

INVITED LECTURE

Vagaries of elastomer service life predictions

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Generally, the useful life of a rubber component is governed by its susceptibility to failure by either mechanical or chemical deterioration. There are well established laboratory tests to address the failure properties of elastomers – fracture mechanics analyses for mechanical durability and accelerated aging tests for chemical degradation. However, laboratory predictions are reliable only to the extent that the relevant failure mechanisms are identified and all contributing factors are accounted for. This paper describes two case studies, one concerning fatigue failure of an elastomeric mechanical capacitor and the other thermal oxidation of a radiant heating hose. Ironically only the latter case, in which redundant laboratory testing provided accurate lifetime predictions, involved product failure with consequent extraordinary financial losses.

Keywords: Service life predictions, Thermal oxidation, Fracture, Fatigue, Arrhenius equation

Introduction

Predicting the service life of a rubber component invariably requires laboratory tests, with simulated use testing employed for more accurate predictions. Commonly such testing falls into one of two categories: fracture mechanics analyses if the lifetime will be governed by the mechanical durability of the elastomer, or accelerated aging tests if chemical deterioration is the expected limiting factor. There are well established methods to address either mode of failure and the underlying science is well understood.

Materials can alleviate mechanical stresses by the growth of cracks, initiating from pre-existing flaws. Rubber is different from most materials, in that the input strain energy is dissipated viscoelastically, with only a negligible amount expended on the breaking of chemical bonds. A first principles description of rubber fracture is not generally feasible, given the complexity of the stress field in the vicinity of the fracture plane in nonlinear, viscoelastic rubber. For this reason tearing and cut growth are treated using a global energy criterion, as first proposed by Griffith,¹ who assumed that the crack front translates without change, obviating explicit consideration of the crack tip. Cracks convert stressed material to an unstressed condition, with the input strain energy equated to the energy expended for crack propagation. This leads to an expression for the rate of crack propagation in terms of the magnitude of the tearing energy, G , defined as the amount of elastically stored energy released per unit increase in crack area^{2–5}

$$G \approx l \times W \quad (1)$$

where W is the strain energy and l is a dimension. In equation (1) both l and the (implied) proportionality

constant (which has a magnitude on the order of unity) depend on the test piece geometry. This simple energy balance approach to crack growth has been successfully applied to various rubbers subjected to various modes of deformation.

When the tearing energy is substantial, so that the crack growth rate, \dot{c} ($=dc/dN$ for cyclic strains where N is the number of cycles), is purely mechanical, the behaviour can be described by a power law^{2–5}

$$\dot{c} = aG^b \quad (2)$$

where a and b are constants, the former depending on the formulation and the latter specific to the polymer. If these cut growth constants are known for a given elastomer, it is only necessary to deduce the tearing energy operative for the application in order to predict the service life. For example, the fatigue life is obtained by integrating equation (2) from the initial flaw size to some macroscopic length scale. The experiments can be accelerated by using larger value of G during laboratory testing, although usually this is unnecessary if only a rate, rather than a lifetime, is measured. The major difficulty in applying fracture mechanics is determining the mode of deformation, so that G can be calculated for a given W ; that is, the value of l and the exact form of equation (1) must be known.

When the tearing energy falls below about 50 J m^{-2} , cut growth typically becomes slow enough for chemical effects to become dominant.⁶ For $l \sim 1 \text{ cm}$, this threshold value of G corresponds to a strain of about 10%. For lower strains the failure will be strongly affected by environmental factors such as the ozone and oxygen levels. Even for G much larger than the threshold value, oxygen can exert a measurable effect by reducing the inherent strength of the polymer backbone.⁷

In a laboratory study chemical degradation can be accelerated by aging the compound at temperatures higher than the intended service temperature. Such accelerated testing has a long history in the rubber industry.^{8–11} The short time, high temperature

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degradation behaviour is extrapolated to yield predictions of the property deterioration expected for long time, lower temperature exposure, with quantitative predictions of lifetimes obtained through use of the Arrhenius relation (see below). Of course the method assumes that the chemical deterioration induced in the lab testing is the factor determining the service life in the field.

