INTERNATIONAL STANDARD

ISO 9924-3

First edition
2009-03-15

Rubber and rubber products — Determination of the composition of vulcanizates and uncured compounds by thermogravimetry —

Part 3:

Hydrocarbon rubbers, halogenated rubbers and polysiloxane rubbers after extraction

Caoutchouc et produits à base de caoutchouc — Détermination de la composition des vulcanisats et des mélanges non vulcanisés par thermogravimétrie —

Partie 3: Caoutchoucs hydrocarbonés, caoutchoucs halogénés et caoutchoucs polysiloxanes après extraction

Reference number
ISO 9924-3:2009(E)

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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.

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 9924-3 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

ISO 9924 consists of the following parts, under the general title *Rubber and rubber products — Determination of the composition of vulcanizates and uncured compounds by thermogravimetry*:

- *Part 1: Butadiene, ethylene-propylene copolymer and terpolymer, isobutene-isoprene, isoprene and styrene-butadiene rubbers*
- *Part 2: Acrylonitrile-butadiene and halobutyl rubbers*
- *Part 3: Hydrocarbon rubbers, halogenated rubbers and polysiloxane rubbers after extraction*

INTERNATIONAL STANDARD **ISO 9924-3:2009(E)**

Rubber and rubber products — Determination of the composition of vulcanizates and uncured compounds by thermogravimetry —

Part 3:
Hydrocarbon rubbers, halogenated rubbers and polysiloxane rubbers after extraction

WARNING — Persons using this part of ISO 9924 should be familiar with normal laboratory practice. This part of ISO 9924 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 to ensure compliance with any regulatory conditions.

CAUTION — Certain procedures specified in this part of ISO 9924 may 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 part of ISO 9924 specifies a thermogravimetric method for the determination of the main constituents of rubber compounds such as elastomer(s), carbon black and mineral filler.

It establishes the “fingerprint” of the tested material. However, the result does not always correspond exactly to the theoretical formula of the rubber.

This method applies to raw or compounded rubbers, vulcanized and unvulcanized, after preliminary extraction.

This method applies to rubbers with hydrocarbon backbones (NR, BR, SBR, IIR, EPDM, ACM, AEM, etc.) used alone or as mixtures. For the mixtures, the polymer content corresponds to the total rubber, and it is not usually possible to identify individual polymers.

This method applies to rubbers with halogenated hydrocarbon backbones (CR, CSM, FKM, CM, CO, ECO, etc.) or containing nitrogen (NBR, HNBR, NBR/PVC, etc.), as well as to their mixtures. However, these rubbers often form carbonaceous residues which interfere with the analysis. Application of an appropriate procedure minimizes these interferences.

This method also applies to rubbers with a polysiloxane backbone (VMQ, etc.) and to rubbers not listed above.

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 1407, *Rubber — Determination of solvent extract*

ISO 23529, *Rubber — General procedures for preparing and conditioning test pieces for physical test methods*

3 Principle

A weighed test portion is heated following a pre-set programme in a known atmosphere.

Initial pyrolysis in an inert atmosphere (nitrogen) is followed by combustion in an oxidizing atmosphere.

Generally, the reactions that generate mass variations are decompositions, oxidations, or reactions volatilizing a constituent.

The loss in mass as a function of temperature indicates a quantitatively usable thermogram which is characteristic of the material.

4 Reagents

4.1 Nitrogen of minimal purity 99,995 % mass fraction, with an oxygen content of less than 10 mg/kg (ppm) and hydrocarbon content less than 1,5 mg/kg (ppm).

4.2 Dry air, with no detectable trace of oil.

The air used may be reconstituted nitrogen and oxygen of purity minimum 99,5 % mass fraction. In some cases, pure oxygen may be used.

5 Apparatus

5.1 Thermogravimetric analyser.

5.1.1 General. Various types of analyser are commercially available. The basic components of an analyser are listed in 5.1.2 to 5.1.8.

5.1.2 Thermogravimetric balance, comprising a microbalance provided with a pan made from a nonoxidizable material, that can weigh up to 50 mg, is readable to the nearest 1 µg, and equipped with an oven capable of being maintained at temperatures from room temperature to approximately 1 000 °C.

5.1.3 Appropriate enclosure allowing the sample to be kept under a specified atmosphere.

5.1.4 Pan or **crucible** of size suitable to accommodate the sample and small enough to reduce the influence of buoyancy.

