TECHNICAL SPECIFICATION

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Rubber, unvulcanized — Determinations using a shearing-disc viscometer —

Part 4: Determination of the Mooney stress-relaxation rate

Caoutchouc non vulcanisé — Déterminations utilisant un consistomètre à disque de cisaillement —

Partie 4: Détermination du taux de relaxation de contrainte Mooney

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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.

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/TS 289-4 cancels and replaces ISO 289-4:2003, which has been technically revised.

The main changes are:

— publication as an ISO Technical Specification instead of an International Standard;

— the addition of Annex B.

A list of all parts in the ISO 289 series can be found on the ISO website.

Introduction

Mooney viscosity, as defined in ISO 289-1, is one of the most widely accepted rubber characterization parameters. However, Mooney viscosity alone is usually insufficient to guarantee that other rheological properties are well controlled[2]. It does not give any information about the elasticity of raw and unvulcanized rubbers[3]. Viscosity and elasticity can change independently; therefore, it is important to have test procedures available that are able to measure both properties independently.

Mooney viscosity is measured at one specific shear rate and rubbers exhibit shear rate-dependant viscosity. Sophisticated test equipment to measure the viscosity of a rubber as a function of the shear rate is available. Generally speaking, this type of equipment, its operation and the interpretation of the results are too complicated to be used as a standard quality control tool at present.

As described in the literature[4], the Mooney stress-relaxation is related to the elastic effects in the rheology of unvulcanized rubbers. It can be measured relatively easily and only takes a few seconds extra at the end of a standard Mooney viscosity measurement. The Mooney stress-relaxation rate (MSR) parameter is independent from Mooney viscosity.

Mooney stress-relaxation, combined with the conventional Mooney viscosity, gives a better description of the visco-elastic behaviour of uncompounded as well as compounded, unvulcanized rubbers[5]. Mooney stress-relaxation measurements have been proposed as a quality control tool[6][7].

The short interval method as described in this document is a refinement of the evaluation procedures for Mooney stress-relaxation measurements. Short interval evaluation leads to higher reproducibility compared to using an extended interval.

Using a short interval, a major parameter relevant to rubber rheology can be obtained from Mooney stress-relaxation experiments *viz*. the Mooney stress-relaxation rate, i.e. the rate of decay of torque versus time[8][9][10][11].

The Mooney stress-relaxation rate also has been referred to as "slope", where the latter is sometimes presented as a positive and sometimes as a negative value. As the method described in this document uses a specific evaluation interval and the parameter is always referred to as a positive value, a new distinctive name has been chosen[12][13][14][15].

Data are available to show that the described method distinguishes polymers (EPDM) with different high molecular weight fractions despite the short evaluation interval.

The decision to publish this document as a Technical Specification instead of an International Standard is based on the fact that the method in this document was new and not widely enough practised at the time of development.

Rubber, unvulcanized — Determinations using a shearing-disc viscometer —

Part 4: Determination of the Mooney stress-relaxation rate

1 Scope

This document specifies a method of use of a shearing-disc viscometer for measuring the Mooney stress-relaxation rate (MSR) of uncompounded or compounded, unvulcanized rubbers, characterizing the elastic response of those materials next to the viscous response as measured by the Mooney viscosity. The intended use of this document is on quality control measurements.

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 289-1:2015, *Rubber, unvulcanized — Determinations using a shearing-disc viscometer — Part 1: Determination of Mooney viscosity*

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

3 Terms and definitions

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

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

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

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

3.1
Mooney stress-relaxation rate
MSR
absolute value of the slope of the linear regression line of the log(torque) versus log(time) plot over a specified time interval after stopping the rotor at the end of a Mooney viscosity measurement

Note 1 to entry: The MSR measurement is a stress relaxation measurement which covers a broad spectrum of relaxation times and is sensitive to polymer structure at a specified relaxation time interval.

