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

Part 4:
Determination of the Mooney stress-relaxation rate

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

Partie 4: Détermination du taux de relaxation de contrainte Mooney

Reference number
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Foreword

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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.

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ISO 289-4 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analyses*.

ISO 289 consists of the following parts, under the general title *Rubber, unvulcanized — Determinations using a shearing-disc viscometer*:

⎯ *Part 1: Determination of Mooney viscosity*

⎯ *Part 2: Determination of pre-vulcanization characteristics*

⎯ *Part 3: Determination of the Delta Mooney value for non-pigmented, oil-extended emulsion-polymerized SBR*

⎯ *Part 4: Determination of the Mooney stress-relaxation rate*

In this corrected version of ISO 289-4:2003, the following changes have been incorporated:

page iv: corrected spelling of the TC title;

pages v, 1, 2, 3, 6, 7: modifications of bibliographic reference numbers;

page 2: addition of the word "thickness" to NOTE 2;

page 3: change of symbol for Mooney units – from M to T;

page 4: Figure 1, addition of symbol t, to the key for the abscissa;

page 6: subclause A.2.1, new text;

page 8: Table A.1, deletion of the second line of the table title and also of the word "NOTE" above the table footnotes;

pages 9 and 10: Bibliography, change in order and numbering of references, deletion of former reference [6], detailed changes in former references [1] [9] [12] [15] [17] [18].

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 [1]. It does not give any information about the elasticity of raw and unvulcanized rubbers [2]. 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 is too complicated to be used as a standard quality control tool at present.

As described in the literature [3] 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 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 [14]. Mooney stress relaxation measurements have been proposed as quality control tool [4] [5].

The short interval method as described in this part of ISO 289 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 (MSR) i.e. the rate of decay of torque versus time [16] [17] [18] [19].

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 part of ISO 289 uses a specific evaluation interval and the parameter is always referred to as a positive value, a new distinctive name has been chosen [6] [7] [8] [15].

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

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

Part 4:
Determination of the Mooney stress-relaxation rate

1 Scope

This part of ISO 289 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.

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 289-1:1994, *Rubber, unvulcanized — Determinations using a shearing-disc viscometer — Part 1: Determination of Mooney viscosity*

3 Terms and definitions

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

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   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 [9].

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.

NOTE 1   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.

NOTE 2   The use of a barrier film is recommended. The polymer type and the thickness of such a film have an influence on the results. This part of ISO 289 was developed using a polypropylene film of 20 μm thickness, with a DSC peak temperature of 161 °C (second heating curve).

6   Preparation of test piece

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

7   Temperature and duration of the test

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

8   Procedure

Conduct the test following the procedure described in Clause 7 of ISO 289-1:1994.

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

NOTE 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 2   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 must be controlled automatically.

The relaxation data shall be collected starting 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.

NOTE 3   The use of different evaluation intervals and or different data sampling schemes result in different Mooney stress-relaxation rate values. Longer evaluation intervals may 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 part of ISO 289 has been based on EPDM. It might be anticipated that for other polymers different evaluation intervals and/or different sampling schemes are more appropriate [10] [11]. Deviations from this document should be agreed upon between the supplier and customer and always mentioned in the test report.

9   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 2, and b) calculating the constants of the power law model of material response, as represented by Equation (1).

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

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.

If Equation (1) is transformed by taking the log of both sides, Equation (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 2, 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 $\pm$ 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:

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

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 [12].

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

10 Test report

The test report shall include the following information.

a)   all of the information described in Clause 10 of ISO 289-1:1994;

b)   reference to this part of ISO 289, i.e. ISO 289-4;

c)   manufacturer and model of the viscometer used;

d)   relaxation time interval used if it differs from the one stated in Clause 8;

e)   Mooney stress-relaxation rate (MSR) rounded to the nearest third decimal;

f)   standard error for the MSR as calculated as part of the regression analysis rounded to the nearest third decimal;

