INTERNATIONAL STANDARD

ISO 6914

Second edition
2004-04-01

Rubber, vulcanized or thermoplastic — Determination of ageing characteristics by measurement of stress relaxation

Caoutchouc vulcanisé ou thermoplastique — Détermination des caractéristiques de vieillissement par mesurage de la contrainte de relaxation

Reference number
ISO 6914:2004(E)

Contents

Page

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 6914 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses*.

This second edition cancels and replaces the first edition (ISO 6914:1985), which has been technically revised.

Introduction

The stress in a rubber test piece at a given elongation changes with time as a result of a combination of simultaneous physical and chemical processes. Chemical processes predominate in the case of thin test pieces exposed to an atmosphere containing oxygen at an elevated temperature for relatively long periods of time. Thus, the ageing characteristics of the rubber may be determined by measurement of the change of stress in a thin test piece deformed in tension after periods of exposure under such conditions.

There are two variants of the technique. Measurements of stress may be made under either

a) continuous strain conditions;

or

b) intermittent strain conditions.

In the case of a), continuous strain conditions, the test piece is held in extension throughout the ageing period in the oven. In the case of b), intermittent strain conditions, the test piece is aged in the oven in the unstressed state, but, at periodic intervals, it is stretched to a fixed extended length for a short time in order to determine the stress. Hence, this latter method is a measure of the change in modulus as a function of time.

NOTE 1 The terms "continuous stress relaxation" and "intermittent stress relaxation" are commonly used to describe the two principal variants of the technique. The latter term, "intermittent stress relaxation", is a misnomer since no true relaxation of stress occurs and indeed the measured stress may increase with time. For this reason, the use of this term has been avoided in this document although it is fairly well established in the literature.

In a second version of the intermittent test, the test piece is periodically removed from the accelerated ageing atmosphere and the stress is measured under normal laboratory conditions. The advantage of this method is that it does not require the use of special apparatus since a conventional tensile testing machine can be used for the measurement of stress.

Measurements made in accordance with the methods described in this International Standard provide information about the structural changes that occur in the rubber during ageing.

Under continuous strain conditions, provided physical relaxation processes are not dominant, the decay of stress provides a measure of the degradative scission reactions in the network. Any new networks formed as a result of crosslinking reactions are considered to be in equilibrium at the test strain with the main network and therefore do not impose any new stresses.

NOTE 2 Even under conditions conducive to chemical processes, some physical relaxation may occur. The extent to which it does so will depend on the viscoelastic characteristics of the rubber and on the test conditions and care must be exercised in the interpretation of the results. Physical relaxation is increased by fillers and will be more evident at short times and at lower temperatures. It is often found to be proportional to logarithmic time and is less temperature sensitive than chemical relaxation.

Under intermittent strain conditions, the decay of stress provides a measure of the net effect of both degradative scission and crosslinking reactions.

The validity of the methods described in this International Standard depends on the uniformity of degradation in the rubber. For this reason, the thickness of the test pieces used is 1,0 mm to minimize the effect of oxygen diffusion on ageing.

The change in stress may be of direct interest, but the relative resistance of rubbers to ageing will depend on the properties being measured or required by the application. This International Standard should therefore be regarded as complementary to ISO 188.

In addition, a distinction should be made between this test and the stress relaxation in compression tests as specified in ISO 3384, *Rubber, vulcanized or thermoplastic — Determination of stress relaxation in compression at ambient and at elevated temperatures*, which is primarily intended for the testing of rubbers in applications, for example as seals, where resistance to stress relaxation is a functional property.

The lifetime of the material, if this is to be investigated, can be determined using the procedures described in ISO 11346.

The most important factor in achieving good repeatability and reproducibility when making these tests is to keep the temperature and the elongation constant during all measurements.

Rubber, vulcanized or thermoplastic — Determination of ageing characteristics by measurement of stress relaxation

1 Scope

This International Standard describes three methods for the measurement of the change of stress in a test piece at a given elongation for the purpose of determining the ageing characteristics of the rubber vulcanizate.

— Method A is intended for measurement under continuous strain conditions.

— Method B is the preferred method for measurement under intermittent strain conditions.

In the case of both methods A and B, a stress relaxometer is used to record the stress at the temperature of ageing.

— Method C is an alternative to method B for measurement under intermittent strain conditions in which the test piece is removed from the ageing environment for measurement of the stress at the standard laboratory temperature.

The necessary calibration schedule for this type of measurement is given in Annex A.

Measurements at a single elevated ageing temperature may be used for quality control purposes as a measure of heat-ageing resistance. Measurements at a number of temperatures may be used for research and development purposes to estimate long-term ageing characteristics in accordance with the procedures described in ISO 11346.

No agreement between the three methods should be inferred. The method used will depend on the purpose of the test.

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 471:1995, *Rubber — Temperatures, humidities and times for conditioning and testing*

ISO 5893:2002, *Rubber and plastics test equipment — Tensile, flexural and compression types (constant rate of traverse) — Specification*

ISO 18899:—[1)], *Rubber — Guide to the calibration of test equipment*

3 Apparatus

3.1 Stress relaxometer (for method A or B), consisting of two grips which hold the test piece without slipping at a fixed extended length (to within ± 1 %) together with a means of measuring and recording the force on the test piece.

