INTERNATIONAL STANDARD

ISO 12493

Third edition
2023-01

Rubber, vulcanized or thermoplastic — Determination of stress in tension under non-isothermal conditions

Caoutchouc vulcanisé ou thermoplastique — Détermination de la contrainte en traction dans des conditions non isothermes

Reference number
ISO 12493:2023(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This third edition cancels and replaces the second edition (ISO 12493:2017), which has been technically revised.

The main changes are as follows:

- another method (method B) for measuring tensile stress under non-isothermal conditions has been added. In this method, the change of stress is measured at a given strain and under variation of temperature at a given heating rate as a function of temperature.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Usually, stress relaxation tests (see ISO 6914) are performed at constant temperature conditions because temperature has a strong impact on the relaxation time constants of rubber materials. Depending on the respective relaxation time constant or, more realistic, relaxation time spectrum, those measurements are more or less time consuming and can require testing times of several days, weeks or even months. Accelerated stress relaxation tests can be performed under non-isothermal conditions, if the temperature is increased at a certain constant heating rate, because relaxation processes are thermally activated and therefore occur faster at higher temperatures. Thus, the entire stress relaxation behaviour of the material can be scanned within a short period of time, typically a few hours. This method is designated as the temperature scanning stress relaxation (TSSR) test method and offers the ability to characterize rubber — vulcanized or thermoplastic — by short-term measurements. TSSR tests cannot replace conventional isothermal stress relaxation measurements, but are considered as a comparative test method, e.g. for the purpose of material pre-selection or in order to determine the state of crosslink density — which is an important reason for ageing phenomena — of a sample.

During non-isothermal testing, the material undergoes not only stress relaxation, but additional phenomena occur which need to be considered by adequate corrections. Most important in this case is an increase of retractive forces due to the Gough-Joule effect and thermal expansion of the sample. Whereas the latter can be numerically compensated by considering a proper value of the coefficient of thermal expansion (CTE), the increase of retractive forces offer the opportunity to calculate the crosslink density of the material, based on fundamental theory of rubber elasticity. Furthermore, an enhanced sensitivity of the test, with respect to specific relaxation processes is achieved by determination of the first derivative of the measured stress–temperature curve. Similar to stress relaxation measurements in the time domain, the latter can be used to calculate a corresponding relaxation temperature spectrum, instead of a relaxation time spectrum.

Rubber, vulcanized or thermoplastic — Determination of stress in tension under non-isothermal conditions

WARNING 1 — Users of this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of users to establish appropriate safety and health practices and determine the applicability of any other restrictions.

WARNING 2 — Certain procedures specified in this document can involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This document describes two methods for measuring stress in tension under non-isothermal conditions.

- Method A: The thermal stress is measured for various pre-strain and temperature conditions as a function of time.
- Method B: The change of stress is measured in a test piece at a given strain and under variation of temperature at a given heating rate as a function of temperature. In this way, the determination of the thermal-mechanical behaviour of a rubber can be accelerated, e.g. for the purpose of comparative testing of aging or estimating the upper limit of the operating temperature.

The measurement device, which is equipped with a suitable heating chamber, is used to record the stress as a function of time or temperature until the sample breaks or the stress has approached zero or for a certain time.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 188:2011, *Rubber, vulcanized or thermoplastic — Accelerated ageing and heat resistance tests*

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

ISO 18899:2013, *Rubber — Guide to the calibration of test equipment*

ISO 23529, *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.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.1
thermal stress

σ_T

force per initial unit area that is developed in the test piece upon heating

Note 1 to entry: It is expressed in N/m^2 or Pa.

3.2
maximum thermal stress

$\sigma_{T,max}$

peak value of the thermal stress recorded during the test

3.3
thermal stress after a specified time

$\sigma_{T,t}$

stress induced in the test piece upon heating for a specified time t

3.4
pre-strain

strain to which the test piece is subjected at the beginning of the test

Note 1 to entry: It is expressed as:

$$\frac{l_f - l_i}{l_i} * 100$$

where

l_i is the initial length;

l_f is the length after strain.

3.5
pre-stress

force per initial unit area that results from the pre-strain

Note 1 to entry: It is expressed in N/m^2 or Pa.

