Stress relaxation of a nitrile rubber surrounded by an oil that increases the network density

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(Received 1 September 1988; revised 21 November 1989; accepted 8 January 1990)

When a rubber item is subjected to a periodically varying deformation, the restoring force can exhibit a much more rapid decay than when the deformation is held constant. This is studied by dynamic mechanical stress relaxation. Based on well known relations from statistical rubber elasticity theory, a theory for the dynamic mechanical stress relaxation is proposed. In this paper it is shown that the special dynamic stress-relaxation behaviour has network degradation as its origin at elevated temperatures, and that data from measurements of continuous stress relaxation and intermittent stress relaxation can be related to results from measurements of dynamic stress relaxation. Results are reported from stress-relaxation measurements on nitrile rubber surrounded by a naphthenic oil with a gear-lubricant additive, which is found to be the origin of a reaction that increases the network density in the nitrile rubber.

(Keywords: stress relaxation; intermittent; continuous; dynamic; relations; nitrile rubber; degradation; oil gear-lubricant additive)

INTRODUCTION

The environment can have a detrimental effect on technical rubber products[1–3]. In this study, stress relaxation has been measured on nitrile rubber surrounded by a naphthenic oil with a gear-lubricant (GL) additive, which is found to be the origin of a reaction that increases the network density in the nitrile rubber[4]. Nitrile rubbers with three different network densities were studied.

Nitrile rubber is the standard material used for rubber components that will be in contact with oil, for example in sealings Recently published books in rubber technology are good sources for general information about nitrile rubbers[5–7]. Stress relaxation is regarded as the most convenient method of evaluating rubber materials for sealing applications[8]. Results from measurement of intermittent stress relaxation, continuous stress relaxation and dynamic stress relaxation will be reported here and the methods described. Dynamic stress-relaxation studies show that during a periodically varying deformation the restoring force from a deformed rubber item can exhibit a much more rapid decay than when the deformation is held constant[9–15]. This rapid decay is especially important regarding rubber goods for sealing applications. Data from measurements of continuous stress relaxation and intermittent stress relaxation can be related to results from measurements of dynamic stress relaxation[16]. These relations, based on the statistical rubber elasticity theory[17] and with basic ideas in common with Tobolsky's 'two-network theory'[18,19], are presented in the paper.

DYNAMIC STRESS-RELAXATION MEASUREMENT

The principle of the measurement of dynamic stress relaxation is shown in *Figure 1*. The cylindrical rubber specimen with undeformed length L_u is compressed to a prestrain S. A sinusoidally varying strain with amplitude A is then superimposed on this prestrain, so that the deformation varies between a maximum compression when the specimen length is L_a and a minimum compression when it is L_i. The restoring force is continuously measured by a load cell, and periodically recorded at its minimum and maximum values. Distinct measurements of the maximum and minimum values of the restoring force over extended periods of time are thus obtained. When the results are presented, these points are linked in a diagram by two lines, one for the maximum and one for the minimum values. The maximum and minimum stress values occur slightly after the maximum and minimum, respectively, of the deformation because rubber materials are viscoelastic rather than purely elastic.

Dynamic stress relaxation of rubber materials has been studied in a group of papers[10–16]. It is found that the level of minimum stress exhibits a more rapid decay than the maximum stress level, when normalized values are compared.

Tobolsky has used the statistical rubber elasticity theory to relate the results of continuous and intermittent stress relaxation on the one hand and permanent set on the other. In this paper, the statistical rubber elasticity theory is used to derive an approximate relation between continuous, intermittent and dynamic stress relaxation, and thus to show that the special dynamic stress-

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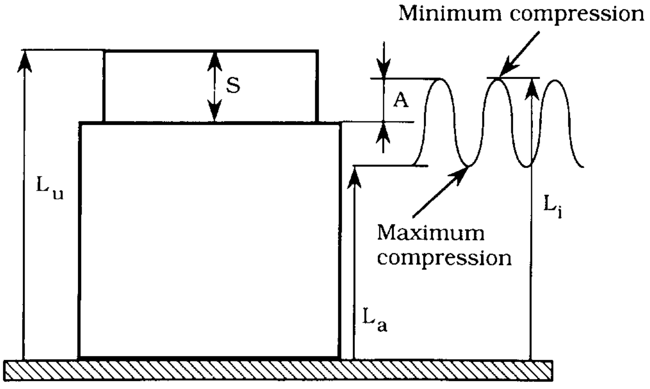

Figure 1 Dynamic compression

relaxation behaviour is of chemorheological nature with network degradation as its origin.

CONTINUOUS STRESS RELAXATION

Continuous stress relaxation of rubber materials at elevated temperatures was first investigated by Tobolsky and coworkers[19,20]. After a constant deformation is applied to a specimen, the retractive force and its change with time are recorded. The retractive force is usually found to decrease with time. In the statistical theory of rubber elasticity[17], from which equation (1) emanates, it is claimed that the stress acting on a uniaxially strained rubber item is completely determined by the tension, the temperature and the network density:

$$f/A = \sigma_{\mathrm{nom}} = \nu RT[L_x/L_u - (L_u/L_x)^2] \quad (1)$$

This equation fits well to experimental data in both compression and tension[17]. In equation (1), f is the force, A is the original cross-sectional area of undeformed specimen, σ_{nom} is the nominal stress, ν is the network density (i.e. network chains per unit volume), R is the gas constant, T is absolute temperature, L_u is the undeformed length and L_x is the deformed length of the specimen.

Entanglement effects, conformational changes and alignment of polymer chains have an influence on the modulus of the rubber[21], at least at shorter times, but these effects may be difficult to analyse in a reproducible way. After some time, these effects no longer dominate the stress relaxation, especially not at higher temperatures. A way of minimizing these complicating effects is to normalize the data, which means that all measured values are divided by the value at a certain time, e.g. 10 min after applying the deformation.