g)   any operation not included in this part of ISO 289 or regarded as optional.
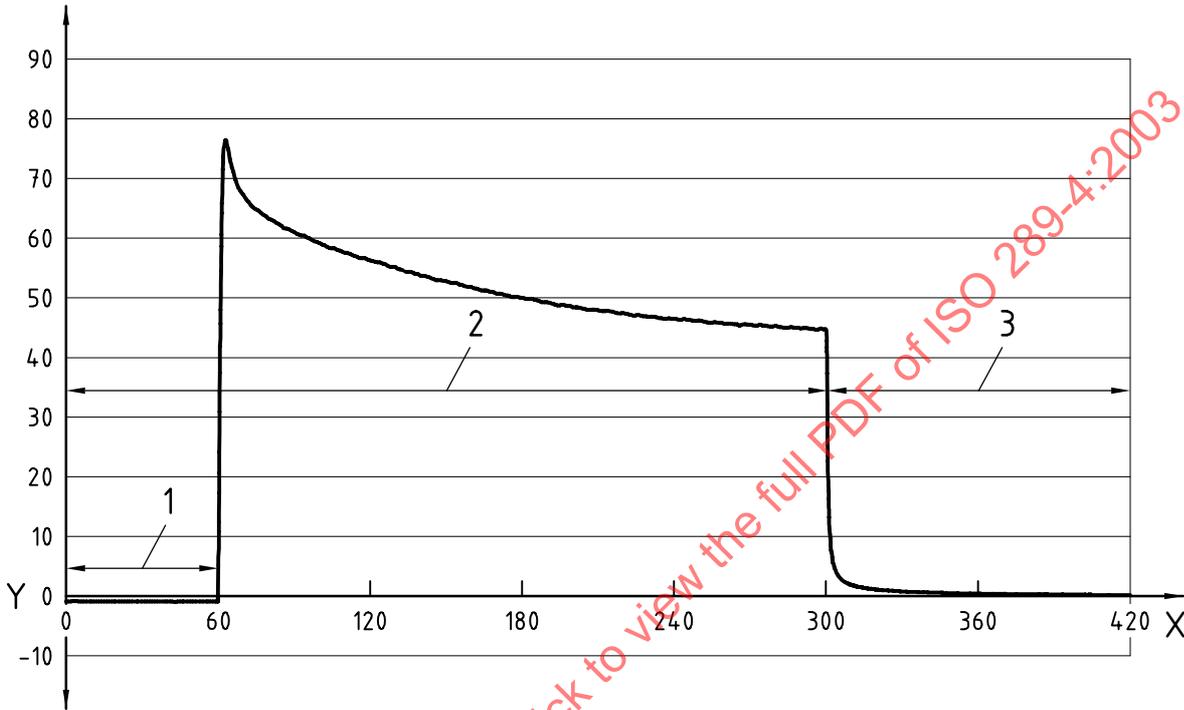
Key

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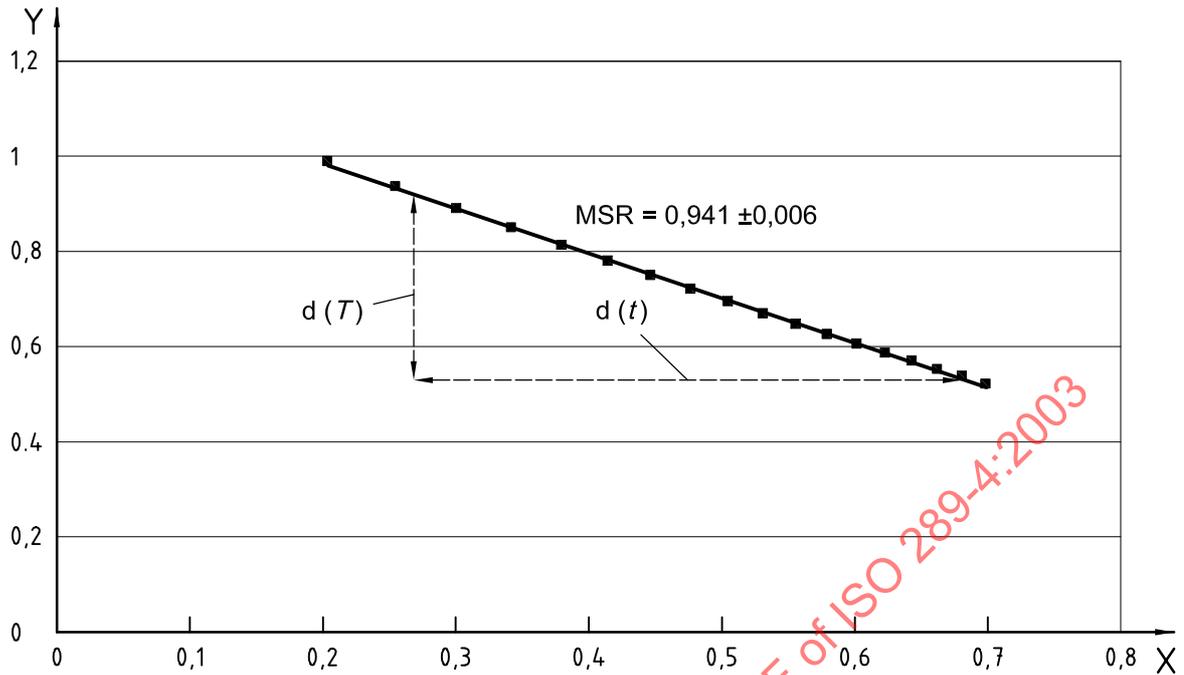
$y = -0,941\,4\,x + 1,172\,4$; $R^2 = 0,999\,4$; standard error = $0,005\,9$

X   log (t)
Y   log (T)

Figure 2 — Mooney stress-relaxation rate parameters

5

Annex A
(informative)

Precision statement

A.1 The test programme

The interlaboratory test programme (ITP) for precision evaluation for Mooney stress-relaxation rate was conducted in 2001 using the procedures and guidelines as described in ISO/TR 9272 [14].

