CHAPTER 7
Durability

Andrew Stevenson and Robert Campion

Materials Engineering Research Laboratory Ltd., Tamworth Road, Hertford, SG13 7DG, England

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7.1 Introduction

Durability assessment should be an integral part of the engineering design process with elastomers. All polymers, and elastomers in particular, are potentially sensitive to the temperatures, fluids, and mechanical conditions they are likely to encounter in service, and they can undergo changes in properties large enough to cause failure. This sometimes surprises engineers whose professional training in materials science has been restricted to metals and may lead to the false conclusion that polymer engineering components are always unreliable. Most of these changes are understood scientifically and can be predicted if the material has been adequately characterized.

Durability then is defined here as the resistance to any change in properties due to the service environment. Elastomers vary widely in their resistance to specific environments, depending on the material composition. The detailed composition and microstructure of elastomeric materials, which are essentially created during the manufacture of the component, depend on both the ingredients selected for the compound and the forming process used. This again is different from metals, where components are generally formed from materials whose composition is not substantially changed by the forming process. It is important for engineers to appreciate the factors that may affect the durability of the main categories of elastomers in different service environments. Different elastomers can vary in their properties as widely as different metals (e.g., gold, copper, steel). There is at present no accepted standardization of elastomer compounds, and these formulations are usually proprietary secrets of component manufacturers.

In practice, assessment of durability is often qualitative and derived from simply cataloguing changes in standard test properties. Although this does give some guidance, and some such information is included in this chapter, it is nevertheless inadequate for critical engineering components with demands for quantitative life assessment. Such life assessment requires first identifying the properties that will determine the function of the component and then defining acceptable limits within which they may change. Tests may then be devised to measure rates of change in these properties, and these rates may be used for quantitative life prediction.

One of the most important changes that can limit component durability is the growth of cracks in the material. These normally arise due to oscillating or static mechanical conditions of service. Cracks may grow in any mode of deformation, and growth rates may be either slow and stable, or catastrophic. Use of fracture mechanics is the most scientific approach to the characterization of fatigue life, defined by the growth of cracks. This approach has been used with success for elastomeric components, and there is a growing body of literature documenting a wide range of case studies [1 to 5]. This topic is covered in Chapters 5 and 6, and so is not considered here. Reference [1] describes a case history in which fracture mechanics was used successfully to predict the life of critical components in the offshore oil industry.

In addition to crack growth, other physical and chemical processes may cause elastomer properties to change with time in service environments. Some of these processes, such as physical creep and stress relaxation and crystallization, are in principle reversible and should not cause permanent damage. However, they may cause changes to properties that diminish the ability of a component to function and, in that sense, limit component durability: moreover, in practice, it may be impossible to reverse the process. An example is a bearing in service. The consequences of either crystallization due to cold environments or age hardening due to aerobic effects in hot sunny climates may double the elastomer modulus (stiffness); the reduction in service performance would then be the same in both cases, even though the stiffening was due to a theoretically reversible process in the first case and an irreversible process in the second.

Service environment also significantly affects durability. Aerobic attack is one example of chemical degradation that causes permanent changes in property levels. Oxygen is the most common factor in age hardening of elastomers. However, other permanent chemical changes can occur in anaerobic conditions at high enough temperatures by the continuation of cure or because of the presence of other chemical species, such as hydrogen sulfide as a vulcanization by-product in natural rubber. The consequences of certain, purely physical, effects can also cause permanent changes. Large amounts of swelling can occur in hydrocarbon liquids, and this causes weakening. Gases can permeate elastomers to a considerable extent at high pressures, and a rapid removal of these pressures can quickly change a hitherto stable situation into an unstable one, resulting in fracture and breakup of the elastomer in extreme cases.

Assessment of the overall durability of an elastomeric component should take account of the mechanical effects of fatigue crack growth and strength and environmental durability in service fluids and temperatures. In the wider sense, the term "durability" covers both types of process. Interactions between these two mechanisms of deterioration need also to be considered in detail for some applications. An improved appreciation of mechanisms of deterioration and factors limiting durability allows engineers to design elastomeric components for more critical applications and with increased reliability. This approach to reliability analysis is beginning to be required in some documents of the International Standards Organization (ISO).

This chapter focuses on describing mechanisms affecting durability that are not directly involved with crack growth. Other chapters deal with fracture mechanics and crack growth mechanisms. Discussions on interactions between fluid aging and fracture mechanisms are a more advanced topic, and beyond the scope of this book.

7.2 Creep, Stress Relaxation, and Set

Creep is a time-dependent increase in deformation under constant load, while stress relaxation is a time-dependent reduction in stress under constant deformation. Both are referred to as "relaxation" phenomena. Theoretical relationships between creep and stress relaxation rates are mathematically complex, but in practice either rate can be deduced from the other if the shape of the force-deflection curve is known (see Section 7.2.2). Set is "permanent" deformation, which remains when a material is released from the strain imposed. These phenomena occur in all materials, but are often more evident in elastomers because of the high initial deformations to which they may be subjected.

7.2.1 Creep

If an elastomeric component is subjected to a static preload, then this load causes a progressive increase in deformation as a function of time. This can be important in a wide variety of applications, from building mounts to automotive suspensions and engine mounts to elastomeric tensioners for oil platforms [2]. Creep is usually expressed as a percentage of the initial deflection. Thus,

$$\text{creep at time } t = \frac{x_t - x_o}{x_o} \times 100\% \tag{7.1}$$

where x_o is the initial deflection, and x_t is the deflection at time t.