When effects of viscoelasticity are neutralized in this way, it is mainly chemical degradation of the network that contributes to stress relaxation. The ratio of the stress at a certain time to the stress at the normalization time is thus the same as the ratio of the network density at the same measurement time (ν_u) to the network density at the normalization time ($\nu_{u,0}$), as indicated in the equation:

$$(f/f_0)_{\mathrm{cont}} = \nu_u/\nu_{u,0} \quad (2)$$

where $(f/f_0)_{\mathrm{cont}}$ is the normalized continuous stress relaxation. This analysis of chemical rupture in a rubber network is the idea behind Tobolsky's concept of chemical stress relaxation[19,22]. The force f_0 is the retractive or restoring force at the normalization time, at which $\nu_{u,0}$ is the network density of the original network in its equilibrium position at L_u. At an arbitrary time at which the network density attains the value ν_u the retractive force is f.

The rubber network can degrade with different types of reactions[22]. Scission reactions can occur either randomly along the main chains or at the junction points of the network. Crosslinking reactions can generate a secondary network. Sometimes the crosslinking reaction is started by a scission reaction, so the scission will be reversible. When random scission along the main chains is the predominant degradation mechanism, a comparison of normalized stress-relaxation results shows that a vulcanizate of low network density exhibits a greater decay than an otherwise identical vulcanizate with higher network density. When scission at the junction points is the predominant degradation mechanism in a rubber network, normalized stress-relaxation curves for vulcanizates with different network densities give concurrent results. The shapes of the stress-relaxation curves for these different mechanisms are illustrated in *Figure 2*.

INTERMITTENT STRESS RELAXATION

When intermittent stress relaxation is measured[19], the specimen is maintained in a relaxed, undeformed condition at a suitable constant temperature. At widely spaced time intervals, a fixed deformation is applied to the specimen and the equilibrium stress is rapidly measured. The specimen is then quickly unloaded. This is an intermittent measurement of the modulus of the network under conditions in which the duration of the stress measurement is very short compared with the time intervals between the measurements. Nearly all scission and crosslinking may be considered to occur when the network is in its undeformed state. The values measured after different ageing times are normalized with respect to the first measured value, so that normalized intermittently measured stress-relaxation data are obtained:

$$(f/f_0)_{\mathrm{int}} = (\nu_u + \nu_x)/\nu_{u,0} \quad (3)$$

where ν_u and $\nu_{u,0}$ are as in equation (2) and ν_x is the network density for a formed secondary network.

Crosslinking reactions are detected by intermittent stress relaxation as an increase in retractive force (because of increasing network density or secondary crosslinking reactions), although the continuous stress relaxation is unaffected.

The secondary network formed by a crosslinking reaction will here be ascribed a network density ν_x as in equation (3) and $(f/f_0)_{\mathrm{int}}$ is stress relaxation as measured intermittently. In measurements of intermittent stress

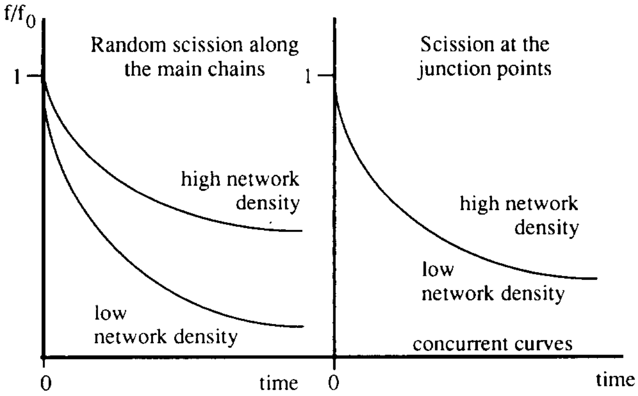

Figure 2 Typical shapes of normalized stress-relaxation curves for materials of low and high network density when degraded by random scission along the main chains and by scission at the junction points

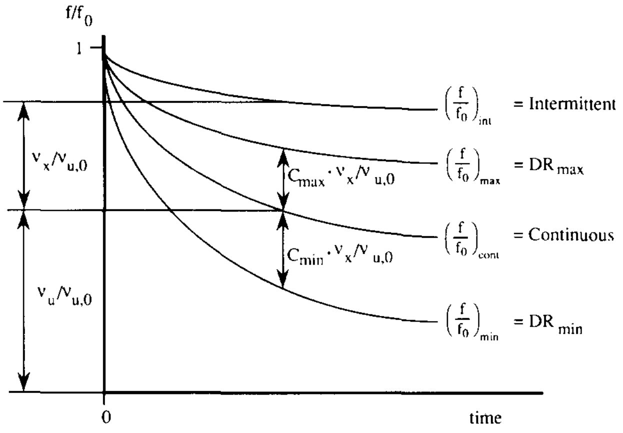

Figure 3 A graphical presentation of the terms in equations (2), (3), (4), (16) and (17). DR_{min} (and DR_{max}) are normalized values of the minima (respectively maxima) of the restoring force during dynamic stress relaxation

relaxation it is assumed that the network formed has its equilibrium position at the undeformed length L_u. By combining normalized results from continuous stress-relaxation (equation (2)) and intermittent stress-relaxation measurements (equation (3)), the relative difference in network density between these two networks can be evaluated[19]:

$$\nu_x/\nu_{u,0} = (f/f_0)_{int} - (f/f_0)_{cont} \quad (4)$$

The ratio $\nu_x/\nu_{u,0}$ is an estimate of the network density of a secondary network normalized with respect to the network density at the normalization time of the original network. The different terms of equations (2), (3) and (4) are presented in *Figure 3*.

