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Rubber, vulcanized or thermoplastic — Estimation of life-time and maximum temperature of use

Caoutchouc vulcanisé ou thermoplastique — Estimation de la durée de vie et de la température maximale d'utilisation

Reference number
ISO 11346:2004(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11346 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This second edition cancels and replaces the first edition (ISO 11346:1997), which has been technically revised.

This corrected version of ISO 11346:2004 incorporates the following corrections:

- the text of Clause 9, which was incorrect, has been replaced by a new text;
- ISO 471, which was withdrawn in 2004, has been replaced by ISO 23529 (see Clauses 2 and 8);
- in Subclause 11.1, line 16, the sentence: “An example is given in Figure 1.” has been deleted;
- in the key to Figure 3, the words “as a fraction of initial value” have been deleted;
- in Subclause 11.2, last-but-one paragraph, the word “equation” has been inserted after WLF.

Introduction

The rate of a chemical reaction normally increases with increase in temperature. By exposing test pieces to a series of elevated temperatures, the relation between the reaction rate of degradative mechanisms and temperature can be deduced. Estimates can then be made by extrapolation of the degree of degradation after a given time at a given temperature or the time at a given temperature to reach a given degree of degradation.

The reaction rate/temperature relationship can often be represented by the Arrhenius equation. The reaction rate at any given temperature is obtained from the change in the value of a selected property with exposure time at that temperature. The reaction rate can be represented by the time to a particular degree of degradation (threshold value) and this may be the only measure to use if the property/temperature relation is complex.

The Arrhenius approach is only suitable for chemical degradation reactions and may give wrong results for tests where physical (viscoelastic) changes cannot easily be separated from chemical changes.

An alternative approach for rubbers is to use the Williams Landel Ferry (WLF) equation. This equation performs a time/temperature transformation and no assumptions are made as to the form of the property/time relation at any temperature. Hence, in principle, it can be applied to any physical property, including set and relaxation, or where the property/time relation is complex. Further explanation of the use of the WLF equation can be found in the literature [1].

During the preparation of this International Standard, account was taken of the contents of ISO 2578 [2] and IEC 60216 [3].

Rubber, vulcanized or thermoplastic — Estimation of life-time and maximum temperature of use

1 Scope

This International Standard specifies the principles and procedures for estimating the thermal endurance of rubbers from the results of exposure to elevated temperatures for long periods.

Two approaches are specified (see also the Introduction):

- one using the Arrhenius relation;
- the other using the WLF equation.

In this document, the estimation of thermal endurance is based solely on the change in selected properties resulting from periods of exposure to elevated temperatures. The various properties of rubbers change at different rates on thermal ageing, hence comparisons between different rubbers can only be made using the same properties.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 188:1998, *Rubber, vulcanized or thermoplastic — Accelerated ageing and heat resistance tests*

ISO 23529:2004, *Rubber — General procedures for preparing and conditioning test pieces for physical test methods*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
life-time
time at which the material under test has reached the specified threshold value for the property tested at the temperature of use

3.2
maximum temperature of use
temperature at which the material under test has reached the specified threshold value for the property tested after the specified time

3.3
threshold value
particular degree of degradation which is taken as the maximum acceptable for the property being tested

NOTE The time to reach the threshold value can be used to represent the reaction rate.

4 Principle

At a chosen test temperature, the variations in the numerical value of a chosen property, for example a mechanical or viscoelastic property, are determined as a function of time.

The testing is continued until the relevant threshold value of that property has been exceeded.

Further tests are carried out at at least two other temperatures.

For the Arrhenius procedure, the measures of the reaction rates obtained are plotted logarithmically as a function of the reciprocal of temperature and the straight line obtained is extrapolated back or interpolated to the temperature of use.

For the WLF procedure, the shift constants are calculated and used to transpose the property/time relation to the temperature of use.

5 Selection of tests and ageing oven

The tests chosen should preferably relate to properties which are likely to be of significance in practice. Wherever possible, use shall be made of methods of test specified in International Standards.

For general evaluations, hardness and tensile stress-strain properties are commonly used, but stress relaxation or set in compression, for example, is desirable for sealing applications.