The initial deflection must be measured at a defined initial time t_0, which should be about 10 times longer than the time taken to apply the deformation. Creep rate is expressed as creep divided by a function of time. This function may be the logarithm of time if the relaxation mechanism is physical or time if it is chemical.

Creep in rubber consists of both physical creep (due to molecular chain slippage) and chemical creep (due to molecular chain breaking). Physical creep rates (A) decrease in time and are usually expressed as a percentage of the original deflection per decade (factor of 10 increase) of time. Chemical creep rates (B) at a constant temperature are approximately linear with time, and thus the total creep is given by

$$\text{creep } (\%) = A \log_{10}\left(\frac{t}{t_0}\right) + B(t - t_0) \tag{7.2}$$

This approach has proven successful in characterizing large-scale components, and good correlations between laboratory expectations and site measurements exist for up to 15 years' service in building mounts [6].

7.2.2 Stress Relaxation

When an elastomer is held at a constant deformation, there is a decrease in stress as a function of time. This phenomenon can be of great importance in sealing applications, where the material of the seal is required to maintain a specific level of sealing force to prevent leakage. Stress relaxation can be the dominant factor that limits the effective life of the seal.

Stress relaxation is usually defined as the loss in stress expressed as a percentage of the initial stress. Thus,

$$\text{stress relaxation } = \frac{\sigma_0 - \sigma_t}{\sigma_0} \times 100\% \tag{7.3}$$

The rate of stress relaxation is then the stress relaxation divided by some function of time.

Stress relaxation and creep rates are related to one another if the shape of the force-deflection curve is known, using a method proposed by Gent in 1962 [7]. According to this, the relationship between the two parameters is determined by the incremental stiffness at the point on the force-deflection curve relevant to the stress relaxation or creep measurement. Thus

$$C = \frac{\sigma}{\varepsilon}\left(\frac{d\varepsilon}{d\sigma}\right)S \tag{7.4}$$

where C is the creep rate, S is the stress relaxation rate, ε is the strain and σ is the stress. Since it has been established that creep and stress relaxation can be related in this way, in the following discussion both are referred to as relaxation processes.

7.2.3 Physical Relaxation

Relaxation mechanisms are usually divided into two categories, namely physical and chemical. Physical relaxation is not very sensitive to temperature at normal operating temperatures, whereas chemical relaxation is. Physical relaxation is associated with reorientation of the molecular network under strain, with the disengagement and rearrangement of chain entanglements, and with the breaking of bonds due to secondary valence forces between chains, between filler particles, or between chains and filler particles. The strain history of the material can also have an impact. These processes are relatively rapid initially and slow down with time. Physical relaxation usually decreases linearly with the logarithm of time. Figure 7.1 shows the stress relaxation of two elastomers at elevated temperature. In each case the behavior is initially log-linear, and can be described by the relation

$$\frac{\sigma_0 - \sigma_t}{\sigma_0} = A \log_{10}\left(\frac{t}{t_0}\right) \tag{7.5}$$

where A is the stress relaxation rate in percent per decade of time (ppd).

The proximity of the service temperature to the glass transition temperature T_g is normally the dominant factor in determining physical relaxation rate. Thus, physical rates are high near to T_g and decrease as the temperature rises and molecules become more mobile.

The degree and type of crosslinking of the elastomer also affect the relaxation rate, with increasing crosslink density decreasing the relaxation rate. Since fillers cause additional relaxation mechanisms, filled elastomers have higher physical relaxation rates. Relaxation rates are not generally strongly dependent on strain or the mode of deformation: compression, tension, or shear.

Physical relaxation rates may be affected by the absorption of small amounts of fluids, such as water vapor. Thus, a natural rubber vulcanizate in 88% relative humidity has been shown [8] to absorb less than 1% of water, but this increased stress relaxation by 60% compared to dry conditions.

Although physical relaxation rates are not very temperature sensitive, temperature cycling while an elastomer is under stress or strain does indeed affect physical relaxation significantly, and so careful temperature control is essential when making measurements [9].

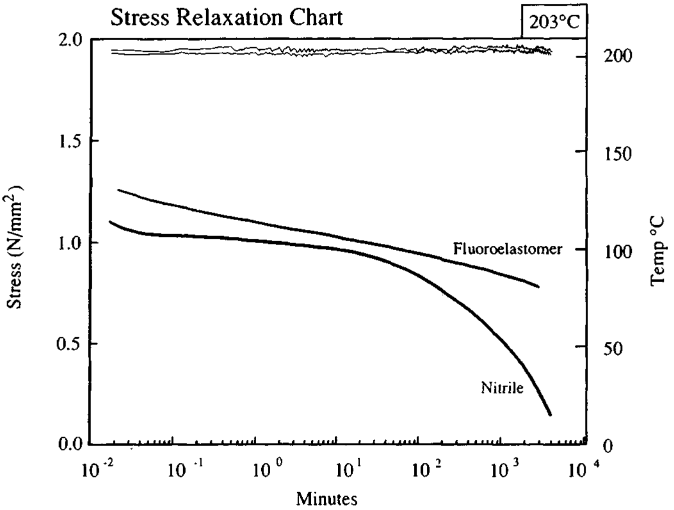

Figure 7.1 Stress relaxation of acrylonitrile-butadiene rubber (NBR) and a fluoroelastomer (FKM) at 203 °C (upper thin traces: in situ thermocouple outputs); lower bold traces: typical stress relaxation data for NBR and FKM elastomers.

