1. Introduction

Rubber materials tend to degrade according to various complicated mechanisms involving electrical or mechanical factors, as well as oxygen concentration, heat, water, ozone, light, gas, chlorine, chemicals, radiation, metals, and microorganisms. Selection of an optimal rubber material, which meets the requirements under various usage conditions, is therefore required. In this situation, it is essential to evaluate the performance of rubber materials under conditions close to actual usage ones.

The physical properties of rubber materials presented by rubber manufacturers are the initial ones attained by rubber-test methods mainly complying with the Japanese Industrial Standards (JIS). In consideration of the long-term stability, it is difficult to estimate the fundamental lifetime of a rubber material from its initial physical properties. For that reason, a method for estimating the lifetime of rubber materials is required.

Toshiba has formulated a lifetime-estimation method that uses the compression set ($Cs$) as an index for evaluating seal performance and selecting a substitute oxidation-resistant rubber material, and its effectiveness as a way of estimating $Cs$ of rubber material used in certain equipment was confirmed. This report describes the lifetime-estimation method and results of an evaluation of the effects of temperature change and differing levels of oxygen concentration on lifetime.

2. Evaluation index for seal performance and lifetime-estimation method

As for rubber materials used in power transmission and transformation systems, sufficient seal performance against gas and oil over a long time is required. As a means of evaluating seal performance, under the assumption that degradation in seal performance can be regarded as the lifetime of the seal, we have carried out compression-set tests in accordance with the JIS K 6262. As for evaluating lifetime, it is necessary to establish a lifetime-estimation method and a method for accelerated degradation of materials and to set a determined value for the lifetime. Accordingly, we have used the general Arrhenius equation(1) as a lifetime-estimation method using temperature acceleration to accelerate the degradation of rubber materials. As for determining lifetime, the time point at which $Cs$ reaches 80% (namely, when seal performance starts to decrease owing to the thermal degradation of rubber materials) was set as the judgement value(2).
2.1 Lifetime evaluation of ethylene propylene diene monomer (EPDM) O-ring

An EPDM O-ring was fitted in a compression jig corresponding to an actual machine (Figure 1), and the jig was placed in a constant-temperature bath and subjected to heat-accelerated degradation tests under various temperatures. After being subjected to accelerated heating for a predetermined time, the compression jig was removed from the bath, the O-ring was extracted and its thickness was measured, and $C_s$ was calculated from the O-ring thicknesses before and after the test.

$$K = Ae^{\frac{E}{RT}}$$

(1)

$$\ln K = \frac{-E}{R} \frac{1}{T} + \ln A$$

(2)

where, $K$ is a chemical reaction rate constant, $A$ is a frequency factor, $E$ is activation energy (J/mol), $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), and $T$ is absolute temperature (K) (Celsius temperature: $T_c = T - 273.16°C$). Since $K$ and lifetime $t$ are reciprocally related as $K = \frac{1}{t}$, Equation (2) can be expressed as Equation (3) and then by Equation (4) as follows:

$$\ln \left( \frac{1}{t} \right) = \frac{-E}{R} \frac{1}{T} + \ln A$$

(3)

$$\ln (t) = \frac{E}{R} \frac{1}{T} - \ln A$$

(4)

where, $E/R$ represents an inclination and $-\ln A$ an intercept of the Arrhenius plot.

The Arrhenius plot, namely $\ln(t)$ given by Equation (4) against the inverse of heat-accelerated-degradation temperature, when $C_s$ reaches 80% is shown in Figure 3. The lifetime at a given temperature can be estimated from the approximation in Figure 3. Here, since $C_s$ does not reach 80% at 70°C and 90°C, the time that $C_s$ reaches 80% was obtained by extrapolation.

As shown in Figure 3, the two Arrhenius equations with a different inclination in the low-temperature range (70–90°C) and the high-temperature range (90–130°C), respectively, were obtained. As for the reason for these two equations (lines), it is considered that the form of degradation and deteriorative-chemical-reaction rate of the rubber material change at a certain temperature boundary (i.e., 90°C). As for the form of degradation, it is considered that the degradation reaction is mainly propelled by oxygen in the low-temperature range, but it is mainly propelled by heat in the high-temperature range. The degradation-reaction rates can be compared in terms of activation energy.