For the ageing of test pieces, a circulating-air oven meeting the requirements of ISO 188 shall be used.

6 Selection of threshold value

The threshold value shall be chosen as the degree of degradation that is the maximum acceptable for the property being tested and the end use. Commonly, 50 % of the initial value of the property is chosen.

NOTE The test should normally be continued for a long enough period for the threshold value to be reached. Although it is possible to extrapolate to greater degrees of degradation, this is not recommended.

7 Test pieces

7.1 The dimensions and method of preparation of the test pieces shall be in accordance with the relevant test method standard.

7.2 The minimum total number, n, of test pieces required for a destructive test method depends on:

- the number of test pieces, a, required for a single test in accordance with the test method standard;
- the number of different ageing periods, b, necessary to obtain the property/time relationship at any one exposure temperature;
- the number of exposure temperatures, c.

The minimum number of test pieces required is given by:

$$n = abc + a$$

It is recommended that additional test pieces are aged at each temperature in case problems occur after several weeks, months or years of ageing or an extra exposure temperature is required to improve precision.

The minimum number of test pieces required for a non-destructive test method is normally given by:

$$n = ac$$

When measuring compression set, tension set and relaxation, the tests are preferably done on the same test pieces, at the different times, to reduce the number of test pieces needed. This also reduces variations in the test results.

It may be necessary, in addition, to carry out trial runs to determine the exposure temperatures and the number of test points required at each temperature.

NOTE Whilst it is possible to reduce the number of test pieces for each test from that given in the test method standard to economize on testing, extrapolation of the results requires the best possible precision and in some circumstances it may be advisable to increase the number of test pieces.

8 Exposure temperatures

Selection of the exposure temperatures involves knowing beforehand the approximate ageing characteristics of the material under test. With no previous knowledge of the material, exploratory tests will have to be carried out. This information will assist in selecting the exposure temperatures best suited for the evaluation of the material.

Test pieces shall be aged at not fewer than three temperatures covering a range adequate to establish the life-time estimation by extrapolation with the required degree of accuracy. The lowest exposure temperature shall be chosen so that the time taken to reach the threshold value is at least 1 000 h. Likewise, the highest temperature shall be chosen so that the time taken to reach the threshold value is not shorter than 100 h. The temperatures used should preferably be standard test temperatures taken from ISO 23529.

NOTE To obtain an estimate of the life-time with adequate precision will often require more than three test temperatures.

9 Exposure times

The properties chosen to measure the reaction rate shall be tested after each of at least five different exposure times at each temperature, but more exposure times will normally be needed if the shape of the property/time curve is to be established.

The exposure times shall be such as to enable the property chosen to measure the reaction rate to be characterized adequately. For thermo-oxidative ageing, a linear progression will be satisfactory in many cases. For physical relaxation, a logarithmic progression would be more appropriate. The requirements concerning minimum exposure times in Clause 8 shall be respected.

10 Procedure

Measure the selected properties using unaged sets of test pieces conditioned as required by the relevant test method standards.

Place the required number of test pieces in each of the ovens maintained at the selected temperatures.

At the end of each exposure time, condition the test pieces to be examined as required by the relevant test method standard and measure the selected properties.

Continue this procedure until the required number of sets of test pieces have been tested.

11 Expression of results

11.1 Arrhenius procedure

The Arrhenius relation can be written as:

$$\ln K(T) = B - \frac{E}{RT}$$

where

$K(T)$ is the reaction rate (min^{-1});

B is a constant;

E is the activation energy (J/mol);

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

T is the absolute temperature (K).

The stage the reaction has reached is given by the relation:

$$F_x(t) = K(T) \times t$$

where

$F_x(t)$ is a function describing the stage, x, the reaction has reached;

t is the reaction time (min).

There will be different reaction rates, $K(T)$, corresponding to different temperatures, T.

For each exposure temperature, plot the results for each property against time. For each plot, determine the reaction rate.

Often, a convenient measure of the reaction rate is the time for the property to reach the threshold value, determined by interpolation as illustrated in Figure 1.