5.1.5 Temperature-control system, allowing heating rates to be controlled from 10 °C/min to 50 °C/min.

5.1.6 Gas selector allowing successive introduction of the inert gas and oxidizing gas while controlling the flow rate.

5.1.7 Measurement equipment for gas flow rate in the range 10 cm^3/min to 250 cm^3/min.

5.1.8 Data acquisition and processing system.

6 Preparation of samples

6.1 Conditioning of samples

Test samples should be conditioned in standardized laboratory conditions of temperature and humidity in accordance with ISO 23529. These conditions are preferred, but are not mandatory.

6.2 Extraction of samples

A preliminary extraction of plasticizers and additives shall be performed in accordance with ISO 1407 using the appropriate solvent. Conventionally, the amount of extract is denoted w_1.

6.3 Test portion

After extraction (6.2), prepare a test portion of 8 mg ± 3 mg cut into a single piece.

NOTE The preparation of the test portion can influence the kinetics of the phenomena.

7 Procedure

7.1 General

Considering the variety of the decomposition modes linked to the nature of polymers, two procedures are defined:

a) procedure A for carbon rubbers;

b) procedure B for polysiloxane and fluorocarbon rubbers.

If procedure A does not result in a thermogram that achieves constant mass at 600 °C, procedure B shall apply.

A non-exhaustive list of the recommended procedures for each of the various rubber families is given in Table A.1.

7.2 Description of the procedures

Table 1 gives details of the operating steps for procedures A and B.

Table 1 — Operating steps

Step	Units	Procedure A	Procedure B
Initial temperature	°C	35 ± 10	35 ± 10
Heating rate under nitrogen	°C/min	20	20
Target temperature under nitrogen	°C	600	800
Maintenance time at target temperature under nitrogen	min	0	5
Cooling under nitrogen	°C	600 to 400	800 to 400
Temperature at the change of atmosphere	°C	400	400
Maintenance time at atmosphere change temperature under air	min	2	2
Heating rate under air	°C/min	20	20
Final temperature under air according to the equipment [a]	°C	800 to 850	800 to 850
Maintenance time at the final temperature under air	min	10 to 20	10 to 20

[a] If procedures do not result in a thermogram that achieves constant mass at final temperature under air, maintain the final temperature condition until constant mass is achieved.

7.3 Test procedures

7.3.1 Connect the apparatus and adjust (5.1.6) the gas flow to a rate between 20 cm^3/min and 250 cm^3/min (5.1.7). Set the parameters according to the chosen process.

The recommended flow rate is 100 cm^3/min.

7.3.2 Before the test, ensure that the pan (5.1.4) or the crucible is clean and empty.

7.3.3 Close the thermobalance oven (5.1.2), purge with a nitrogen (4.1) flow at the preset rate. Wait until stabilization. Adjust the zero to compensate for the mass of the pan or the crucible.

7.3.4 Place the test piece prepared in accordance with 6.3 in the pan or the crucible and weigh it under the conditions specified in 7.3.3. Record the mass, m_0.

7.3.5 Conduct the test by following the operating steps specified in Table 1.

7.3.6 At the end of the test, allow the oven to cool to room temperature, open it and clean the pan or the crucible.

8 Expression of results

8.1 Recordings

Make two different types of recording to enable the necessary calculations to be made:

a) a plot of the percentage variation in mass fraction, w, vs. temperature or time;

b) a derivative plot, $\mathrm{d}w/\mathrm{d}T$.

These will be used to derive the content of the various compound ingredients.

8.2 Calculation of the mass change from curves

An example of a thermogram is given in Figure B.1.

The derivative plot shall be used to define particular points on the mass variation plot as follows.

Identify on the derivative plot the minima A'_0, A'_1, A'_2, and A'_3, corresponding to the closest points to return to zero of the derived function. Note these points on the main curve of mass change. Report A_0, A_1, A_2, and A_3 on the ordinate and read the corresponding masses m_0, m_1, m_2, and m_3, where

m_0 is the initial mass of the test piece;

m_1 is the mass of the test piece remaining after pyrolysis;

m_2 is the mass of the test piece remaining after pyrolysis and carbon black combustion;

m_3 is the mass of the residue yield.