4 Principle

A test piece is held at a constant pre-strain in a tensile mode at a constant temperature. When the pre-stress resulting from the given pre-strain has reached an apparent equilibrium value, the temperature of the test piece is increased. In method A, the test temperature is reached as quickly as possible, in method B, heating is carried out at a constant rate. The thermal stress developed at the elevated temperature is measured.

5 Apparatus

5.1 Test machine

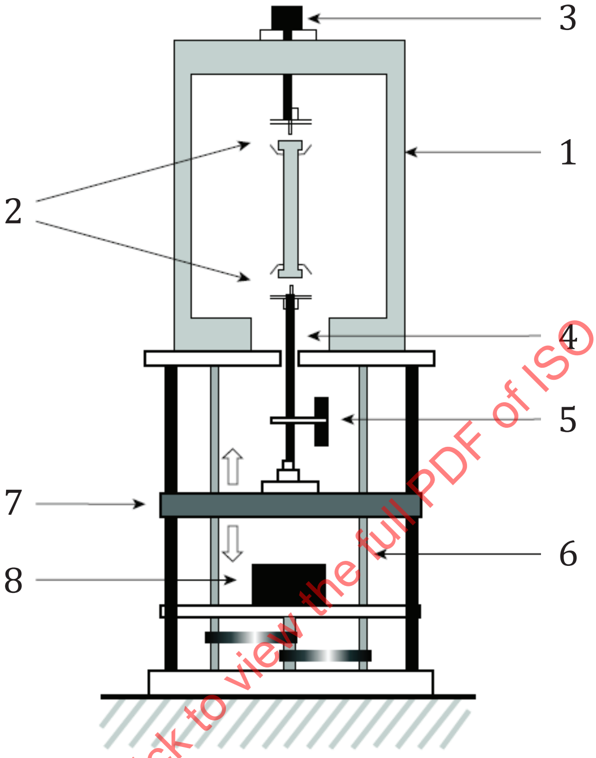
5.1.1 General

The setup of the measuring devices can be done in different ways. Two possibilities are described below.

5.1.2 Thermal-stress testing machine

An example of a test machine for measuring the thermal stress developed in rubbery materials when heated is shown in Figure 1. Two clamps hold the test piece in a temperature-controlled chamber, with the upper clamp connected to a load cell and the bottom clamp connected to a crosshead. The crosshead is moved using a screw driven by a motor to impose a pre-strain on the test piece. The thermal stress developed when the temperature is raised is transmitted to the load cell and the output is recorded to give the variation in stress as a function of time.

The test machine shall be in accordance with ISO 5893 with force measurement to class 1 and the machine shall be capable of setting the pre-strain to within ±0,1 at a speed of (20 ± 2,5) mm/min.



Key

1	temperature-controlled chamber
2	clamps
3	load cell
4	rod
5	linear variable differential transformer
6	screw
7	crosshead
8	motor

Figure 1 — Example of thermal-stress testing machine

The temperature-controlled chamber shall be capable of raising the temperature at a rate of at least 30 K/min and maintaining the test piece at the required temperature as specified in ISO 23529. A suitable volume for the chamber is 3 l to 5 l. A temperature-sensing device shall be located within the chamber near the test piece.

Load cell and crosshead shall be in accordance with ISO 18899:2013.

5.1.3 Stress relaxometer

Another example of a test machine consists of an electrically driven linear actuator equipped with 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.

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 ±1 % of the force reading throughout the duration of the test.

The force measuring system and strain measuring system shall be in accordance with the requirements specified for ISO 18899:2013.

5.2 Oven

The oven shall be in accordance with ISO 188:2011, cell-type oven, for testing of a single test piece. For the heating chamber, other shapes than cylindrical are acceptable.

5.3 Thickness- and width-measuring devices

Instruments for measuring the thickness and width of the test piece shall be in accordance with ISO 23529.

6 Calibration

The test apparatus shall be calibrated in accordance with the schedule given in Annex A.

7 Test piece

7.1 Dimensions

7.1.1 Method A:

The test piece shall be prepared by cutting from moulded flat sheet and shall have the shape and dimensions shown in Figure 2. In addition, the thickness shall be (2 ± 0,2) mm. The test piece shall have a smooth surface and be free from irregularities.

