INTERNATIONAL STANDARD

ISO 6502-1

First edition
2018-07

Rubber — Measurement of vulcanization characteristics using curemeters —

Part 1:
Introduction

Caoutchouc — Mesure des caractéristiques de vulcanisation à l'aide de rhéomètres —

Partie 1: Introduction

Reference number
ISO 6502-1:2018(E)

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Published in Switzerland

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Foreword

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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).

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

For an explanation on 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 the following URL: 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 first edition of ISO 6502-1 cancels and replaces the fourth edition of ISO 6502:2016, which has been technically revised to keep consistency within the ISO 6502 series.

A list of all parts in the ISO 6502 series can be found on the ISO website.

Introduction

An International Standard specifying requirements for the use of oscillating disc curemeters was established in 1977 as ISO 3417, *Rubber — Measurement of vulcanization characteristics with the oscillating disc curemeter*. Later, when various rotorless curemeters were developed and became popular, an International standard for these instruments was produced as ISO 6502, *Rubber — Measurement of cure characteristics with rotorless curemeters*. However, because of the variety of available instruments that differed in geometry and construction, ISO 6502 was not able to specify such requirements in detail. In 1999, it became clear that a number of different rotorless curemeters were available and that significant developments had taken place and were continuing. Hence, it was concluded that, rather than specify individual rotorless instruments, possibly restricting future developments, a more general document was required. Accordingly, it was decided to provide guidance and assistance in the design and use of curemeters generally, and the title of ISO 6502 was changed to *Rubber — Guide to the use of curemeters*. As the use of rotorless curemeters has become more mature, it has now been decided to revise the Guide as Rubber — Measurement of vulcanization characteristics using curemeters — Part 1: Introduction, with subsequent parts for oscillating disc curemeters and rotorless curemeters.

Rubber — Measurement of vulcanization characteristics using curemeters —

Part 1: Introduction

WARNING 1 — Persons using 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 the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

WARNING 2 — Certain procedures specified in this document might 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 provides an introduction to the determination of vulcanization characteristics of rubber compounds by means of curemeters.

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 1382, *Rubber — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1382 and the following apply.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
oscillating-disc curemeter
ODC
curemeter consisting of a biconical disc oscillated within a temperature-controlled die cavity containing the test piece

Note 1 to entry: An oscillating-disc curemeter is also known as an oscillating disc rheometer (ODR).

3.2
rotorless curemeter
RCM
curemeter consisting of two dies forming a temperature-controlled cavity, one of which is moved relative to the other to apply a stress or strain to the test piece

Note 1 to entry: A rotorless curemeter is also known as a moving die rheometer (MDR).

3.3
marching-modulus cure
type of vulcanization during which the modulus does not reach a maximum value but, after a rapid rise, continues to rise slowly at the vulcanization temperature

3.4
vulcanization characteristics
characteristics which can be taken from a vulcanization curve

Note 1 to entry: See Figure 1.

Note 2 to entry: More explanations are given in Clause 4.

3.5
stiffness
measure of the resistance offered by rubber to deformation

Note 1 to entry: Force and torque have not been defined since they have a generally accepted scientific meaning.

4 Basic principles

The properties of a rubber compound change during the course of vulcanization, and the vulcanization characteristics can be determined by measuring properties as a function of time and temperature. Vulcanization characteristics are most commonly determined using instruments known as curemeters in which a cyclic stress or strain is applied to a test piece and the associated strain or force is measured. Normally, the test is carried out at a predetermined constant temperature and the measure of stiffness recorded continuously as a function of time.

The stiffness of the rubber increases as vulcanization proceeds. Vulcanization is complete when the recorded stiffness rises to a plateau value or to a maximum and then declines (see Figure 1). In the latter case, the decrease in stiffness is caused by reversion. In cases where the recorded stiffness continues to rise (marching-modulus cure), vulcanization is deemed to be complete after a specified time. The time required to obtain a vulcanization curve is a function of the test temperature and the characteristics of the rubber compound. Curves analogous to Figure 1 are obtained for a curemeter in which strain is measured.

Direct proportionality between torque and stiffness cannot be expected under all conditions and all instruments because, particularly at in high torque ranges, elastic deformation of the disc shaft and driving device has to be taken into account, Moreover, in cases of small amplitudes of deformation, the strain can be expected to have a considerable elastic component. However, for routine control purposes, corrections are not necessary.