RELATION BETWEEN DIFFERENT TYPES OF STRESS-RELAXATION MEASUREMENTS

Tobolsky[18,19] has deduced that scission and crosslinking reactions can occur simultaneously in a rubber network, and that the rate of crosslinking is quite unaffected by the elongation of the sample. He proposed that in a strained network the crosslinks form in such a way that the network produced is in a relaxaed position with respect to the momentary geometrical restraints on the sample. Tobolsky stated that it is possible for degraded rubber vulcanizates to have two networks that are in equilibrium at different deformations. This theory is applied to predict the permanent set (PS) of rubber items, defined in equation (5), when data for continuous and intermittent stress relaxation are known[18]:

$$PS = 100(L_s - L_u)/(L_x - L_u) \quad (5)$$

In this equation, L_s is the new equilibrium length of a rubber item of original length L_u that has been stored for an extended period at the deformed length L_x. The equation for calculating permanent set is given in equation (6):

$$PS = \frac{100}{L_x/L_u - 1}\left[\left(\frac{(L_x/L_u)^3 - 1}{(L_x/L_u)^2 \nu_u/\nu_x + 1}\right)^{1/3} - 1\right] \quad (6)$$

This equation is commonly presented in introductory books in polymer physics[23–25] and the predicted values fit well to experimental data.

A rubber cylinder (*Figure 1*) with length L_u in the undeformed state is dynamically compressed between two extremes, minimum compression at a length L_i and maximum compression at a length L_a. Note that the sine curve (*Figure 4*) for most of the time is at a value quite near its extremes.

When crosslinking or rearrangement reactions occur under these conditions, a certain amount of the crosslinks will therefore be formed when the material is strained to the vicinity of maximum compression and a certain amount of the crosslinks will be formed when the material is strained to the vicinity of minimum compression. The discussion of secondary networks formed during varying compression can be simplified if it is assumed that two secondary networks are formed, one with its equilibrium at L_a and one with its equilibrium at L_i. The rubber item is thus assumed to have three networks in equilibrium at different lengths: the original network with its equilibrium position at L_u and the two secondary networks with equilibrium positions at L_a and L_i respectively.

The two idealized secondary networks can be handled in the same way as the single secondary network in Tobolsky's theory for the prediction of permanent set, presented by Andrews *et al.*[18]. According to the statistical rubber elasticity theory[17], equation (7) is an expression of the true or actual stress in a rubber vulcanizate:

$$\sigma' = \nu RT[(L_x/L_u)^2 - L_u/L_x] \quad (7)$$

At minimum compression (for equilibrium at L_u) the retractive stress from the original network will be $\sigma'_{u,min}$ and at maximum compression it will be $\sigma'_{u,max}$, as stated in equations (8) and (9):

$$\sigma'_{u,min} = \nu_u RT[(L_i/L_u)^2 - L_u/L_i] \quad (8)$$

$$\sigma'_{u,max} = \nu_u RT[(L_a/L_u)^2 - L_u/L_a] \quad (9)$$

It should be noted that ν_u in these equations decreases as degradation of the rubber progresses. The secondary networks that are formed at minimum and maximum compression contribute to the minimum and maximum values respectively of the retractive stress. The network in equilibrium at minimum compression (i.e. at length L_i) can be ascribed a network density of ν_i and the network in equilibrium at maximum compression (i.e. at length L_a) a network density of ν_a. The network in equilibrium at maximum compression contributes $\sigma'_{a,min}$ to the retractive stress at minimum compression, given by the equation:

$$\sigma'_{a,min} = \nu_a RT[(L_i/L_a)^2 - L_a/L_i] \quad (10)$$

The network in equilibrium at minimum compression

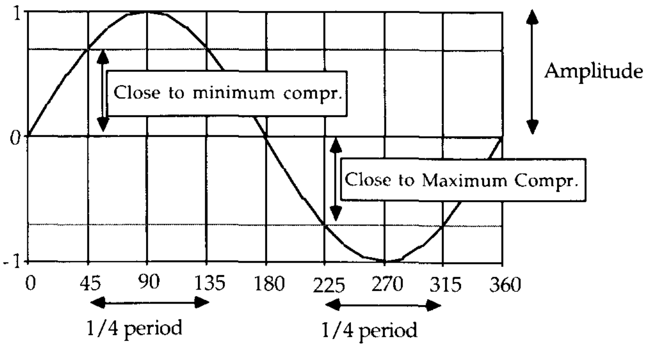

Figure 4 A sine curve is for most of the time at a value quite near its extremes

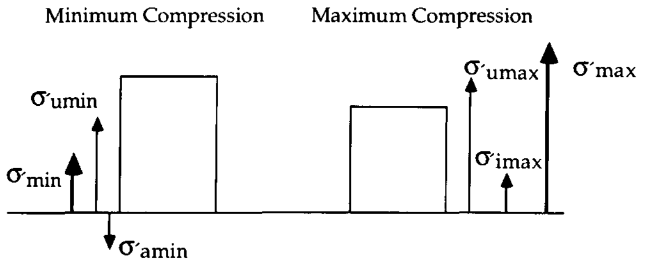

Figure 5 Stresses at maximum and minimum compression according to equations (8) to (13)

contributes $\sigma'_{i,max}$ to the retractive stress at maximum compression, given by equation (11):

$$\sigma'_{i,max} = \nu_i RT[(L_a/L_i)^2 - L_i/L_a] \qquad (11)$$

The signs of these contributions are indicated in *Figure 5*, showing that at minimum compression $\sigma'_{a,min}$ acts in the reverse direction to $\sigma'_{u,min}$. At maximum compression, $\sigma'_{i,max}$ and $\sigma'_{u,max}$ act in the same direction. Equations (12) and (13) give the total retractive stresses at minimum and maximum compression respectively:

$$\sigma'_{min} = \sigma'_{u,min} + \sigma'_{a,min} \qquad (12)$$

$$\sigma'_{max} = \sigma'_{u,max} + \sigma'_{i,max} \qquad (13)$$

The data presented from dynamic stress relaxation are normalized with respect to values measured 10 min after starting the dynamic deformation. At this time there are probably still no secondary networks, so the network densities ν_i and ν_a can be regarded as being zero. The retractive stresses at the normalization time are designated $\sigma_{min,0}$ for the minimum values and $\sigma_{max,0}$ for the maximum values. The original network density is $\nu_{u,0}$. For minimum values of retractive stress, equation (14) applies, and analogously equation (15) for maximum values:

$$\left(\frac{f}{f_0}\right)_{min} = \frac{\sigma'_{min}}{\sigma'_{min,0}} = \frac{\nu_u RT[(L_i/L_u)^2 - L_u/L_i] + \nu_a RT[(L_i/L_a)^2 - L_a/L_i]}{\nu_{u,0} RT[(L_i/L_u)^2 - L_u/L_i]} = \frac{\nu_u}{\nu_{u,0}} + \frac{\nu_a}{\nu_{u,0}}\left(\frac{(L_i/L_a)^2 - L_a/L_i}{(L_i/L_u)^2 - L_u/L_i}\right) \qquad (14)$$

$$\left(\frac{f}{f_0}\right)_{max} = \frac{\sigma'_{max}}{\sigma'_{max,0}} = \frac{\nu_u}{\nu_{u,0}} + \frac{\nu_i}{\nu_{u,0}}\left(\frac{(L_a/L_i)^2 - L_i/L_a}{(L_a/L_u)^2 - L_u/L_a}\right) \qquad (15)$$

where $(f/f_0)_{min}$ and $(f/f_0)_{max}$ are normalized stress relaxations at minimum and maximum compressions. The two quotients $\nu_a/\nu_{u,0}$ and $\nu_i/\nu_{u,0}$ are idealized values, and are not experimentally accessible. They are, however, related to the ability of the material to form a secondary network. As indicated in equations (2) to (4), the relative density of a secondary network can be calculated from results of intermittent and continuous stress relaxation according to the Tobolsky two-network theory[18,19]. The replacement of $\nu_a/\nu_{u,0}$ and $\nu_i/\nu_{u,0}$ by $\nu_x/\nu_{u,0}$ in equations (14) and (15) can be justified, not because they are equal, but because they should be of the same order owing to the fact that the molecular processes behind their formation are the same. Actually $\nu_x/\nu_{u,0}$ should be larger than $\nu_a/\nu_{u,0}$ and $\nu_i/\nu_{u,0}$.

In the following equations, expressions for dynamic stress relaxation at minimum and maximum compression are given in the same way as in equations (14) and (15), but the expressions containing L_u, L_i and L_a are replaced by two coefficients, C_{min} and C_{max}, and with $\nu_i/\nu_{u,0}$ (respectively $\nu_a/\nu_{u,0}$) replaced by $\nu_x/\nu_{u,0}$:

$$\left(\frac{f}{f_0}\right)_{min} = \frac{\nu_u}{\nu_{u,0}} - \frac{\nu_x}{\nu_{u,0}} C_{min} \qquad (16)$$

$$\left(\frac{f}{f_0}\right)_{max} = \frac{\nu_u}{\nu_{u,0}} + \frac{\nu_x}{\nu_{u,0}} C_{max} \qquad (17)$$

where C_{min} (and C_{max}) are coefficients relating data for intermittent and continuous stress relaxation to values for stress relaxation at minimum (respectively maximum) values of dynamic stress relaxation. The two coefficients C_{min} and C_{max} are both greater than zero, and the minus sign in equation (16) comes from $\sigma'_{a,min}$, which acts in the reverse direction to $\sigma'_{u,min}$, as shown in *Figure 5*. The relations in equations (16) and (17) are shown graphically in *Figure 3*. A way of testing the validity of this relation is to check whether data for dynamic, continuous and intermittent stress relaxation can be adapted to equations (16) and (17), giving reasonable values for C_{min} and C_{max}. Equations (18) and (19), derived from equations (2), (4), (16) and (17), show how this can be done:

$$C_{min} = \frac{(f/f_0)_{cont} - (f/f_0)_{min}}{(f/f_0)_{int} - (f/f_0)_{cont}} \qquad (18)$$

$$C_{max} = \frac{(f/f_0)_{max} - (f/f_0)_{cont}}{(f/f_0)_{int} - (f/f_0)_{cont}} \qquad (19)$$

C_{min} and C_{max} calculated in this way exhibit a considerable numerical sensitivity when the numerical values of the different normalized stress-relaxation quantities are close to each other.

C_{min} and C_{max} can be estimated theoretically if $\nu_i/\nu_{u,0}$ and $\nu_a/\nu_{u,0}$ are assumed to be equal to $\nu_x/\nu_{u,0}$. With this assumption, an expression for C_{min} (equation (20)) is derived from equations (14) and (16) and an expression for C_{max} (equation (21)) from equations (15) and (17):

$$C_{min} = -\frac{(L_i/L_a)^2 - L_a/L_i}{(L_i/L_u)^2 - L_u/L_i} \qquad (20)$$

$$C_{max} = \frac{(L_a/L_i)^2 - L_i/L_a}{(L_a/L_u)^2 - L_u/L_a} \qquad (21)$$

Values of C_{min} and C_{max} for different prestrains and different amplitudes calculated with these equations are given in *Figure 6*. Both C_{max} and C_{min} increase when the

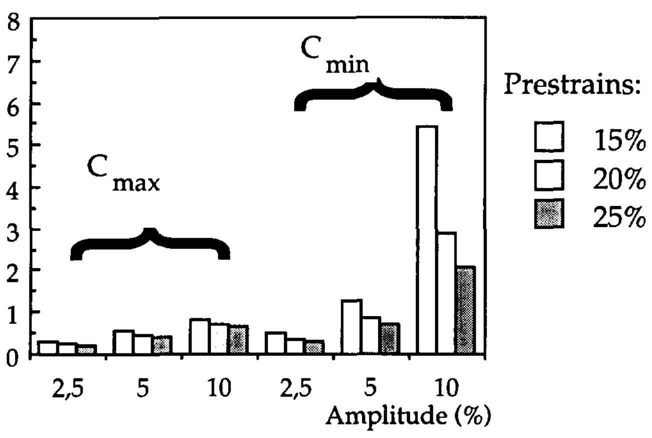

Figure 6 Theoretical values of C_{max} and C_{min} for different prestrains and amplitudes calculated using equations (20) and (21)

amplitude is increased and decrease when the prestrain is increased.

