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Estimation of Life of an Elastomeric Component: A Stochastic Model

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ABSTRACT

Life of equipment has been an area of great importance to engineers, however, largely unexplored. In the case of elastomers, this becomes more critical because of faster degradation in properties of the elastomers, and thereby performance of the elastomeric item, when compared to metals–the degradation referred to as aging of the elastomer. The present work focuses on the development of a stochastic model for estimating life of a vibration isolator, which finds many defence applications, to attenuate noise and vibration from the machinery. A majority of the vibration isolators use rubber for attenuation, and therefore, the life of the isolator invariably depends on the life of the rubber. The methodology of life estimation has been based on the Arrhenius theory of chemical kinetics and is applicable where the material degrades relatively faster at higher temperature so that the degradation rates can be studied. Statistical techniques have been applied to arrive at a reliable estimation. The method can be used for reliable estimation of storage life of elastomeric products, and thereby help to maintain cost-effective inventory.

Keywords: Elastomer, Arrhenius model, accelerated aging, Gaussian distribution, elongation at break, dynamic modulus, damping factor

1. INTRODUCTION

Elastomeric products, like vibration isolators, rubber seals, etc., are commonly used for long-term applications in the industry/defence. A vibration isolator provides attenuation to the vibration and noise generated by the machinery and finds a number of applications in the defence sector, like onboard naval ships, missiles, etc. The key element in majority of the vibration isolators is the rubber, an elastomer, which dampens the vibration considerably, and thus provides attenuation. Similarly, seals of various types and other elastomeric products are used extensively in defence. When the elastomeric products are manufactured, these are supplied to the user in an optimum state for the desired performance. Before being put to service, many a times, these products are stored for a considerable period of time. However, the physical and dynamic properties of these products degrade with time and the performance deteriorates, mainly due to the degradation of the elastomeric material. The degradation of the elastomeric material is commonly referred to as ageing. Various factors contribute to the ageing of an elastomer, the important ones being oxygen, temperature, UV rays, ozone, etc. Therefore, it is imperative for the user to know the storage life, also called the shelf life, of these products. Interest in this area is high and a number of papers have been published on the estimation of shelf life as well as the service life of an elastomer by various authors, using the principle of accelerated ageing. These tests are carried out for two distinct purposes. Firstly, these are intended to measure changes in the elastomer at the (elevated) service temperature or, secondly, these can be used as accelerated tests to estimate the degree of change, which would take place over much longer times at normal ambient temperature[1]. A series of accelerated exposure tests were performed by Itoh[2], *et al.* on various rubber materials including high damping rubber (HDR) to investigate the degradation due to different environmental factors. It was found that the thermal oxidation is the most predominant degradation factor affecting the HDR material.

Mainly two models exist in the literature on life estimation of an elastomer, namely, Arrhenius model and WLF model. There are also some variants to these main models. Le Huy[3], *et al.* carried out research work on shelf life and service life estimation of rubber using Arrhenius and WLF models. They have concluded that WLF model is appropriate for lifetime predictions when polymer ageing is controlled by a viscoelastic process (e.g., relaxation, creep), as in the case of service life. On the other hand, when physio-chemical mechanisms are dominant, the Arrhenius model is the most widely used model for evaluating accelerated test results involving the effect of temperature. Mandel[4], *et al.* studied the tread wear of tires, i.e. the service life. These works mainly indicate the methodologies to be followed for life estimation. The aim of the present work is to augment the work carried out by other researchers in the field by making the estimation of life reliable. The shelf life of nitrile rubber, used in various engineering applications, has been studied using the technique of accelerated ageing and subsequent application of Arrhenius theory. The estimate

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of shelf life has been rendered more reliable by developing a stochastic model, incorporating the statistical techniques.

The work gains significance because it being a reliable estimate of the shelf life of the elastomeric products, inventory of these products can be judiciously maintained. Not only this, as noted earlier, some of the products, like vibration isolators are used onboard naval ships, where it is required to be known whether a particular isolatormount can be stored safely for a certain duration of time before putting it into service.