The following vulcanization characteristics can be taken from the measure of stiffness against time curve (see Figure 1).

Minimum force or torque	F_L or M_L
Force or torque at a specified time *t*	F_t or M_t
Scorch time (time to incipient cure)	t_{sx}
Time to a percentage *y* of full cure from minimum force or torque	$t'_c(y)$
Plateau force or torque	F_{HF} or M_{HF}
Maximum force or torque (reverting cure)	F_{HR} or M_{HR}
Force or torque value attained after a specified time (marching-modulus cure)	F_H or M_H

The minimum force or torque F_L or M_L characterizes the stiffness of the unvulcanized compound at the curing temperature.

The scorch time (time to incipient cure) t_{sx} is a measure of the processing safety of the compound.

The time $t'_c(y)$ and the corresponding forces or torques give information on the progress of cure. The optimum cure is often taken as $t'_c(90)$.

The highest force or torque is a measure of the stiffness of the vulcanized rubber at the curing temperature.

NOTE The term *F* denotes force and the term *M* denotes torque.

The scorch time t_{sx} is the time required for the force or torque to increase by *x* units from F_L. It might be convenient to define the scorch as a given percentage, e.g. 2 % or 5 %, of the total cure.

The time to a percentage of full cure from minimum force, $t'_c(y)$, is the time taken for the force (or torque) to reach:

$$F_L + 0{,}01\, y (F_{HF} - F_L) \quad (1)$$

or

$$M_L + 0{,}01\, y (M_{HF} - M_L) \quad (2)$$

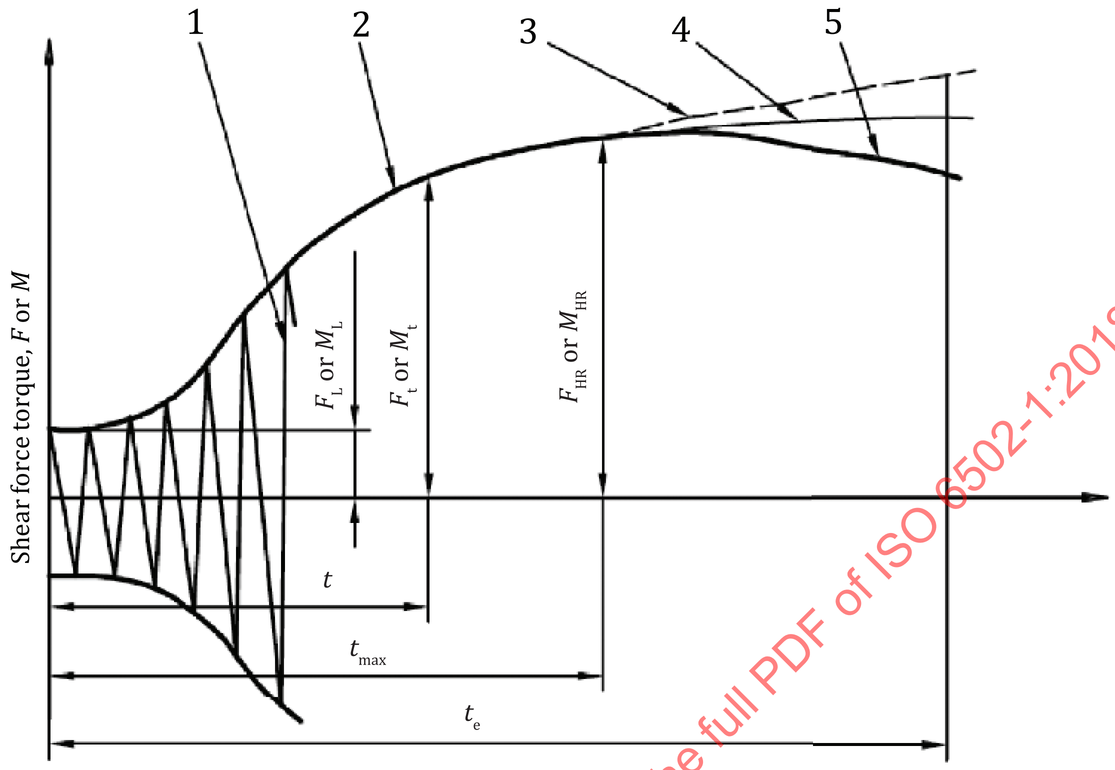
— $t'_c(10)$ is a measure of the early stages of cure.

