

Properties of Rubber Compounds for Engineering Applications

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The performance of elastomeric engineering components generally depends on their having the correct force–deformation behaviour. This can only be achieved if the stress–strain behaviour of the elastomer is appropriate and well characterised. This is taken to include the effects of frequency and hysteresis as well as the quasi-static elastic behaviour.

Extreme temperatures, oils and oxygen may alter the stress–strain behaviour of the elastomer either reversibly or irreversibly and hence degrade the performance of the component, or even result in its failure. The constraints these considerations make on the choice of compound are briefly described.

Even if the properties of the elastomer do not deteriorate, the component may fail by rupture of the elastomer. The theoretical framework for describing such failure is briefly presented and its implications for component design and choice of compound mentioned.

Most physical tests cited in specifications are appropriate to achieving quality control rather than being directly related to the performance or longevity of the component. This paper aims at restoring the balance by reviewing how the performance of the component is related to the properties of the rubber.

STRESS–STRAIN BEHAVIOUR

Quasi-static Force–deformation Behaviour of Mounts

The basic design feature of most engineering components is the stiffness, that is the ratio of force to deflection, also known as the spring rate. The stiffness of a component scales with the modulus of the rubber, that is the ratio of stress to strain. Unfortunately rubber technologists usually refer to the stress (rather than the ratio of stress to strain) at a specified strain as being the 'modulus'.

Rubber mounts are required to bear a dead load, and it is important that the static deflection should be limited to an acceptable level. However, the dynamic stiffness (determined in part by the tangent to the load-deflection curve) must be sufficiently low to achieve effective vibration isolation if the function of the component is to isolate in the same direction as the dead load is supported. These considerations mean that for a highly variable dead load (for example, for a truck suspension spring) a rising rate is appropriate (*Figure 1*) so that the natural frequency is not dependent on load (for small vibration amplitudes)¹. For a well-defined dead load a high initial stiffness followed by a plateau region (achieved by a buckling mode of deformation) may be appropriate (*Figure 2*) so that the static deflection is small (corresponding to the high initial stiffness) as also is the dynamic stiffness for small amplitude vibrations about the static deflection^{2,3,4}.

Either way it is desirable that the quasi-static force–deformation behaviour of the

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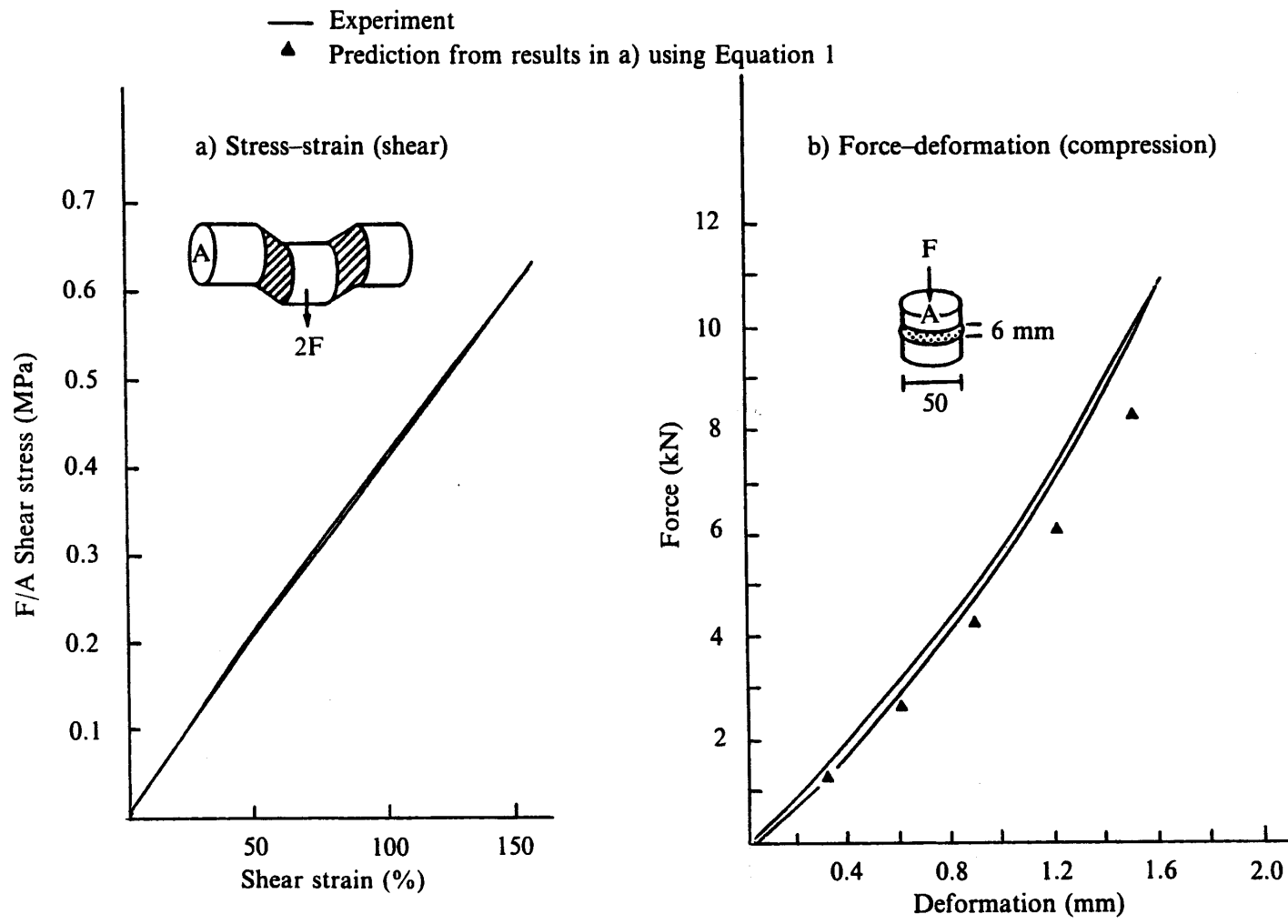


Figure 3. Tenth cycle quasi-static deformation of unfilled natural rubber a) stress-strain in simple shear and b) force-deformation in compression (shape factor ≈ 2).

component is calculable. On the assumption of linear stress-strain behaviour, many formulae have been derived⁵, and these are largely satisfactory for unfilled natural rubber (*Figure 3*). However, when a reinforcing filler is used the stress-strain behaviour of the rubber is non-linear, and this results in an extra contribution to any non-linearity associated with the geometry of the component (*cf Figures 3 and 4*). At low strains, the shear modulus of filled rubber is high because of carbon black interactions which progressively break down as the strain is increased⁶, resulting in a strain softening. This effect can rarely be exploited to practical advantage. One exception is the use of highly filled natural rubber for seismic isolation bearings, for which the high stiffness at low strains limits the deflection caused by wind loading to an acceptable level⁷.

At high strains, the modulus of filled rubber again increases due to finite extensibility of the polymer chains, which occurs at much lower strains for a highly filled rubber because of the strain amplification effect of the filler⁸. For the rubber in *Figure 4*, it is seen that this effect occurs at shear strains above 100% whereas usually the strain levels in service are less than 100%. The detailed shape and position of the upturn in the stress-strain curve depends on the previous strain-history of the sample⁸.

Non-linearity of the stress-strain behaviour means that the modulus will depend on the strain. The formulae derived assuming linear stress-strain behaviour may still provide a useful estimate for the force-deformation behaviour of non-linear rubbers if the modulus inserted into them is chosen at an appropriate strain⁹. Such a representative shear strain $\bar{\gamma}$ may be defined by

$$\bar{\gamma} = \sqrt{(k/G)/V} x \quad \dots 1a$$

where V is the volume of rubber in the component

x is the deflection of the component

and the ratio k/G is taken to be the stiffness for unit modulus derived on the basis of linear stress-strain behaviour.

Having found the representative strain $\bar{\gamma}$ using *Equation 1a*, the shear modulus to be used in predictions of stiffness of the components can be obtained from the measured shear stress/shear strain behaviour of the rubber. The modulus is calculated from the shear stress $\sigma(\bar{\gamma})$ at $\bar{\gamma}$ according to

$$G_{\text{chord}} = \sigma(\bar{\gamma})/\bar{\gamma} \quad \dots 1b$$

Equation 1 appears to be successful, at least at moderate deformations of the component given in *Figure 4*. Fortunately, it is the behaviour at moderate deformations which is required in practice.

Thus while reinforcing fillers cause the stress-strain behaviour to be non-linear, it is still possible to use existing formulae for the force-deformation behaviour of components, provided that the compound is characterised by the full stress-strain behaviour and not just by a single number, such as hardness.

Hardness can be used⁹ to estimate the shear modulus (in Nm^{-2}) at a strain of about 5% and an equation giving an approximate fit to the theoretical relationship is

$$\log_{10} (G_{5\%}) \simeq \frac{\text{IRHD} + 228}{47} \quad \dots 2$$

for $35 < \text{IRHD} < 80$

Very rough estimates of shear modulus at other strains can only be made from the hardness value by appealing to prior experience of similar compounds.