7.2.4 Chemical Relaxation

At high temperatures and long times, chemical relaxation usually predominates over physical relaxation. The rate of chemical relaxation is approximately linear with time, at least in the early stages. Chemical relaxation has the usual sensitivity to temperature associated with chemical reactions: the rate can almost double with a 10 °C change in temperature (but see Section 7.6.4 and Chapter Problem no. 3). Chemical relaxation is associated with a scission of chemical bonds, either in the polymer chains or in the crosslinks. Scission is mostly oxidative, although this is not always the case, since breakdown may be anaerobic. Except for anaerobic relaxation, chemical relaxation is strongly affected by specimen thickness because the chemical degradation process needs to be supplied by the fluid (e.g., oxygen) which activates it, and only the thinnest sections have sufficient supply to measure a "true" chemical relaxation rate. For specimen thicknesses above about 0.25 mm, oxygen cannot diffuse in fast enough to sustain the highest possible chemical relaxation rates, and so the reaction is "diffusion controlled." This effect becomes most important at higher temperatures. For example, the chemical rate for natural rubber in air at 110 °C has been found [8] to be about 50% less for a 7 mm thick section than for a 0.25 mm thick section.

A total relaxation rate can be determined by combining physical and chemical rates. Thus

$$\text{total relaxation} = A \log_{10}\left(\frac{t}{t_0}\right) + B(t - t_0) \tag{7.6}$$

(where A is the physical relaxation rate and B is the chemical relaxation rate) is the general form of Eq. (7.2).

Figure 7.1 illustrates the type of relaxation behavior that may occur in nitrile rubber when chemical mechanisms become important. The influence of the second coefficient B

may be seen in the departure from logarithmic/linear behavior beyond a certain time. The greater chemical resistance of FKM is shown by the lack of such a change. In-situ test techniques are required to provide relaxation charts of the type illustrated in Fig. 7.1.

7.2.5 Compression Set and Recovery

Theoretically, set is the deformation that remains after an imposed strain has been removed. Thus, set measures the ability of the elastomer to recover its original dimensions. When the deformation is compressive, it is referred to as compression set. Hence, compression set is defined as

$$\text{set} = \frac{t_o - t_r}{t_o - t_s} \times 100\% \tag{7.7}$$

where t_o is the initial thickness, t_r is the recovered thickness, and t_s is the compressed thickness.

Practically, the recovered thickness increases as a function of time from release of compression. Hence, appropriate recovery times need to be specified. In "standard" testing (e.g., ASTM), rubber disks are compressed by 25% at room temperature, then exposed to the test temperature for a specified time (e.g., 24 hours), and released to allow recovery. Then t_r is measured after a 30 minute recovery at room temperature.

The main use of the standard test is to provide a quality control check on the state of cure. An undercured specimen shows excessive set because of the formation in the compressed state of extra crosslinks, which prevent recovery. Attempts to interpret the standard test beyond this can be meaningless. The large specimen size means that oxidative effects do not occur evenly because the time scale of the test is usually too short for oxygen to be present at equilibrium other than at the surface.

Compression set does not measure the same changes as stress relaxation and there is no reason any correlation should exist between the two properties. After compression of an elastomer to a fixed deformation, breakdown of the network of long-chain polymer molecules occurs, and this is to some extent measured by stress relaxation. However, crosslinks may form in the strained state and form a "second network." These crosslinks have no effect on stress relaxation, but can dominate the value of compression set, since the bonds so formed oppose recovery after release of compression.

In sealing applications, the ability of the seal to recover can be important if there is movement in the surrounding metalwork. Whether instant recovery or just the ability to recover at all is more important depends on the design and the application. In either case, recovery at 30 minutes is not a useful measure, as it represents a mixed case between instant and permanent recovery. Where ability to recover is more important than speed of recovery, it is recommended that the set 24 hours after release be used as a measure of "permanent" set. Where speed of recovery is important, then the set 10 seconds after release may be used, which requires *in situ* measuring equipment.

If temperatures fall below T_g (see Section 7.4.1) and then increase again, a form of compression set can occur from physical reasons only. Again, this may be important in some sealing applications.

7.2.6 Case Study

A detailed case study has been made of a set of building mounts over a period of 15 years [10, 6]. The building, Albany Court in London, was supported by 13 bearings with a capacity between 60 and 200 tons, which isolated the building from vibrations from an underground railway ("tube") line, as shown schematically in Fig. 7.2. Provision was made for easy access to the bearings with jacking points to facilitate replacement, should this prove necessary. One of the main concerns was that creep in the rubber should be neither excessive nor uneven, since this could cause uneven settlement and structural damage to the building. Extensive laboratory tests were performed to establish the creep rates for the rubber compound used. The physical creep rate A was measured as $6.6 \pm 1.2\%$ per decade and the chemical creep rate B was $0.47 \pm 0.2\%$ per year. Using these laboratory values, calculations were made for the full-scale building mount, which led to estimates that creep in the rubber bearings would be not more than 6 mm after 100 years' service.

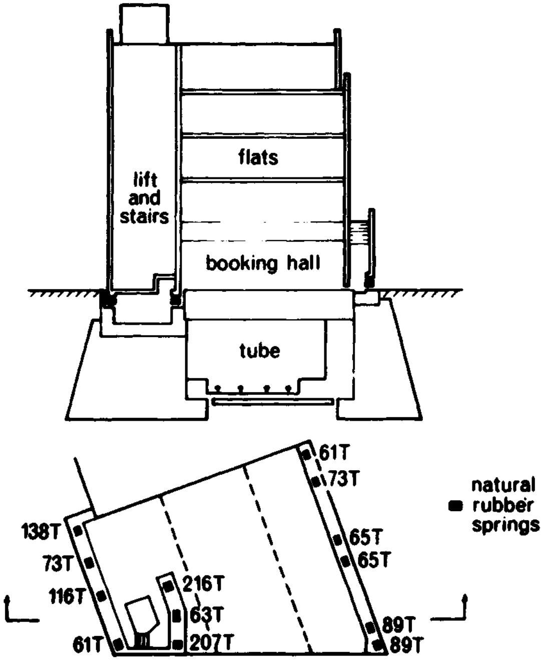

Figure 7.2 Albany Court building mounts: schematic views showing the locations (■) of the rubber bearings in the building.