Although oxidation of rubber is fairly complex,^{12,13} thermally activated processes can be described using the Arrhenius equation if certain conditions apply. Two obvious requirements are that the rate of each chemical step involved in the oxidation process (initiation, oxygen uptake, chain scission, termination) must respond the same to changes in temperature and that the oxidation proceeds uniformly throughout the material (homogeneous reaction). When these assumptions hold, the rate of oxidative aging, r , at the use temperature, T_1 , can be determined from the aging rate measured in the lab at a test temperature T_2 , from the Arrhenius equation^{14,15}

$$r(T_1) = r(T_2) \exp \left[-E_a / R (T_1^{-1} - T_2^{-1}) \right] \quad (3)$$

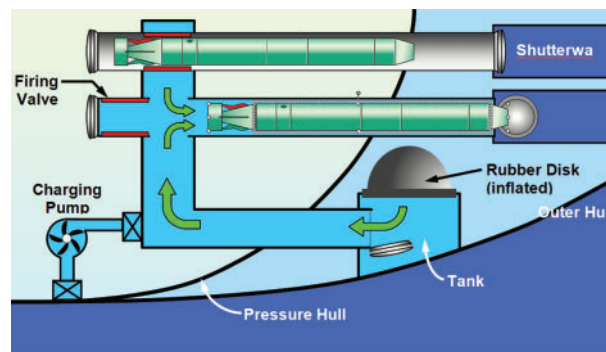
where E_a is the activation energy and R the gas constant. Fortuitous circumstances often give rise to effectively Arrhenius behaviour even when the thermal degradation process is more complicated.¹⁶ In this case the measured E_a is only an effective activation energy, but nevertheless still useful for predictions.

Although fracture mechanics and Arrhenius extrapolations are both firmly based on well understood principles, service life predictions are reliable only to the extent that the relevant failure mechanisms are identified, all contributing factors accounted for, and the samples used for laboratory test are representative. This paper describes two case studies in which rigorous, competent testing did not prevent product failure, but did lead to an understanding of the cause.

Case I – mechanical fatigue failure

Elastomeric materials are attractive for energy storage devices, due to their ability to store and quickly return substantial quantities of energy. The US Navy developed an elastomeric mechanical capacitor to eject torpedoes from submarines.¹⁷ This application requires sufficient power to accelerate a 1600 kg torpedo to an exit velocity of $\sim 13 \text{ m s}^{-1}$ in one second. There are several advantages of an elastomeric system over conventional ejection methods, including lower weight and cost and, most importantly, superior acoustic properties. The elastomeric ejection system (EES) is illustrated in Fig. 1. A small ($\sim 50 \text{ kW}$) pump inflates the rubber disk, which is 2 m in diameter and 20 cm thick. Although a higher strain to volume ratio could be achieved with a spherical geometry, a disk avoids any potential for buckling. In retrospect a geometry that deforms the rubber in shear may have been a better choice, since the performance would be less sensitive to cracking of the elastomer.

The rubber formulation was chosen to meet various requirements. Natural rubber (NR) was selected as the base polymer, given its resilience and toughness. Deproteinised NR was used since its salt water absorption is one-quarter that of conventional NR.¹⁸ Curing of the thick disk required 14 h at 135°C for complete



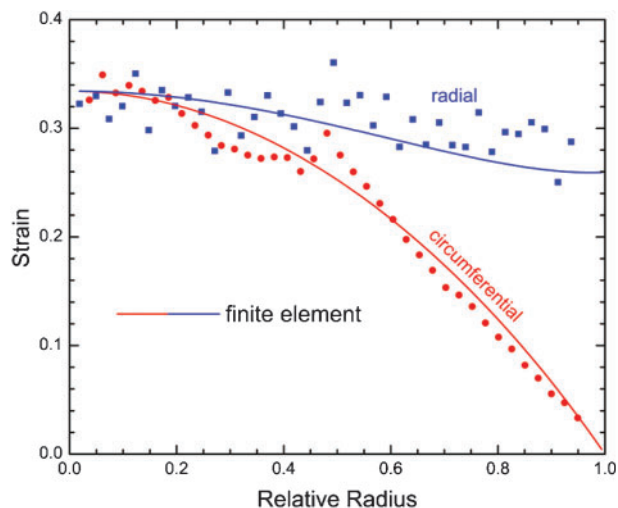
1 Schematic depiction of elastomeric ejection system

vulcanisation; in order to avoid reversion (dissociation of the crosslinks), a low sulphur, ‘semi-EV’ cure system was used. This also improves resilience by minimising the concentration of mechanically labile polysulphidic crosslinks. The final compound had a modulus, calculated as twice the elastic strain energy divided by the square of the strain, equal to 2 MJ m^{-3} at 130% tensile strain. The EES would be inflated during operation to a biaxial strain of 100%, which yields the same strain energy as a tensile strain of 130%. The energy loss (hysteresis) during a stress–strain cycle was less than 10%.