Dynamic Stiffness and Dynamic to Static Ratio

Vibration amplitudes are typically much smaller than the quasi-static deflections of vibration isolation springs. Thus even if

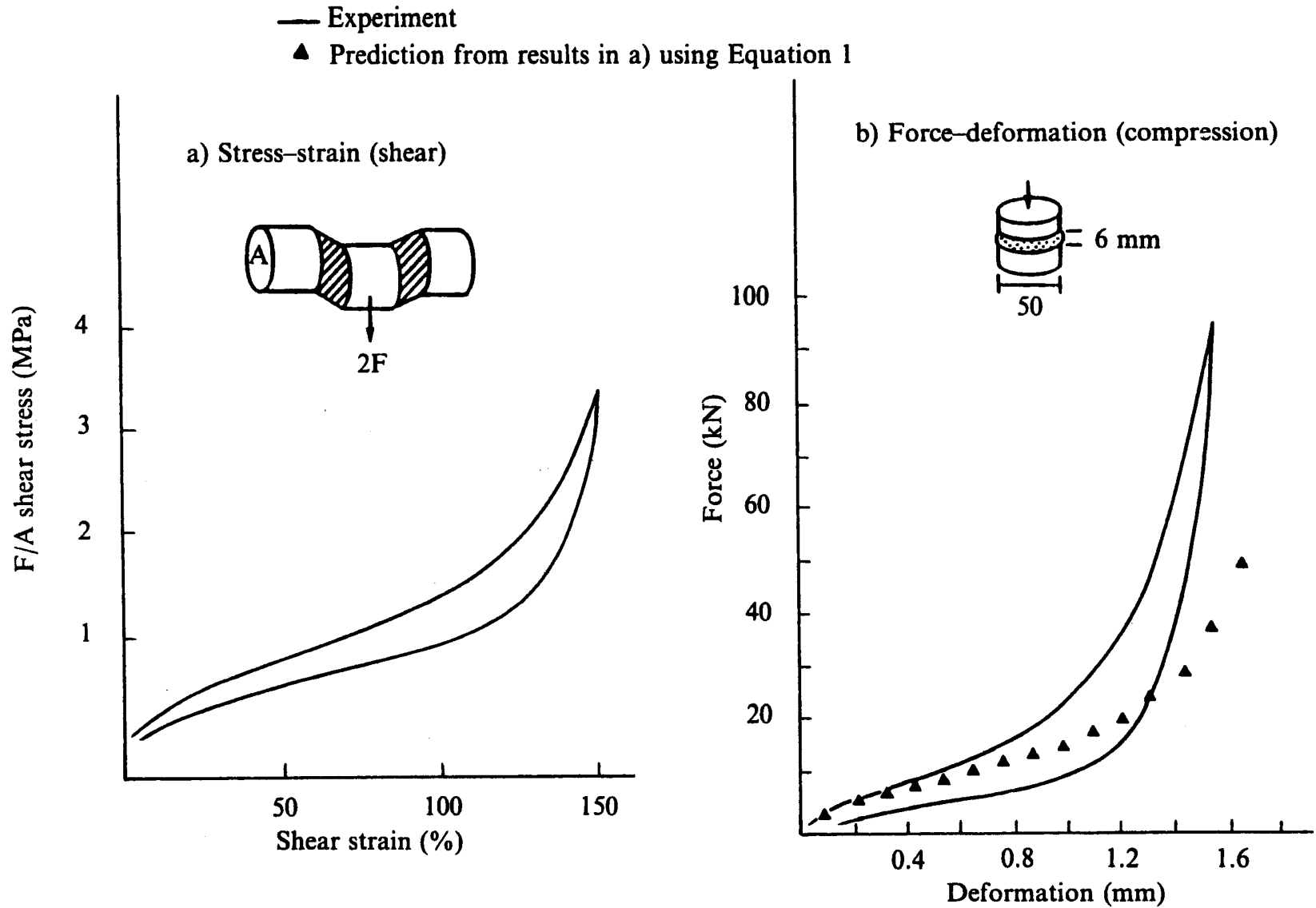


Figure 4. Tenth cycle quasi-static deformation of natural rubber + 75 p.h.r. N330 black
 a) stress-strain in simple shear and b) force-formation in compression (shape factor ≈ 2).

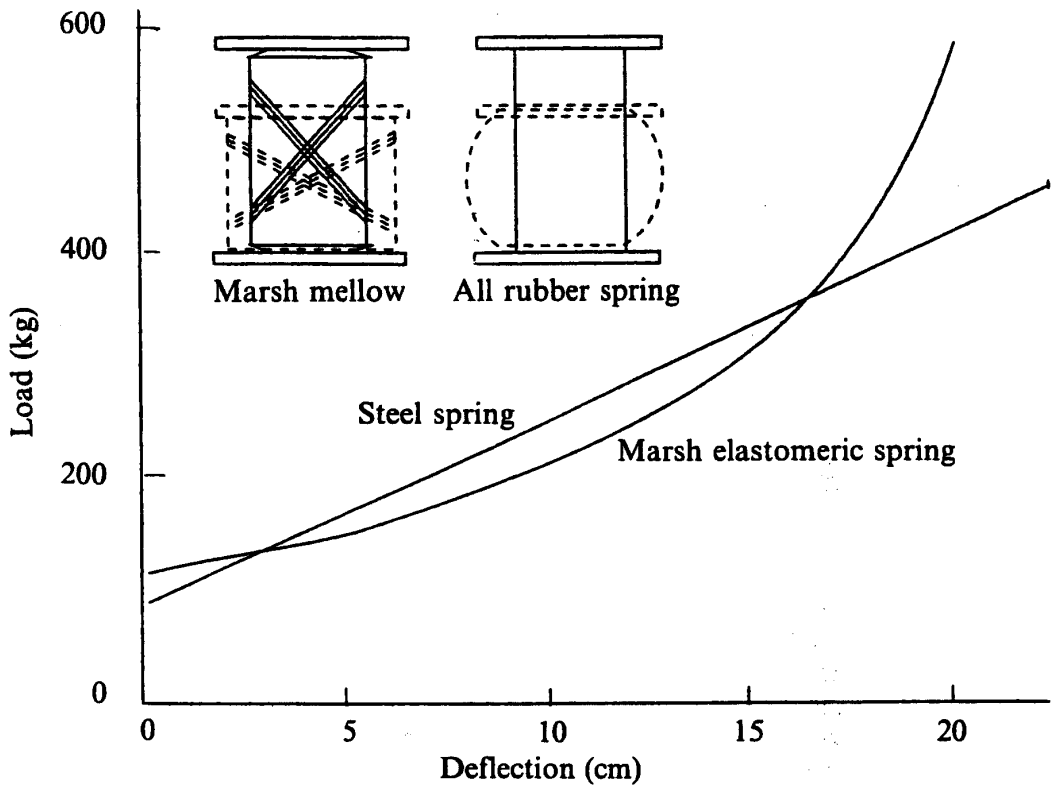


Figure 1. Load-deflection curve of Marsh Mellow spring, showing non-linearity. Insert: Marsh Mellow spring showing how pantographing cords restrict bulging of the rubber under load, causing an extra contribution to the non-linearity¹.

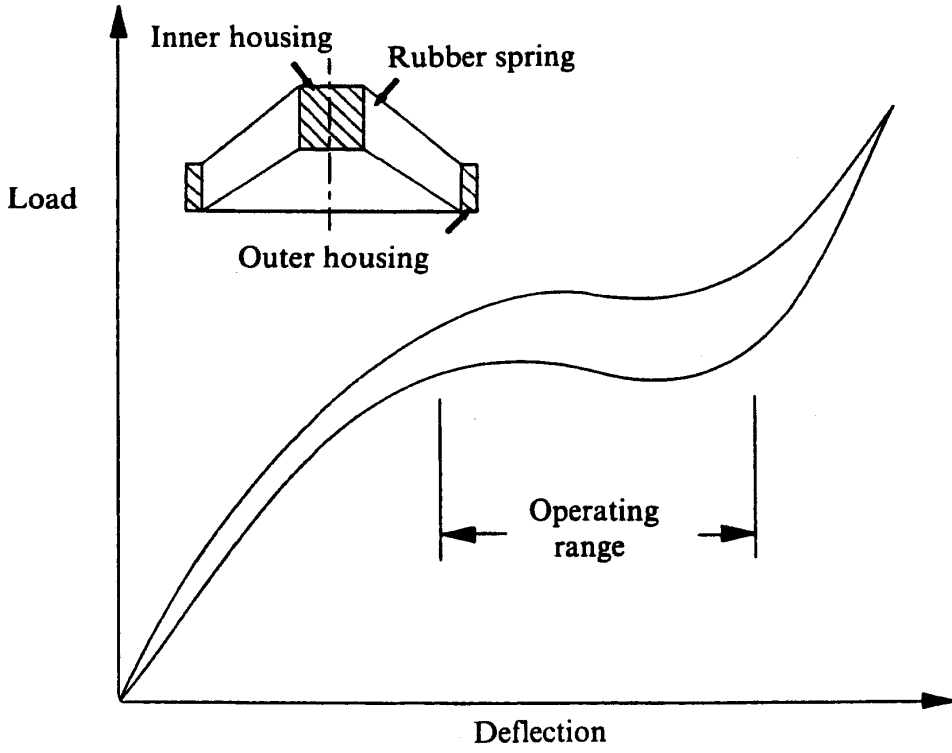


Figure 2. Load-deflection curve for axially compressed conical rubber shear bushing³.

the overall quasi-static force-deformation behaviour is non-linear, vibration isolation theory based on the assumption of linearity usually suffices. The stiffness k to be used in formulae derived from this theory (*Figure 5*) must, however, be appropriate to the particular frequency and amplitude of the vibration and to the static deflection of the spring. This value of k is called the 'dynamic stiffness'.

For springs that are non-linear for geometric reasons only (*Figures 1 and 2*), the dynamic stiffness is determined by the tangent stiffness to the quasi-static force-deflection curve. Some elastomers (including all those with a high T_g , such as ENR 50) also show a strong effect of frequency, the dynamic stiffness being higher at higher

frequencies, but for NR (filled or unfilled), this effect is weak.