The relations presented in equations (14) to (21) are derived using assumptions similar to those used for the predictions of permanent set[18,19]. Permanent set, defined in equation (5), can be predicted using values of $\nu_u/\nu_{u,0}$ and $\nu_x/\nu_{u,0}$ and the formula given in equation (6). A comparison between experimental and calculated values of permanent set provides a check on the relevance of these assumptions to the system studied.

When the relations are valid, some conclusions can be drawn about dynamic stress relaxation. The minimum of the restoring force should decay more than the maximum when normalized values are compared. Extensive crosslinking in a material should lead to a greater decay of the minimum of the restoring force, and a greater initial network density should give a smaller decay of the minimum of the restoring force, because any secondary network formed would then have less influence. Reversion should also be small for minimizing the decay of the minimum of the restoring force. An increase in the value of C_{min} increases the decay of the minimum value, and an increase in C_{max} reduces the decay of the maximum value. Both an increase in the prestrain and a decrease in the amplitude of a dynamic deformation make C_{min} smaller, as indicated in *Figure 6*. These should thus be methods to moderate the decay of the minimum force.

APPLICATION OF THE RELATIONS TO RESULTS FOR NATURAL RUBBER

When these relations were applied to data from studies of stress relaxation on natural rubbers (both conventionally vulcanized and EV vulcanized) it was found that C_{min} increased with increasing amplitude, as predicted theoretically, and also that C_{max} increased with increasing amplitude in accordance with theoretical estimations[16]. Values of C_{max} and C_{min} calculated using data for different prestrains for the conventionally vulcanized material are shown in *Figure 7*. C_{min} decreased when the prestrain was increased, in agreement with the theoretical values given in *Figure 6*.

EXPERIMENTAL

Rubber specimens

Three different nitrile rubber compounds were made, resulting in vulcanizates with different network densities.

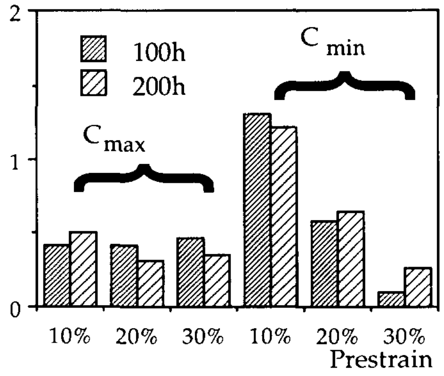

Figure 7 Experimental values of C_{max} and C_{min} at different prestrains at 5% amplitude calculated from data for natural rubber[16] using equations (18) and (19)

Table 1 Recipes of the rubber compounds

	Material 1 (phr)[a]	Material 2 (phr)	Material 3 (phr)
Perbunan 2807 (NBR)[b]	100	100	100
ZnO	3	3	3
Stearic acid	0.5	0.5	0.5
TMTD[c]	1	3	4.5

[a] phr means part per hundred parts of rubber
[b] Perbunan 2807 is a nitrile rubber with 28% by weight of acrylonitrile
[c] TMTD is tetramethylthiuramdisulphide

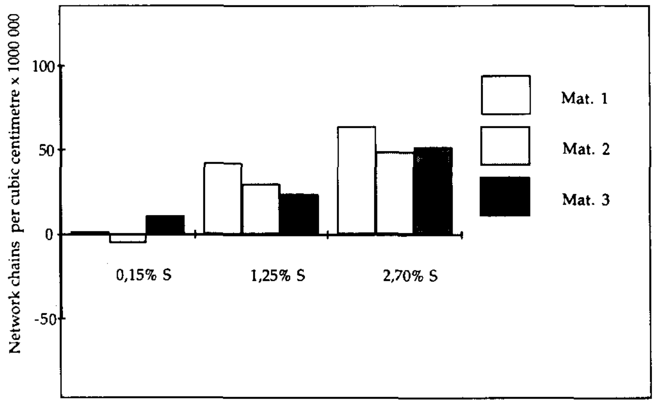

Figure 8 Differences between network densities of fresh specimens and of specimens immersed for 336 h in oils with different levels of GL additive

The recipes are given in *Table 1*. The rubber was moulded into cylinders with length and diameter equal to 20 mm for the stress-relaxation measurements. Sheets with a thickness of 2 mm were moulded for the stamping of tensile test specimens, type C according to ASTM 412. The tensile test specimens were used for the measurement of network density both mechanically and by swelling in order to investigate further how the rubber was influenced by the oil with a GL additive. The cylinders were vulcanized for 1 h at 185°C and the sheets for 30 min at 174°C.

Test methods for network density

Network density was determined by a tensile test with the specimens strained to 100% elongation, the force being recorded 3 min after the elongation and the network density being calculated from the statistical rubber elasticity theory[17] (equation (1)). These measurements were made in an Instron testing apparatus.

Swelling tests were also carried out in order to calculate network density using the Flory–Rehner equation[26]. The rubber was swollen in methylene chloride at 25°C. In the calculations, an interaction parameter value of 0.314 was used[27] for butadiene–acrylonitrile 70/30 at 25°C.