— $t'_c(50)$ can be determined accurately providing the slope of the curve is greatest at this point.

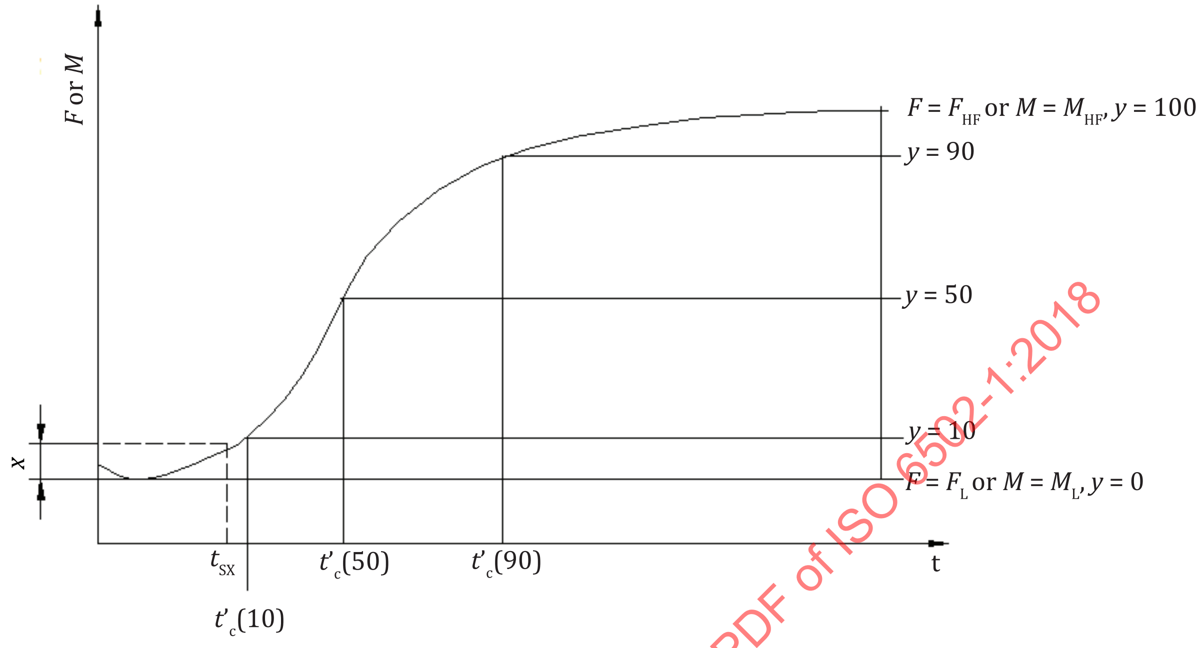
— $t'_c(90)$ is often used as an indicator of optimum press cure.

The cure rate index is the average slope of the rising curve and is given by:

$$100 / \left[t'_c(y) - t_{sx} \right] \quad (3)$$



a) Vulcanization curve *F* or *M* = *f*(*t*)



b) Method of evaluation

Key

1 sinusoidal curve

2 envelope curve

3 vulcanization curve with steady increase to F_H or M_H at time t_e at end of test (marching-modulus cure)

4 vulcanization curve with plateau at F_{HF} or M_{HF} (plateau cure)

5 vulcanization curve with maximum F_{HR} or M_{HR} at time t_{max} (reverting cure)

Figure 1 — Typical vulcanization curve and method of evaluation

5 Types of curemeter

Three types of curemeters have found widespread use:

— oscillating-disc;

— reciprocating-paddle;

— rotorless.

Other geometries are possible, for example with a vibrating probe or needle.

The reciprocating-paddle type was popular, but is now more or less obsolete and is not considered further in this document.

The oscillating-disc curemeter consists of a biconical disc that oscillates in a closed cavity. It was for many years the most widely used type of instrument.