In consideration of an expected lifetime of ten years, the fatigue life required for the EES was 1500 inflation cycles. While laboratory testing was carried out at 130% tensile strain to match the strain energy for 100% biaxial inflation, the relevant quantity is the tearing energy (equations (1) and (2)). For uniaxial extension the relation between W and G is well known,^{3,4} but it cannot be obtained analytically for biaxial strain. However, a prediction based on uniaxial tension measurements is expected to underestimate the biaxial fatigue lifetime, since failure properties generally are greater for biaxial than uniaxial tension.^{19,20} This is due to the fact that crack growth in a biaxially strained elastomer does not make the material adjoining the crack free of stress; thus, the driving force for crack propagation is smaller than for uniaxial tension at equal W . And since G is proportional to strain energy for both deformation modes, the biaxial fatigue life should be equal to or larger than the uniaxial fatigue life.

The uniaxial tension fatigue life was determined to be 5200 ± 1500 cycles. This is consistent with the result, 4900 cycles, obtained from integration of equation (2) using the experimentally determined cut growth constants for the compound. For a sulphur cured NR this is a relatively low fatigue life, a result of the ‘tight’ network designed to give low mechanical hysteresis. Before construction of a full size prototype of the EES, limited fatigue testing was done on $\frac{1}{4}$ scale disks cycled at 100% inflation. The result was ~ 4500 cycles to failure, consistent with the uniaxial testing. During cyclical inflation of these small disks, cracks developed in the central portion (pole), where the stresses are highest. Daughter cracks subsequently developed in random directions but none propagated in any particular direction. This behaviour reflects the fact that under biaxial tension no material becomes stress free from the growth of a crack.

Since the laboratory tests indicated the fatigue life was well above the required 1500 cycles to failure, full size



2 Strains measured in inflated rubber membrane as a function of radial position. Equal biaxial deformation is limited to vicinity of pole, while at circumference strain mode is pure shear. Solid curves are finite element calculations

(3300 kg) disks were constructed. After curing the disks were inspected using ultrasound to ensure an absence of voids. Material properties were confirmed by measurements on 100 small specimens dissected from various radial and axial locations on a sacrificial disk. Either of two clamping methods, an external compression clamp and a bonded metal ring with bolt holes, was found to be satisfactory. The disks were initially inflated with water only to low strains, in order to measure the pressure–volume behaviour, which governs the ability to accelerate a torpedo. For strains below the maximum, the volumes and deflections of the disk were very close to finite element calculations using the Ogden equation to model the rubber.

It was intended to determine the failure performance of the fullscale disks by cyclic inflation to 100%; however, before full inflation all disks failed during the first cycle. Notwithstanding a fatigue life in uniaxial and biaxial lab tests exceeding 4000 cycles, the full scale disk could not attain the same strain energy without rupture. This failure occurred independently of the method of clamping the disk, even though fracture always initiated from the disk periphery. Since this is not the location of the highest stress, the suggestion is that the mode of deformation differs here; that is, it is not uniformly biaxial. Since the biaxial fatigue life was substantially larger for ¼ scale samples, there must be a variable that depends on the dimensions of the disk that affects performance.

In a disk geometry, a constant circumference must be maintained at the outer periphery, since the clamped rubber can not contract laterally. This means that near the outer edge only transverse strains can Poisson contract during inflation. Such a condition corresponds to pure shear deformation (also known as planar extension). This is illustrated in a plot (Fig. 2) of the radial and circumferential strains measured as a function of position in an inflated rubber film.²¹ This conclusion that the outer regions of the disk are subjected to pure shear is borne out by finite element modeling.²¹

For a pure shear strain, the characteristic dimension in equation (1) relating the strain energy and the tearing energy is the height of the sample²⁰

$$G = h \times W \quad (4)$$

in which h is parallel to the applied load. For a disk geometry, h corresponds to the radial distance over which a pure shear condition prevails. As seen in Fig. 2, this is a substantial fraction of the entire sample. More importantly, h scales with the total specimen size. At a constant strain energy, this means that larger disks experience proportionally larger tearing energies. The exponent in equation (2) $b=4$; thus, we expect a 16-fold decrease in fatigue life in going from ¼ to full scale disk geometry. This accounts at least in part for the disconnect between the laboratory and ‘field’ performance of the disk.