The oil, and its influence on the rubber

The surrounding oil was a hydrated naphthenic oil. To this was added a GL additive (gear lubricant) based on sulphur–phosphorus chemistry. The amount of additive was such that the sulphur content in the oil became 2.7%. The sulphur content in the oil was originally 0.15%. The influence on the network density of the nitrile rubber vulcanizates of oils with different levels of GL additive has been reported in an earlier paper[4]. *Figure 8* shows with data from that paper how the network density, measured with the swelling test, was changed after 336 h immersion at 70°C. The network density of the samples was not influenced when they were immersed in the oil with no additive (0.15% S), but a significant increase in network density was observed for specimens immersed in the oils with GL additive. At this temperature, an increase in the level of GL additive gives a greater increase in network density. It can thus be concluded that at this temperature the GL additive in the oil is the origin of the secondary crosslinking reactions in the rubber. Investigation of the chemical mechanisms leading to this secondary crosslinking was outside the scope of the study.

Equipment for stress-relaxation measurements

The apparatus used for the measurement of intermittent stress relaxation, continuous stress relaxation and dynamic stress relaxation on specimens surrounded by oil is shown in *Figure 9*. The overview is given to the left in the figure. An electric motor equipped with an electronic speed regulation device gives the motion that is needed when dynamic stress relaxation is measured. A drive-shaft passes vertically through the apparatus from the motor to the gear housing. Above the gear-box there is a flywheel. From the gear-box, shafts with cam discs go out in four directions. The eccentricity of these cam discs is adjustable so that sinusoidally varying axial motions of different amplitudes can be produced. The cam discs are also used for setting the amount of deformation when intermittent stress relaxation is measured.

The can in which the specimen and the oil are placed is shown in the right-hand part of *Figure 9*. The specimen is inserted between two plates in the can. The upper plate is connected to a rod that transfers the motion from the cam-wheel. The prestrain is adjusted by a bolt with a scale graduation on this rod. The lower plate stands on a filament at the bottom that separates the oil chamber from the load cell. After the specimen has been inserted, the hand hole cover is screwed on, the thread being sealed with PTFE tape. The preheated liquid is fed in through the nipple at the top of the can. The tap at the bottom is for draining the liquid after the measurements are completed. An electric heating element is wrapped around the can, and the temperature is kept constant to 70±0.5°C with an electric device with a PT100 thermometer fitted in the back of the can.

Performance of stress-relaxation measurements

All stress-relaxation measurements were carried out in the apparatus presented in *Figure 9*. The temperature equilibrium, at 70°C, was achieved 30 min after a specimen was inserted. The specimens were cylinders with length and diameter equal to 20 mm. Continuous stress relaxation and intermittent stress relaxation were measured with 20% compressive strain. For continuous stress relaxation, the restoring force was recorded immediately after the specimen was compressed.

When intermittent stress relaxation was measured, the specimens were fixed with a small amount of cement in order to avoid dislodgement during the testing period. The intermittently measured restoring force was recorded 3 min after loading, after which the specimens were kept unloaded until the next measurement.

When dynamic stress relaxation was measured, the dynamic compression was built up of a 20% prestrain (4 mm), on which a sinusoidally varying strain of amplitude 2.5% (0.5 mm) was superimposed. The frequency was 2 Hz. The difference between maximum compression and minimum compression was twice the amplitude, i.e. 1 mm. This means that the force was recorded when the specimen was compressed 17.5% (minimum compression) and 22.5% (maximum compression).

Results from continuous and dynamic stress relaxation are reported normalized with respect to the restoring force 10 min after the specimen was compressed. Results for intermittent stress-relaxation measurements are reported normalized with respect to the first data point. Measurements were extended to 160 h.

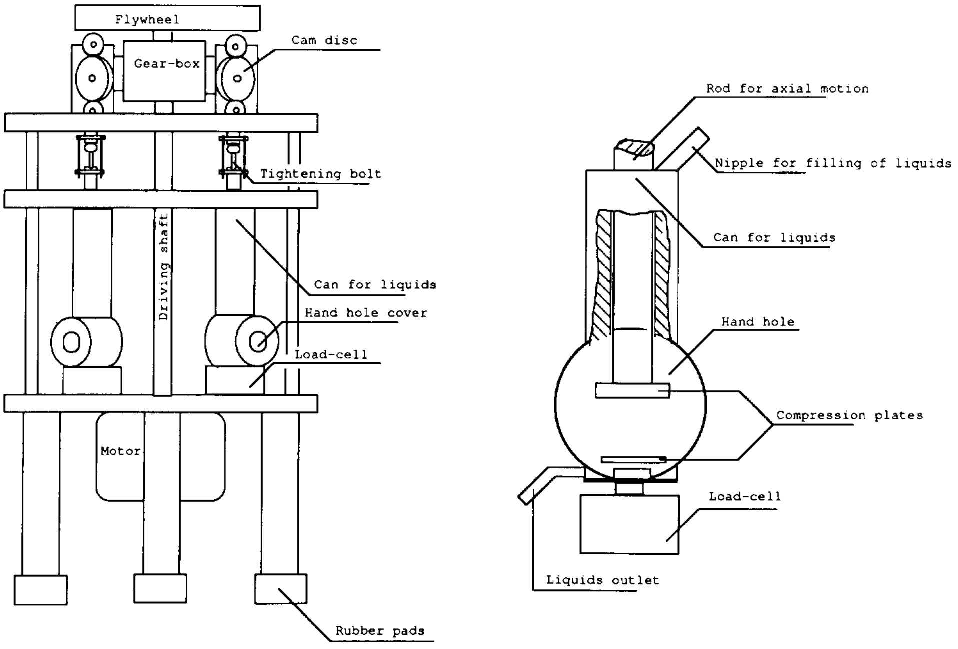

Figure 9 Apparatus for stress-relaxation measurements in specimens surrounded by oil

RESULTS AND DISCUSSION

Network densities measured mechanically and by swelling on both fresh material and material aged in the oil with additive are given in *Table 2*. Mechanical measurements gave higher absolute values than swelling measurements, which can be anticipated because of entanglement effects in the rubber[28]. The results are the mean values of triplicate tests, with a reproducibility in the range of ±10%. Ageing of material 2 in oil without any sulphur additive gave changes in network density much smaller than the reproducibility of the results, indicating no influence of this oil on network density. With the exception of the swelling test on material 1, the network densities exhibit almost the same increase with time for all three materials regardless of the initial network density. The process induced by the oil to increase the network density can thus be studied by both mechanical tests and swelling.