2. ACCELERATED AGEING

The method of accelerated ageing involves first heating the elastomer samples at higher temperatures, so that the degradation of a property is faster. This can then be related to similar level of degradation at a lower temperature, but at scaled-up time. In other words, if the degradation of a property is studied at an elevated temperature, it is possible to predict the time at which a similar degradation can be expected at the actual temperature. Hence, this can be used to predict life, if cut-off level for the drop in property is defined. The underlying assumption is that the mechanism for the degradation of the rubber property remains the same at different elevated temperatures as that at the storage temperature.

3. THE ARRHENIUS MODEL

The test methodology for life estimation of an elastomer is traceable to Arrhenius' theory of thermal acceleration of reaction kinetics and the concept of the activation energy of a process[5]. With rise in temperature, the state of a chemical reaction increases. For many organic-chemical reactions, a temperature rise of 10 °C translates to about 2 to 3 times higher reaction rate[6]. The temperature dependence of chemical reactions is described by the Arrhenius equation[6] as:

$$K(T) = A.e^{-E/RT} \quad (1)$$

where, $K(T)$ is reaction rate constant (min^{-1})

A is pre-exponential factor (min^{-1})

E is activation energy (J/mol)

R is gas constant (8,314 J/mol K)

T is absolute temperature (K)

The following relation gives the state of a chemical reaction[6]:

$$F_x(T,t) = K(T).t \quad (2)$$

where, $F_x(T, t)$ is function of the state of the reaction x, and t is reaction time (min)

The state of the reaction, $F_x(T, t)$ may be related to the value of any property of interest. Consequent to different reaction rates K_i for different temperatures T_i, the threshold value F_a of a reaction will be reached at different reaction times t_i (equal-value times), e.g., t_1 to t_4 as shown in Fig. 1 ($T_1 > T_2 > T_3 > T_4$).

The threshold value is given by the equation

$$F_a(T_i, t_i) = K_i(T_i).t_i \quad (3)$$

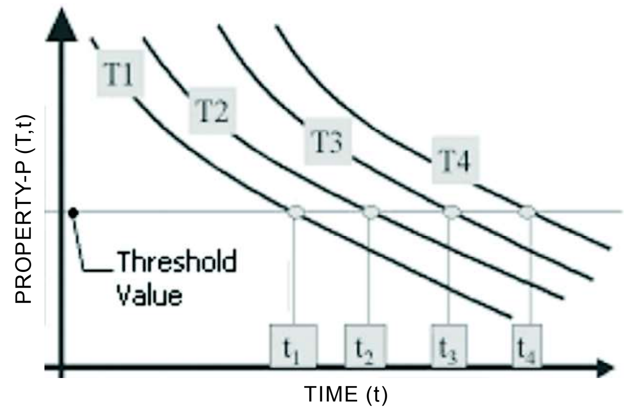

Figure 1. Degradation of property with time.

The Arrhenius equation Eqn (1) can be substituted in Eqn (3) as follows :

$$F_a(T_i, t_i) = A.e^{-E/RTi}.t_i \quad (4)$$

or, in logarithmic form with the constant terms combined in one term B, we get

$$\ln t_i = E/RT_i + B \quad (5)$$

Hence, a plot of ln(t) versus $1/T$ gives a straightline with the slope being E/R, known as the Arrhenius plot, a sample plot shown in Fig. 2. Extrapolating this line to the temperature of interest (T_s) can indicate the estimated life (t_s).

Therefore, if the degradation in a property of an elastomer is taken as thermally-activated molecular process with constant activation energy, the Arrhenius equation can be used to estimate long-term behaviour of the elastomer.

4. VARIOUS TESTS CONDUCTED

Among different degradation factors noted above, it was found by Yoshida[7], *et al.* that thermal oxidation changes the HDR properties more than the other factors, resulting in an increase in HDR's stiffness and a decrease in elongation at break as well as tensile strength. In the present work, too accelerated tests were performed on rubber samples, focusing on the most significant degradation factor, i.e. thermal oxidation.