The material contribution to non-linearity (induced by the use of reinforcing filler) affects the dynamic stiffness in a more complicated way. For clarity, this will be illustrated for simple shear (*Figure 6*), a mode of deformation for which there is no geometric contribution to non-linearity. While for unfilled NR the dynamic modulus is equal to the quasi-static modulus (*Figure 6a*), for filled NR, the dynamic modulus is closer to the tangent modulus at zero shear strain rather than to the tangent modulus at the specified (non-zero) static strain (*Figure 6b*). The behaviour is reminiscent of a spring with friction, which will have an extra high stiffness at the start

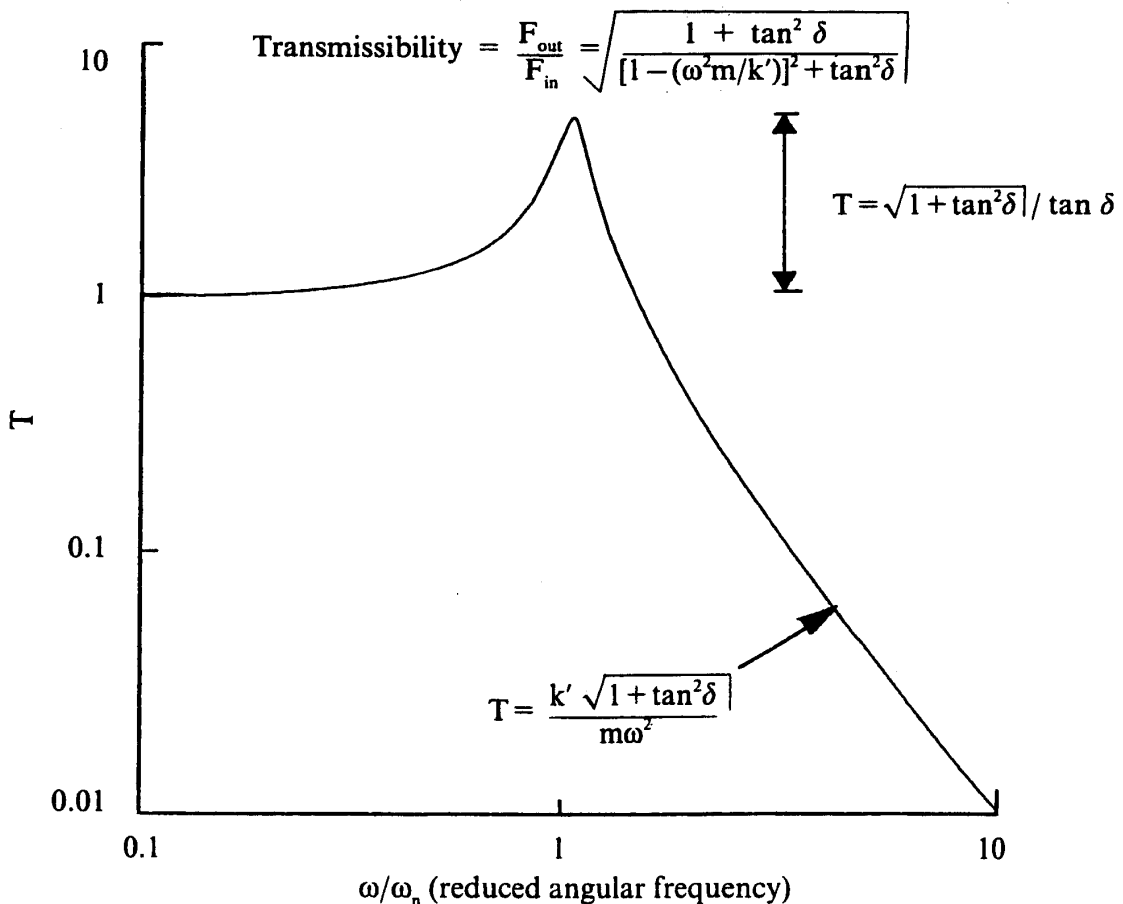


Figure 5. Schematic diagram to show effects of damping ($\tan \delta$) and dynamic storage stiffness (k') on vibration isolation.

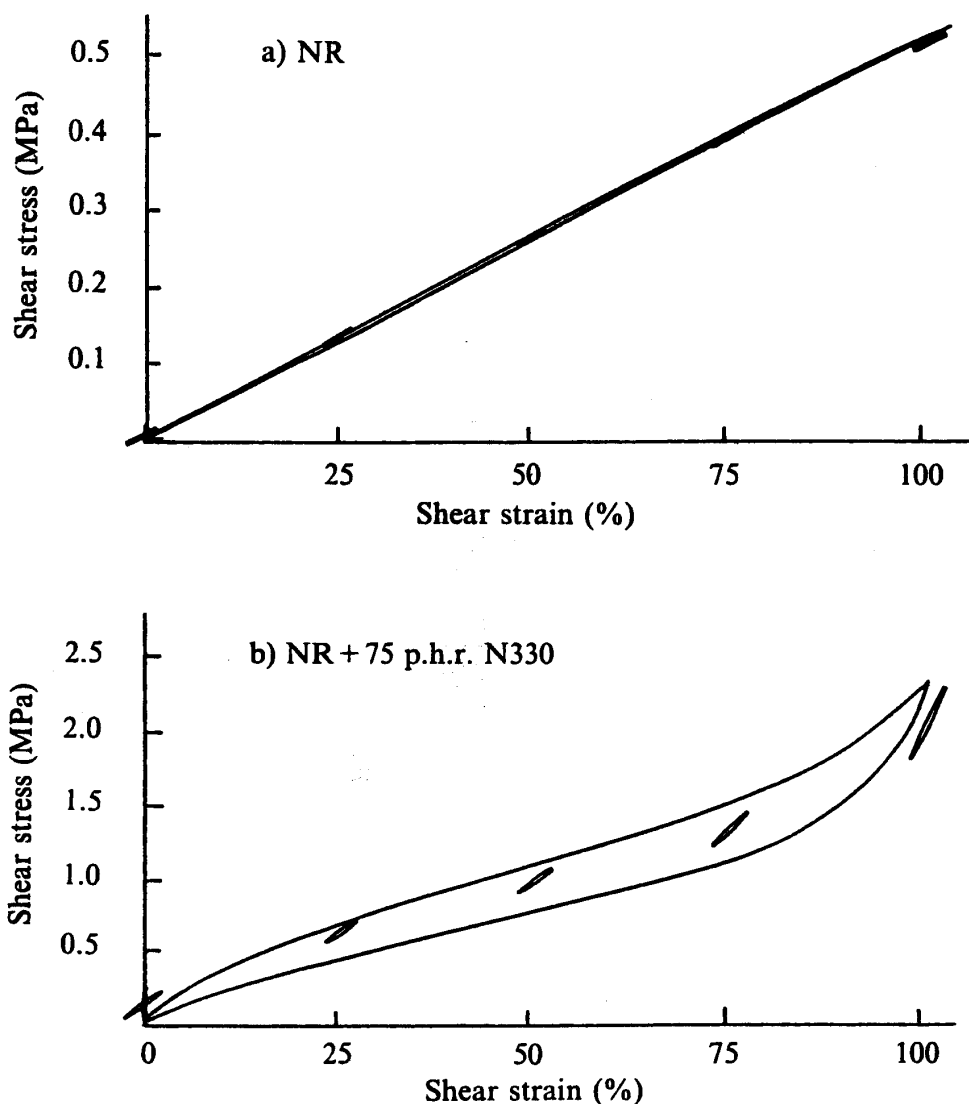


Figure 6. Tenth cycle shear stress-strain curves with cycles of $\pm 2\%$ shear strain superimposed about static strain of 0%, 25%, 75% and 100%; a) unfilled natural rubber and b) natural rubber + 75 p.h.r. N330 black.

of extension and at the start of retraction. The dynamic stiffness is strongly influenced by the retraction stiffness. However, carbon-black interactions cause time-dependent effects¹⁰ as well as such 'frictional' effects.

The ratio of dynamic stiffness to the slope of the quasi-static force-deformation curve is sometimes known as the 'dynamic to static ratio'. Use of this term may imply an assumption of linearity of the quasi-static

force-deformation curve, so that whether the chord or tangent slopes are specified for the static stiffness is left open.

The word 'dynamic' suggests the departure of the ratio from unity is a consequence of frequency dependence of the elastic properties. Although this may be the case for high T_g rubbers, for filled NR the amplitude effects are much more important than the frequency effects.

Figure 7 shows effects of dynamic amplitude (at zero static pre-strain) and filler loading on the 'dynamic to static ratio' in shear, choosing the tenth cycle chord modulus at 50% shear as a measure of static stiffness. The effect of static pre-strain on the dynamic modulus is relatively small and has been neglected for the purposes of Figure 7. Fortunately, the rise in dynamic modulus as the amplitude is decreased becomes less rapid for strains below 1%, and the dynamic modulus reaches a limiting value at about 0.1% strain according to Payne⁶.

The fact that the dynamic to static ratio is greater than unity for filled rubber is not a desirable feature, since for effective isolation of noise and vibration, the dynamic stiffness must be of a specified, low magnitude. It is difficult, and perhaps impossible, to correctly design the dynamic stiffness to have the specified level, bearing in mind that it depends on dynamic amplitude (which for high frequencies may be extremely low), static amplitude, recovery time after subjection to higher amplitude and temperature.

These complications may severely limit the usefulness of any constitutive equation intended to describe black filled rubber.

Thus, the use of significant amounts of reinforcing filler at best complicates the design for satisfactory performance considerably, and at worst, may prevent the optimum performance being achieved. Fortunately for natural rubber it is not essential to use filler, since the unfilled vulcanisate has adequate strength properties, unlike non-crystallising rubbers.

Damping

It is apparent from the formula in Figure 5 that in addition to the dynamic stiffness k , the loss tangent, $\tan \delta$, is an important parameter in determining the transmissibility. The loss tangent may be defined by the following equation relating the force F required to deflect a linear rubber spring with a sinusoidal amplitude A and angular frequency ω :

$$F = kA \sin \omega t + k' \tan \delta A \cos \omega t \quad \dots 3a$$

$$k = k' \sqrt{1 + \tan^2 \delta}$$

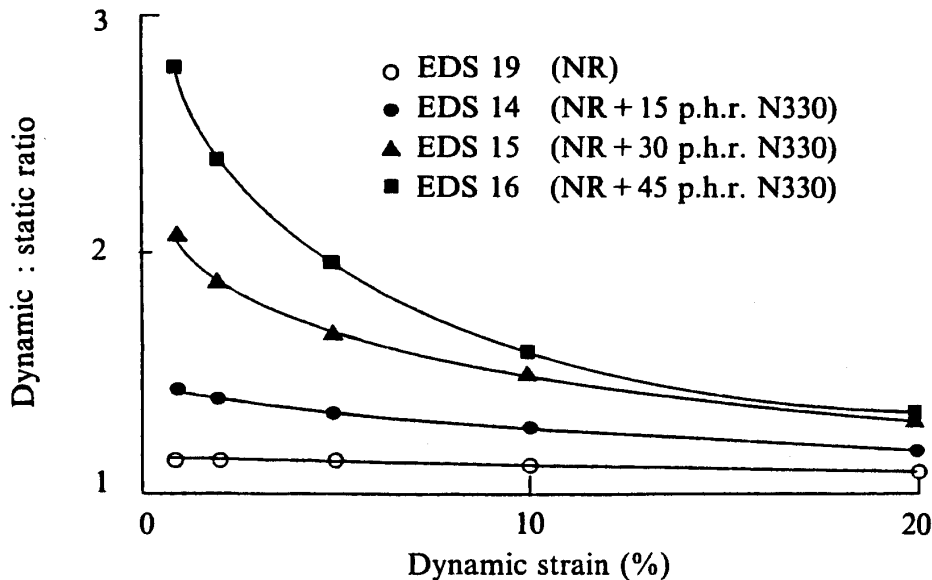


Figure 7. Effect of dynamic strain and carbon black loading on the ratio of complex dynamic shear modulus (at 1 Hz) to the tenth cycle quasi-static chord shear modulus at 50% shear⁴¹.