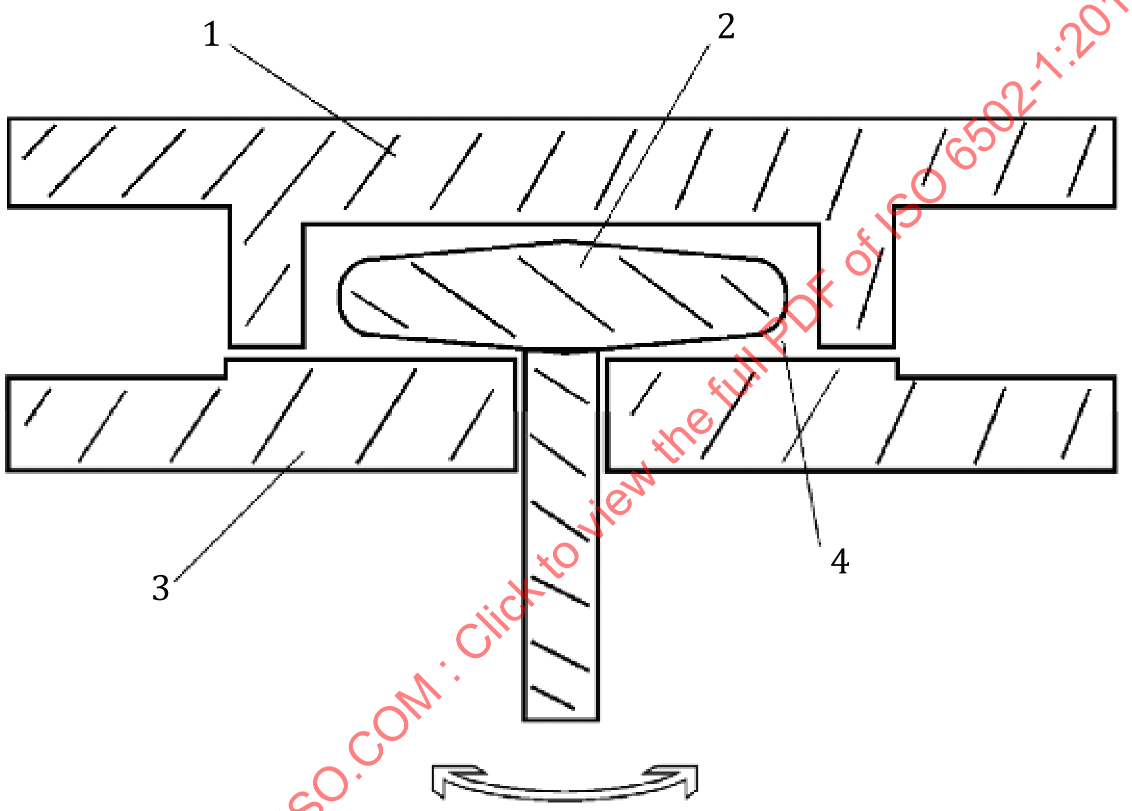
In rotorless curemeters, one half of a die enclosing the test piece, rather than a disc within the test piece, oscillates or reciprocates. The rotorless type of curemeter has increased greatly in popularity, largely because of its advantages of the specified temperature being reached in a shorter time after insertion of the test piece into the die cavity and better temperature distribution in the test piece (see Annex A).