Following construction, detailed measurements of creep were taken at regular intervals on site for up to 15 years. The results of these measurements were in good agreement with the predictions from laboratory tests and consistent with the prediction that creep would be less than 6 mm after 100 years' service. There was no evidence of a diffusion control mechanism at this temperature. The results are shown in Fig. 7.3. The upper and lower bounds of the laboratory predictions are shown by the solid curves, while the site measurements are represented by circles. After 15 years, the amount of creep is close to the predicted value and the trend is still consistent with the ultimate prediction of "less than

6 mm after 100 years." All the measurements shown are averages from readings on seven different bearings and all have been corrected for seasonal fluctuations in temperature. The general condition of the rubber in all these bearings still appears to be excellent, and no replacement has proved necessary. There is thus good evidence that creep in elastomers over long periods of time can be correctly predicted from short-term laboratory tests.

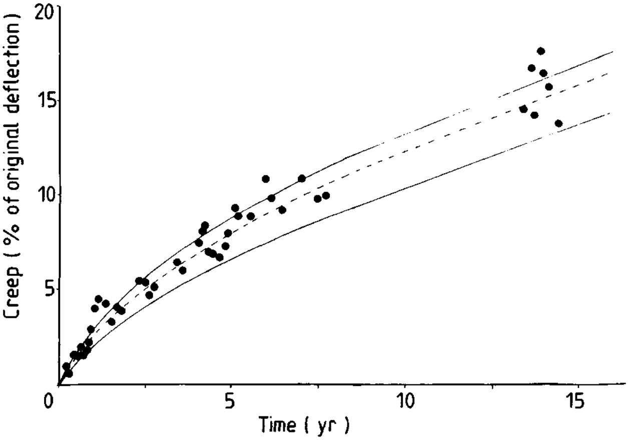

Figure 7.3 Creep of building mounts after 15 years service in Albany Court: circles show site measurements on building; curves indicate envelope and median of laboratory predictions made before building construction.

7.3 Longevity of Elastomers in Air

7.3.1 Durability at Ambient Temperatures

There is also evidence that rubber can survive very long periods in service at ambient temperatures up to at least 30 °C without any measurable deterioration. A range of polychloroprenes and fluoroelastomers have been characterized in 14-year trials of longevity at an outdoor weathering site in Panama [11]. Natural rubber and polychloroprene bridge bearings have now been in continual service for more than 30 years with no need for maintenance or replacement. However, durability at ambient temperatures can be affected adversely by poor processing (e.g., incomplete cure). Slow continued crosslinking may then occur, causing hardening. Some elastomer compounds are more vulnerable to this than others. Results from thin standard test pieces can be misleading when attempting to judge the durability of real engineering components. Some case studies follow.

7.3.2 Sunlight and Weathering

Effective protection against direct sunlight is given by the carbon black filler incorporated in most rubber compounds. Carbon black filters ultraviolet radiation. Additionally, rubber components are often placed so that they are shielded from direct sunlight.

Surface degradation of rubber, variously described as perished, cracked, crazed, or weathered, can normally be attributed to attack by atmospheric ozone, oxygen, and sunlight. This can occur particularly in rubbers not protected by antioxidants and antiozonants. However, this phenomenon affects only the relatively thin outer layer of rubber, and so may remain only a surface effect for structural bearings. Bearing pads of natural rubber installed in 1890 have been examined, and although the outer 1 to 2 mm of rubber had degraded after 96 years of exposure to the atmosphere, the inner core of rubber was still in good condition. Most likely, oxidation was so limited because diffusion of oxygen through oxidized rubber is much slower than through new rubber; the oxidized material had formed a thin protective skin on the surface of the bearing.

Some standard aging tests on thin strips of rubber can be very misleading because of these skin effects. They do, however, provide a guide to the relative weather resistance of thin sections of different types of rubber.

7.3.3 Ozone Cracking

Minute concentrations of ozone in the atmosphere can cause cracking within a few weeks in unprotected rubber components (i.e., with no antiozonant in the formulation). For this to occur requires the presence of a minimum surface tensile strain; the cracks then grow perpendicular to the strain (see Fig. 5.14). This characteristic distinguishes ozone cracks from crazing induced by sunlight. The rate of crack growth depends on the type of rubber and on the ozone concentration. Nitrile rubber and natural rubber are intrinsically less resistant to this effect than polychloroprene or ethylene-propylene diene monomer (EPDM). Protection can be provided by waxes or chemical antiozonants added to the formulation.

Ozone cracking is not considered here in detail because it is covered as a crack growth mechanism in Chapters 5 and 6. Most national standards for bridge bearings require a certain level of ozone resistance, as judged by an accelerated test in a high ozone concentration. The best level of protection is required by the German standard DIN 1400, which lists resistance to 200 parts per hundred million (pphm) concentration of ozone for elastomeric bridge bearings.

7.3.4 Structural Bearings: Case Studies

7.3.4.1 Natural Rubber Pads on a Rail Viaduct after 100 Years of Service

Pads of natural rubber were installed in 1889 between the steel superstructure and the supporting piers in a rail viaduct between Flinders Street and Spencer Street, Melbourne, Victoria, Australia (see Fig. 7.4). The viaduct was opened to traffic in 1891 and is still one of the most heavily traveled structures of the Victoria Railway system, with up to 30 trains per hour. It is believed that the rubber pads were installed to absorb impact and noise rather than to accommodate any temperature-induced horizontal movement of the cross-girder relative to the piers. In those days, there was no satisfactory method of bonding rubber to metal plates, and so unbonded pads were used, which have now in places squeezed out from beneath the steel plates of the superstructure. This enabled a sample of rubber to be cut away from one edge and tested in the laboratory.