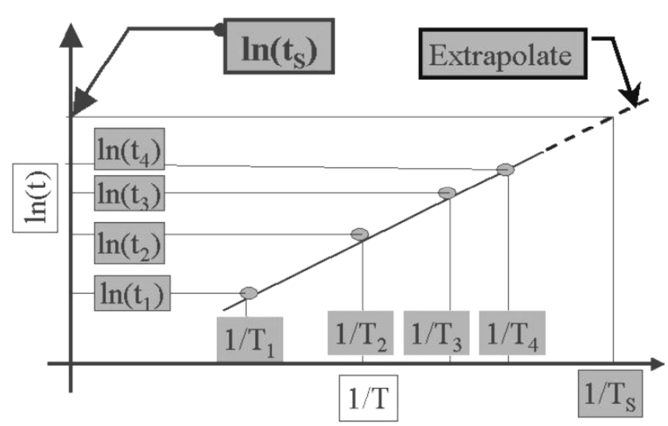

Figure 2. Arrhenius plot for life estimation of an elastomer.

4.1 Selection of Various Parameters

4.1.1 Selection of the Ageing Temperatures

The ageing temperatures were so chosen such that the chemical reaction at each temperature was identical to the one at the shelf temperature[6]. For nitrile rubber, beyond 110 °C-120 °C, there is a change in the type of reaction, which has implications. Hence this limits the maximum ageing temperature. The ageing temperatures should be chosen such that[6]:

- The time to attain the threshold values at the lowest ageing temperature is at least 1000 h.
- Likewise, the highest temperature should be chosen such that the time taken to attain the threshold is not <100 h.

In view of the above considerations, a range of 60 °C to 120 °C was chosen. The ageing temperatures selected thus were 120°C, 100°C, 90°C, 80°C, 70°C and 60°C.

4.1.2 Selection of Properties for Life Estimation

The properties chosen should be of significance. Their selection varies from product to product. In the present study, a number of static and dynamic properties were chosen. Under the static properties, the study was carried out for tensile strength, elongation at break, hardness, and stress relaxation in compression. In the dynamic category, dynamic modulus and damping factor were studied. A survey of the literature indicated that the elongation at break had been preferentially used for prediction of long-time behaviour of rubber. Results of the study for five rubbers have been given by Mandel[4], *et al.* in which elongation at break was used as the measure of degradation. In the present work, though the study has been conducted for a number of properties, it was observed that the elongation at break gave the best representation of the state of degradation for studying the shelf life. This has been discussed further.

4.1.3 Selection of Threshold Value of Life

The threshold value should be chosen to suit the conditions of use. It was selected as 50 per cent of the initial value of the property[6].

4.2 Experimental Procedure

The test specimens for different tests were made from the rubber blocks, which were used in the manufacture of the vibration isolator. The test specimens were prepared in line with applicable ASTM standards, indicated below. The ageing studies of the test specimens were carried out in air circulating ovens. Tests for tensile strength and elongation at break were conducted using the Universal Testing Machine, as per ASTM D 412[8]. The hardness test was performed on hardness tester, as per ASTM D 2240[9]. Test for stress relaxation was carried out using stress relaxometer, in accordance with ASTM D 1390[10], while the dynamic tests for dynamic modulus and damping factor were performed using dynamic mechanical analyser, as per ASTM D 5992[11].

5. TEST RESULTS AND PRELIMINARY DATA ANALYSIS

It may be noted that out of the six properties measured, four properties namely, tensile strength, elongation at break, hardness, and stress relaxation are related to the static performance of the mounts while dynamic modulus and damping are related to the dynamic performance of the mounts. Dynamic modulus and damping were measured to gain an inside view of the dynamic property of the rubber material. However, these two properties were not studied for shelf life estimation, as no dynamic loading is applicable during the storage period, and the data showed considerable scattering.