Dimensions in millimetres

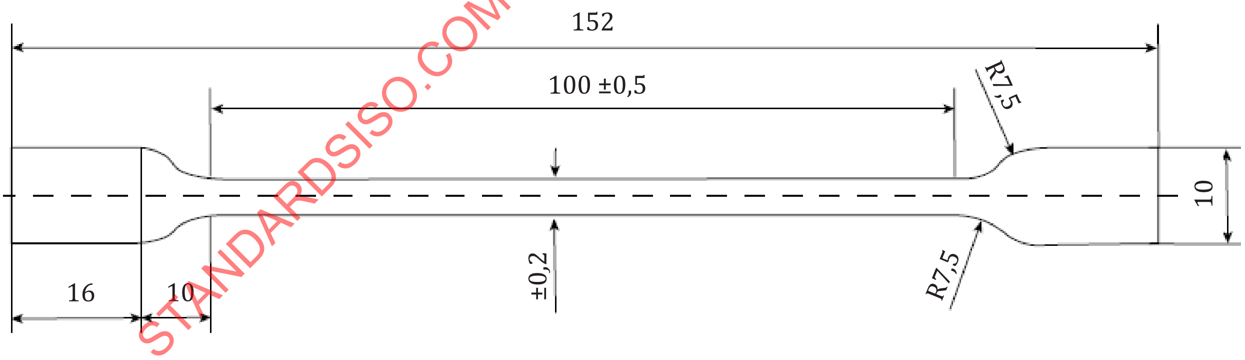


Figure 2 — Test piece for thermal-stress measurements

7.1.2 Method B:

Wherever possible, the test specimens shall be dumb-bell-shaped, e.g. types 2 or 4 in accordance with ISO 37:2017. The test piece shall be prepared by cutting from moulded flat sheet. In addition, the thickness shall be (2 ± 0,2) mm. The test piece shall have a smooth surface and be free from irregularities. For certain applications, both smaller and larger samples can be used.

7.2 Number of test pieces

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

7.3 Time lapse between moulding and testing

The time interval between vulcanization and testing shall be in accordance with ISO 23529.

7.4 Conditioning

Test pieces shall be protected from light as completely as possible during the interval between vulcanization and testing.

Test pieces shall be conditioned at a standard laboratory temperature for at least 3 h immediately before being measured and tested.

If the test is to be carried out at a starting temperature other than a standard laboratory temperature, the test pieces shall be conditioned at the test temperature immediately prior to testing for a period sufficient to ensure that they have reached the test temperature (see ISO 23529).

If materials are tested, which need a relaxation process after sample manufacturing (e.g. injection molding for thermoplastic elastomers), a tempering process of 2 h at 80 °C is recommended to reduce the variation of the measurement results.

8 Test conditions

8.1 Heating rate and temperature interval under investigation

Method A: The elevated temperatures shall be selected from those specified in ISO 23529 unless otherwise necessary for technical reasons. Recommended test temperatures are 60 °C, 100 °C and 140 °C.

Method B: The duration of test depends on the heating rate and on the temperature interval under investigation. Preferably, a heating rate of 2 K/min shall be applied, if appropriate. The temperature interval under investigation shall be adapted to the decay of the stress.

The test shall be stopped at sample rupture or when the stress approaches zero. Alternatively, the test can be stopped when the stress indicator, expressed as the ratio of the force, F_t, at time t to the initial force, F_0, reaches a predetermined value (e.g. 0,5).

During the entire test, the force shall be monitored as a function of temperature, where the data acquisition rate shall be sufficiently high. For tests performed with a heating rate of 2 K/min, the data acquisition rate shall have a value of at least 1 data point per second. In case of other heating rates, data acquisition rate shall be adapted appropriately.

8.2 Strain of the sample

Method A: A minimum of three pre-strains at each temperature shall be selected. Recommended pre-strains are 20 %, 40 % and 60 %.

Method B: Preferably, a strain of 50 % should be applied to the sample. Alternatively, in case of filled vulcanizates, a strain of 100 % might be more appropriate in order to reduce the influence of filler–filler interactions. The strain ε_t is defined as the percentage difference of the distance L between the clamps in the final position, and the distance of the clamps L_0 in initial position, with reference to the distance L_0. Other strain values are acceptable, if appropriate. For instance, in case of samples of very high hardness or low value of ultimate strain, lower strain values are recommended.