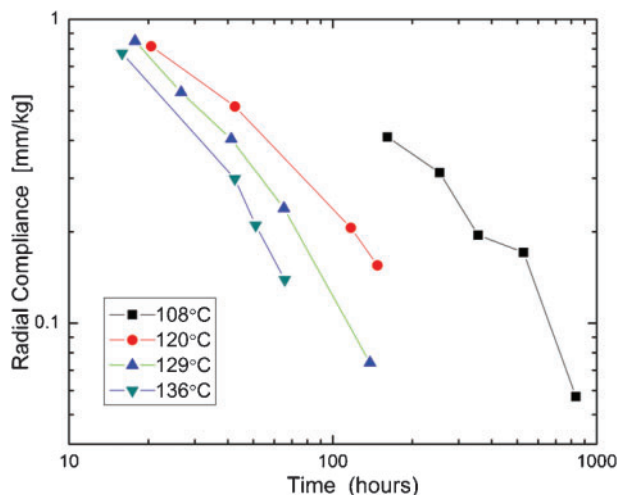
To overcome this failure problem the crosslink density of the compound was reduced, in combination with more carbon black reinforcement. The result was a ‘tougher’ rubber with substantially longer fatigue life, 2500 cycles for the full size disk inflated to 100%. The drawback to increasing the toughness of the material is greater hysteresis, which increases the demand on the inflating pump and limits the time between inflation and launch. The latter is required to maintain the EES in a pressurised ‘delivery-ready’ mode, a desirable but not essential feature.

Case II – thermal oxidative degradation

Radiant hydronic systems, in which heat is radiated from hoses containing flowing liquid, are an increasingly popular method for home heating, as well as snow melt applications. They have several advantages over convection heating, including less heat loss through walls and windows, minimising vertical thermal gradients, and better retention of humidity. Typical operating temperatures for the fluid in a radiant heating system are in the range from 60 to 85°C. Since the hose is exposed to ambient air, the possibility exists for thermal oxidation of the hose material during service. This is a potentially devastating problem because the hose is installed under floors and behind walls, so that its replacement requires deconstruction of the building.

Beginning in 1989, 10 000 radiant heating systems (comprising 25 million feet of hose) were installed in the United States and Canada using a particular nitrile rubber (NBR) compound. Subsequently, the hose began to harden and crack, leading to fluid leakage and ultimately system failures. The resulting lawsuits culminated in a class action settlement in excess of \$300 million dollars, along with several other judgments against the hose manufacturer and supplier. Nitrile rubber is an unsaturated rubber and as such is well known to be susceptible to oxidative degradation.^{22,23} The question is whether the failure of this radiant heating hose could have been predicted by laboratory tests.

A condition of the rubber (e.g. brittleness or hardness) is assumed that corresponds to a degree of deterioration likely to cause product failure. The service life is then estimated as the time for the material to reach this condition at the service temperature. For example, to predict the condition of the rubber after 20 years at



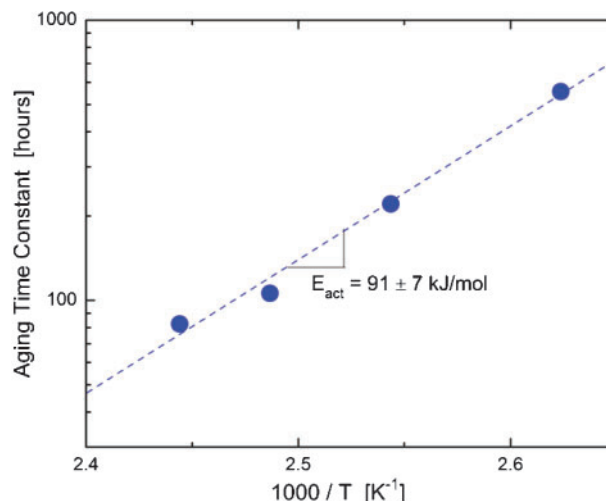
3 Transverse compliance of NBR hose as a function of aging time at indicated temperatures