6 Apparatus

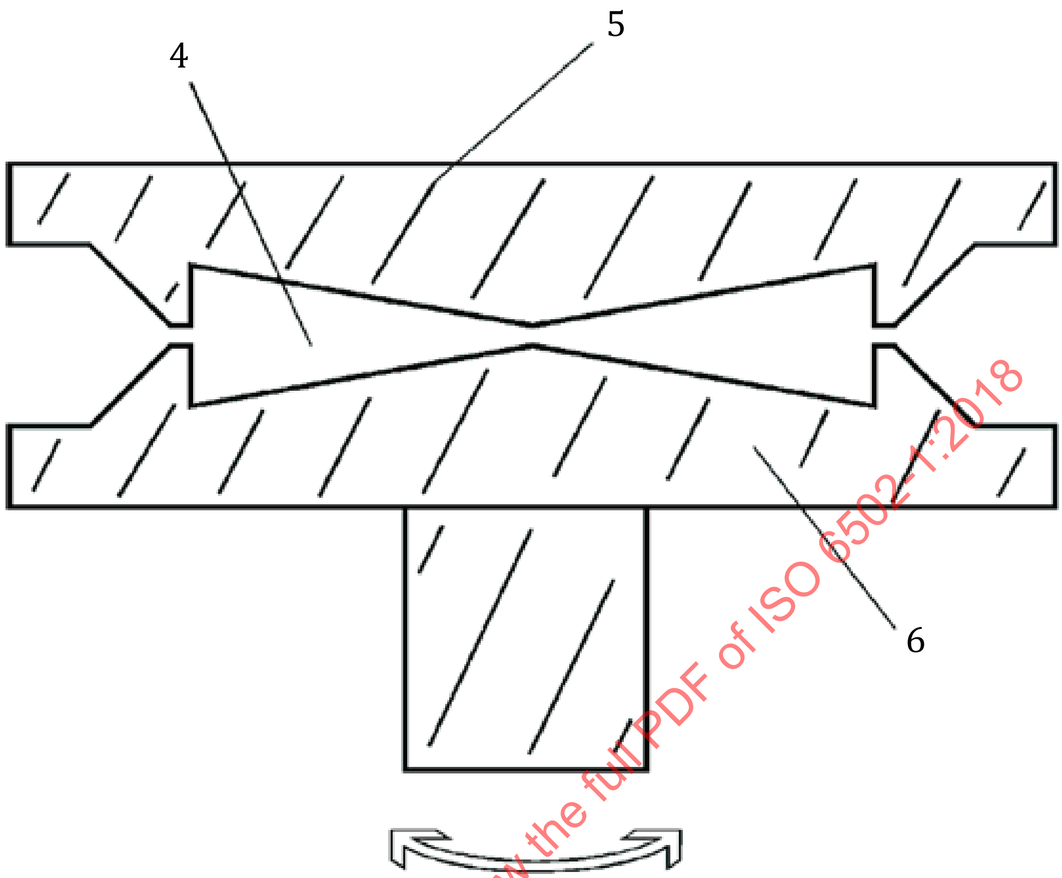
6.1 General

A curemeter consists of two heated dies with means of closing them under a specified force to form a die cavity containing the test piece, a means of oscillating a rotor within the cavity, or alternatively oscillating or reciprocating one of the dies relative to the other, and a means of measuring and recording the force or torque required to produce the relative movement, or the movement produced by a given applied force or torque. In addition, with sealed rotorless torsion systems, reaction torque on the stationary die opposite the moving die can be measured.

The general principles of oscillating-disc and rotorless curemeters are shown in Figure 2.



a) Oscillating disc



b) Oscillating die

Key

1 upper die
2 oscillating disc
3 lower die
4 test piece
5 fixed die
6 oscillating die

Figure 2 — Principles of curemeters

6.2 Dies

The dies shall be manufactured from a non-deforming material. The surface of the dies shall be such as to minimize the effect of contamination and be hard so as to prevent wear. A minimum Rockwell hardness of 50 HRC, or equivalent, is recommended. The tolerances necessary on the dimensions of the dies will depend on the particular design, but as a general guide the dimensions of the cavity should be controlled to ±0,2 %.

The top and bottom surfaces of the cavity shall have a pattern of grooves of dimensions sufficient to prevent slippage of the rubber test piece.

Holes shall be provided in both the upper and lower dies to accommodate temperature sensors. The positions of the sensors relative to the cavity shall be such as to ensure reproducible response.

In the case of oscillating-disc instruments, one die requires a central hole to allow insertion of the die stem. A seal of suitable low, constant friction shall be provided in this hole to prevent material leaking from the cavity.

Suitable means shall be employed by design of dies or otherwise to apply pressure to the test piece throughout the test to minimize slippage between the disc and the rubber. A positive pressure is also important to exclude air which can affect the cure of, for example, peroxide-cured rubbers and to prevent any tendency for the rubber to become porous.

The die cavity can be checked by measuring the dimensions of the vulcanized test piece. For biconical-die rotorless curemeters, particular attention needs to be paid to the thin central portion, the thickness of which depends on the die gap. For oscillating-disc curemeters, the vulcanized test piece should be cut in half and checked to see that it is symmetrical. Any asymmetry indicates that the rotor height has been set incorrectly.

The dimensions of the cavity and of the vulcanized test piece will not be identical because of the effect of mould shrinkage.

6.3 Die closure

The dies are closed and held closed during the test by, for example, a pneumatic cylinder.

A force of 11 kN ± 0,5 kN is recommended for oscillating-disc instruments with a mating-surface area between the dies of approximately 1 400 mm^2.