Note that due to thermal expansion of the material, the initial length L_0 of the sample increases if a temperature scan is performed starting at initial temperature T_0 up to higher temperatures T. In consequence, the thermal expansion of the sample leads to a decrease of strain, and thus contributes to a decrease of stress, independently of the (true) stress relaxation of the sample. The thermally induced variation of strain during a non-isothermal TSSR (temperature scanning stress relaxation) test can be given by Formula (1):

$$\varepsilon_t(T)=\frac{L}{L_0(1+\alpha\cdot(T-T_0))}-1 \quad (1)$$

where

L_0 is the initial distance at temperature T_0;

L Is the final distance of the sample holders at temperature T_0;

α is the coefficient of linear thermal expansion of the sample. For rubber, typical values for α are in the range of 1 to 3 x 10^{-4} K^{-1}[4].

To minimize the influence of thermal expansion, TSSR experiments is not performed at strains below 50 %. The initial length of the sample is the free length of the parallel part of the dumbbell test piece. Because of the form-fitting connection between sample and sample holder, the initial distance of the clamps (sample holders) and the free length of the parallel part of the dumbbell test piece are identical.

9 Procedure

9.1 Method A

Mount a test piece in the clamps at a standard laboratory temperature and elongate it to the required pre-strain by movement of the crosshead at a speed of (20 ± 2,5) mm/min, as shown in Figure 3. Hold the test piece at the constant pre-strain until the pre-stress resulting from the pre-strain reaches an apparent equilibrium value. This will be after about 30 min. Then, reset the load cell to zero and increase the temperature to the required test temperature. Start recording the thermal stress immediately after the heating begins (designated as zero time). Monitor the development and decay of the thermal stress as a function of time. The minimum duration of the test shall be 30 min.

Unless otherwise specified, carry out the test to obtain results at a minimum of three temperatures, with three pre-strains at each temperature.

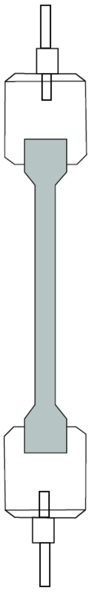


Figure 3 — Schematic diagram of a test piece with clamps at a constant pre-strain

9.2 Method B

9.2.1 Isothermal test period

Short-term relaxation processes lead instantly to a more or less strong decay of stress after a rubber sample has been elongated to a certain strain. At room temperature, the time constants of the majority of relaxation processes are very high. Consequently, the instantaneously stress decay is limited and the sample reaches a quasi-equilibrium state within a period of some hours. Therefore, the isothermal test period is used for conditioning the sample before the non-isothermal test (temperature scan) is started. The test is carried out in the following manner.

a) Mount the test piece in the sample holder in the unstrained condition.

b) After inserting the test piece stretch the test piece to a strain within 1 % of the preferred strain of 50 %. The final strain shall be reached within 1 min. A smaller strain can be used, for instance in the case of rupture of the test pieces, when (20 ± 1) % is preferred. The initial force, F_0, is taken to be that (5 ± 0,5) min after stretching the test piece.

c) Record the force, F_t, on the test piece as a function of time for the duration of the test, preferably 2 h.

NOTE If the isothermal test period is less than 2 h, the decay of stress due to short-term relaxation processes can have a strong influence on the results of the subsequently performed non-isothermal test. Therefore, test results are only comparable if the tests were performed with equal duration of the isothermal test period.

9.2.2 Non-isothermal test period (TSSR, temperature scanning stress relaxation test)

Immediately after the isothermal test period has been completed, the non-isothermal test period is started in the following manner.

a) Record the initial force, $F_{0,\mathrm{N}}$.

b) Increase the temperature of the oven with a constant heating rate of (2 ± 0,05) K/min. If required, other heating rates are acceptable.

NOTE The heating rate has an influence on the results of the non-isothermal test period. Results, which were obtained with different heating rates, are not comparable.

c) Stop the test at sample rupture, when the force approached zero or when the force ratio $F_{t,\mathrm{N}}/F_{0,\mathrm{N}}$ reaches a predetermined value (e.g. 0,5 or 0,1).