82°C, laboratory tests could be carried out for one month at a higher temperature. The value of this higher temperature is calculated from equation (3), using E_a for thermal oxidation of NBR. There are possible three sources for this activation energy:

- (i) literature value. This assumes the compounding ingredients have negligible effect on E_a , a reasonably accurate assumption. However, the acrylonitrile content of NBR varies and this does affect E_a . Goh²⁴ reported values for thermal oxidation of NBR ranging from 82 kJ mol⁻¹ at 21% acrylonitrile content to 100 kJ mol⁻¹ for 45% acrylonitrile. We will assume for argument sake that the acrylonitrile content of the radiant hose is proprietary and thus unknown (although of course it could be readily determined). Gillen *et al.*¹⁶ suggested a value of 88 ± 4 kJ mol⁻¹ for generic NBR, which from equation (3) gives 162°C as the temperature for the accelerated aging tests
- (ii) thermal analysis. During calorimetry measurements on an organic compound a strong exothermic peak is observed at the temperature of maximum oxidation. If the heating rate of the calorimetry experiment is increased, this peak shifts to higher temperatures, reflecting the kinetic nature of the oxidation phenomena. Thus, a series of rates and temperatures can be obtained, with the activation energy in equation (3) given by

$$E_a = \frac{R}{\log(e)} \frac{d \log(r)}{dT^{-1}} \quad (5)$$

where e is the base of the natural logarithm. This calorimetric method is equivalent to a highly accelerated aging test, with the material lifetime in principle estimated directly from the data. However, the very large extrapolation from the measurements to the service condition (experiments with a duration of about one hour used to predict degradation transpiring over decades of time) can lead to large errors. One source of error is that the degradation in service may involve different chemical reactions than the lab tests. Notwithstanding this concern, calorimetry



4 Arrhenius plot of aging time for tenfold decrease in hose compliance (from Fig. 3), yielding indicated activation energy for oxidation of hose rubber

measurements on the hose compound give $E_a = 119 \pm 5$ kJ mol⁻¹, from which an accelerated aging test temperature of 138°C is obtained.

- (iii) air-oven aging. Even when the activation energy for thermal oxidation is known, it is still necessary to carry out at least one aging experiment at the temperature calculated from E_a . Alternatively, aging experiments can be conducted at a series of temperatures to obtain both E_a and the material lifetime from the same data. Toward this end the hose was exposed to air at four temperatures in the range from 108 to 136°C. These temperatures are arbitrary; higher values would expedite the experiments but at greater risk of introducing new degradation mechanisms. Figure 3 shows the radial compliance of the hose measured after various aging times. Aging rates corresponding to a tenfold decrease in hose compliance (that is, the initial compliance of 1.17 mm radial deflection per gram load is reduced to 0.117 mm g⁻¹) were extracted from the data and these yield an activation energy = 91 ± 7 kJ mol⁻¹ (Fig. 4). Using this E_a , we calculate that one month oxidation at 159°C is equivalent to 20 years at 82°C.

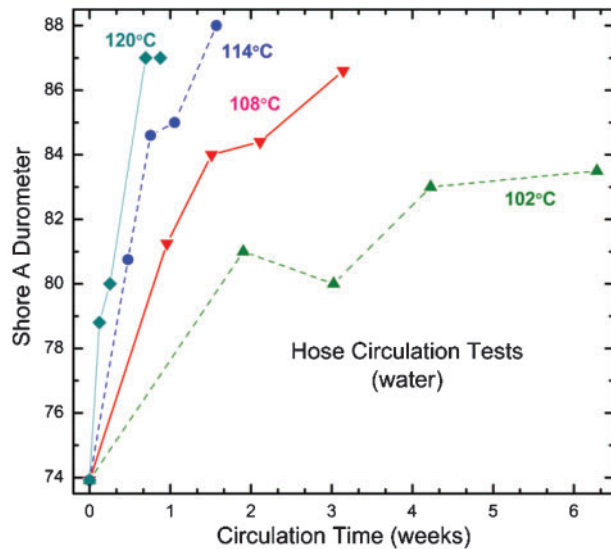
The various activation energies and laboratory aging temperatures are summarised in Table 1. Although the different aging conditions would lead to different predictions of the product lifetime, the differences turn out to be small compared to the expected service life of a radiant heating system. To make a specific prediction of this lifetime requires specifying a condition equating to

Table 1 Various methods of Arrhenius extrapolation

Method	E_a , kJ mol ⁻¹	T^* , °C	Predicted service life†
Literature	88 ± 4	162	5.8 ± 0.3
Calorimetry	119 ± 5	138	7.8 ± 0.4
Oven aging	91 ± 7	159	6.0 ± 0.5

*Temperature giving same degree of oxidation in one month as 20 years at 82°C.

