Fig. 11. The dynamic storage (a) and loss (b) moduli of NR59, swollen in DBA to different volume fractions as a function of strain.
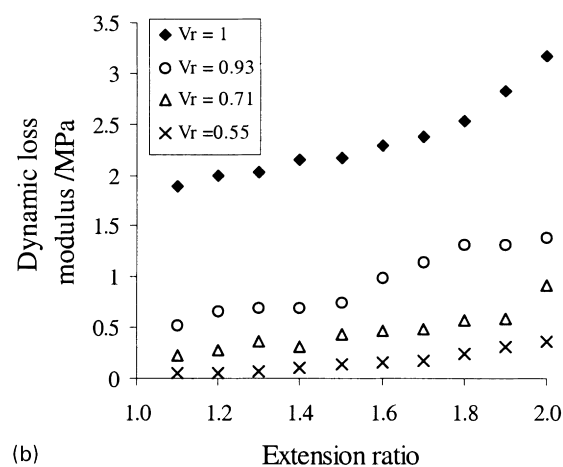
'dynamic/static ratio'. This is a somewhat misleading term as it suggests that the effect is associated with an influence of the frequency of the oscillation. From results quoted in the previous paragraph and from other published work by Medalia [3] it can be seen that any influence of this sort would contribute only a small fraction to this effect. It is generally thought [4] that the slope of the retraction stress–strain curve is the determining factor in the dynamic modulus as measured here.

Fig. 6 shows the extension and retraction curves for NR59. The straight lines indicate the relevant extension and retraction moduli. The retraction modulus is measured in this way for a range of strains, and a comparison is made between this and the dynamic storage modulus in Fig. 7. This figure shows that these two quantities are in fact closely similar. The high slope of the retraction curve at the pre-strain point is a consequence of the Mullins [5] effect shown by filled rubbers.

The dynamic properties of the three unswollen rubbers were measured over a range of pre-strains, and the results are shown as the variation of E' and E'' in Fig. 8a and b. The

expected marked increase in both E' and E'' due to the filler is clear. There is a similar qualitative dependence on strain to that found for the unfilled material by Davies et al. [1]. There is a region at low to moderate strains where both E' and E'' are approximately constant, and at higher strains both show marked increases.

Comparison with the earlier work on unfilled materials shows that the upsweep occurs at lower strains with the present filled materials. This can be attributed to what has been termed by Mullins and Tobin [6] as the strain amplification effect. This recognises that the average strain in the rubber matrix is greater than the overall strain of the filled material because of the presence of the inextensible filler; thus any high-strain non-linearity in the behaviour of the rubber itself will appear at a lower overall strain.

Some measurements have been done over a range of temperature (23–70°C) with the results shown in Fig. 9a and b. The storage modulus E' shows a decrease with increasing temperature, the effect being more pronounced at higher pre-strains. A similar effect is found for E''. An unfilled rubber will normally show an increase in modulus with temperature in accordance with the statistical theory of
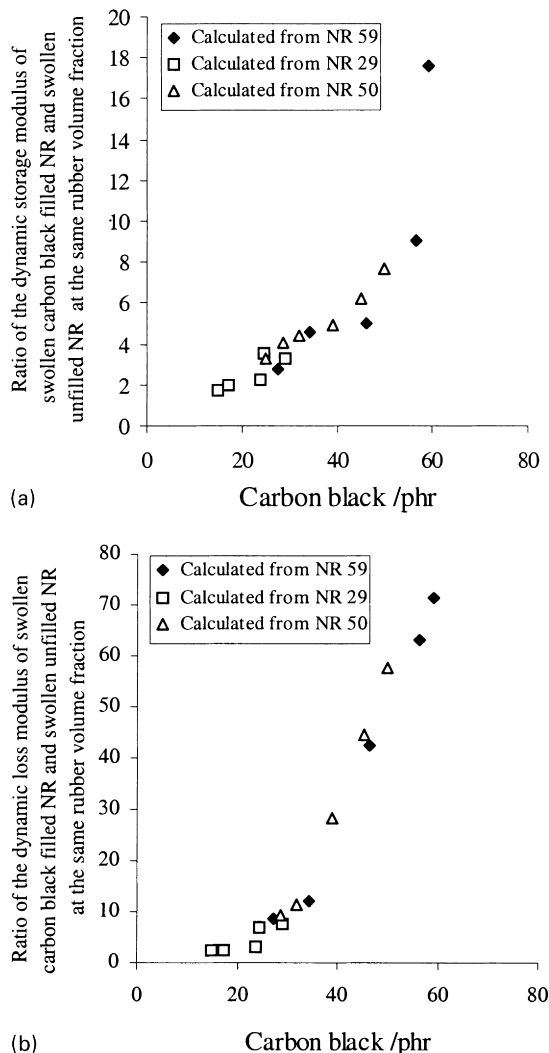
Fig. 12. The dynamic storage (a) and loss (b) moduli plotted as a function of rubber volume fraction.