The percentage mass fraction loss, w_2, due to pyrolysis is given by:

$$w_2 = \frac{m_0 - m_1}{m_0} \times 100 \qquad (1)$$

The percentage mass fraction loss, w_5, due to carbon black combustion is given by:

$$w_5 = \frac{m_1 - m_2}{m_0} \times 100 \qquad (2)$$

The percentage mass fraction loss, w_7, due to partial or total decomposition of mineral components is given by:

$$w_7 = \frac{m_2 - m_3}{m_0} \times 100 \qquad (3)$$

The percentage mass fraction, w_8, corresponding to the residue yield, is given by:

$$w_8 = \frac{m_3}{m_0} \times 100 \qquad (4)$$

The sum of the percentage mass fractions, $w_2 + w_5 + w_7 + w_8$, shall correspond to 100 % (not including the analytical errors).

NOTE These operations can be calculated by computer.

8.3 Interpretation

8.3.1 General

A simple interpretation of the thermogram shall give pyrolysable, non-pyrolysable mass fraction losses and the residue.

8.3.2 Rubbers with hydrocarbon backbones (Figures B.2 and B.3)

a) Under nitrogen

The first loss in mass fraction, w_2, corresponds to the pyrolysis of one or several polymers. The end of the polymer decomposition is arbitrarily taken at the end of the heating step under nitrogen.

b) Under oxidizing atmosphere

1) w_5 is the loss in mass fraction, due to carbon black combustion (if any is present in the compound)

2) w_7 is the loss in mass fraction, due to the partial or total decomposition of mineral components (e.g. $CaCO_3$), (see Figure B.3)

3) w_8 is the residue yield at 800 °C

4) w_6 is the mineral content, equal to $w_7 + w_8$

8.3.3 Rubbers with a nitrogenous hydrocarbon backbone (Figure B.4)

For nitrogen-containing hydrocarbon rubbers, the thermogram produced while nitrogen is flowing is similar to that described in 8.3.2. However, during pyrolysis, carbonaceous residues may be generated. These residues usually oxidize at lower temperatures than carbon black. If the resolution of the derivative plot allows, the corresponding mass fraction loss, w_3, shall be added to the pyrolysate yield, w_2.

8.3.4 Rubbers with a halogenated hydrocarbon backbone (Figure B.5)

For rubbers with a halogenated hydrocarbon backbone, the pyrolytic decomposition of the polymer takes place in several steps, in particular with:

a) generation of volatile halogenated fragments;

b) formation of carbonaceous residues.

The percentage mass fraction lost of halogenated volatile components, w_4, shall be taken into account for the calculation of the content of polymer which is then equal to $w_4 + w_2$.

As the carbonaceous residues can hardly be distinguished from the carbon black, the total content of carbon black shall be taken as $w_3 + w_5$.

8.3.5 Rubbers with a hydrocarbon, nitrogenous and oxygenated backbone

The thermogram is expressed in a similar way as for some rubbers with a hydrocarbon backbone (see 8.3.2).

8.3.6 Rubbers with a hydrocarbon and sulfurated backbone

The thermogram is expressed in a similar way as for some rubbers with a hydrocarbon backbone (see 8.3.2).

8.3.7 Rubbers with a polysiloxane backbone

The thermogram is expressed in a similar way as for some rubbers with a hydrocarbon backbone (see 8.3.2).

8.4 Expression of results

8.4.1 Result obtained from the TGA curve

Indicate, where necessary, the following conventional values:

a) w_2 content lost due to pyrolysable part of polymer(s);

b) w_3 content lost due to combustion of any carbonaceous residues;

c) w_4 content lost due to driving off any halogenated volatile fragments;

d) w_5 content lost due to combustion of carbon black;

e) w_6 content of mineral fillers and metallic salts;

f) w_7 content lost due to mineral filler decomposition;

g) w_8 mineral residue yield at 800 °C or 850 °C under air.

8.4.2 Correction for extract in calculated percentage mass fractions of material

It is necessary to take into account the amount of extract in the calculation of the percentages. Calculate the extract-corrected mass fractions, w_n', using the equation

$$w_n' = \frac{w_n\,(100 - w_1)}{100} \tag{5}$$

where

n is 2 to 8 (for definitions of the individual parameters, see 8.4.1);

w_1 is the extractable matter content, as a percentage mass fraction, determined by solvent extraction.

9 Test report

The test report shall contain at least the following information:

a) sample details:
  1) full description of the sample and its origin,
  2) conditions of preparation of the sample,
  3) the extraction solvent with the method used;

b) test method:
  1) a full reference to the test method used, i.e. the number of this International Standard,
  2) the method used (A or B);

c) test details:
  1) the laboratory temperature,
  2) the time and temperature of conditioning prior to test,
  3) the temperature of test, if other than standard laboratory temperature,
  4) type of equipment used,
  5) details of any procedures not specified in this International Standard as well as the possible incidents;

d) test results:
  1) the number of test pieces used,
  2) the individual test results,
  3) the date of test.