†Months at 82°C.

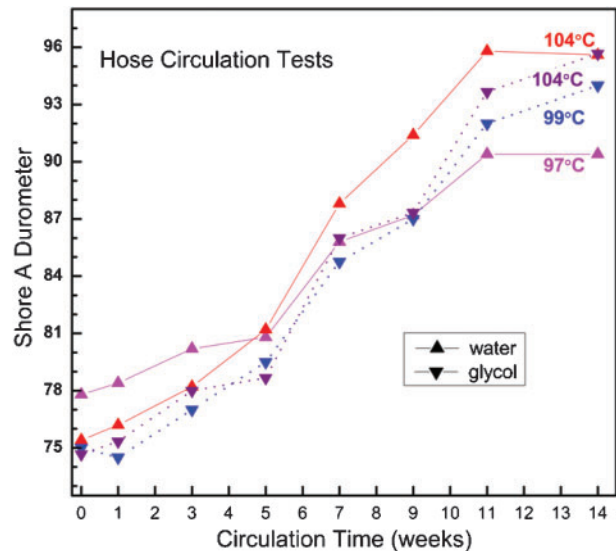


5 Hose hardness measured during simulated use of radiant heating hose with water as circulating fluid

hose failure. This condition can be based on analysis of failures in the field, although usually product life predictions are done before commercialisation of a product. Since embrittlement and loss of sealing ability occur simultaneously with hardening of the hose, we can adopt a particular value of hardness as equivalent to a failed condition. We assume that tenfold stiffening of the hose rubber makes it too stiff to reliably function; this order of magnitude change corresponds to an increase in the Shore A hardness of the rubber from its initial value of 75 ± 2 to a value above 90, for which the accuracy of the durometer scale is poor. Using the E_a value determined from oven aging, we predict at 180°F the hose will attain this loss of flexibility in one-half year. The corresponding predictions using the other methods of determining the activation energy for thermal oxidation are listed in the table.

All results indicate a service life of less than one year, which is far below expectations for a radiant heating system. To corroborate the Arrhenius oven aging method, experiments were carried out in which fluid was circulated through the hose to simulate the application. Two such simulated service tests were conducted, one by the manufacturer of the hose and the other at the behest of end-users, with the intent of carrying out the test for very long times. The condition of the rubber was monitored continuously during the testing, with the results displayed in Figs. 5 and 6. The presence of the system fluids (water or water/glycol mixtures) may introduce additional effects, such as extraction of plasticisers and antioxidants or swelling of the hose; nevertheless, both circulation tests show that the hose approaches a hardness of 90 or greater in only a few months time. This confirms the prediction of laboratory accelerated aging tests that the hose will fail prematurely in this application.

A potential problem not accounted for in this analysis is any batch to batch nonuniformity of the hose rubber. The lab tests were done on a single sampling of the material, assumed to be representative. We expect hoses experiencing the same conditions in the field to age similarly. While the extent of batch to batch uniformity can often be assessed from analysis of quality control



6 Hose hardness measured during simulated use of radiant heating hose with either water or water/propylene glycol as circulating fluid

data obtained during product manufacture, it is not straight forward to account for the effect any non-uniformities might have on product performance. This introduces some uncertainty into the accelerated aging methodology, without necessarily obviating its utility.

Concluding remarks

Two examples of service life predictions were described. The first concerned fatigue failure of an elastomeric mechanical capacitor, intended to launch torpedoes from Navy submarines. Predictions based on fracture mechanics overestimated the lifetime of the elastomer component by three orders of magnitude. However, simulated use testing identified the error and its origin; thus, problems in the field were avoided and modifications enabled a reliable product to be achieved.

The second example involved thermal oxidation of a radiant heating hose. Extensive testing, both laboratory scale and simulated use, revealed that the product lifetime would be unacceptably low. However, this testing was done subsequent to sale and use of the hose in radiant heating systems. The consequence was field failures involving about 29 million feet of hose. The utility of the testing was limited to identifying the cause of the failures.

Acknowledgements

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