In unsealed rotorless instruments, the dies are not completely closed but a small clearance is left which shall be between 0,05 mm and 0,2 mm. For sealed cavities, no gap shall exist at the edges of the die cavity. The minimum closing force required depends on the clearance area. As a general guide, a minimum of 7 kN to 8 kN is recommended.

6.4 Moving member

The disc in an oscillating-disc instrument shall be manufactured from a non-deforming material having a minimum hardness of 50 HRC. Both the top and bottom surfaces shall have a pattern of grooves to prevent slippage of the rubber test piece.

The disc shall be biconical in shape to give an approximately uniform shear rate, and its diameter shall be controlled to ±0,03 % and the cone angle to ±1,3 %.

The moving member in a rotorless instrument is one of the dies. The shape of the die cavity shall be a plane disc for reciprocating types and either biconical, flat plate or “top hat” in the oscillating type to produce a substantially uniform shear rate.

The drive linkage shall be sufficiently stiff to prevent significant deformation.

6.5 Movement

The frequency of oscillation or reciprocation shall be between 0,05 Hz and 2 Hz, and tests can be made at two or more frequencies. If a single frequency is selected, 1,7 Hz ± 0,1 Hz is recommended.

Generally, greater sensitivity can be obtained with larger amplitudes, but the amplitude that can be used in practice is restricted by the possibility of slippage between the test pieces and the die surface or rotor.

For oscillating-disc curemeters, an amplitude of ±1° is recommended but ±3° might be possible and advantageous in some circumstances.

For rotorless curemeters, the range shall be between ±0,1° and ±2° or, for reciprocating types, between ±0,01 mm and ±0,1 mm.

The tolerance on amplitude shall be ±2 %, and the drive shall be sufficiently powerful and stiff to substantially maintain the amplitude under load.

With different frequencies and amplitudes, different results will be obtained.

6.6 Stiffness measurement

The means of measuring force or torque shall be rigidly coupled to a die or rotor and be capable of measuring the resultant force or torque to an accuracy of ±1 % of the force or torque range. This tolerance shall include any errors due to deformation of the measuring device and its coupling and of the output device.

The force or torque shall be monitored and recorded continuously. Any recorder used for this purpose shall have a response time for full-scale deflection of 1 s or less.

6.7 Heating and temperature control

The heating and temperature control system shall be capable of producing a reproducible and evenly distributed temperature in the dies and permit rapid and reproducible temperature recovery after insertion of the test piece. Close control of these parameters is necessary for the precise measurement of vulcanization characteristics.

The temperature-measuring system shall enable temperature to be measured to a resolution of ±0,1 °C over the range 100 °C to 200 °C. The temperature controllers shall enable the dies to be controlled to an accuracy of ±0,3 °C at the steady-state. The temperature of the dies shall recover after insertion of a test piece at 23 °C ± 5 °C to within 0,3 °C within 3 min for biconical-die rotorless instruments. For flat-plate-die rotorless instruments, the recovery range shall be ±1 °C within 1,5 min at the test temperature of 150 °C.

The effect of temperature distribution on measured cure rate is discussed in Annex A.

6.8 Calibration

Calibration of curemeters shall be carried out in accordance with the manufacturer's instructions and considering ISO 18899. The force or torque should be determined at several points over the range(s) used but, additionally, it can be useful to have provision for making in-use checks.

Stable standard rubber compounds can also be tested periodically to check for consistent performance.

7 Test piece

The test piece shall be homogeneous and as far as possible free from trapped air. The test piece volume shall be slightly larger than the die cavity volume such that a small amount of material is extruded between all edges of the dies when they are closed. The optimum volume should be determined by preliminary tests, and test pieces of equal volume should be used to obtain reproducible results. Oversize test pieces might cool the cavity excessively during the early part of the test cycle.

The test piece shall be cut from sheeted material by an appropriate device which ensures the production of test pieces of constant volume.

Normally, one test piece is taken from each rubber sample, but if this might not be representative of the batch then further test pieces should be taken.

8 Vulcanization temperature

The vulcanization temperature is chosen as that appropriate for the rubber compound being tested and intended processing. This will normally be 100 °C to 200 °C.

9 Conditioning

The rubber sample shall be conditioned at 23 °C ± 5 °C for a minimum of 3 h before testing.

10 Procedure

10.1 Preparation for test

The temperature of both dies shall be brought to the test temperature with the cavity closed and, in the case of oscillating-disc curemeters, with the disc in place, and allowed to stabilize.