10 Precision

See Annex C.

Annex A
(informative)

Recommended procedures

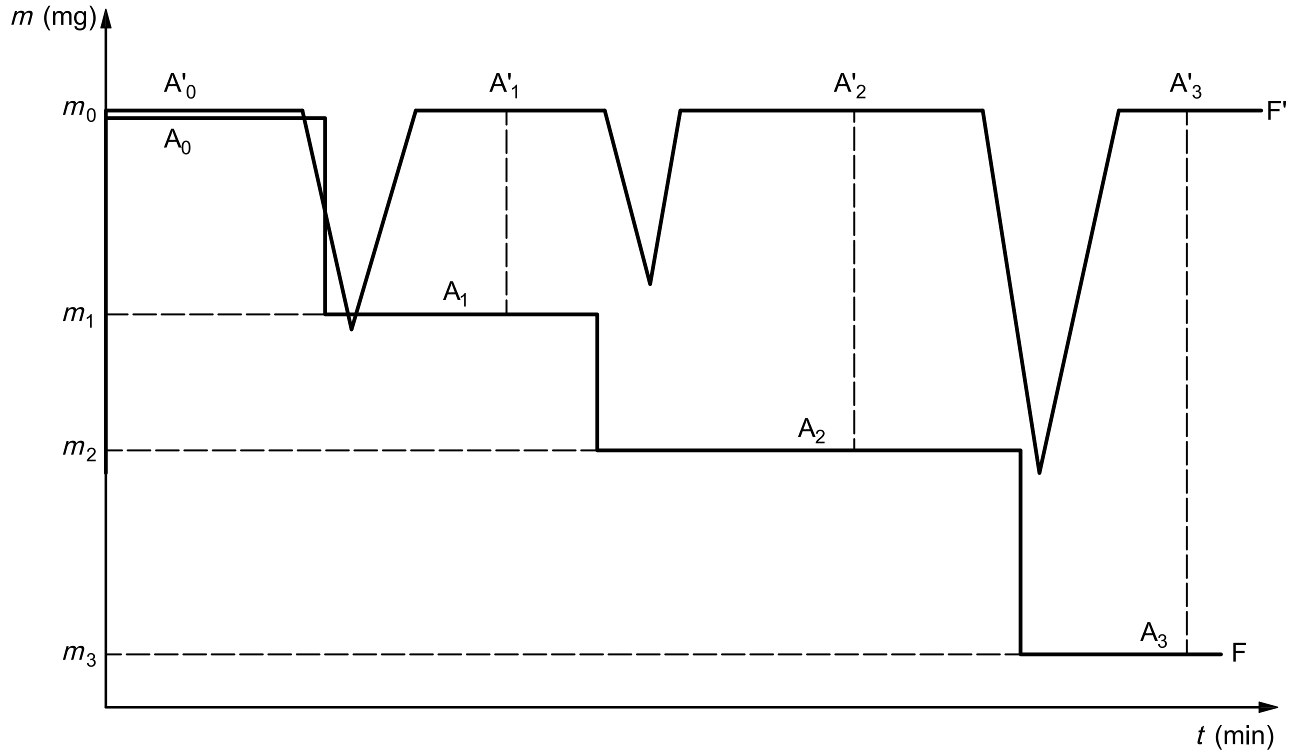
Table A.1 — Recommended procedures according to rubber families (non-exhaustive list)