From the tests, it was found that the tensile strength data did not follow proper trend, it increased and decreased abnormally. This property, therefore, was not used for further study. The data pertaining to hardness and stress relaxation showed relatively less fluctuation, however the Arrhenius plots for these properties were observed to be deviating considerably from straight lines. Figures 3 and 4 show the respective Arrhenius plots. These properties too, therefore, were abandoned from the scope of study.

As indicated in Section 4.1.2, elongation at break has been used by various authors for life estimation study of elastomers. In the present case too, it was observed that the data pertaining to elongation at break were very much consistent at each temperature. Therefore, further study was carried out with this property.

The ageing data at 120 °C was found to be inconsistent when viewed with the data at other temperatures. It was observed that this temperature is too high for the present rubber sample where 50 per cent drop in the property was observed within just three days, and therefore, the test data at 120 °C were rejected for further analysis. On the other hand, degradation at 60 °C was observed to be very slow, and therefore, was not considered for further analysis.

In view of the observations made, analysis of test results as per Arrhenius model was restricted to four temperatures, i.e. 100 °C, 90 °C, 80 °C and 70 °C. The curves of elongation at break versus time data (log h) have been

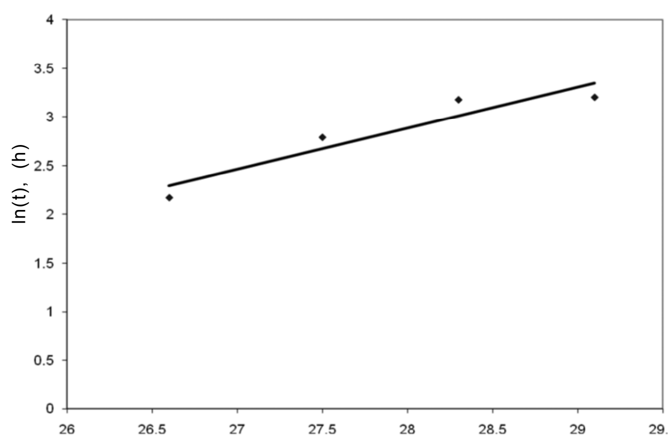

Figure 3. Arrhenius plot for hardness.

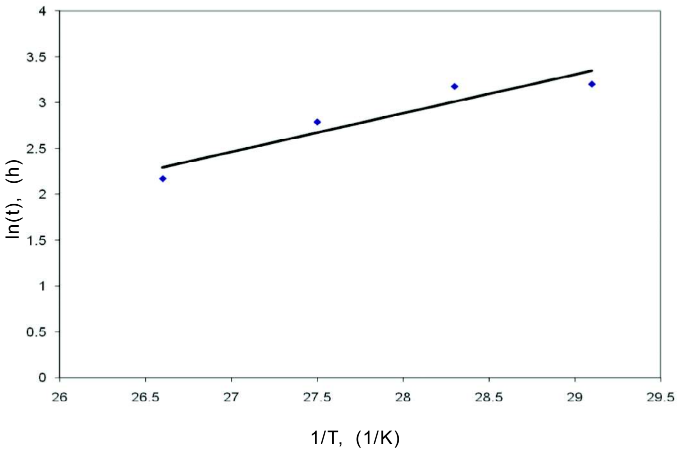

Figure 4. Arrhenius plot for stress relaxation.

plotted and shown in Fig 5. The degradation curves for elongation at break at 70 °C, 80 °C and 90 °C were observed to be of similar pattern, except for that at 100°C. If the patterns of curves are the same at different temperatures, then identical reaction of the rubber may be considered, which is a precondition for Arrhenius model. Therefore, it was concluded that reaction at 100 °C was not the same as that at other temperatures. Thus, data at 100 °C were not considered for further analyses.