Fig. 13. The dynamic storage (a) and loss (b) moduli for NR29 plotted against rubber volume fraction for a range of different viscosity oils.

rubber-like elasticity, although viscous effects may mask this behaviour if measurements are made at too high a frequency or too low a temperature. In contrast, filled rubbers are known to show a decrease of modulus with temperature, the mechanism for which is not completely clear. One possible mechanism is that slippage of the rubber over the filler surface may occur more readily at high temperatures, thus reducing the stiffening effect of the filler. Another possibility is that filler aggregates, which are known to be present, may be disrupted by the application of a small stress, and the strength of these aggregates may decrease with temperature due to thermal agitation. It is not easy to distinguish between these mechanisms by purely mechanical measurements in the absence of quantitative theories. However, electrical conductivity data reported by Donnet et al. [7] suggest that significant aggregate disruption does occur with the application of small strains of only a few percent. Thus, thermal agitation may be potent enough to give an appreciable weakening of the filler aggregate. The
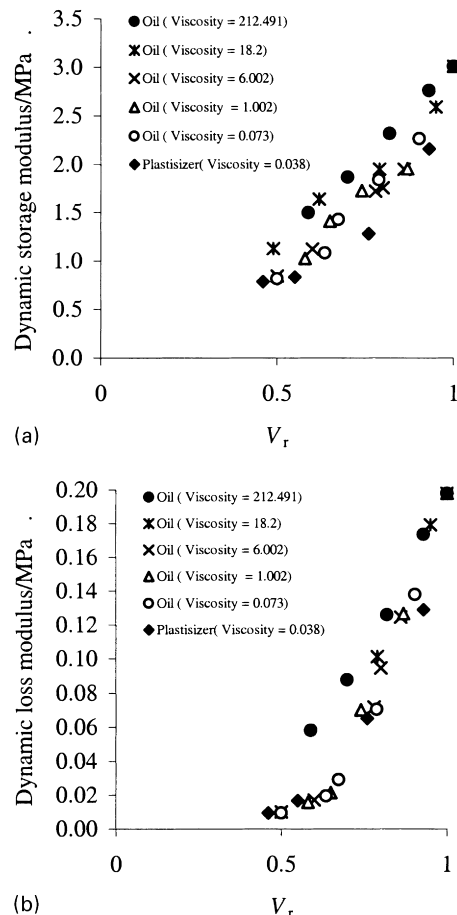
dissipative process determining E'', which will involve the breakage and reformation of the aggregate, may be expected to parallel the E' behaviour.