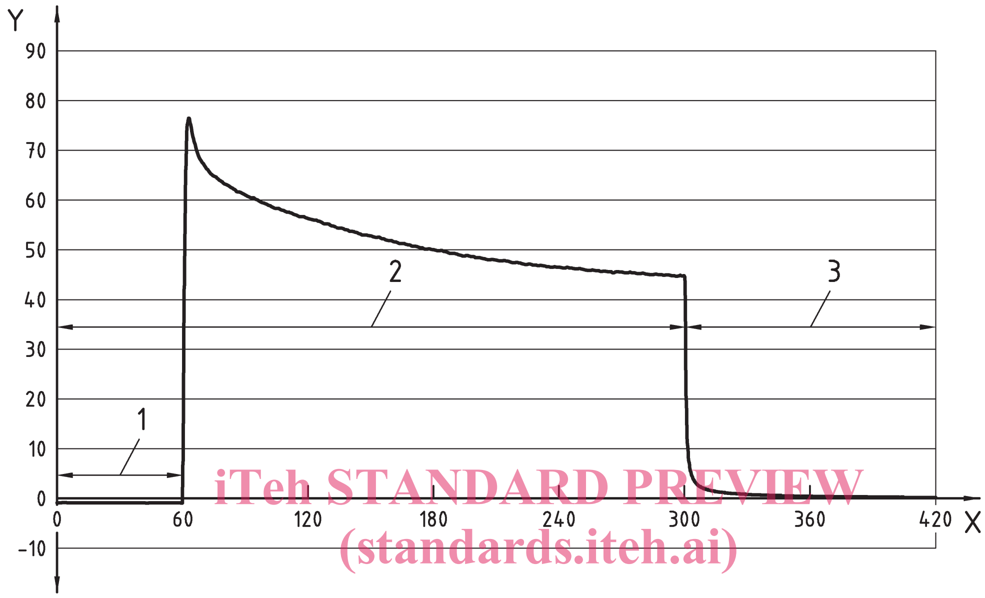
4 Principle

The test consists of determining the decay of the Mooney torque immediately after the determination of the Mooney viscosity. After abruptly stopping the rotor at the end of the Mooney viscosity measurement, the decrease in torque is recorded as a function of time. The rate of change of the torque is evaluated over a short time interval assuming power law validity, in accordance with theoretical predictions[16].

5 Apparatus

The apparatus specified in and calibrated in accordance with ISO 289-1 shall be used. Furthermore, the apparatus shall be able to stop the rotation of the disc within 0,1 s, reset the zero torque point to the static zero for a stationary rotor and record the torque at least every 0,2 s after stopping the rotor.

There is a difference in zero torque for a stationary and a rotating rotor. Resetting of the zero torque point for the rotating rotor before every measurement is recommended. This results in a negative torque signal during the preheating time as can be seen in Figure 1.



Key

1 preheating time
2 Mooney viscosity part
3 stress relaxation part
X time, *t*, s
Y torque, *T*, Mooney units

Figure 1 — Mooney viscosity curve with Mooney stress-relaxation part

The use of a barrier film is recommended. The polymer type and the thickness of such a film might affect the test results as described in ISO 289-1.

As stated above, the apparatus should be able to stop the rotation of the disc within 0,1 s. Figure 2 a), b), c) and d) clearly indicate that this is not always the case. Measurements with certified butyl IRM241D on an apparatus of which the motor (old) was replaced with a different type of motor (new) resulted in different MSR values, respectively 0,662 vs 0,702. As shown in Figure 2 b), different log-log plots of the torque versus time were found for the old and new motor. Analysis of the individual measurement data showed different slopes in the relaxation curves in the range of 301,6 s and 305 s [Figure 2 c)]. Analysing the moment of stopping of the motor showed that the old motor stops 0,1 s to 0,2 s before and the new motor 0,3 s to 0,4 s after the pre-described moment of stopping of 300 s. In principle, both types of motor do not meet the stopping requirements. Hence, care should be taken when comparing MSR data from different apparatus. Apparatus influences should be investigated first.

In an attempt to compare the data obtained with the different motors, the MSR curves were shifted over each other and the MSR data were recalculated [Figure 2 e) and f)]. This kind of curve fitting could be a solution.