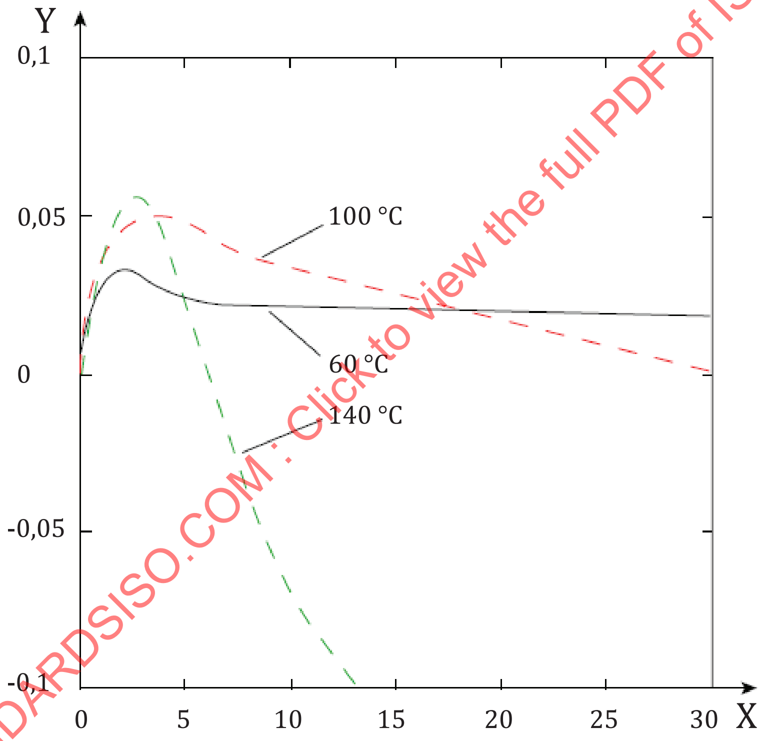
d) Record the force, $F_{t,\mathrm{N}}$ on the test piece, and the temperature T, measured by means of a sensor placed close to the surface of the sample, as a function of time for the duration of the test. The sampling rate of the data acquisition should be one data point per second of each quantity in case of a heating rate of 2 K/min. In other cases, the sampling rate shall be adapted accordingly.

10 Evaluation of the data and expression of results

10.1 Method A

Plot the thermal stress in the test piece as a function of time. From the graph, obtain the maximum thermal stress, the time to reach the maximum thermal stress, and the thermal stress at a specified time, which shall be taken as 20 min unless otherwise specified.

An example of the thermal stress of an unfilled natural rubber (NR) vulcanizate at a pre-strain of 40 % is shown in Figure 4 as a function of time at three different temperatures.



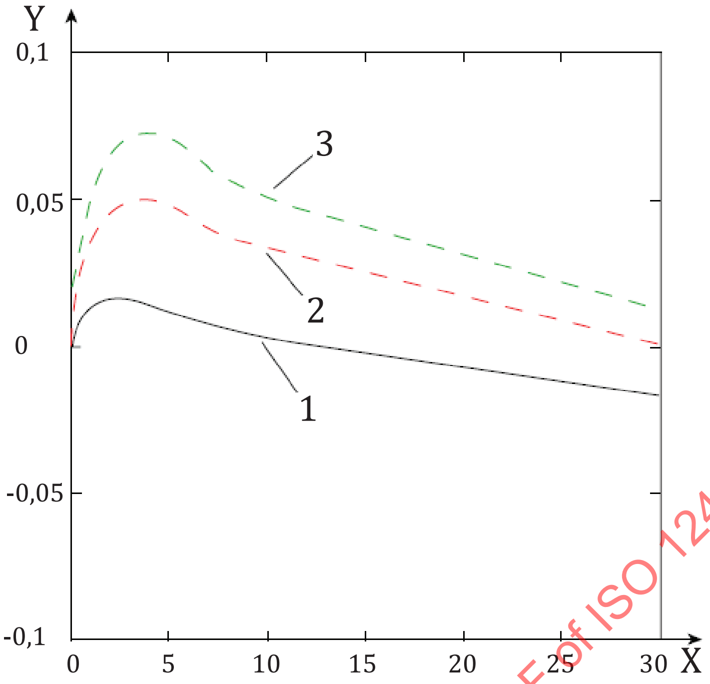
Key

X t, min

Y σ_{T}, MPa

Figure 4 — Thermal stress at various temperatures of an unfilled NR vulcanizate at a pre-strain of 40 %

Another example of the thermal stress of an unfilled NR vulcanizate at a test temperature of 100 °C is shown in Figure 4 as a function of time at three different pre-strains.