The rubber pads were about 0.5 in. thick and made from "best red rubber," composed of natural rubber, clay, sulfur, and iron oxide. The sulfur level was found to be several times higher than in modern NR compounds, and there were no added antioxidants. Although the surface of the rubber is now hard and shows evidence of oxidation, below a depth of about 1.5 mm, the rubber is free from such degradation and has a hardness of only 63 IRHD (International Rubber Hardness degrees). There is no evidence of significant deterioration of the rubber below this depth or in the center of the pad. This convincingly illustrates that weathering of rubber in normal conditions is limited to the surface regions. It suggests also that so-called accelerated tests exposing thin rubber sheets to elevated temperatures can give a misleadingly pessimistic view of the longevity of rubber pads for civil engineering applications. The skin of oxidized rubber, which forms as a result of aging, can act as a protective layer to inhibit further ingress of oxygen to rubber deep inside a thick block. It is, of course, the bulk stiffness of the pads that determines whether they continue to function satisfactorily in this type of application, not the appearance of a surface skin.

The rubber pads discussed here were made from what would today be considered to be an inferior and unprotected compound. Yet they are still functioning satisfactorily 100 to 110 years after installation. Modern elastomer compounds with chemical antioxidants are expected to show even greater durability. Compounds of synthetic elastomers, such as polychloroprene, can also be used as coatings to reduce degradation in the outer skin of a large bearing based on natural rubber.

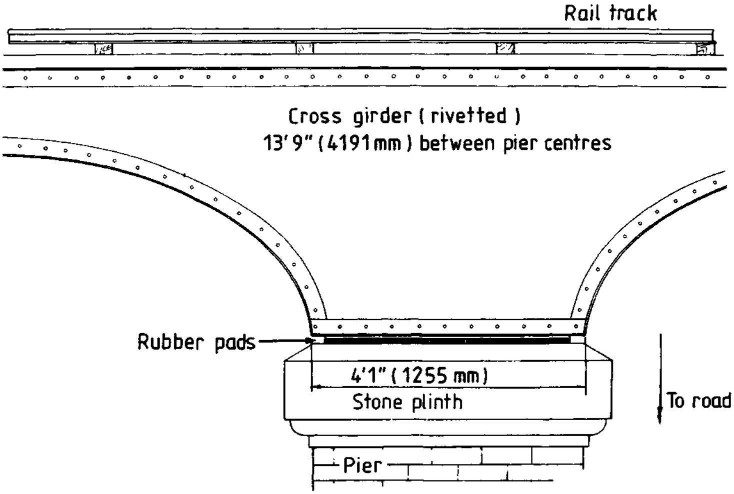

Figure 7.4 Location of 100-year-old rubber rail pads in bridge in Melbourne, Australia.

7.3.4.2 Laminated Bridge Bearings after 20 Years of Service

Laminated polychloroprene and natural rubber bearings have been in documented service for more than 30 years in the U.S. and in the United Kingdom with no reports of serious deterioration. A detailed case study [6] was made of natural rubber bridge bearings taken from a bridge along the main London-to-Kent M2 Motorway. The specimens were removed for laboratory study in December 1982 after 20 years' service. The study was commissioned by the British Department of Transport to help assess any future needs for replacement of elastomeric bearings in bridges. The bridge is 52 m long and has twin two-lane carriageways with hard shoulders. There are 32 bearings located in two rows, one row at each end of the bridge deck. Figure 7.5 shows a close-up view of a bearing in situ supporting the bridge deck. For a period of one year, detailed measurements were made of the functioning of the bearing using displacement transducers, positioned to monitor shear movements in the bearing.

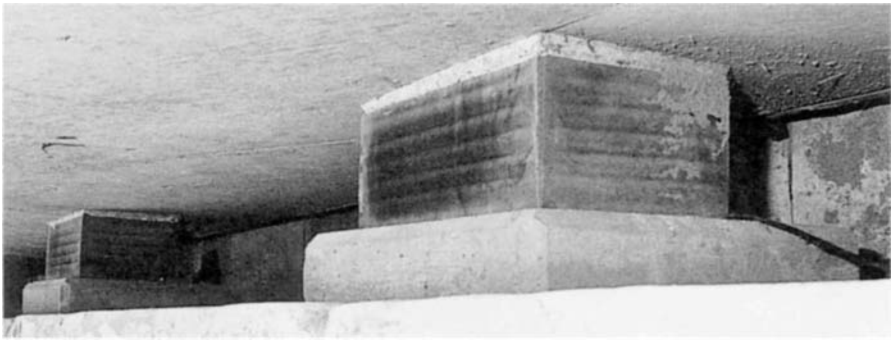

Figure 7.5 Close-up of 20-year-old rubber bearing under bridge deck in England.

Two bearings were removed by raising the bridge deck using hydraulic jacks. The compression and shear stiffnesses of the removed bearings were measured, and one bearing was sectioned to study the condition of the rubber. Figure 7.6 shows the results for that bearing. The compression stiffness was within the range of original test results quoted by the manufacturers for this set of bearings prior to installation and also within the design limits for the bridge. Tests on whole bearings gave no evidence of any significant change in either shear or compression stiffness. The stiffnesses of the 20-year-old bearing were also very close to that of new replacement bearings supplied by the manufacturers (Andre Rubber Ltd.).