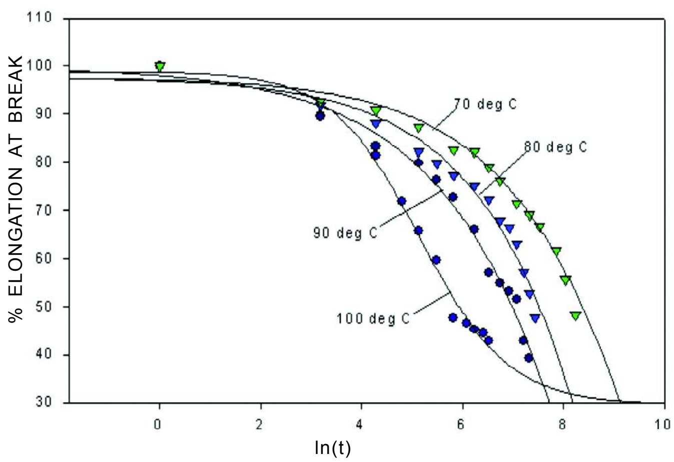

Figure 5. Experimental plot of elongation at break.

The Arrhenius plot based on the three remaining temperatures, namely 90 °C, 80 °C and 70 °C is shown in Fig. 6. On examining Fig. 6, it was observed that the three data points corresponding to 90 °C, 80 °C, and 70 °C were almost in a straight line, i.e., the best-fit line was passing very closely through the data points. This was reflected in the R^2 value (= 0.992) also, which was very close to unity. The value of R^2 quantifies goodness of fit, having a fractional value between 0.0 and 1.0. A higher value indicates that the model fits the data better. The straight line through the three data points was extrapolated to the storage temperature, i.e. 27 °C, and the life from the curve worked out to be 13.24 years for 50 per cent degradation as the threshold for life.

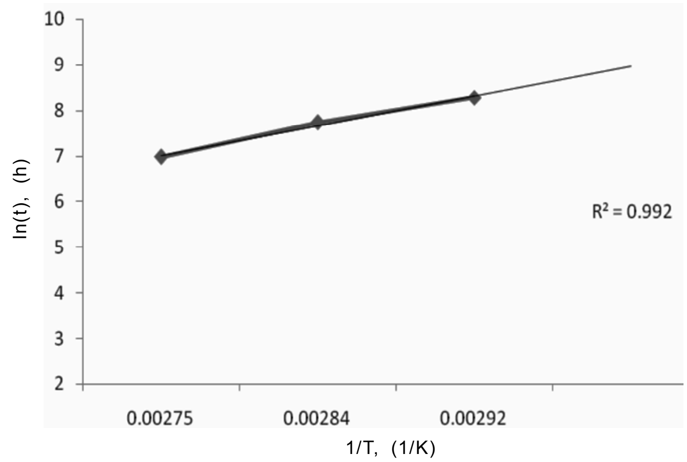

Figure 6. Arrhenius plot considering three temperatures.

6. STATISTICAL EVALUATION

Historically, the vast majority of accelerated ageing studies have utilised the Arrhenius methodology. However, as pointed out by Wise[12], *et al.*, the estimation by this method may give little confidence due to non-Arrhenius behaviour. As experienced by the authors, the non-Arrhenius behaviour, however, can partly be avoided by discarding temperatures where the degradation pattern differs substantially from that at other temperatures, and also by selecting the ageing temperature closer to the shelf temperature or the temperature of use. In addition, the estimation can be rendered more reliable by incorporating statistical techniques, as elaborated here.

It may be noted that at each temperature, measurement of the property at a particular time was carried out on several samples. Therefore, for an ageing temperature, a set of values of the property, i.e. elongation at break, was available at a particular time. The mean of these property values was obtained at each time to generate the degradation plot of the property, i.e., the property *vs* time plot at that particular temperature. Thus, essentially the raw data points were replaced by corresponding averages. This may be said to be an exercise in point estimation. However, each datum point is actually representative of a data distribution. A sample raw data plot for a particular temperature is indicated in Fig. 7.

From the Fig. 7, it is evident that the raw data varies within some range; simple averageing may not be appropriate to estimate life and statistical techniques could be employed for a more reliable estimate. This has been discussed below wherein the concepts of sample/ population mean and confidence interval have been employed for working out a reliable model of shelf life estimation.