An alternative definition of $\tan \delta$ is in terms of the stress response to a sinusoidal strain. For example, in simple shear, the stress response $\bar{\gamma}$ to a sinusoidal strain of amplitude γ_0 is

$$\sigma = G' \gamma_0 \sin \omega t + G'' \gamma_0 \cos \omega t \quad \dots 3b$$

where G' is the storage modulus and G'' is the loss modulus. In general, G' and G'' are functions of ω . The ratio G''/G' may be identified as $\tan \delta$.

Equation 3b can also be expressed as

$$\sigma = \frac{\sqrt{(G'^2 + G''^2)}}{\sigma_0} \gamma_0 \sin(\omega t + \delta) \equiv \sigma_0 \sin(\omega t + \delta) \quad \dots 3c$$

where σ_0 is the amplitude of the sinusoidal stress and δ is the loss angle.

For unfilled elastomers well above their T_g , such as natural rubber at room temperature, $\tan \delta$ is fairly independent of frequency but rather low. Carbon black increases the level of $\tan \delta$, and the insensitivity to frequency is largely retained. For many applications, this is a distinct advantage over achieving high damping by choice of an unfilled high T_g polymer, since then both the in-phase modulus and $\tan \delta$ increase rapidly with frequency, and the isolation of higher frequencies will be impaired (Figure 5). However, if very high values of $\tan \delta$ (e.g. > 0.2) are required and the temperature and frequency ranges are not too extended it may be preferable to use a high T_g elastomer (such as ENR) rather than face the problem of amplitude dependence of stiffness (discussed above) associated with high loadings of filler.

Creep and Stress Relaxation

Creep is often an undesirable feature for load bearing components such as mounts, since extra clearance is required to accommodate the creep deflections. Differential creep may also lead to redistribution of the loads on the mounts. Stress relaxation is an undesirable feature

for components such as seals which are held at a constant deformation and must maintain an adequate stress for their function.

Creep and stress relaxation may be related as follows¹¹. The rate of creep C at a constant stress σ is defined as the relative slope of the strain *versus* time curve:

$$C = (1/e) (\partial e / \partial t)_\sigma \quad \dots 4$$

where e is the strain at time t after the stress σ is imposed. The rate of stress relaxation S at a constant strain e is defined similarly:

$$S = -(1/\sigma) (\partial \sigma / \partial t)_e \quad \dots 5$$

It follows that

$$C = [(\sigma/e) / (\partial \sigma / \partial e)] \cdot S \quad \dots 6$$

Wherever the terms stress and strain occur in the above, they can be replaced by force and deflection respectively. It can be concluded from Equation 6 that the creep rate of a spring depends not only on the stress-relaxation rate of the rubber but also on the degree of non-linearity of the spring's force-deformation behaviour. Springs with a falling rate will suffer more from creep than springs with a rising rate, while for linear springs the creep rate will be equal to the stress-relaxation rate.

It is generally found that the relaxation modulus $G(t)$ [that is, $\sigma(t)/e$] for rubbers well above their T_g decreases approximately linearly with $\ln(t)$:

$$\partial G(t) / \partial \ln t \approx -G_0 \quad \dots 7$$

provided the relaxation time is not very long, so that Equation 7 is valid in the restricted time range $t_1 < t < t_2$.

Using the theory of linear visco-elasticity, it can be shown¹² that Equation 7 corresponds to

$$G''(\omega) \approx G_0 \pi/2 \quad \dots 8$$

$$dG'(\omega) / d \ln(\omega) \approx G_0$$

where $t_1 \ll 1/\omega \ll t_2$. Substitution of Equation 7 into Equation 5 gives

$$tS \approx G_0/G(t)$$

The right hand side can be approximately expressed in terms of $\tan \delta$ [that is $G''(\omega)/G'(\omega)$] using Equation 8:

$$tS \approx \frac{2}{\pi} \tan \delta \quad \dots 9a$$

Because of Equation 7, it is customary to

$$\text{refer to } S_{\%} = -\frac{100}{\sigma} \frac{\partial \sigma}{\partial \log_{10} t} \equiv 100 \ln(10) tS$$

(a dimensionless quantity having units of % relaxation per decade of time) as being the stress-relaxation rate.

Substituting Equation 9a into this definition of $S_{\%}$ leads to

$$S_{\%} \approx 147 \tan \delta \quad \dots 9b$$

Gent¹¹ has shown that for a wide range of unfilled NR vulcanisates and for an unfilled SBR vulcanisate, Equation 9b is reliable to 20%. However, for black filled NR vulcanisates, the measured stress-relaxation rates can be lower than those predicted by Equation 9b by a factor of three to five¹³. Stress-relaxation rates are increased by increase in the filler loading, but the effect is smaller than would be anticipated from the accompanying increase in $\tan \delta$. This observation shows that linear viscoelasticity is not applicable to filled rubbers, suggesting that the origin of the extra damping is 'frictional' rather than viscoelastic. The combination of relatively low stress-relaxation and creep rates with high values of $\tan \delta$ may mean that the use of filler to achieve damping is preferable in some applications to using a high T_g polymer.

The above discussion concerns 'physical relaxation'. After long periods of time, it can be seen from Equation 9a that the physical relaxation rate becomes very small. Ultimately another process, 'chemical relaxation',

which is characterised by a linear dependence of relaxation with time [rather than $\log(\text{time})$] becomes the dominant relaxation mechanism and the relaxation process is better described by

$$\frac{G(t_1) - G(t)}{G(t_1)} \approx A \log_{10}(t/t_1) + B(t - t_1) \quad \dots 10$$

A may be identified as $S_{\%}$ above. B , the chemical relaxation rate, rises more strongly with temperature than A . This makes the interpretation of accelerated tests at raised temperatures difficult. For a typical NR vulcanisate at 10°C, the rate of physical relaxation falls to about the same level as that of chemical relaxation after one or two years¹⁴.

Applications Requiring High Damping

There is a tendency to regard creep, stress relaxation and compression set as undesirable for any rubber. However, in some applications, the primary requirement of the engineer is for high damping, and the creep rate may be of secondary importance or even irrelevant.

One such example is the 'vibration absorber'. The function of this device is to prevent the amplitude of a resonance in an engineering structure from becoming unacceptably large. This is achieved by dissipating some of the excitation energy in a sprung mass 'absorber' tuned close to the resonant frequency¹⁵. Often the resonant frequency is rather high, so that the static deflection of the spring is very small and creep deflections are negligible. This is fortunate, as optimising the spring properties requires very high levels of damping.

Seismic isolation bearings are another example⁷. Here the requirement is for a low horizontal stiffness together with very high damping. Creep in the horizontal direction should not occur since there is no static horizontal loading. The bearings must support a high vertical load, but the vertical creep deflections can be kept to acceptable

levels by making the bearings very stiff vertically.

In other cases, it may be possible to combine a highly elastic compound in parallel with a highly hysteretic compound (the analogue of an oil-filled damper). This could be done, for example, by using multiple laminations of the flexible rubber-steel laminated spring¹⁶ depicted in *Figure 8*.

DEGRADATION OF PERFORMANCE:
EFFECT OF THE ENVIRONMENT

Swelling by Oils

If a rubber absorbs a large volume of liquid it will become very 'weak' and useless for most engineering applications. Equilibrium swelling is the conventional measure of swelling resistance. However, such a test does not take into account that throughout the life-time of bulky elastomeric engineering components only the outermost rubber will become swollen to anything like the equilibrium level. Swelling is a diffusion-controlled process and the depth of penetration of the swelling liquid is proportional to the square root

of time for which the rubber has been immersed. The diffusion coefficient, and hence the time required to penetrate a certain depth, is related to the viscosity of the liquid¹⁷ as shown in *Figures 9* and *10*. It is apparent that a natural rubber component (if 20 mm or more in thickness) will not be seriously affected by splashes of engine oil during a life-time of ten or more years. For more aggressive environments, measures may be adopted ranging from use of an oil-resistant paint to choice of an oil-resistant elastomer (ENR or NBR). Natural rubber is swollen by most hydrophobic liquids (but not by castor oil or silicone oil).

Oxidation

As with other unsaturated polymers, natural rubber and ENR are prone to oxidative degradation, at a rate which increases with temperature. However, the depth to which oxidative degradation takes place is controlled by diffusion slowed down by consumption by chemical reactions. Degradation of bulky rubber components is, therefore, generally restricted to the surface layers, this may be unacceptable

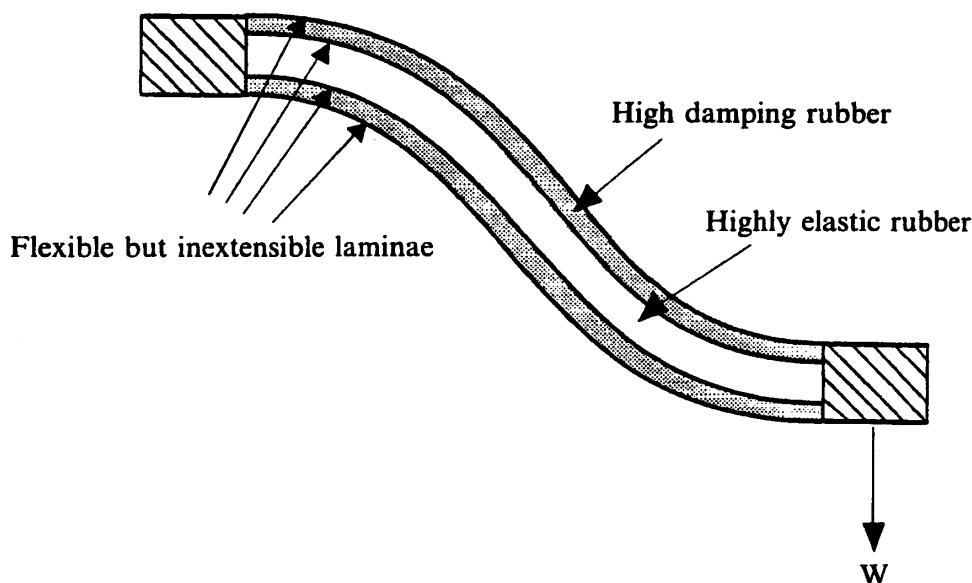


Figure 8. Flexible rubber-steel sandwich spring¹⁶.