Key

X t, min

Y σ_T, MPa

1 pre-strain 20 %

2 pre-strain 40 %

3 pre-strain 60 %

Figure 5 — Thermal stress at various pre-strains of an unfilled NR vulcanizate at a test temperature of 100 °C

10.2 Method B

If desired, the data of the isothermal test period may be evaluated in accordance with ISO 6914:2013, Clause 8. Otherwise, only the data acquired during the non-isothermal test period are subject of evaluation.

The tensile stress, σ_T, at a specified temperature, T, of testing is expressed as the ratio of the measured force, $F_{t,N}$, at the corresponding temperature and the cross section, A_0, of the sample in the unloaded initial state.

The initial tensile stress, σ_0, is the stress measured at time of start of the test, and corresponds to the initial temperature T_0.

The relaxation modulus, E_T, at a specified temperature T, is given by the ratio of the stress σ_T and the strain ε_t.

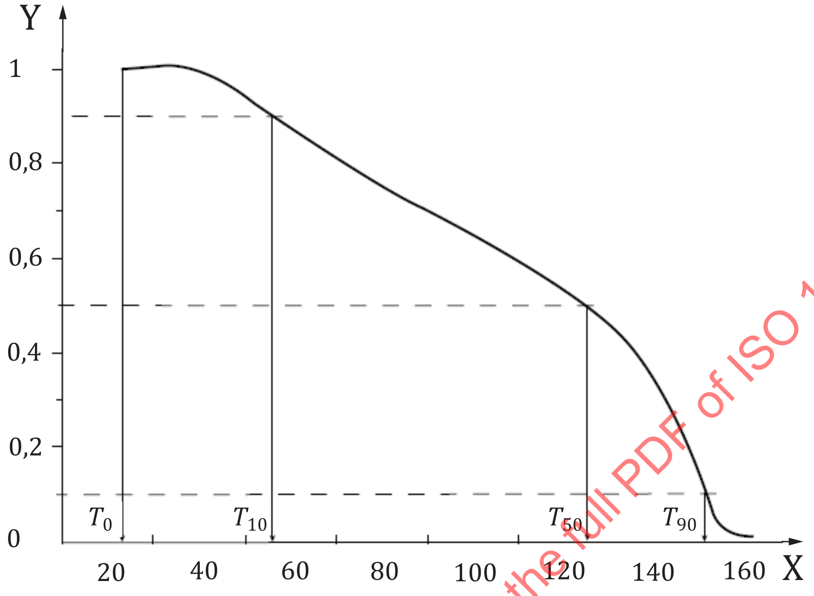
The tensile stress ratio, σ_T/σ_0, is plotted graphically as a function of temperature. A curve, obtained from a thermoplastic elastomer, is shown in Figure 6.

The selected temperature, T_x, i.e. T_{10}, T_{50} or T_{90}, stands for the temperature at which the tensile stress ratio, σ_T/σ_0, has decreased about x % with respect to the initial tensile stress σ_0.

The TSSR index, is given by Formula (2).

$$\frac{\int_{T_0}^{T_{90}} \frac{\sigma_T}{\sigma_0} dT}{T_{90} - T_0} \tag{2}$$

NOTE The TSSR index is sometimes called the relaxation index (RI).



Key

X T, °C

Y σ/σ_0

Figure 6 — Typical stress ratio curve of a thermoplastic elastomer

In case of rubber, vulcanized and thermoplastic, an increase of stress due to its entropy elastic behaviour, is observed. During the TSSR test, the increase of stress is more or less overcompensated by the phenomenon of stress relaxation. Nevertheless, the initial slope of the tensile stress curve, described by the temperature coefficient, κ_0, gives information about the entropy elastic behaviour of the material.