The dynamic behaviour of the swollen materials over a range of strain and degrees of swelling has also been examined with the results shown in Figs. 9–11. The amount of swelling is expressed as the volume fraction of rubber v_r in the rubber phase. The liquid used in the data shown is dibutyl adipate. The general behaviour is similar to that of the unfilled rubber, but the dependence of both E' and E'' on swelling is much stronger, particularly for the more highly filled materials. This is perhaps to be expected, because when the material is swollen not only is the modulus of the rubber matrix decreased but also the effective volume fraction of the carbon black filler is reduced. A lower filler content will of course lead to decreases in E' and E'', as found above. It is possible to check whether a combination of these effects is sufficient to account for the observed changes. Fig. 12a and b show E' and E'', respectively, for the filled swollen materials (at low extensions) divided by the corresponding values for the unfilled materials at the same degree of swelling. These reduced values are plotted
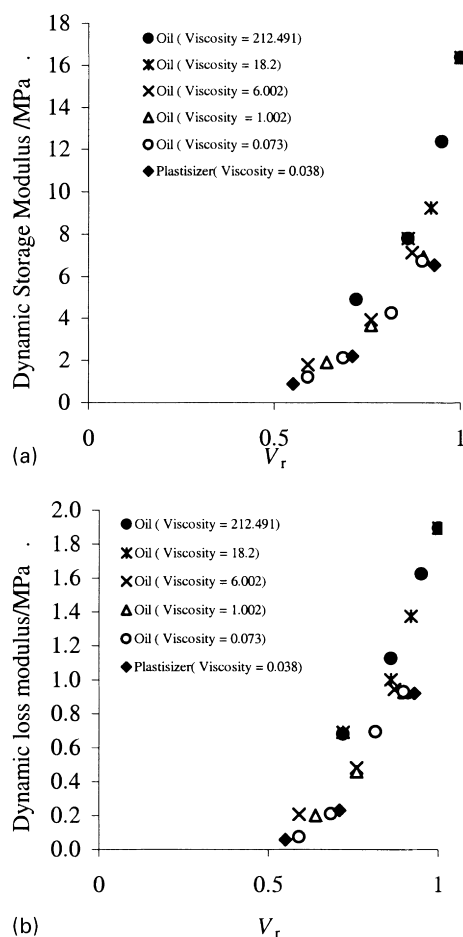
Fig. 14. The dynamic storage (a) and loss (b) moduli for NR59 plotted against rubber volume fraction for a range of different viscosity oils.

against the volume fraction of filler, allowing for the decrease in the filler loading due to the swelling. If the combination of the effects of swelling suggested above is correct then all the data for the various degrees of swelling and filler loadings will be consistent with a single curve. Fig. 12 suggests that this is at least approximately true for both the storage and loss moduli.

The effect of the viscosity of the swelling liquid has been studied by using a number of oils which range in viscosity from that of the plasticizer used earlier (0.038–212 Pa s). The materials NR29 and NR59 were swollen and tested as before with the results shown in Figs. 13 and 14. As might be expected, the higher viscosity oils gave rather higher loss moduli, but the effect is not very great. The tensile loss modulus at a frequency of f for a liquid of viscosity η is $6\pi f \eta$, and under the present test conditions where f is about 10 Hz the contribution to the measured E'' of the most viscous liquid will be about $(0.04 \text{ MPa}) \times (1 - V_r)$. This may be significant for highly swollen NR29 but for NR59, and for other liquids, the effect is negligible.

This could account for the modest influence of liquid viscosity on loss modulus. The main effect of adding a liquid appears to be as a diluent, combined with the

influence of altering the free volume available for the movement of the rubber chains, as discussed by Davies et al. [1].

There seems to be a slight effect of liquid viscosity on E'. This is perhaps surprising as the nature of the swelling liquid has been reported by Gumbrell et al. [8] to have no discernible effect on the stress–strain behaviour of unfilled rubbers, and the statistical theory of rubber elasticity would not predict one. However, measurements with highly viscous liquids, and on filled rubbers, do not appear to have been made previously, so there are no strictly comparable results. It is possible that the swelling liquids affect the filler–filler or the filler–rubber interaction, and this might influence E'.

4. Conclusions

The dynamic behaviour of natural rubber vulcanisates containing several levels of filler (HAF carbon black) loading has been studied for small oscillations superposed on a range of tensile pre-strains. The storage and loss moduli, E' and E'', do not depend strongly on pre-strain at small pre-strains, which is qualitatively similar to the behaviour of unfilled rubber [1] although the increases at higher strains occur earlier in the filled case. This is probably ascribable to the strain amplification effect usually invoked to explain the general stress–strain behaviour of filled rubbers. Increases in temperature produce substantial decreases in both E' and E''.

Swelling the materials in non-volatile liquids produces relatively large decreases in E' and E'' compared with the corresponding changes in unfilled rubbers. These decreases can be at least approximately ascribed to a combination of the softening effect of swelling on the rubber matrix and the decrease, with swelling, in the effective volume fraction of filler. The liquids used covered a wide range of viscosity— more than a thousand to one—but the effect of this variable on E'' was relatively slight. Only the most viscous liquid in the least filled material at the highest liquid content produced a significant increase, an effect that can be understood in terms of the high effective internal viscosity of the rubber.

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