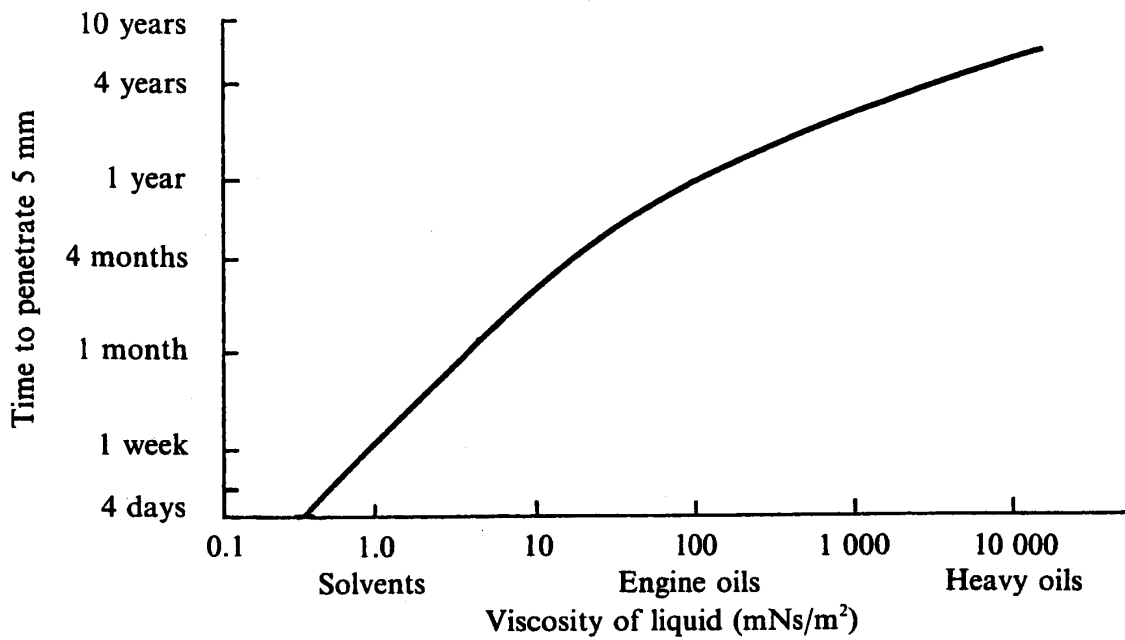


Figure 9. Effect of oil viscosity¹⁷ on the time taken to penetrate NR to a depth of 5 mm.

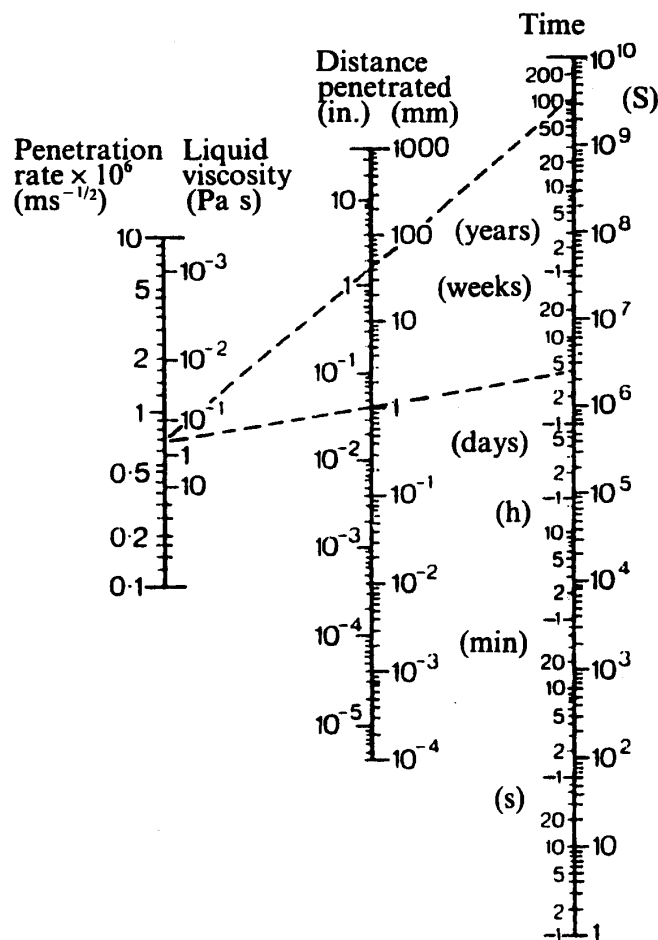


Figure 10. Nomogram relating oil viscosity, penetration distance and time for swelling of NR by oils¹⁷.

on cosmetic grounds but may not seriously affect performance.

Effective antioxidants are available, but they generally act in a sacrificial manner. This means that their effectiveness may be under-estimated by tests on thin rubber sheets since in a bulky component, constant replenishment of the antioxidant in the surface layers can occur by diffusion from the interior. Oxidation can cause both scission and further crosslinking. The balance depends on the polymer and temperature; natural rubber softens at elevated temperatures (except when oxidation has progressed to an extreme extent¹⁸), but oxidation may directly cause hardening at lower temperatures. Extensive oxidation, for example at elevated temperatures, can produce a brittle surface layer, which acts as a barrier to further ingress of oxygen¹⁹. The time required for such a layer to form for a bulky natural rubber component formulated with antioxidant is predicted to be hundreds of years at ambient temperatures¹⁸.

Oxidation is increased by ultra-violet radiation, but this effect can be eliminated by the presence of at least some carbon black in the compound (>1 p.p.h.r.) to make it opaque.

Ozone Attack

Ozone reacts with the carbon-carbon double bond extremely rapidly and causes direct cleavage of the bond. Attack on unstretched rubber is, therefore, restricted to a very thin surface layer, and is thus of no practical consequence. However, if the rubber is stretched above a threshold strain, cracking occurs. This results in much more efficient utilisation of the available ozone for destructive purposes. In static tests, the threshold strain at which cracking occurs may be increased substantially by dialkyl p-phenylene diamine antiozonants. However, these antiozonants may also induce a dependence of the threshold strain on the ozone concentration so that static tests in high concentrations of ozone may not be a reliable guide to performance at

ambient ozone concentrations. Hydrocarbon waxes may also prevent ozone cracking under static conditions and the effect can be especially great when used together with p-phenylamine antiozonants. The effectiveness of waxes depends strongly on the temperature, and this must be borne in mind on choosing the temperature of accelerated tests. As with antioxidants, antiozonants and antiozonant waxes depend for their efficiency on diffusion to the surface. This means that bulky components will have the advantage of a large internal reservoir of antiozonant for replenishment of the surface layers²⁰. If the threshold strain is exceeded, antiozonants can reduce the rate of cracking. Protection against ozone attack under dynamic conditions is more difficult than under static conditions. P-phenylenediamine antiozonants are particularly helpful in reducing the dynamic crack growth rate, but the dynamic strain below which no cracking occurs remains too low to be of practical significance.

Effect of Water

Pure polyisoprene is not swollen by water, but natural rubber does contain a few percent of hydrophilic material (such as proteins) so that some water is absorbed. This may lead to an increase in the rates of creep and stress relaxation, but other physical properties are not seriously affected for typical vulcanisates, even after immersion for forty-two years²¹. In some environments, there may be some microbial attack, paraffinic compounding ingredients such as fatty acids and wax providing the main nutrients, but the consequences for the physical properties of natural rubber are again slight. An effect of immersion that may cause problems for thin walled components (such as inflatable boats) is the leaching of antioxidants and antiozonants. Since the efficiency of antidegradants depends in part on their mobility, some of the best flex-cracking antioxidants are the most easily leached out (notably IPPD)²⁰.

There is a possibility that water may precipitate failure of rubber-metal bonds. For

this reason, automotive bonded components are sometimes tested in an environment of salty spray. However, in a study involving immersion in sea water for two years, no degradation of natural rubber-steel bonds (using Chemlok 205/220 adhesive system) was observed even when the metal was partly exposed and had become corroded²². If, on the other hand, cathodic protection was used to suppress corrosion of the exposed steel then bond failure did occur. In another study, NR/steel bonds (using Chemosil 211 + 231 adhesive system) were exposed to fresh water at 70°C or 85°C; subsequent tests on the dried test-pieces did show a decline in 'stripping force' after a few days' exposure²³.

Effect of Low Temperatures

All rubbers undergo an almost instantaneous reversible increase in the storage modulus as the temperature is lowered towards the T_g , due to an increasing internal energy contribution to the work of deformation. For natural rubber (with a T_g of -72°C), this effect is small down to -40°C , while ENR 50 (with a T_g of about -20°C) is then a brittle, glassy material with a shear modulus about 1000 times greater than the value at ambient temperature. The very high dynamic stiffness of rubbers with reinforcing filler becomes even more pronounced as the temperature is lowered, as seen in *Figure 11*. It appears that the reinforcing effect becomes stronger at lower temperatures.

Another reversible but time-dependent effect of low temperature undergone by only some rubbers (notably polychloroprene and natural rubber) is stiffening due to crystallisation²⁴. The rate of crystallisation of natural rubber is a maximum at around -25°C (vulcanisates then taking several days to several months to reach equilibrium). The melting temperature of the crystallites is higher the higher the temperature at which they were formed²⁵, but a temperature of $+30^\circ\text{C}$ is generally sufficient to cause

melting. Crystallisation of natural rubber during seasonal periods of low temperature can be reduced to insignificant levels by choosing a high sulphur vulcanising system (which causes a relatively high degree of polymer chain modification)²⁴. The use of efficient vulcanisation (EV) systems should be avoided in products exposed for long periods to low temperatures.