2.2 Lifetime estimation by using Arrhenius equation

Change of $C_s$ in accordance with heat-accelerated degradation with time ($t$) is plotted in Figure 2. The Arrhenius equation for calculating the rate of a chemical reaction under a certain temperature is given as Equation (1) below, and taking the natural logarithms on both sides of Equation (1) gives Equation (2):

Figure 1. O-ring compression jig for life tests.
The O-ring is inserted in the compression jig (corresponding to an actual machine), pressurized, and evaluated.

Figure 2. Relationship between $C_s$ and $t$.
As temperature of heat-accelerated deterioration increases, the time to reach the end of the lifetime shortens.

Figure 3. Arrhenius plot for the O-ring when $C_s$ reaches 80%.
Activation energy can be calculated from the inclination of the Arrhenius plot.
in the low- and high-temperature ranges are formulated, and the activation energies listed in Table 1 are calculated from the inclinations given by each one. The two Arrhenius equations are given as Equations (5) and (6) in the low- and high-temperature ranges, respectively, as follows:

For the 70–90°C range,

\[ \ln(t) = 46.38 \times \left(\frac{10^3}{T}\right) - 115.82 \quad (5) \]

For the 90–130°C range,

\[ \ln(t) = 12.47 \times \left(\frac{10^3}{T}\right) - 22.57 \quad (6) \]

Since activation energy in the high-temperature range is lower than that in the low-temperature range, the degradation reaction proceeds more easily; in other words, the degradation-reaction rate is higher. This result confirms that the reaction rate changes at the boundary temperature of 90°C.

3. Estimation of \( C_s \) from \( T_C \) and \( t \)

As for an O-ring installed in equipment, it is often the case that it is replaced at the end of its lifetime (unless the equipment is dismantled due to incompatibility found during periodic inspection). To estimate \( C_s \) of an O-ring in the fitted condition, we have investigated a method for calculating \( C_s \) from temperature and time without dismantling the equipment. \( C_s \) is expressed as a function of \( T_C \) and \( t \) given as:

\[ C_s = b(T_c) \times t^a(T_c) \quad (7) \]

Here, \( a \) is the inclination of the approximation taken as the logarithm of \( C_s \) at various temperatures in Figure 2, and \( b \) is the intercept at time \( t = 1 \) hour. The relationships of \( a \) and \( b \) with \( T_C \) are plotted in Figure 4. The relationships between \( T_C \) and \( a \) and between \( T_C \) and \( b \) are given by Equations (8) and (9), respectively.

\[ a(T_C) = 0.43 \times \ln(T_C) - 1.73 \quad (8) \]

\[ b(T_C) = 44154 \times T_C^{-1.97} \quad (9) \]

Incorporating Equations (8) and (9) into Equation (7) gives the following expression for the relation between \( C_s \) and \( T_C \) and \( t \):

\[ C_s = (44154 \times T_C^{-1.97}) t^{0.43 \ln(T_C) - 1.73} \quad (10) \]

A graph for estimating \( C_s \) by inserting a certain time of continuous use (\( t \)) into Equation (10) is shown in Figure 5. According to the graph, \( C_s \) of a rubber subjected to 10 years (87 600 hours) of continuous use at 80°C is estimated to be about 46%. The expression relating \( C_s \) with \( T_C \) and \( t \), is considered to be an effective method for estimating \( C_s \) of an O-ring in the equipment-fitted condition without having to dismantle the equipment.

4. Assessing effect of temperature variation on \( C_s \)

Except in the case of special temperature control, a rubber material built into equipment is subjected to the effects of either daily or yearly temperature variations. Accordingly, variation in \( C_s \) in the case that the rubber material is subjected to simulated temperature variations was investigated.

First, a right circular cylinder of button rubber made of EPDM (JIS K 6262; large-sized test specimen; diameter: 29.0±0.5 mm; thickness: 12.5±0.5 mm) was compressed. The specimen was then alternatively placed into constant-temperature baths at 70°C and 130°C for 500 hours in each bath. Variation of \( C_s \) in the case that

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70–90</td>
<td>385.6</td>
</tr>
<tr>
<td>90–130</td>
<td>103.7</td>
</tr>
</tbody>
</table>

Figure 4. Changes in \( a \) and \( b \) with \( T_C \).