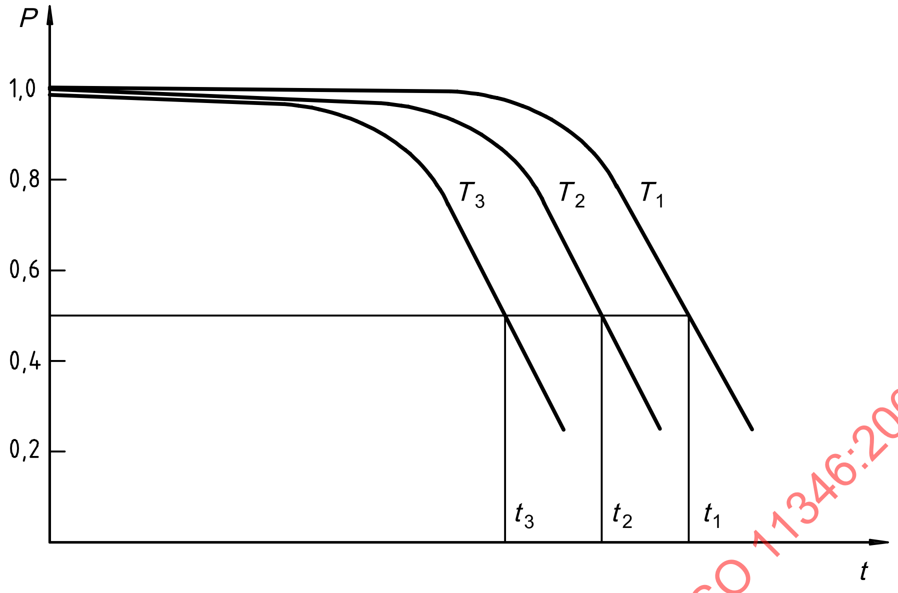
NOTE The ideal measure of the reaction rate would be the slope of the property-time plot, but this is rarely linear [i.e. $F_x(t)$ is rarely linear]. It may be possible to fit a convenient relationship to the data or to obtain a convenient plot by plotting on a logarithmic scale.

Plot the logarithm of the reaction rate (e.g. time to threshold value) against the reciprocal of the absolute temperature and construct a best-fit straight line through the points by established statistical methods. An example is given in Figure 2. If the data deviates from a straight line, this indicates that different reactions are taking place at the different temperatures and extrapolation of the data is invalid.

The life-time is estimated by extrapolation of the line to the temperature of use. The reaction rate at that temperature will give the time to reach the threshold value.

The maximum temperature of use is estimated by extrapolation of the line to a specified reaction rate or time to reach the threshold value. A time of 20 000 h is commonly used when establishing a general maximum temperature of use.

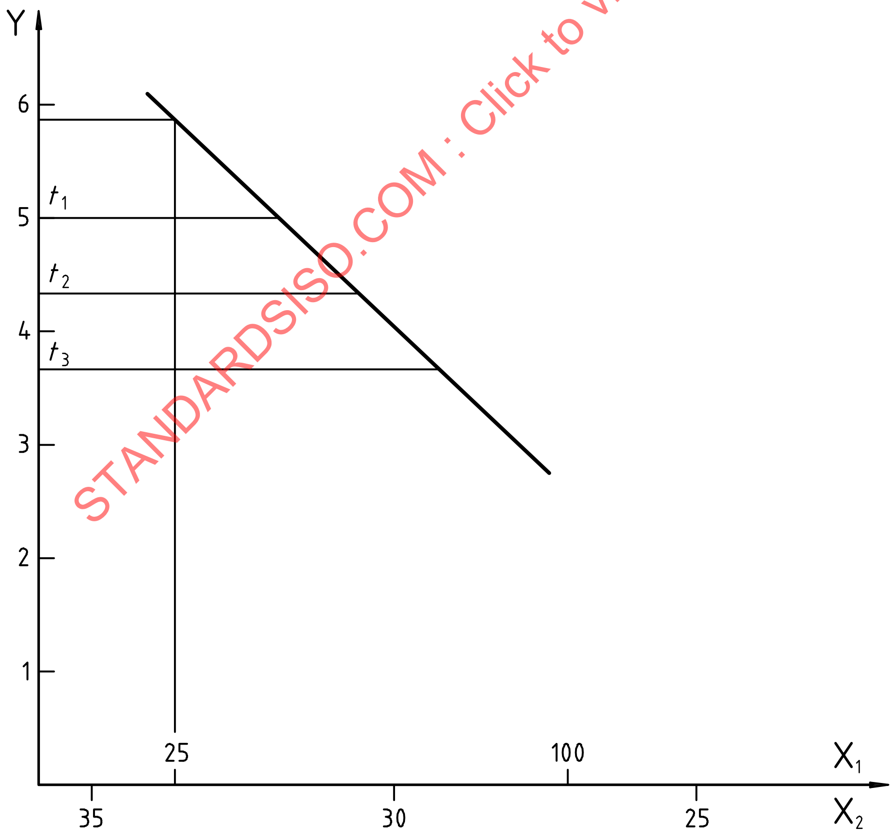
The activation energy is obtained by dividing the slope of the line by R, the gas constant.