7. DEVELOPMENT OF STOCHASTIC MODEL FOR LIFE ESTIMATION

As noted above, each datum point is characterised by ageing temperature at which the relevant samples have been aged (T), the time duration for which the samples have been aged (t), and different sample values of the

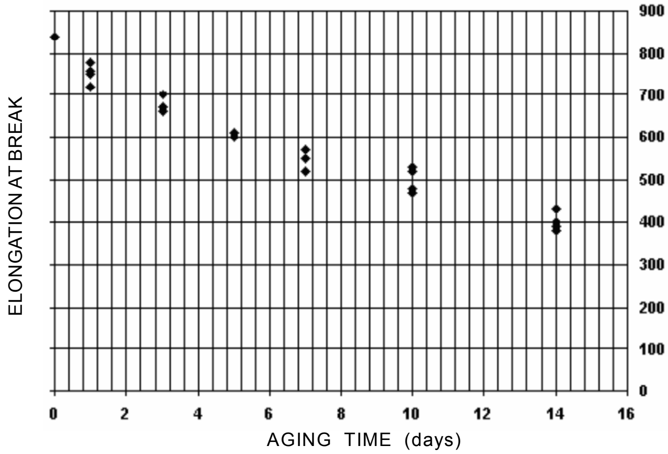

Figure 7. Elongation at break data at a particular temperature for different samples.

property. The values of the property at a particular temperature and time are theoretically expected to be identical for all the samples, but are observed to be different in practice even though enough care is taken in following the correct experimental procedure. This is in line with the normal experimental method. The difference is attributable to various causes, like difference in curing of different rubber samples, error in measurement, air flow variation at different locations within the oven, localised variations in temperature inside the oven, etc. Hence, the different experimental values can be treated as a statistical data distribution.

For cases in which the errors are likely to be equally positive as well as negative, the smooth distribution of an infinite number of readings coincides with the Gaussian or normal distribution[13, 14]. The Gaussian distribution has been found to describe more real cases of experimental and instrument variability than any other distribution and is the one assumed in the present work.

The equation for the Gaussian distribution is

$$f(X) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(X-\mu)^2/2\sigma^2} \tag{6}$$

where, $f(X)\,dX$ is the probability that a single measurement of X will lie between X and $X + dX$, μ is the distribution mean and σ is the distribution standard deviation.

The above description assumes a Gaussian parent population, which would be well-described if infinite number of samples are taken. However, it is not possible to take infinite number of samples. Thus, the concept of sample population and sample standard deviation comes into the picture. The mean or average of the sample population is defined by

$$\bar{X} = \frac{1}{N}\sum_{i=1}^{N} X_i \tag{7}$$

where, N is the number of individual readings X_i. The sample standard deviation is given by

$$S_X = \left[\frac{1}{N-1}\sum_{i=1}^{N}\left(X_i - \bar{X}\right)^2\right]^{1/2} \tag{8}$$

According to the central limit theorem of statistics, irrespective of the shape of the distribution of the population or universe, the distribution of average values of samples drawn from that universe will tend toward a normal distribution as the sample size grows without bound[15].

7.1 Confidence Intervals in Sample Populations

The confidence interval of the mean defines a band about the calculated sample mean within which the population mean is expected to lie for a given sample confidence/ probability level. This interval can be defined for each datum point, i.e. for each mean value of the property at a particular temperature and at a particular time. Mathematically, it is denoted as follows[14]:

$$\alpha = N(p) \times \sigma / \sqrt{n} \tag{9}$$

where, $N(p)$ is the value of normal function for a probability p, σ is the standard deviation of the sample and n is the sample, size.

From above, it may be deduced that one can define a standard normal distribution for each datum point. This will enable one to indicate the expectation for values of elongation at break at that duration and temperature of ageing, i.e., it is possible to have a maximum value, a minimum value, and a mean value of the expected population mean of elongation at break, aged at a temperature, T for duration t, for a particular confidence level, and thus three estimates of life can be made.