Any necessary zeroing and selection of range of the force- or torque-measuring device shall be made before loading the test piece.

10.2 Loading the curemeter

The loading of the test piece and the closure of the dies shall be carried out as quickly as possible. The dies shall be closed immediately after insertion of the test piece. The whole cycle, from opening to closure, shall not exceed 20 s.

The vulcanization time should preferably be recorded from the instant the dies are fully closed. Oscillation of the movable die or disc should be started before or at the instant of die closure.

After removal of the cured test piece, a further sample may be inserted immediately if the temperature of the dies has remained within ±0,3 °C of the set value. If not, the dies should be closed and the temperature allowed to recover to the test value.

A deposit of material from the rubber compound can build up on the dies (and disc) which might affect the final torque values. The use of a standard compound can be used to detect this occurrence. If such contamination develops, it can be removed by very light blasting with a mild abrasive, ultrasonic cleaning or non-corrosive cleaning fluids. Great care should be taken with cleaning, and the manufacturer's advice followed. If fluids are used, the first two tests after cleaning shall be rejected. Running a natural-rubber gum compound can be used to remove debris. In some cases, a protective film can be used to prevent contamination. For biconical-die rotorless curemeters of the sealed-cavity type, the use of protective film (for example, polyester of thickness <0,03 mm) is strongly recommended.

11 Expression of results

All or some of the cure characteristics given in Clause 4 shall be taken from the cure curve. Times shall be given in minutes, force in newtons and torque in newton metres.

Annex A
(informative)

Effect of thermal parameters on measured cure properties

A.1 General

Curing (vulcanization) is the basic product-forming process in the rubber industry. In order to calculate the cure profile in an article, and hence the optimum cure schedule, it is necessary to know the relationship between cure, time and temperature for the rubber compound under isothermal conditions. In current industrial practice, the basic cure parameters for rubber are determined from measurements made on curemeters. These instruments measure a property, which can be called stiffness, which is approximately proportional to the hot-shear modulus. The sample has a stiffness before any crosslinking takes place, and stiffness increases from this minimum value to a maximum during the course of the curing reaction, giving rise to the familiar S-shaped curve. The cure time at a given temperature is the time taken to reach 90 %, say, of this stiffness change. The material should be characterized by making measurements at different temperatures.

A.2 Deviation from isothermal conditions

The majority of curemeters do not operate under isothermal conditions. In any instrument, this deviation is a result of the finite time required for the sample to reach thermal equilibrium. During this heating-up period, the stiffness decreases [see Figure 1 b)]. As a rule of thumb, a 1 mm-thick sheet heated from both surfaces would take about 6 s to heat up. Time increases as the square of the thickness, and a 6 mm-thick sheet would take about 4 min. The heating-up time for a particular curemeter thus depends on the thickness of the test piece. It becomes more important at higher temperatures because the time needed to heat the sample is a larger fraction of the cure time.

There is an additional problem with curemeters with a rotor. Heat is lost continuously by conduction from the rotor down the drive shaft, causing the rotor to be cooler than the platens. The average temperature of the test piece is, therefore, less than the set temperature, and the curing process is slower.

The gap between the platens in a rotorless curemeter should be set so that the test piece remains under a positive pressure during the measurement. This is not only to eliminate problems with porosity, but also because it has been reported that lack of pressure gives cure times which are too long[4]. Pressure can have a direct effect on the curing-reaction rate, or it can affect the heat transfer between the platen surfaces and the test piece.

If the curemeters are only being used for quality control, the above considerations might not matter, unless results from different types of instrument are being compared. To accommodate this, the following action may be carried out. To obtain vulcanization characteristics comparable with those obtained with the oscillating-disc curemeter described in ISO 6502-2, the heater of the rotorless curemeter should be adjusted so as to heat the test piece to the specified temperature in 6 min. This has given comparable results with a number of compounds of medium filler content of the most important rubber types. This procedure should only be adopted with extreme caution.

If, on the other hand, curemeter results are to be used for calculating cure times, operators should be aware of the size and effect of any deviations from isothermal conditions[5]. For example, at 150 °C an oscillating-disc curemeter can overestimate the cure time by a factor of about two[6][7]. The factor increases at higher temperatures. The relationship is not linear and should be determined experimentally.