Effect of High Temperatures

As the temperature is increased, the loss modulus of a rubber decreases and the entropic contribution to the elastic modulus increases. Well above the T_g , where the entropic contribution is dominant, the elastic modulus of unfilled vulcanisates is proportional to the absolute temperature.

The strength of an elastomer generally declines as the temperature is increased (*Figure 12*), because it is related to the amount of hysteresis (at the high strains around the crack tip). However, the effect is much more marked for non-crystallising rubber than for natural rubber, which even at temperatures as high as 140°C can apparently strain-crystallise at crack tips²⁶. This aspect is not usually covered by specifications, which concentrate on the irreversible effect of exposure to high temperatures on the properties subsequently measured at room temperature.

Irreversible changes (often called 'ageing') are a consequence of both oxidation (discussed above) and anaerobic chemical reactions. The anaerobic reactions are the more serious limitations, since they proceed independently of the bulk of the rubber component. They proceed especially rapidly at temperatures of the order of the vulcanisation temperature ($\sim 150^\circ\text{C}$). For conventionally cured natural rubber, some crosslinks are lost altogether while others are reduced from polysulphides to disulphides or monosulphides. This results in a reduction in both the modulus and resilience. EV systems provide improved resistance.

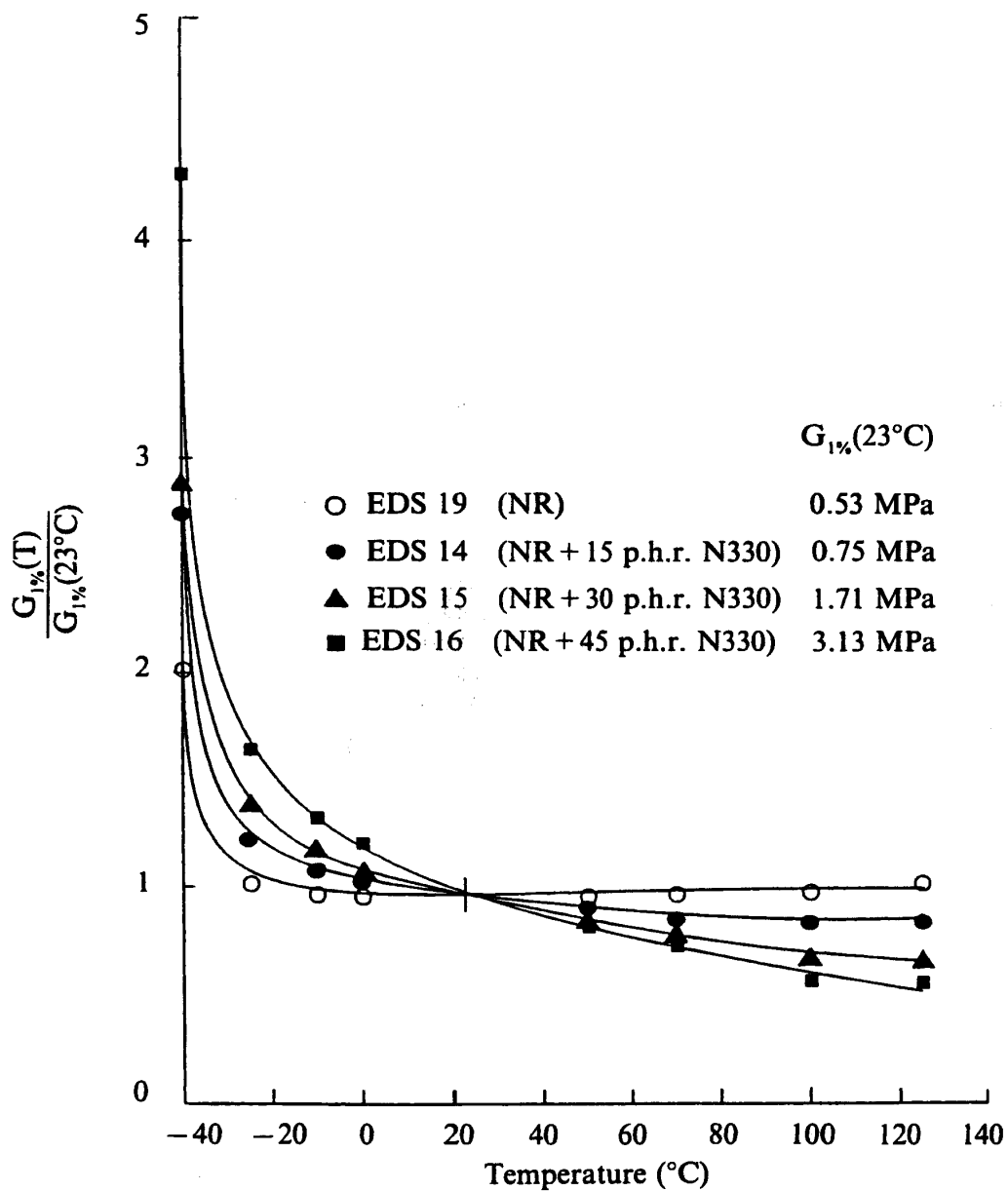


Figure 11. Effect of temperature and loading of carbon black on the complex shear modulus (1 Hz, 1% strain) of natural rubber vulcanisates¹¹.

Hysteretic Heating and Heat Build-up

In extreme cases (such as solid tyres) hysteretic loss can result in high temperatures, and runaway heat build-up may occur, especially if there is a tendency for the modulus and resilience to fall on exposure to high temperatures. For natural rubber compounds, the thermal runaway

process begins only when the temperature reaches 120°C or more²⁷. Once very high temperatures have been reached the rubber may be pyrolysed to a liquid, and gaseous products may cause mechanical failure (or 'blow-out') of the surrounding rubber²⁸.

When a visco-elastic material is deformed in simple shear with a sinusoidal shear-strain

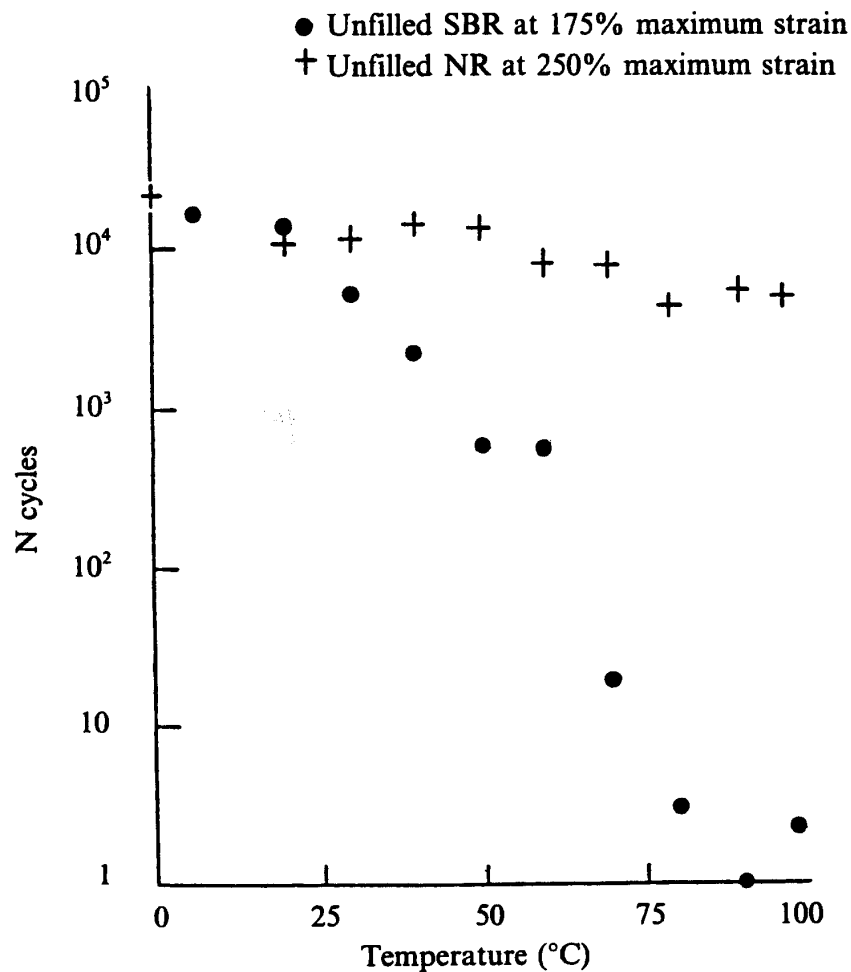


Figure 12. Effect of temperature on the cyclic fatigue life of dumbbell test-pieces at 100 cycles/min for unfilled SBR at 175% maximum strain and unfilled NR at 250% maximum strain; minimum strain zero³⁵.

amplitude γ_o , the energy dissipated by hysteresis per unit volume of rubber is given by

$$\pi \sigma_o \gamma_o \sin \delta = \pi \gamma_o^2 G'' = \frac{\pi \sigma_o^2 G''}{(G'^2 + G''^2)} \quad \dots 11$$

where the symbols are defined as in Equation 3. For non-linear materials, there may be some stress response at harmonics of the displacement frequency, but Equation 11 is still a correct expression for the energy loss provided G' , G'' and δ refer to the stress response at the fundamental frequency²⁹.

The three expressions in Equation 11 are useful according to whether $\sigma_o \gamma_o$, γ_o or σ_o are held constant in the application, corresponding to constant energy, constant strain or constant stress respectively. Thus, under constant energy conditions, the important parameter is the loss angle; under constant strain conditions, the modulus should also be low, while under constant stress conditions a high modulus (and low loss angle) will act to reduce heat build-up. It is important that these distinctions are considered in applications where heat build-up is a problem. Standard tests (such

as Goodrich heat build-up) may not correspond to the conditions for the application of interest, and may thus give misleading information. Ideally, direct measurements of G'' and G' at the relevant elevated temperatures should be made, checking also for effects of exposure time at elevated temperatures on the dynamic properties.

MECHANICAL FAILURE OF THE COMPONENT

Specifications usually stipulate a minimum allowable value for the tensile strength and perhaps also a minimum value for the tear strength. However, in practice the only occasion when the component is likely to fail in such a catastrophic manner is when it is extracted from the mould. For maximum relevance, the tensile or tear strengths should thus be measured at the appropriate elevated temperature which is generally much higher than the service temperature. Since this is not the usual practice, the value of tensile and tear strength tests is restricted to quality control.