The log approximation of \( C_s \) gives a linear function of \( t \), and \( a \) and \( b \) are expressed by the function of \( T_C \).

Figure 5. Estimation of \( C_s \) during continuous use at 80°C. In the case of 10-year use at 80°C, \( C_s \) is estimated to be about 46%.
the specimen was subjected to the temperature variation in the manner just described is plotted in Figure 6. In the case of alternate continuous heating at 70°C and 130°C, \( C_s \) varies intermediately between the cases of continuous heating at a single temperature (70°C or 130°C).

5. Lifetime evaluation of EPDM rubber under various oxygen concentrations

The lifetime of rubber material falls remarkably according to the environment in which it is used, and in such cases, \( C_s \) can be assumed as an index representing lifetime. Accordingly, we have investigated the lifetime of EPDM button rubber under usage environments with varying oxygen concentrations.

5.1 Difference in expected lifetime due to changes in oxygen concentration

As part of the development of gas circuit breakers with lower environmental load, the lifetime of rubber material under different oxygen concentrations was evaluated. Compressed button rubber was placed in a test vessel under different oxygen concentrations. The specimen container was placed in a constant-temperature bath (set at various temperatures) for a predetermined time and subjected to heat-accelerated-aging tests. After a predetermined time under heating, the test vessel was removed from the bath, the button rubber was removed from the test vessel, and its thickness was measured. \( C_s \) was then calculated from the measured thicknesses before and after the test.

The Arrhenius plot when \( C_s \) reaches 80% under accelerated-aging heating is shown in Figure 7. When expected lifetime under continuous use at 80°C is calculated, it is clear that although expected lifetime under oxygen concentration of 20% is about thirty years, that under oxygen concentration of 30% is about three years.

In other words, when oxygen concentration is increased by 10%, expected lifetime is reduced by 90%. It is thus supposed that oxidation degradation of the rubber material is promoted by increasing oxygen concentration.

5.2 Lifetime evaluation of an alternative material

Since it was found that the lifetime of EPDM rubber falls significantly at oxygen concentration of 30%, an alternative material was selected. In consideration of a high-oxygen-concentration environment, fluoro rubber (FKM) was selected as a candidate. In the same manner as explained in Section 5.1, an FKM specimen was subjected to heat-accelerated-aging tests under oxygen concentration of 30%, and the Arrhenius plot when \( C_s \) reaches 80% under accelerated-aging heating is shown in Figure 8. It is clear from the plot that the FKM has...
higher resistance to oxidation and a longer lifetime than those of the EPDM rubber. Furthermore, if expected lifetime is taken as 30 years, although the EPDM rubber can be used at 80°C under oxygen concentration of 20%, FKM can be used in a wider temperature range (up to a maximum of 110°C) under higher oxygen concentration of 30%.

6. Conclusion

An evaluation method using Cs as an index of the performance of rubber seals used in power transmission and transformation systems was formulated and evaluated. It was confirmed that this method improves the precision of estimating expected lifetime of rubber material by long-term testing and can effectively estimate Cs of rubber as-fitted in actual equipment and selected as having resistance to the effects of temperature variation and oxidation. For evaluating long-term seal performance, although a lifetime-estimation method using the Arrhenius plot was shown to be effective, testing of a few thousand hours at least is necessary to estimate lifetime of a rubber seal.

Since rubber is a blended material composed of several ingredients, even if the same kind of rubber polymers are used, when types and content ratios of additive agents, carbon black, filler, etc. vary, initial physical properties, reaction rates, and lifetime vary greatly. Accordingly, the numerical values of the inclination and intercepts of the relational expression between Cs (taken as lifetime in this report) and temperature and time vary in accord with the type of rubber.

Starting with lifetime evaluation, we will carry out various investigations on the cause of incompatibilities and evaluations for selecting appropriate rubber materials, and we will strive to develop evaluation technologies while making efforts to further improve reliability.

References


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