Figure 7.7 shows the structure of the bearing. It had an outer rubber cover about 12 mm thick, for environmental protection. This illustrates the main principle of providing durability for elastomeric structural bearings. All edges of reinforcing metal plates need to be encapsulated and protected from the environment by an outer rubber cover.

The general appearance of the bearings was excellent, with no evidence of any ozone cracks or oxidation. All the bonds to the steel plates still appeared to be in perfect condition, with no evidence of delamination anywhere [6]. In the laboratory, the entire

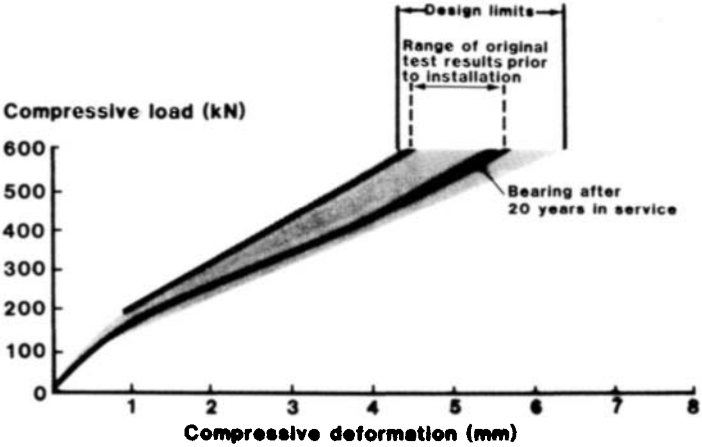

Figure 7.6 Compressive load-deflection characteristics of 20-year-old bridge bearing after removal from bridge deck in Fig. 7.5.

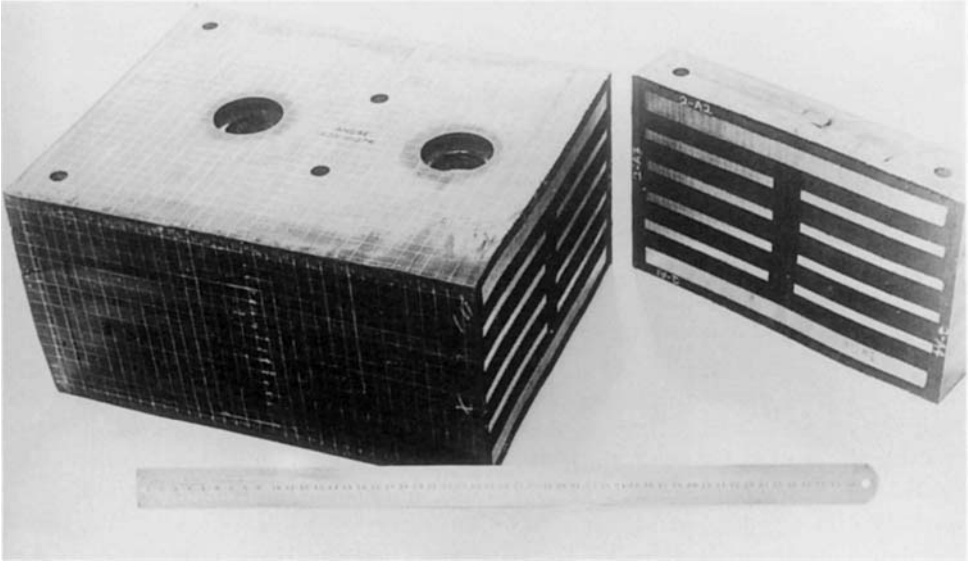

Figure 7.7 Photograph of sectioned 20-year old bearing after tests shown in Fig. 7.6.

outer surface of one bearing was marked with a grid, and hardness and puncture measurements were taken for each grid square. These results enabled contour maps of hardness and puncture strength to be constructed for each surface of the bearing.

Figure 7.8 shows a contour map obtained from the puncture test. Puncture strength is quoted simply as puncture force, but this can be related to tear strength. There was no significant difference in hardness or puncture strength between the outer exposed surface of the rubber and the cut surface from inside the bearing. Apart from a few high and low values, most puncture forces ranged from 15 to 20 N.

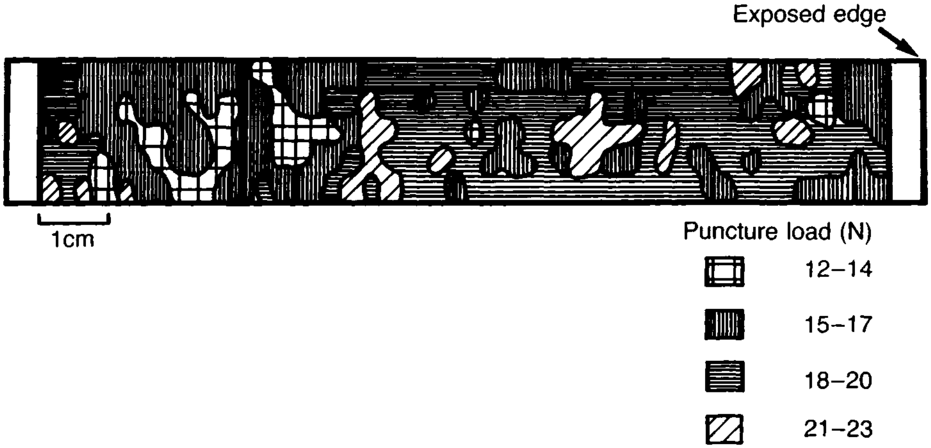

Figure 7.8 Contour maps of puncture strength in 20-year old bridge bearing of Fig. 7.7.