Key

P	value of property (as a fraction of initial value)
t	time
T	temperature

Figure 1 — Change in property against time



Key

X_1	temperature, T (°C)
X_2	$\frac{1}{T} \times 10^4$ (T in kelvins)
Y	time, t

Figure 2 — Arrhenius plot (time against temperature)

11.2 WLF procedure

The WLF equation that is generally used is:

$$\log a_T = \frac{-a(T-T_0)}{b+(T-T_0)}$$

where

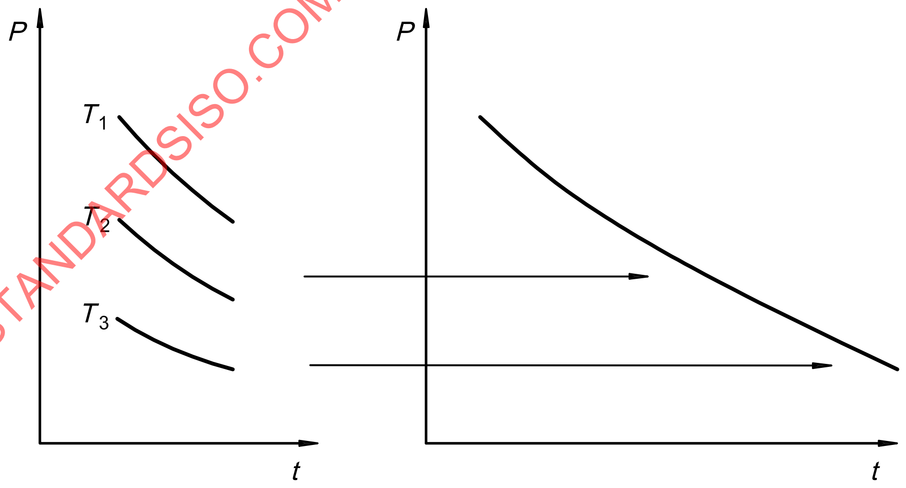
a_T	is a so-called shift factor (see below);
a and b	are constants which depend only on the material;
T_0	is the reference temperature used to create the shift values.

For each exposure temperature, plot the results for each property as a function of time. Typically, a log(time) x-axis is used.

Taking the reference temperature as fixed, slide the lines corresponding to each of the other temperatures in turn horizontally in the x-direction until the best possible overlap with the line at the reference temperature is obtained (see Figure 3). In this way, a "master curve" is constructed, at the reference temperature, which simulates how the material would behave over a much wider time scale than can be investigated by direct experimentation. The amount by which each line at a non-reference temperature is moved (movement in the positive direction is movement towards longer times and movement in the negative direction is movement towards shorter times) is the shift factor, a_T (or, if the x-axis is a logarithmic scale, the log of the shift factor). By definition, when $T = T_0$, $\log a_T = 0$, and there is no shift.

Plot the value of $\log a_T$ for each temperature against the corresponding temperature as shown in Figure 4 (sometimes absolute temperature is used, although mathematically this is unnecessary since the temperatures are in fact temperature differences).

Use standard curve-fitting techniques to determine the best fit for the WLF equation to give values of the constants a and b.



Key

P	value of property
t	time
T	temperature

Figure 3 — Construction of a "master curve"