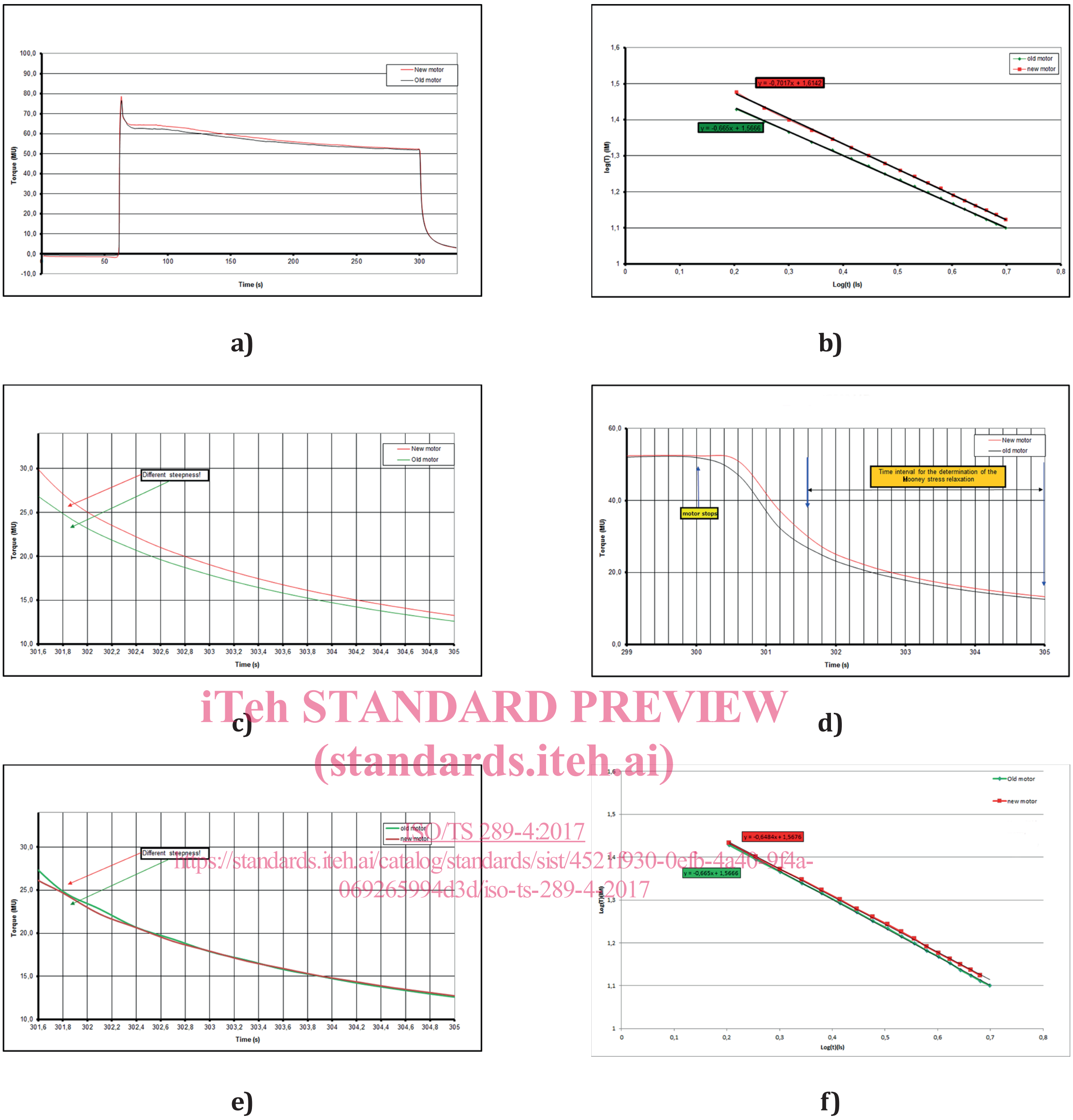


Figure 2 — Illustration of motor influence

6 Calibration

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

7 Preparation of test piece

Run a Mooney viscosity test as described in ISO 289-1.

8 Temperature and duration of the test

Use the test conditions as described in ISO 289-1.

9 Procedure

Conduct the test following the procedure described in ISO 289-1:2015, Clause 7.

If the viscosity has not been recorded continuously, plot the observed Mooney viscosity values as specified in ISO 289-1.

An automatic recorder is strongly recommended. The use of specialized data acquisition software is preferred in order to enable automated calculations.

At the end of the viscosity test, stop the rotation of the disc within 0,1 s, reset the zero torque point to the static zero for a stationary rotor and record the torque at least every 0,2 s.

NOTE Resetting torque to a static zero is necessary because the dynamic zero used for the viscosity test would result in a negative torque value once the material has completely relaxed with a stationary disc. The relaxation of torque for most polymers is so rapid that stopping the rotor, resetting zero and recording the relaxing torque have to be controlled automatically.