Rubber families	Procedure
Rubbers with a hydrocarbon backbone	
Natural rubber (NR) or synthetic isoprene rubber (IR)	A
Polybutadiene (BR)	A
Styrene-butadiene rubber (SBR)	A
Isobutene-isoprene rubber (IIR)	A
Ethylene-propylene-diene terpolymer (EPDM)	A
Copolymer of ethyl acrylate or other acrylates (ACM)	A
Copolymer of ethyl acrylate or other acrylates and ethylene (AEM)	A
Copolymer of ethylene and vinyl acetate (EVM)	A
Rubbers with a nitrogenous hydrocarbon backbone	
Acrylonitrile-butadiene rubber (NBR)	A
Hydrogenated acrylonitrile-butadiene rubber (HNBR)	A
Carboxylic acrylonitrile-butadiene rubber (XNBR)	A
Rubbers with a halogenated hydrocarbon backbone	
Chloroprene rubber (CR)	A
Chlorosulfonylpolyethylene (CSM)	A
Chloropolyethylene (CM)	A
Alkyl chlorosulfonylpolyethylene (ACSM [a])	A
Polychloromethyloxirane (CO)	A
Copolymer of ethylene oxide and chloromethyloxirane (ECO)	A
Acrylonitrile-butadiene rubber/polyvinylchloride blend (NBR/PVC)	A
Isobutene-isoprene rubber brominated or chlorinated (BIIR or CIIR)	A
Fluorocarbon rubbers (FKM)	B
Rubbers with a hydrocarbon, nitrogenous and oxygenated backbone	
Polyester urethane or polyether urethane (AU or EU)	A
Rubbers with a hydrocarbon and sulfurated backbone	
Polysulfide rubber (T)	A
Rubbers with a polysiloxane backbone	
Polymethylvinylsiloxane (VMQ)	B
Polymethylfluorosiloxane (FMQ)	B
[a] Name and abbreviated term do not appear in ISO 1629 [1].	

Annex B
(informative)

Examples of thermogram

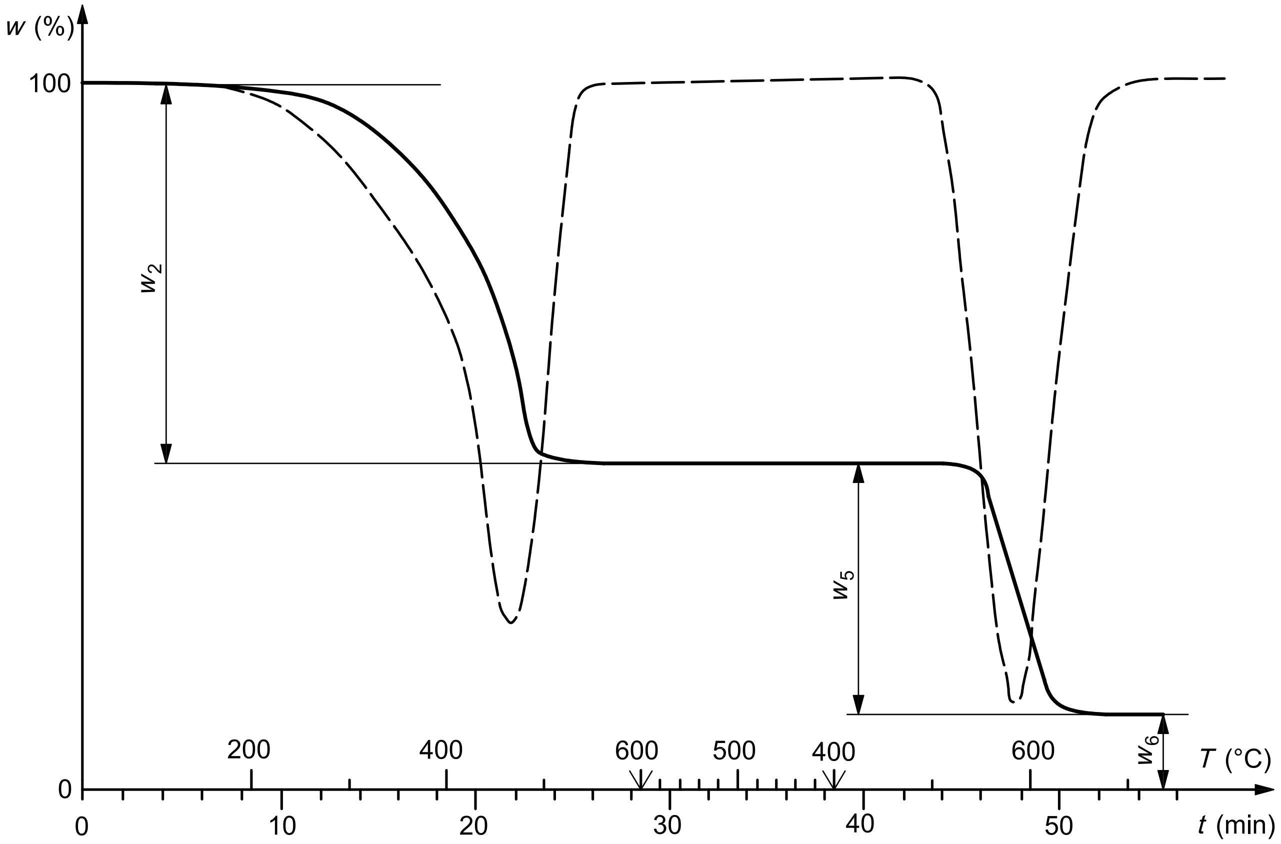
Examples of various thermograms are illustrated in Figure B.1 to B.5