In addition to the contour maps, standard tests were carried out on specimens extracted from the bearing, as required under both past and present British standards. The results are shown in Table 7.1. It was found that the elastomer would still pass standard tests for a new bearing of this type.

After this study, it was concluded that there was no evidence of any significant deterioration of the bearings or of the rubber material over the 20-year period that the bearings had been in service.

Table 7.1 Comparison of Test Data from a 20-year-old Bearing with British Standards

	Original 1952 standard: BS 1154			Results on rubber cut from bearing and ground flat	
Property	Z14	Z15	New 1983 standard: BS 5400	From load-bearing layers between reinforcement inside bearing	From outer rubber cover
Hardness, IRHD	62–70	72–80	66–75	71	68
Tensile strength (TS), MPa	13.8 (min)	10.4 (min)	15.5 (min)	17.1	14.7
Elongation at break (EB), %	350 (min)	250 (min)	300 (min)	439	403
Compression set, %	30 (max)	35 (max)	30 (max)	15	20
Change after 7 days at 70 °C					
Hardness, IRHD	−0, +4	−0, +4	±10 (max)	+2	+3
TS, %	−10, +10	−10, +10	±15 (max)	−8	+1
EB, %	−15, +0	−15, +10	±20 (max)	−5	+8

7.4 Effect of Low Temperatures

7.4.1 Glass Transition

At very low temperatures, all elastomers undergo a rapid transition, occurring across a few degrees only, to the glassy state, becoming brittle and stiffening by factors of up to 1000. In this state, they clearly cannot display elastomeric properties. The temperature range over which this occurs differs widely for different elastomers, depending mainly on the molecular structure of the polymer. Some elastomer glass transition temperatures, T_g, representing the approximate mid-point of this range, are given in the Appendix, Table 1.

There can be significant changes in mechanical properties compared to ambient temperature values at temperatures even 20 °C or more above the actual transitional temperature range to a glassy state as characterized above. Stiffness may increase along with hysteresis, creep, stress relaxation, and set. In dynamic applications, T_g increases, perhaps by many tens of degrees, if frequency is increased. Viscoelastic properties are discussed in Chapter 4. Engineering design with elastomers for dynamic purposes must allow for the associated stiffening at temperatures well above the "static" T_g.

7.4.2 Crystallization

Some elastomers can also crystallize. This occurs at temperatures well above T_g, but can be still below ambient. Polychloroprene (CR) and natural rubber (NR) are the principal types of crystallizing rubbers, having maximum crystallization rates at –10 and –25 °C, respectively. In fact, the extremely good strength and fatigue resistance of CR and NR derive largely from their ability to strain-crystallize locally at a crack tip, even at working temperatures. EPDM can also crystallize, depending on ethylene content (high for crystallization).

While the glass transition is almost instantaneous, crystallization occurs slowly and may take months to reach equilibrium. The most important consequence for engineering applications is an increase of modulus by factors of 1 to 100 [2]. In addition to the choice of elastomer, choice of vulcanization system is important. Natural rubber possesses intrinsically greater resistance to low temperature crystallization than polychloroprene. However, some formulations of NR exhibit greater crystallization (e.g., at –10 °C) than some formulations of CR. The most resistant NR formulations are more resistant than the most resistant CR formulations, which generally are also those with poorer aging resistance at elevated temperatures. Zero-strain crystallization can occur over a temperature range of 70 °C or so, but times to equilibrium are long at the extremes of the range. There can be substantial crystallization in some types of CR and NR after prolonged exposure to a temperature of +3 °C. The resulting stiffening increase should be considered carefully when designing structural bearings for cold climates.

The strong dependence of low temperature resistance on compound formulation means that it is essential to have a performance-related low temperature test for engineering components likely to experience cold environments in service. The most accurate and reliable way to characterize resistance to low temperature crystallization is to measure the elastic modulus directly. Other tests have been used (e.g., low temperature hardness, volume change, low temperature compression set) but, as Fig. 7.9 illustrates, these tests may underestimate the extent of low temperature stiffening.

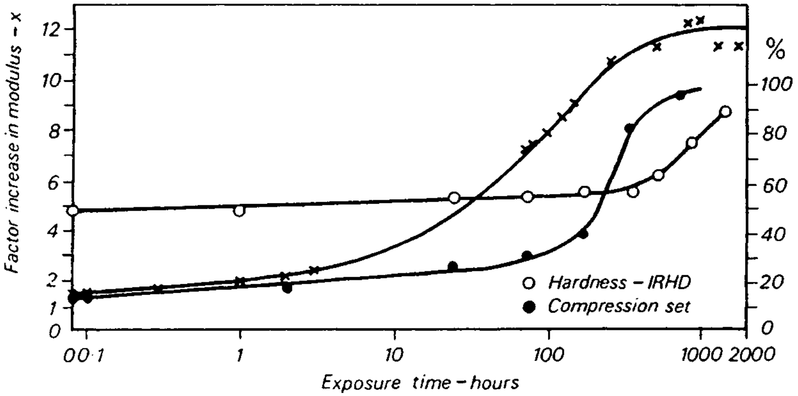

Figure 7.9 Correlation between low temperature modulus increase (x), compression set, and hardness for a natural rubber vulcanizate.

Crystalline rubber still possesses high strength, but it is no longer a large-strain rubbery material. It yields like a plastic above about 7% extension although its degree of crystallinity is, in fact, rather low, below 40% at equilibrium. Melting of the crystallites begins at temperatures 10 °C above the temperature of crystallization. Melting is a much more rapid process than crystallization. During crystallization, rubber possesses very high stress relaxation rates (50% per decade), which can be extremely damaging in sealing functions and some other applications.