Stress-relaxation results are given for the three materials in *Figure 10* (note that the scale on the abscissa is not the same for material 1 as for materials 2 and 3). Material 1, with the lowest network density, exhibits the greatest decay of the continuously measured restoring force, and material 3, with the highest network density, exhibits the smallest. This is a typical result when degradation occurs as random scission along the network chains[22].

The network density ν_x of the secondary network formed by the influence of the GL additive in the cylindrical specimens is shown in *Figure 11*, the values being computed from data for continuous and intermittent stress relaxation given in *Figure 10*, using equations (3) and (4), and with $\nu_{u,0}$ values taken from mechanical measurements in *Table 2*. The increase in ν_x with time is about the same for the three materials, which also supports the statement about the crosslinking effect of the oil with additive.

The permanent set of the cylindrical specimens after 160 h in oil is given in *Figure 12*. Experimental values are compared with values calculated using equation (24) and the data given in *Figure 10*. Agreement between experimental and calculated values is good, which indicates that the Tobolsky two-network theory is applicable to this system of rubber and oil with an additive.

The minimum value for the dynamic stress relaxation, shown in *Figure 10*, exhibits its greatest decay for material 1, with the lowest initial network density, and its smallest decay for material 3, with the highest initial network density. This is in agreement with the relations presented. Values for the coefficients C_{max} and C_{min} calculated using equations (18) and (19) from the data given in *Figure 10* are shown in *Figure 13*. The coefficient C_{max} for the three materials varies between 0.16 and 0.45, and is typically about 0.4 for material 1 and about 0.2 for materials 2 and 3. C_{min} for material 1 is about 1, for material 2 between 0.3 and 0.4, and for material 3 about 0.2.

Table 2 Network densities, measured mechanically and by a swelling test, measured values and changes after ageing in sulphur-containing oil

	Network chains per cubic centimetre (× 10⁶)											
	Material 1				Material 2				Material 3			
	Mechanical		Swelling		Mechanical		Swelling		Mechanical		Swelling	
Time in oil (h)	Measured	Δ	Measured	Δ	Measured	Δ	Measured	Δ	Measured	Δ	Measured	Δ
0	75	–	13	–	114	–	60	–	131	–	81	–
24	50	−25	13	0	120	6	62	2	133	2	91	10
140	74	−1	43	30	133	19	94	34	158	27	118	37
700	166	91	124	111	205	91	160	100	210	79	166	85
Time in oil with no additive (h)												
700					115	1	64	4				

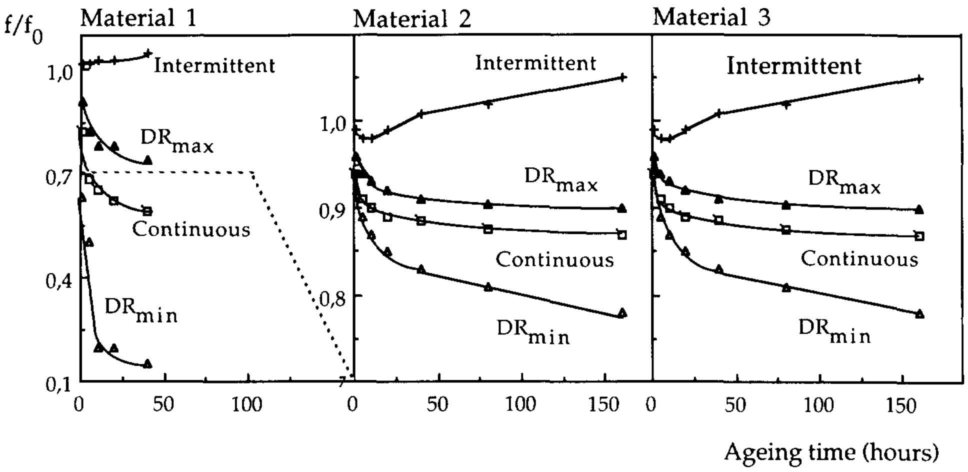

Figure 10 Stress-relaxation results for materials 1, 2 and 3. DR_{max} are maximum and DR_{min} minimum values of the dynamic restoring force

As the coefficients are calculated from differences between normalized values of stress relaxation, the normal scatter in the experimental results can have a considerable influence on the numerical values when differences between dynamic, continuous and intermittent stress relaxation are small, as in the case of material 3. An argument for the relevance of this relation is that the experimental values of C_{max} and C_{min} become fairly constant for each of the materials.

In *Figure 14*, results from measurements of dynamic stress relaxation on material 2 are compared with theoretical curves estimated using equations (16) and (17) with different values of C_{max} and C_{min}, as indicated in the figure. This exemplifies how higher values of C_{min} give a greater calculated stress relaxation at minimum compression, and higher values of C_{max} give a smaller calculated stress relaxation at maximum compression. The calculated curves have the typical shape of curves for dynamic stress relaxation. These different curves also illustrate that some variations in the values of the coefficients can be allowed without making the calculated curves unnatural.

CONCLUSIONS

At this temperature (70°C) the GL additive in the oil induces a crosslinking reaction in rather thick-walled nitrile rubber. This has a great impact on its stress-relaxation properties.

Stress-relaxation studies provide evidence that the original network of the specimens is degraded by random scission along the main chains.