The property which is more appropriate to failure modes of the engineering component in service is fatigue *i.e.* the slow propagation of cracks over many cycles of deformation (or, for static applications, long periods of time). Hysteretic heating of the rubber may mean that the relevant temperature for such tests is greater than the ambient service temperature. Sometimes the hysteretic heating may be so great that failure occurs more due to heat build-up than to crack propagation, although both phenomena are sometimes referred to as fatigue.

Crack Propagation

The rate at which a crack propagates into an elastomer is governed by the strain energy release rate T :

$$T = - \frac{\partial U}{\partial A} \quad \dots 12$$

where U is the total elastic retraction energy, A is the area of one fracture surface, and the partial derivative is evaluated with a fixed boundary to the elastomer so that the external forces do no work.

Examples of test-pieces for which T can be simply expressed are given in *Figure 13*. In deriving the formulae in this figure, the fracture surface area A has been replaced by hc where h is the thickness of the rubber sheet and c is the crack length.

It is found that if T is less than a certain value T_0 (of the order of 0.04 kNm^{-1} for unfilled NR) then the crack will not propagate except by ozone attack³⁰. T_0 depends on the polymer and to some extent on the vulcanisation system, and may for NR be increased somewhat by choice of a suitable antioxidant. Reinforcing blacks increase T_0 for NR by about 50% but other fillers have little effect³⁰.

For $T > T_0$, crack propagation may proceed in a time-dependent manner for non-crystallising rubbers (e.g. SBR or EPDM) held at a constant deformation:

$$dc/dt = f(T) \quad \dots 13$$

where the function f must be found experimentally.

Cycling from $T = 0$ to T_{max} at moderate or high frequencies often results in a much greater increase in crack length per cycle than anticipated from *Equation 13*

$$dc/dn > \int f(T) dt \quad \dots 14$$

It turns out that the increment in crack length per cycle then depends on T_{max} and very little on the period of the cycle or on the detailed path from $T = 0$ to $T = T_{max}$:

$$dc/dn = g(T_{max}) \quad \dots 15$$

For strain-crystallising rubbers, notably natural rubber, but also some grades of polychloroprene and to a less marked extent some grades of synthetic polyisoprene, time-

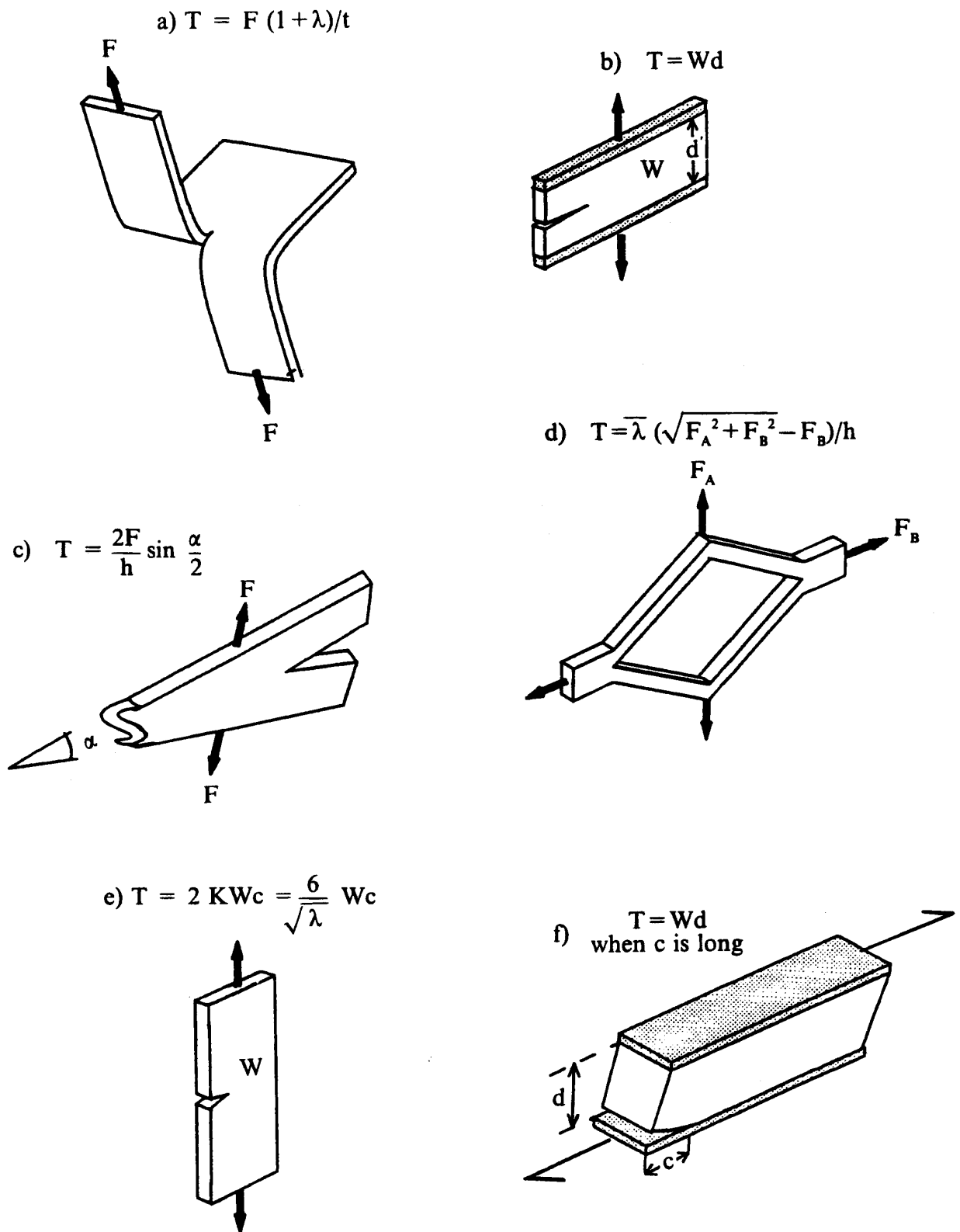


Figure 13. Various fracture test-pieces a) 'trousers', b) pure shear, c) angled, d) split, e) tensile, f) simple shear. In the formulae, h is the thickness of the rubber sheet, c is the crack length, W is the strain energy per unit volume in the region of uniform strain away from the crack and γ is the extension ratio (in the direction of F_B in the case of the split test piece).

dependent mechanical crack growth does not normally occur. The characteristic Equation 14 is also such that dc/dn increases more slowly as T_{max} increases than for the non-crystallising rubbers (Figure 14). Furthermore, under non-relaxing conditions (which is often the case for load-bearing components) strain-crystallising rubber shows a greatly enhanced resistance to crack growth³⁰. For these two reasons, natural rubber is normally preferred for load-bearing components.

Fatigue

Provided a flaw size is put into the theory for crack propagation, the design criterion that throughout the component $T < T^*$ (where T^* is some design value — one suggestion¹⁴ being $T^* = T_0$) may in some cases be reduced to a stress criterion $\sigma < \sigma^*$ which is amenable to finite element analysis of the component. It has been assumed that the flaw size and the strain gradients (in the absence of the flaw) are sufficiently small

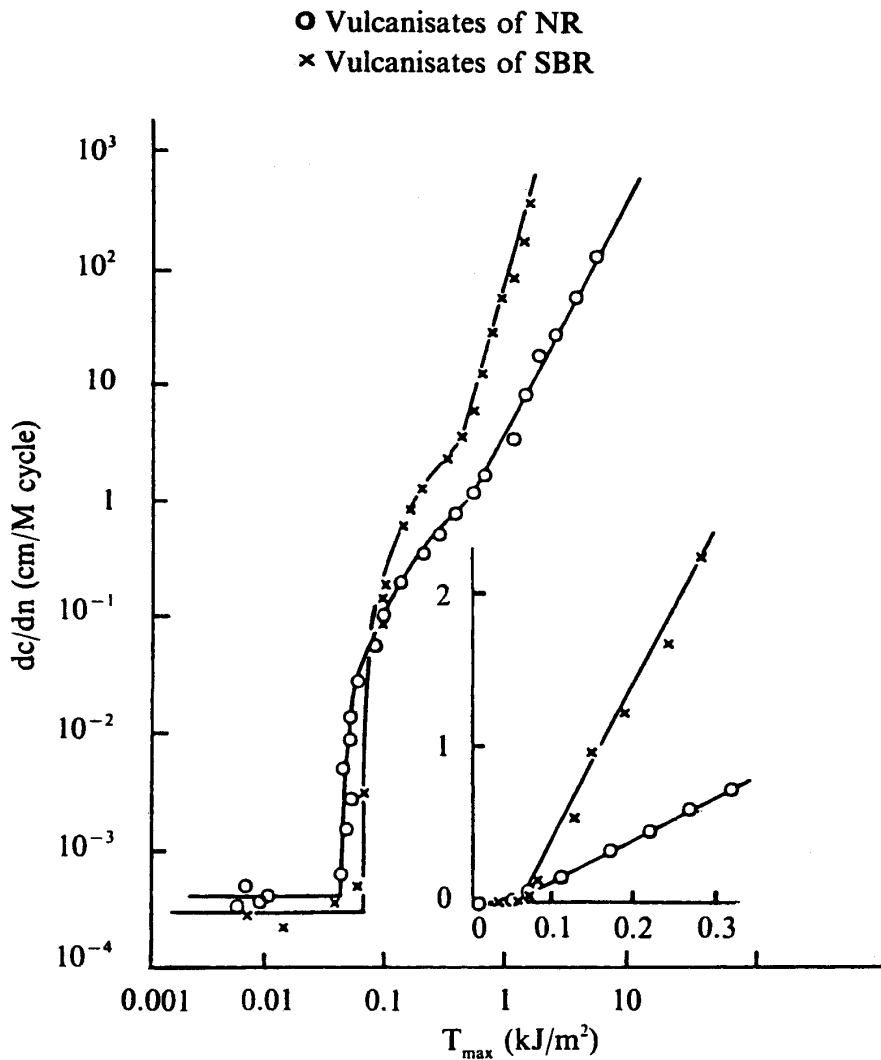


Figure 14. Cyclic crack growth rate dc/dn versus maximum tearing energy of the cycle T_{max} for vulcanisates of NR and SBR. The inset shows the region near T_0 plotted on linear scales³⁷.

that the flaw can be considered to reside in a field of otherwise uniform strain.