7.4.3 Reversibility of Low Temperature Effects

Low temperature stiffening does not in itself damage the rubber, and the effects usually are fully reversible by warming long enough above either T_g or the equilibrium melting temperature of the rubber crystallites. Durability of a component may, however, be adversely affected in an engineering application that requires the semicrystalline bearing to deform to a given extent, causing abnormally high stresses.

7.5 Effect of Elevated Temperatures

At sufficiently elevated temperatures, all types of rubber will undergo degradation reactions, leading to a loss of mechanical properties. Moderately elevated temperatures may cause the exchange of crosslinks and formation of additional crosslinks, leading to some hardening of the rubber. At higher temperatures, scission of crosslinks may outweigh crosslink formation, with a breakdown in structure and a net softening of the rubber. At very high temperatures, the main chains break down and charring and embrittlement of the rubber occurs. Under deformation, all three changes are the basis for compression set testing.

The presence of oxygen is a very important factor in affecting the resistance of rubber to elevated temperatures. In the absence of oxygen, most types of rubber (even natural rubber) could survive temperatures of 175 °C, although degradation would occur very rapidly in the presence of oxygen. Table 7.2 summarizes in general terms the realistic upper service limits of most types of rubber in the context of engineering applications that normally use rubber in reasonable thicknesses. Any such guide has to be approximate, since the actual suitability depends on the properties measured, the exact compounds used (some NR compounds give prolonged service only below 70 °C), and the length of service at that temperature.

Table 7.2 Resistance to Thermal Degradation

Highest service temperature (°C)	Rubber type
75	Polyurethane Styrene-butadiene rubber
85	Butadiene rubber Natural rubber
100	Polychloroprene Epichlorohydrin
125	Nitrile rubber Butyl rubber Ethylene-propylene diene monomer
150	Chlorosulfonated polyethylene Hydrogenated nitrile rubber Polyacrylic rubber
200	Fluoroelastomer Fluorosilicone rubber Terfluoroelastomer copolymer Tetrafluoroethylene-propylene copolymer
250	Silicone rubber
300	Perfluoroelastomer (Kalrez)[a]

[a] DuPont registered trademark

For most engineering applications, oxidative degradation is the most important factor determining durability. For a thick enough section of rubber, the availability of oxygen is limited by diffusion, and components with bulky rubber layers (e.g., engine mounts or bridge bearings) can be considerably more resistant to elevated temperatures than the thin strips of material used in standard tests. As already noted, an outer skin of rubber may form, which can further limit oxygen ingress. Such a skin was found to play an important part in the durability of the 100-year-old bridge pad discussed in Section 7.3.4.1. At high temperatures (e.g., 100 °C), rubber can show surprisingly good resistance because of its low thermal conductivity and tendency to form a charred outer skin, which can act as an intumescent material. Above its highest service temperature, it eventually degrades and becomes sticky.

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Silicone and highly fluorinated elastomers show by far the greatest resistance to high temperatures (⩾ 200 °C). Figure 7.1 illustrates the difference in chemical degradation at 203 °C between typical NBR and FKM compounds. However, at less elevated temperatures, other factors (e.g., mechanical strength) may cause other elastomers to be preferred. Under thermal aging, all chlorine-containing elastomers (e.g., epichlorhydrin) may evolve hydrogen chloride gas if insufficient acid acceptor is present or if temperatures are high enough. Fluorine-containing elastomers may evolve hydrogen fluoride gas, and so, in extreme circumstances, appropriate care should be exercised.

Thermal degradation is an extreme case of the chemical relaxation mechanisms outlined in Section 7.2.4.

7.6 Effect of Fluid Environments

The flexibility associated with an elastomer – essential for performing its many functions (sealing, isolating vibrations, etc) – stems from the 10% or so of space between its molecules – the “free volume.” However, this internal space leads to other, less welcome characteristics: it provides the physical means for fluid molecules to enter the elastomer. No elastomer is completely resistant to chemical and/or physical effects arising from contact with fluids. Different elastomers can withstand such attacks to different extents. If a rubber absorbs a large volume of liquid, it generally becomes weak and useless for most engineering applications. Moreover, chemical attack can cause further deterioration. In either case, initial weakening is progressive; in the latter case, weakening or embrittlement continues throughout service life. It is clear from these observations that the durability of an elastomeric component is affected by its environment. Elastomer selection therefore needs to include a considerations of the service fluid composition. Organic liquids tend to weaken elastomers by physical means only, whereas corrosive liquids, such as acids and alkalis, tend to attack chemically.

Rubber and ebonite are used as coatings and linings to protect chemical plant, pipes, and other equipment against corrosion and abrasion. In that context, they may come into contact with various chemical solutions. Table 7.3 summarizes the resistance at room temperature of several elastomer types to a range of aqueous and other liquids; the behavior may, however, be different at elevated temperatures. Such tables are inevitably very approximate and should be used for preliminary guidance only, since different results may be obtained with different compounds of the same base elastomer. Also, different applications may render the same elastomer compound satisfactory or unacceptable, even with the same liquid. Many such tables are provided by materials producers and manufacturers, and before concluding that the classification is relevant for the application at hand, the engineer should always inquire exactly which tests were performed to determine the classification and whether the formulation of the elastomer compound is suitable.

Oil and gas can come into direct contact with rubber in downhole applications in the exploration for and production of hydrocarbons. The rubber may be exposed in the form of seals, flex joints or flexible pipes, hoses, etc., to crude oil containing methane and other hydrocarbon gases, hydrogen sulfide, and/or carbon dioxide gases, often at elevated