8. STOCHASTIC MODEL

As brought out in section 7 three property degradation curves for each ageing temperature, pertaining to a specific confidence level can be defined. From the three curves for each ageing temperature, three durations of time, namely t_{min}, t_{mean} and t_{max} were obtained at which the respective curves drop to the threshold level of elongation at break. The terms t_{min} and t_{max} represent the bounds of an interval within which the property is expected to drop to the threshold value of life with a defined probability. Plots of the three curves pertaining to the ageing temperature of 70 °C are shown in Fig. 8.

It is clear form the above, that three Arrhenius plots can be made respectively for t_{min}, t_{mean} and t_{max} after obtaining all such values at all ageing temperatures.

The extrapolation of these three plots would give three estimates of life, i.e., l_{min}, l_{mean} and l_{max}. Hence the interval (l_{min}–l_{max}) was obtained within which the life was expected to fall with a defined confidence. The three Arrhenius plots are shown in Fig. 9.

9. RESULTS AND DISCUSSION

In the present work, life has been estimated within a range as against a single value. In statistical terms, interval estimation has been carried out as opposed to point estimation. The lower limit of the range can form a sound basis for the estimation of life. Analysis was carried out at the confidence level of 0.99. The result for

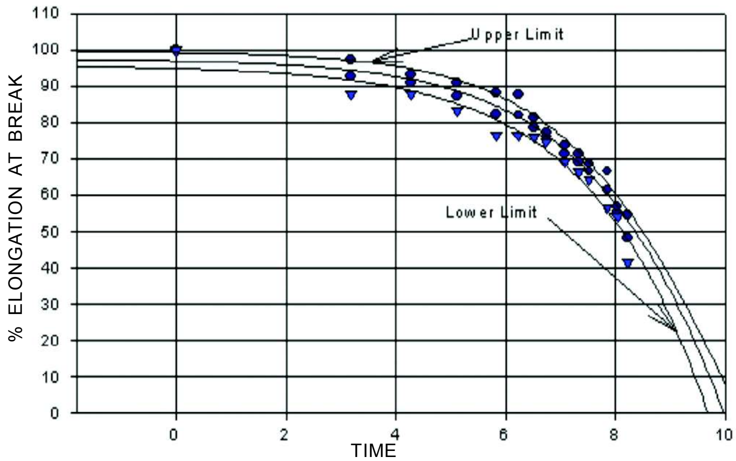

Figure 8. Three curves of the property based on the stochastic model.

99 per cent confidence level is indicated in Table 1. It was observed that if the confidence level was increased further, no appreciable change in the lower limit value was obtained. However, accuracy of this model depends on the number of test samples used for ageing at different temperatures. More the number, more accurate will be the estimate of shelf life.

Arrhenius plots for the lower estimate are shown in Fig. 10.

9.1 Other Environmental Factors

The work described so far relates to estimation of shelf/ storage life considering oxidative ageing only, which has been found to be the maximum contributor for ageing, as noted earlier. Other environmental factors, like moisture, fluids, UV light, microorganisms, ozone, etc. have not been factored into this exercise. Even though the effect of these factors may not be of high order, further study is required to estimate the effect of these factors also.

10. CONCLUSIONS

The methodology for a reliable estimation of life of an elastomeric component/product, e.g., a vibration isolator, based on accelerated thermal ageing and the Arrhenius methodology is described. Life of an elastomeric product