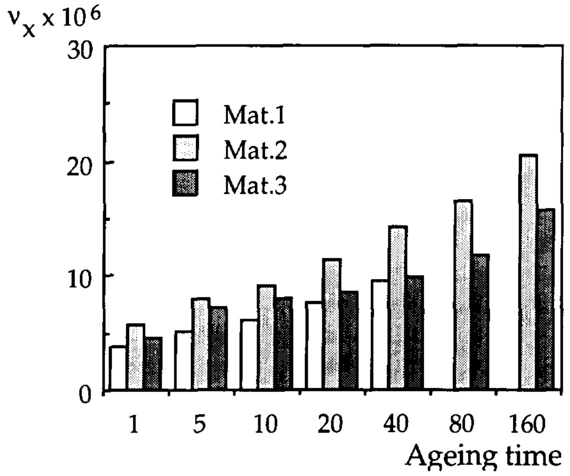

Figure 11 Values of v_x calculated from data in *Figure 10* using equations (3) and (4)

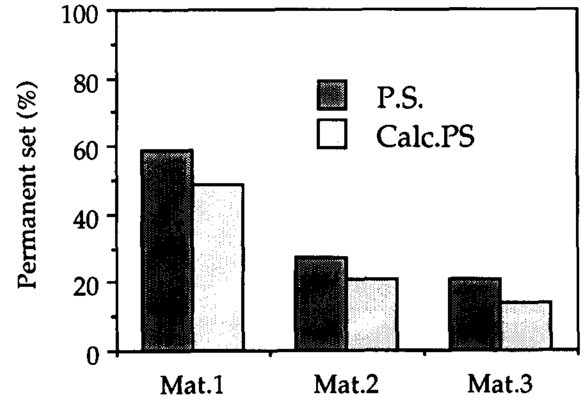

Figure 12 Permanent set, experimental and calculated values

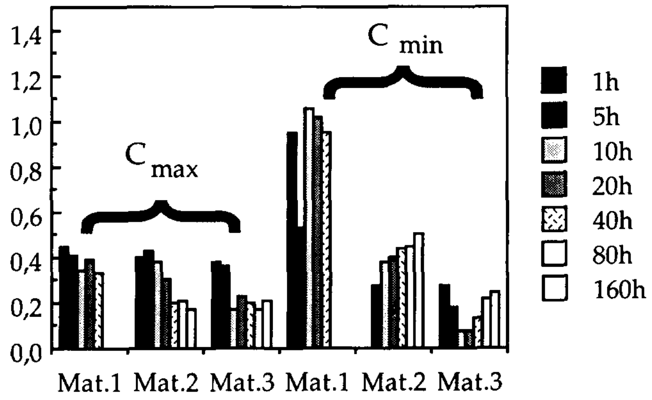

Figure 13 Experimental values of C_{max} and C_{min} calculated from data in *Figure 10* using equations (18) and (19)

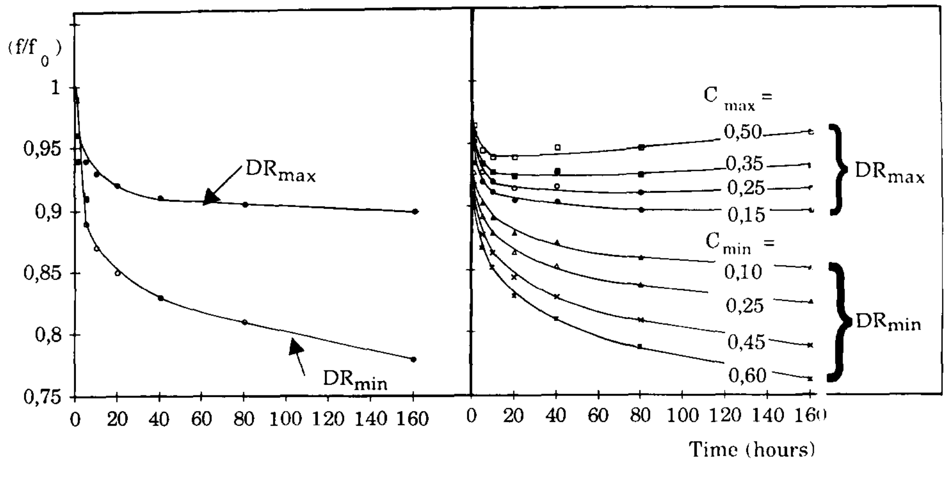

Figure 14 Results of dynamic stress relaxation for material 2 (left) and calculated values for the decay of the maxima and minima of the restoring force when different values of C_{max} and C_{min} are used (right). DR_{max} are maximum values and DR_{min} minimum values of the restoring force. The numbers on the lines in the right-hand side of the figure indicate which values of C_{max} and C_{min} were used when the curves were constructed

The increase in network density induced by the GL additive affects the maximum and minimum values of dynamic stress relaxation, and these are also predicted by the relations presented in this paper.

Dynamic stress relaxation can be reasonably well estimated from data for continuous stress relaxation and intermittent stress relaxation when proper values of the coefficients are used. The relation says that results of both continuous and intermittent stress relaxation are important for predicting the lifetime of a dynamic seal. It says that, when normalized results are compared, the minimum values of the restoring force will have a much greater decay than the maximum values. Normalized continuous stress relaxation will be somewhere between the other two. This is in agreement with experimental results.

From these relations, it can be concluded that in a rubber intended for dynamic seals neither reversion nor secondary crosslinking should be present. The original network density should be high in order to overpower effects of crosslinking induced by factors in the surroundings.

These relations indicate that the special effects that are noted when dynamic stress relaxation is measured have a chemorheological origin.

ACKNOWLEDGEMENTS

We express our gratitude to Nynäs Petroleum, Nynäshamn, Sweden, for the oil, and to Skega AB, Ersmark, Sweden, for the rubber specimens. The financial support from the Swedish Board for Technical Development (STU) is gratefully acknowledged.

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