1) To be published.

The grips shall be arranged such that the test piece can be positioned in an oven. The force measuring system may be, for example, a calibrated spring or electronic load cell, but it shall be accurate and stable to within $\pm$ 1 % of the force reading throughout the duration of the test.

For method B, the stress relaxometer shall, in addition, be equipped with a device such that the test piece can be extended and relaxed at intervals. Repeated extension of the test piece shall be constant to within $\pm$ 1 % of the elongation.

3.2 Tensile testing machine (for method C), using a constant rate of traverse, operating at 50 mm/min and complying with the requirements specified in ISO 5893, force class 1 (measuring force to within $\pm$ 1 % of the measured value).

The machine shall be capable of cycling between fixed strain limits which are accurate to within $\pm$ 1 % of the maximum strain. The grips of the tensile testing machine shall hold the test piece without slippage.

3.3 Oven, complying with the requirements specified for ISO 188:1998, method A (low air speed) or method B (high air speed), for ageing the test piece.

4 Test pieces

4.1 Dimensions

Test pieces shall be parallel-sided strips, cut from a sheet. For the tests described in this International Standard, it is vital to ensure uniform degradation in the rubber. For this reason, the thickness of the test pieces shall be (1,0 $\pm$ 0,05) mm in order to minimize the effect of oxygen diffusion on ageing.

Samples of uniform thickness of less than 1,0 mm, or more than 1,0 mm, may be used, but these may give different results.

The other dimensions of the test pieces, i.e. width and length, shall be chosen to suit the sensitivity of the load-measuring device and the precision of the mechanism used for adjusting the strain, in order that the requirements of 3.1 and 3.2 relating to the accuracy of the force and the strain are satisfied.

4.2 Number

The preferred number of test pieces is three for each test temperature, but for routine and screening tests one or two test pieces are acceptable.

5 Storage and conditioning

The time interval between vulcanization and testing shall be in accordance with ISO 471.

Material and test pieces shall be protected from light as much as possible during the interval between vulcanization and testing. They shall not be allowed to come into contact with test sheets and test pieces of a different composition. This is necessary in order to prevent additives which may affect ageing, such as antioxidants, from migrating from one vulcanizate into other vulcanizates.

Test pieces shall be conditioned for a minimum of 3 h at one of the standard laboratory temperatures as specified in ISO 471 immediately before testing.

6 Test conditions

6.1 Duration of test

The duration of test should preferably be chosen from the following series:

1 h, 2 h, 4 h, 8 h, 24 h, 72 h and 168 h and multiples of 7 d.

For methods A and B, the test period shall be considered to commence when the initial force measurement is made. For method C, the test period shall be considered to be the time in the oven, excluding the time for cooling and the measurement of force.

Alternatively, the test may be stopped when the stress indicator, expressed as the ratio of the force, F_t, at time t to the initial force, F_0 (see Clause 8), reaches a predetermined value (e.g. 0,5).

6.2 Temperature of exposure

The material being tested shall preferably be examined at a series of temperatures at intervals of at least 10 °C. If the test pieces are exposed at only one temperature, this shall be chosen from the following series of temperatures as listed in ISO 471:1995:

standard laboratory temperature (23 °C or 27 °C) or 40 °C, 55 °C, 70 °C, 85 °C, 100 °C, 125 °C, 150 °C, 175 °C, 200 °C, 225 °C, 250 °C, 275 °C, or 300 °C.

The temperature shall be kept as constant as possible during the test, with a tolerance of $\pm$ 1 °C for all elevated temperatures and $\pm$ 2 °C for standard laboratory temperature.

A stable and correct temperature is very important during the test for two reasons.

— First, a temperature deviation of e.g. 1 °C can correspond to about 10 % of the test time.

— Second, the volume expansion of the rubber is 10 to 20 times greater than that of steel, and a temperature variation will cause a variation in the force reading.

As the temperature is increased, the exposure time may need to be reduced. Further, it should be recognized that greater the disparity between the ageing and the service conditions, the less reliable is the correlation between the ageing and the service life.

7 Procedure

7.1 Method A

Method A is carried out in the following manner.

a) Mount the test piece in the preheated grips in the unstrained condition.

b) Position the grips and test piece in the oven preheated to the test temperature.

c) After $(5 \pm 0{,}5)$ min, stretch the test piece, in not more than 1 min, to an elongation between 45 % and 55 % and hold it to within 1 % of that elongation. [A smaller elongation of (20 ± 2) % may also be used in place of (50 ± 5) %.] The initial force, F_0, is taken to be that $(5 \pm 0{,}5)$ min after stretching the test piece.

d) Record the force, F_t, on the test piece as a function of time for the duration of the test.

e) At the end of the test, examine the surfaces of the stretched test piece for signs of cracking using a lens with about 7 times magnification. If cracking is found, it shall be reported in the test report.

With certain types of rubber, stress relaxation additional to that caused by oxygen and heat can occur as a result of surface attack by traces of atmospheric ozone. Cracking may invalidate the test and be the cause of variations between measurements.