The relaxation data shall be collected starting at 1,6 s after the rotor is stopped and continuing until 5,0 s after the rotor is stopped. This normally gives a total of 18 data points. A typical chart of a Mooney viscosity test followed by a stress relaxation test is shown in Figure 1.

The use of different evaluation intervals and/or different data sampling schemes results in different Mooney stress-relaxation rate values. Longer evaluation intervals might result in increased errors. This is due to the lower signal-to-noise ratio at progressing relaxation times. Most of the work done to develop this document has been based on EPDM. It might be anticipated that for other polymers, different evaluation intervals and/or different sampling schemes are more appropriate[17][18]. Deviations from this document should be agreed upon between the supplier and the customer and always mentioned in the test report.

10 Calculation and expression of results

Analysis of Mooney stress-relaxation rate data (torque versus time data) consists of a) developing a plot of torque (Mooney units) versus time in seconds in a log-log plot as shown in Figure 3 and b) calculating the constants of the power law model of material response, as represented by Formula (1).

$$T = k(t)^{\alpha} \quad (1)$$

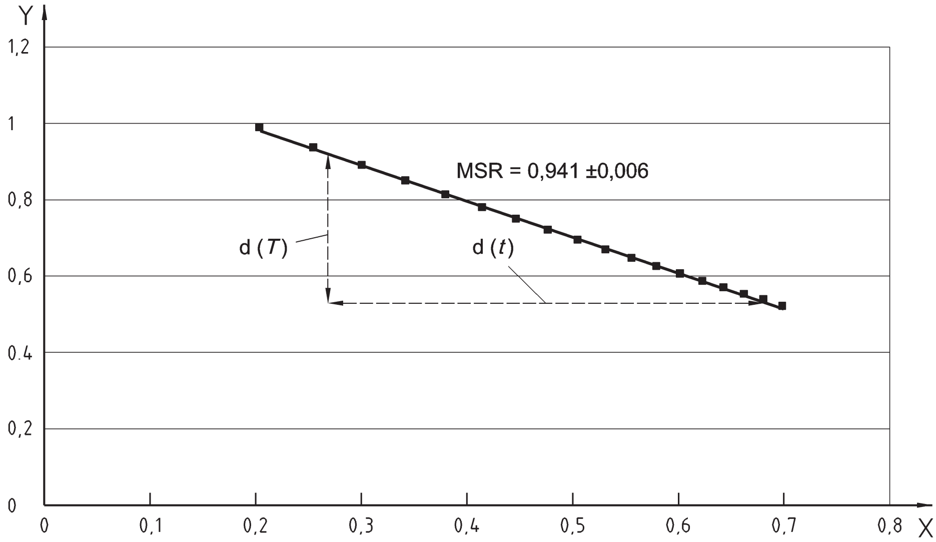
where

T gives the Mooney units (torque) during the stress relaxation test;

k is a constant equal to the torque in Mooney units 1 s after the rotor is stopped;

t is the time after rotor stop, in seconds;

α is an exponent that determines the rate of stress relaxation.



$y = -0{,}941\,4x + 1{,}172\,4$; $R^2 = 0{,}999\,4$; standard error = 0,005 9

Key

X log t

Y log T

Figure 3 — Mooney stress-relaxation rate parameters

If Formula (1) is transformed by taking the log of both sides, Formula (2) is obtained:

$$\log T = \alpha(\log t) + \log k \tag{2}$$

This has the form of a linear regression equation where α equals the slope, log k equals the intercept and log T and log t correspond respectively to the dependent and independent variables. In a plot of log T versus log t, as shown in Figure 3, the slope of the graph, (log T/log t), is equal to α. The absolute value of the slope, $|\alpha|$, rounded to the nearest third decimal is the Mooney stress-relaxation rate.

Report the results of a typical test in the following format:

MSR = 0,941 ± 0,006

NOTE The number 0,006 in this expression stands for the standard error as calculated as part of the regression analysis. It is an estimation of the random error on the MSR value. It is calculated as:

$$\sqrt{\frac{\frac{1}{n-2}\sum e_i{}^2}{\sum (X_\mathrm{i} - \overline{X})^2}}$$

where

e_i is the difference between measured value and the estimated value based on the linear regression, the so-called residual;

n is the number of measurements[19].

The MSR should always be reported in combination with the Mooney viscosity.