There is some hope of using a criterion of the form $\sigma < \sigma^*$ on the free surface of a component, where the rubber will be in a state of biaxial strain and its fracture behaviour may be related to experiments on sheets of rubber in biaxial extension. However, in the interior, the approach is on less certain ground since little work has been done on either calculations of available tearing energy or on fracture propagation.

A stress criterion will not be applicable to stress singularities such as at the junction of the free surface of rubber with a rigid surface to which it is bonded. Lindley and Teo³¹ have analysed this situation for simple shear and reached the conclusion that T reaches a finite limit $0.4Wd$ as $c \rightarrow 0$ (where d is the separation of the shear planes) and at first decreases as c increases. Eventually a minimum value of T is reached (about $0.06Wd$) and T then increases with c until a second (but higher) limiting value is reached ($T = Wd$: Figure 13f). The limiting value of T as $c \rightarrow 0$ can be reduced by means of a fillet, but although strain analysis on fillets has been done³² it has not been extended to cover crack initiation.

Once the locus of the maximum stress has been identified by analytical or numerical means, calculations can be made with cracks of various lengths in that position to find the T value as a function of crack length c (using Equation 12). This has been done in an approximate manner by Stevenson³³ for long cracks in compressed bonded blocks of rubber. T can also be found experimentally, by measuring the effect of crack length on force-deformation behaviour or by measuring the crack-opening area. The relationship of T to crack length c can then be used to estimate fatigue life once mechanical failure has been initiated.

For an edge crack in a tensile test-piece, the fatigue life can be calculated from the crack-growth characteristics as follows³⁴:

$$dc/dn = BT_{\max}^{\beta} \quad \dots 16$$

$$T = 2K Wc$$

$$\Rightarrow dc/dn = B(2KW)^{\beta} c^{\beta} \quad \dots 17$$

Integration from $c = C_0$ (the initial flaw size) gives the number of cycles N to reach $c = C$ as

$$N = \frac{1}{(\beta-1) B(2KW)^{\beta}} \left[\frac{1}{C_0^{\beta-1}} - \frac{1}{C^{\beta-1}} \right] \quad \dots 18$$

At failure $C \gg C_0$ so that the number of cycles to failure is obtained from Equation 18 by taking only the first term in the square brackets. Equation 18 works well at moderate and high strains³⁴ for which Equation 16 is reliable. For SBR, $\beta \approx 4$ and for NR, $\beta \approx 2$. It is apparent that for SBR, the predicted dependence on fatigue life on strain and on flaw size is much greater than for NR. At very high strains, Equation 16 is not appropriate, since there is a value T_c of T at which the crack growth becomes catastrophic. Thus as T_{\max} approaches T_c , the fatigue life will fall below that predicted by Equation 18. Although this regime is not relevant to most engineering components (which are normally required to have a very long fatigue life) progress has again been made in relating fatigue life to crack growth characteristics^{36,37}. For strains below the mechanical fatigue limit (which corresponds to the minimum tearing energy T_0 required for mechano-oxidative crack growth), the fatigue life can be quantitatively predicted by assuming the flaws will grow only by ozone cut growth until T_0 is reached³⁵. The cyclic rate of ozone cut growth is given by

$$dc/dn = \alpha q \tau \quad \dots 19$$

where τ is the time during each cycle for which the test-piece is strained

q is the ozone concentration

α is the ozone cut growth constant for the rubber under static conditions (*i.e.* the rate of growth at unit ozone concentration).

Figure 15 compares the experimental fatigue life of dumbbells of unfilled NR in tension with that predicted. The predictions are based on the experimentally determined crack-growth data for this vulcanisate³⁶, together with a 'single fitting' parameter of $C_o = 25\mu$; the agreement is seen to be good.

Under cyclic conditions (or static conditions for an unprotected rubber), ozone cracking only occurs if T exceeds a threshold value T_z . Unfortunately T_z is so low that it may be difficult to avoid T exceeding T_z on the surface of the component. Exposed rubber to metal bonds are also attacked by ozone³⁸, but only if T exceeds a threshold

value T_b . Fortunately T_b is much greater than T_z and the use of fillets should enable T to be kept below T_b at the bond.

Cavitation

When subjected to a hydrostatic tension of the order of Young's modulus, naturally present cavities in the rubber open up in an unstable manner, resulting ultimately in rupture³⁹. Carbon black suppresses this effect to some extent, but it is still wise to avoid subjecting rubber to hydrostatic tension of this order. Since internal damage will be initiated by a single cycle, it is important not only to avoid excessive

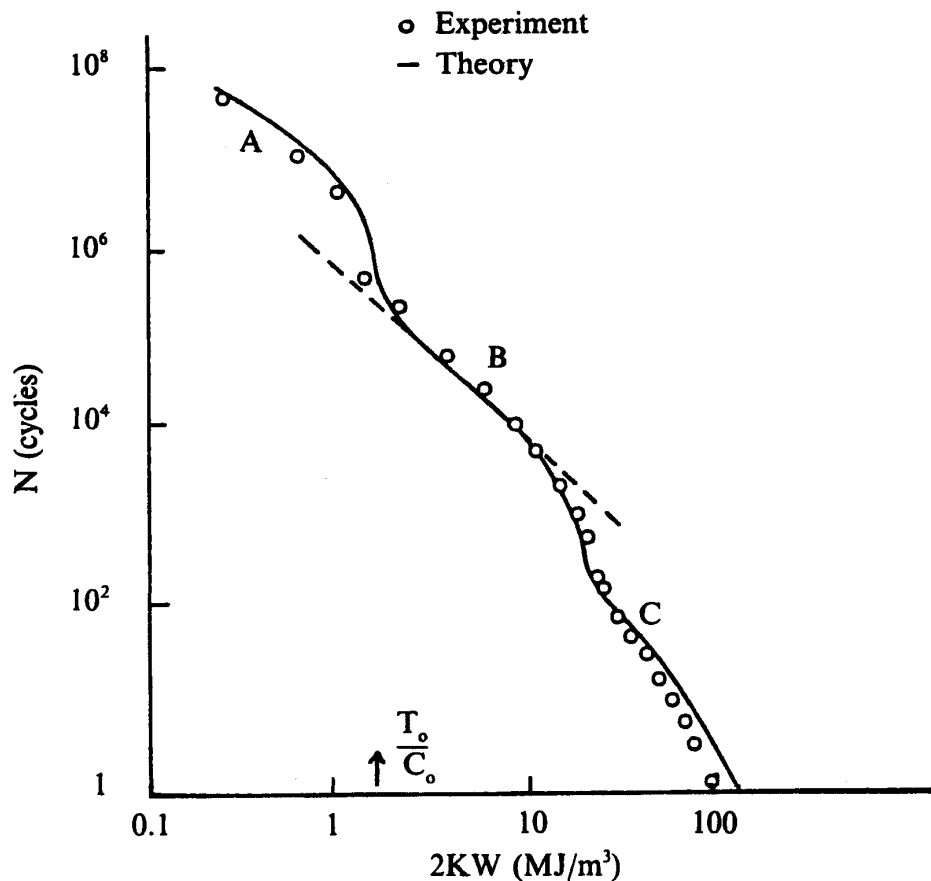


Figure 15. Tensile fatigue life N versus maximum value of strain energy density factor $2KW$ (minimum value zero) for an unfilled NR vulcanisate for maximum strains from about 30% to about 700%³⁵. (Region A — fatigue dominated by ozone cracking Equation 19 Region B — crack growth fatigue mechanism, Equation 18 with $\beta = 2$, Region C — very high tearing energy regime). For the theory, a value of $C_o = 25\mu$ has been taken for the naturally occurring flaw size.

hydrostatic tension in service but also to restrict screening tests for poor bonding to safe levels of tension.

Component Design

Summarising the above, components should ideally be designed such that

- T , for the natural flaw size of $\sim 25\mu$, is less than T_c throughout.
- Fillets and cover layers are used so that the surface values of T are lower still and preferably less than T_c , so that ozone cracking does not reduce the fatigue life or result in unacceptable appearance.
- Hydrostatic tensile stresses should be avoided, or at least be less than the modulus of extension of the rubber.

CONCLUSIONS

Performance of rubber engineering components generally depends on static and dynamic elastic properties and their dependence on amplitude, temperature and (for dynamic properties) frequency. Maintenance of satisfactory performance over long periods of time may depend on proper allowance for creep and stress relaxation. Factors which determine longevity include crack growth characteristics (especially at very low crack growth rates), diffusion rates of antioxidants/antiozonants together with effects of surface area (where the protectants may be lost by weathering, *etc*) and bulk (which provides a reservoir of protectant), diffusion rates of fluids to which the rubber is exposed (as well as equilibrium swelling levels) and leaching of protectants from the rubber by such fluids. All of these factors need to be assessed over the range of service temperatures. The measurements require skill and some may take a long time.

Standard physical tests may be favoured if they are quick, require a minimum of training to perform and yield results with little scatter. The effect of temperature tends

only to be assessed in terms of measurements at laboratory temperature before and after exposure to an extreme temperature. Conditions such as temperature, ozone concentration and tearing energy tend to be so extreme as to make estimation of service performance difficult or impossible. Many standard tests are performed on 2 mm thick sheets and this might lead to rejection of materials which in the bulk form would not be seriously degraded by oxygen, ozone or a swelling fluid. The value of standard physical tests thus lies more in quality control than in providing a reliable guide to performance.

In practice, a compromise may be possible in which only those engineering properties that are crucial for the application are specified. These properties may then be supplemented by standard tests, and perhaps by specifying the polymer selected from experience in such a way as to achieve satisfactory overall performance and quality control.

There are areas where further research is required, particularly relating to longevity of engineering components. Most of the basic studies on fracture of rubber have been done on material in sheet form. Not all failure mechanisms in engineering components can be related to such studies. Another area of uncertainty concerns the durability of rubber-metal bonds. In the usual standard tests of bond strength, failure takes place away from the bond, in contrast to the appearance of automotive components after many years of service⁴⁰. Little basic work has been done on the factors influencing longevity of the bond.

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