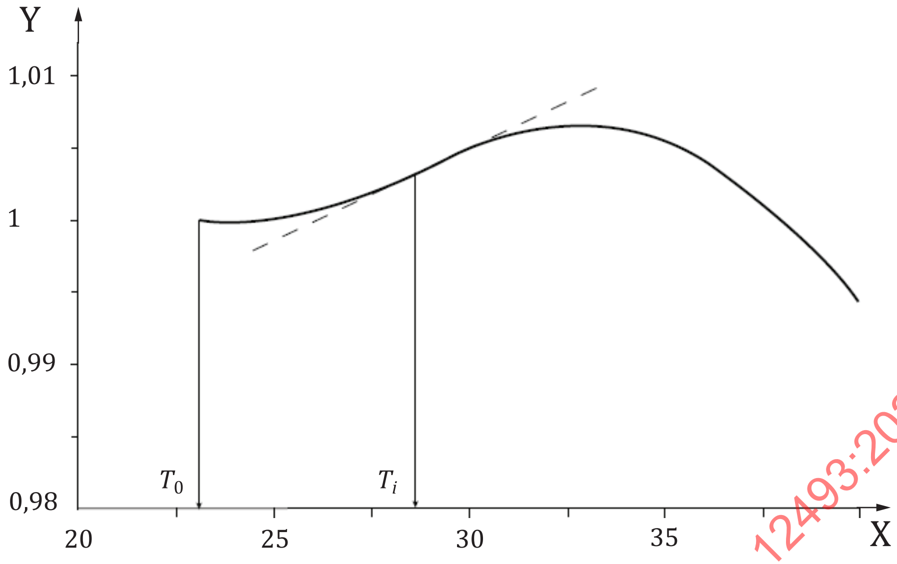
The temperature coefficient is given by Formula (3):

$$\kappa_0 = \kappa_{T_i} = \left(\frac{d\sigma}{dT}\right)_{T_i} \tag{3}$$

where

T_i is the temperature at the first point of inflection of the tensile stress curve, as illustrated in Figure 7.

NOTE 1 The curve illustrated in Figure 6 is typical for thermoplastic elastomers. Vulcanized rubber samples exhibit an extended temperature range, up to a temperature higher than 100 °C, of increasing stress.



Key

X T, °C

Y σ/σ_0

Figure 7 — Illustration of determination of the temperature coefficient, κ_0

NOTE 2 In case of ideal rubber elasticity, almost represented by unfilled rubber networks, according to the statistical theory of rubber elasticity, the temperature coefficient is related to the crosslink density, ν, of the network according to Formula (4):

$$\kappa = (\partial\sigma/\partial T)_\lambda = \nu \cdot R \cdot \left(\lambda - \lambda^{-2}\right) \qquad (4)$$

where R is the universal gas constant and λ is the extension ratio. The strain ratio is defined as the length, L, of the sample divided by its initial length L_0. Thus, the crosslink density of an unfilled rubber network can be determined easily by means of a TSSR test. In the more practical case of filled elastomers, the cross-link density, calculated from Formula (4), gives an apparent value, which can be useful for comparison within a series of samples of almost identical composition.

The value of the non-isothermal relaxation spectrum, H, at a specified temperature, T, is given by Formula (5):

$$H_T = -\Delta T \left(\frac{dE_T}{dT} \right)_{\beta = const} \qquad (5)$$

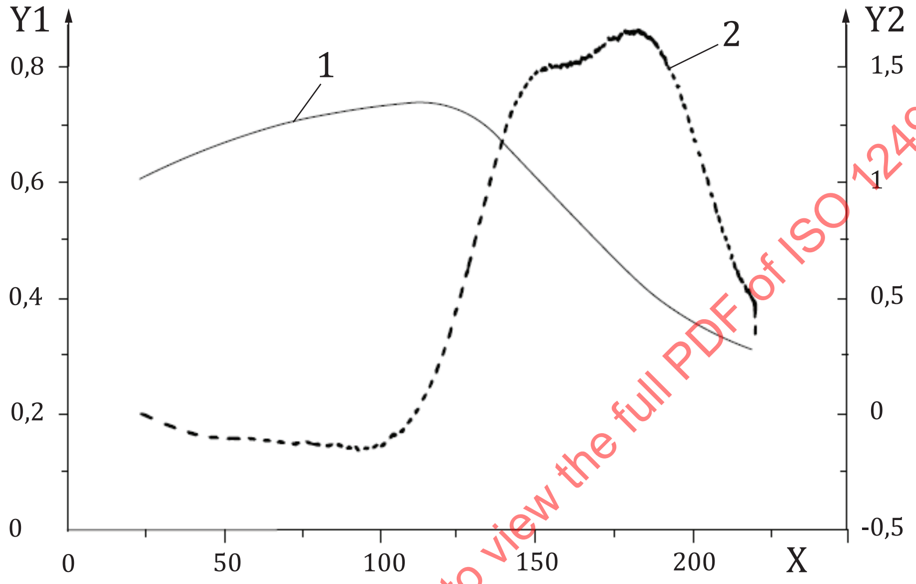
with

$$\Delta T = T - T_0 = \beta \cdot t$$

where

β and t are the heating rate and the time after start of the non-isothermal test period, respectively.