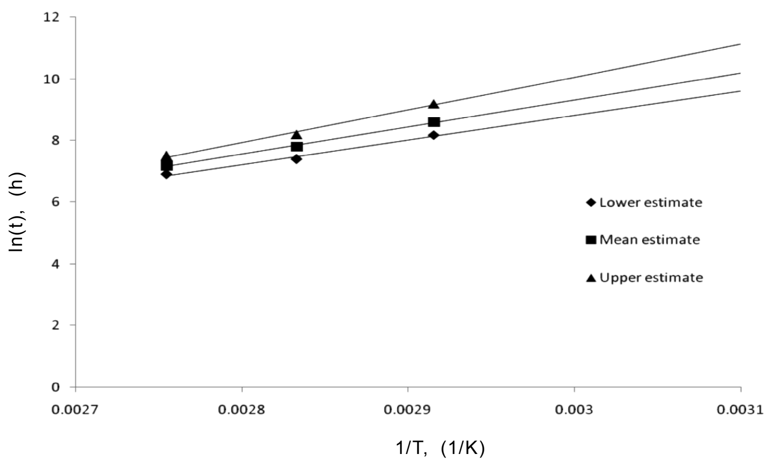

Figure 9. Arrhenius plots based on the stochastic model.

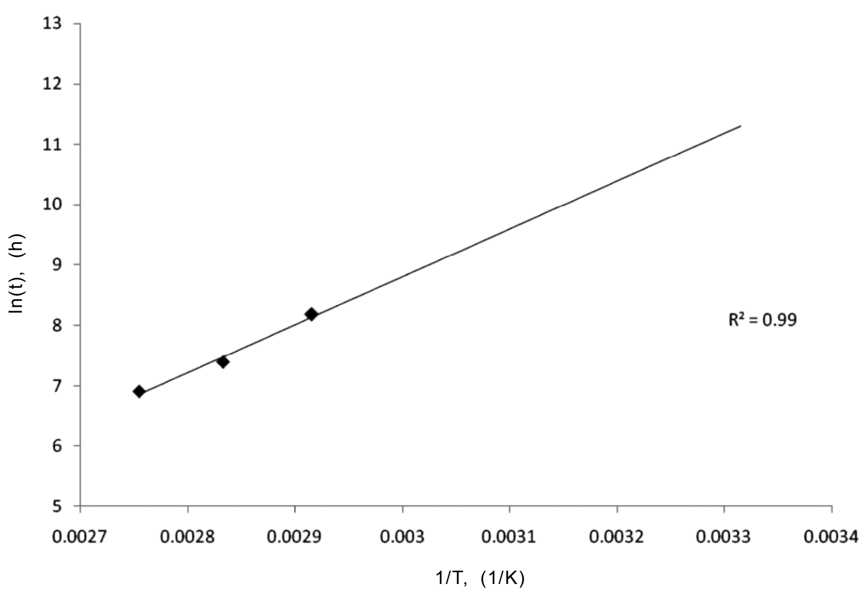

Figure 10. Arrhenius plot corresponding to the lower estimate of shelf life.

Table 1. Life estimates for 99 per cent confidence level

Confidence level	Lower limit of life, l_{min} (years)	Mean life, l_{mean} (years)	Upper limit of life, l_{max} (years)
0.99	11.02	13.24	19.76

essentially means life of the elastomer because of faster degradation of the elastomer when compared to metals. Therefore, tests for life estimation are carried out on the elastomer. In the present study, the tests were carried out on a number of rubber samples, as per ISO/ ASTM guidelines. Several properties of the elastomers were selected for the study. However, it was found that the elongation at break best represents the degradation of the elastomer with time for shelf life study, and therefore, is best suitable for the study of shelf life estimation.

Accelerated ageing tests were carried out at different elevated temperatures. However, data pertaining to some of the temperatures had to be discarded since the application of Arrhenius theory demands that the pattern of degradation of the property should be the same for all the temperatures under consideration. For the discarded temperatures, it was observed that the data did not follow the regular patterns, as demonstrated by other data. Statistical techniques, based on Gaussian distribution, were incorporated to undertake a meaningful study, based on the variation in sample data for a particular temperature and time. This led to the development of a stochastic model for life estimation, wherein three estimates of life were obtained. Out of the three estimates of life, lower estimate can be taken as the more confident estimate of shelf/storage life and a practical decision on inventory of elastomeric items can be taken on the basis of this estimate.

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