The ITP was conducted with 14 polymers. Polymers 1 to 6 were EPDM grade materials and Polymers 7 to 14 were non-EPDM materials. Some details on these polymers are listed in Table A.1. Six laboratories participated in the ITP and Type 1 precision was evaluated for Mooney stress-relaxation rate, with one measurement on each of three separate test days within the time span of two weeks.

The precision results as determined by this ITP may not be applied to acceptance or rejection testing for any group of materials or products without documentation that the results of this precision evaluation actually apply to the products or materials tested.

A.2 Results

A.2.1 General

The precision results are given in Table A.1, for each of the 14 polymers where the precision values are sorted for each category by mean stress-relaxation rate. Repeatability and reproducibility statements are given in A.2.2 and A.2.3.

A.2.2 Repeatability

The repeatability, or local domain precision, of this test method has been established by the values found in Table A.1, for each of the listed polymers. Two single test results (obtained by the proper use of this part of ISO 289) that differ by more than the tabulated values for r, in measurement units and (r), in percent, shall be considered as suspect, i.e. to have come from different populations. Such a decision suggests that some appropriate investigative action be taken.

In general the repeatability (r), is in the 1 % to 6 % range. As an average, the non-EPDM materials have a slightly better repeatability than the EPDM materials.

A.2.3 Reproducibility

The reproducibility, or global domain precision, of this test method has been established by the values found in Table A.1, for each of the listed polymers. Two single test results obtained in different laboratories (by the proper use of this part of ISO 289) that differ by more than the tabulated values for R, in measurement units and (R), in percent, shall be considered as suspect, i.e. to have come from different populations. Such a decision suggests that some appropriate investigative action be taken.

The reproducibility (R), is in the 3 % to 8 % range with one exception — EPDM-5, which has a value of 16 %. There appears to be no difference in overall reproducibility for the two categories of polymers.

A.3 Inter-laboratory agreement

Although all laboratories had good agreement for average slope values for all 14 polymers (only one exception among all labs), two of the laboratories generated outlier values (at the 5 % significance level) for within-lab standard deviations for several of the polymers. These outlier values were replaced with special replacement values by the procedures as outlined in ISO/TR 9272 [13]. For an ITP that has a bare minimum of participating laboratories (i.e. 6) the treatment of outliers by deletion, reduces the degrees of freedom for precision evaluation and therefore seriously compromises the final precision. Thus for any ITP with a bare minimum of participating laboratories, the outlier replacement option is required. This option replaces the outlying value(s) with lower replacement value(s), for either the averages or standard deviations, as obtained by a special procedure that maintains the distributional character of the database as generated by the program.

A.4 Bias

Bias is the difference between a test value and a reference or true value. Reference values do not exist for this test method, therefore bias cannot be determined.

Table A.1 — Type 1: Precision for Mooney stress-relaxation rate

Polymer	ML Mean level	MSR Mean level	Within laboratories			Between laboratories			Number of labs
			s_r	r	(r)	s_R	R	(R)	
EPDM-1	76,9	0,393	0,001 3	0,003 7	0,95	0,004 9	0,013 7	3,49	6
EPDM-2	72,8	0,447	0,001 5	0,004 1	0,91	0,005 1	0,014 2	3,18	6
EPDM-3	80,2	0,538	0,002 4	0,006 8	1,26	0,006 4	0,017 6	3,31	6
EPDM-4	55,5	0,750	0,010 7	0,030 1	4,01	0,016 1	0,045 1	6,01	6
EPDM-5	24,5	0,750	0,012 6	0,035 2	4,69	0,042 5	0,119 1	15,88	6
EPDM-6	46,7	0,931	0,018 8	0,052 7	5,66	0,024 9	0,069 6	7,48	6
IIR-1	78,2	0,234	0,002 2	0,006 2	2,64	0,003 3	0,009 2	3,95	5
IIR-2	51,7	0,623	0,004 7	0,013 2	2,12	0,007 1	0,020 0	3,21	5
SBR 1712	54,2	0,334	0,002 1	0,005 9	1,77	0,004 1	0,011 5	3,45	6
SBR 1500	49,6	0,415	0,002 7	0,007 7	1,86	0,006 9	0,019 2	4,64	6
NBR-1	77,9	0,343	0,002 4	0,006 7	1,95	0,005 1	0,014 2	4,13	6
NBR-2	81,6	0,373	0,001 1	0,003 1	0,84	0,005 2	0,014 5	3,88	6
NBR-3	30,7	0,424	0,004 8	0,013 5	3,18	0,011 9	0,033 2	7,84	6
NBR-4	32,3	0,571	0,003 7	0,010 5	1,83	0,016 0	0,044 9	7,87	6

s_r is the within-laboratory standard deviation (in measurement units)

r is the repeatability (in measurement units)

(r) is the repeatability (in percent of mean level)

s_R is the between-laboratory standard deviation (for total between laboratory variation in measurement units)

R is the reproducibility (in measurement units)

(R) is the reproducibility (in percent of mean level)