NOTE 3 As the relaxation spectrum, *H*, is obtained by differentiation of the stress signal, it is more sensitive with respect to structural changes of the sample than the original stress signal. This is advantageous in the exploration of physical and chemical relaxation mechanisms of rubber, vulcanized and thermoplastic. It has been shown that specific relaxation mechanisms result in well distinguishable peaks, if the relaxation spectrum, *H*, is plotted against temperature. For demonstration, two examples are shown in Figure 8 and Figure 9. In Figure 8 the relaxation spectrum of an unfilled rubber, vulcanized by means of a sulfur cure system is represented. It is seen that the relaxation spectrum exhibits a significant double peak in the temperature range of 150 °C to 200 °C. This is attributed to the cleavage of sulfur bridges and scission of the polymer main chain. In Figure 9 the relaxation spectrum of a commercially available thermoplastic elastomer (TPE), based on a blend of a styrenic block copolymer and polypropylene is represented. Two separated peaks at about 95 °C and 155 °C are clearly recognizable in the relaxation spectrum, which correspond to the glass transition of the styrene–hard phase and the melting temperature of the polypropylene phase, respectively.



Key

X *t*, min

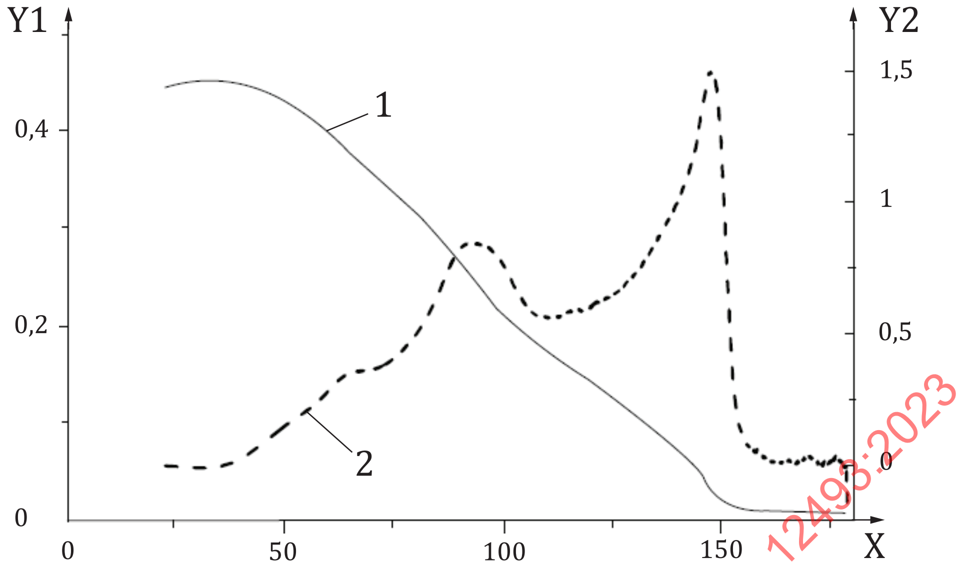
Y_1 σ, MPa

Y_2 *H*, MPa

1 stress

2 relaxation spectrum

Figure 8 — Relaxation spectrum and corresponding stress curve of an unfilled rubber vulcanizate



Key

X	*t*, min
Y_1	*σ*, MPa
Y_2	*H*, MPa
1	stress
2	relaxation spectrum

Figure 9 — Relaxation spectrum and corresponding stress curve of a thermoplastic elastomer based on a SEBS/PP blend

11 Precision

No precision data are currently available for this method.

12 Test report

12.1 Test report Method A

The test report shall include the following information for Method A:

a) a full description of the sample and its origin;

b) a reference to this document, i.e. ISO 12493:—;

c) test details:

  1) the standard laboratory temperature used;

  2) the time and temperature of conditioning prior to the test;

  3) the test temperatures used;

  4) the pre-strains used;

  5) details of any procedures not specified in this document.

d) test results:

  1) the number of test pieces used,