Key

A_0, A_1, A_2, A_3	absolute minima	m_0	initial test piece mass
A'_0, A'_1, A'_2, A'_3	derivative minima	m_1	test piece mass after pyrolysis
F	main curve	m_2	test piece mass after pyrolysis and carbon black combustion
F′	derivative curve	m_3	residue yield mass
m	mass	t	time

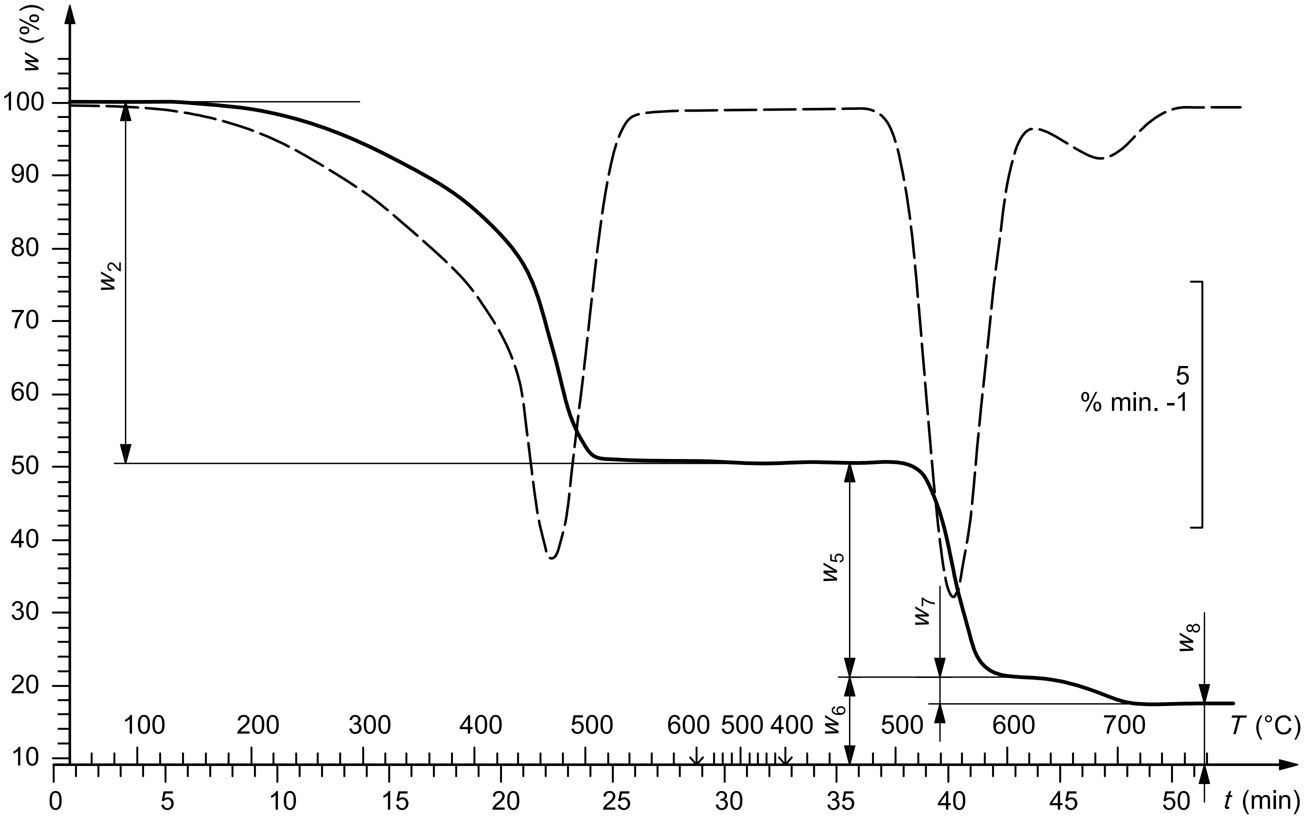
Figure B.1 — Thermal diagram



Key

t	time
T	temperature
w	mass fraction (content)
w_2	content lost due to pyrolysable part of polymer(s)
w_5	content lost due to combustion of carbon black
w_6	content of mineral fillers and metallic salts

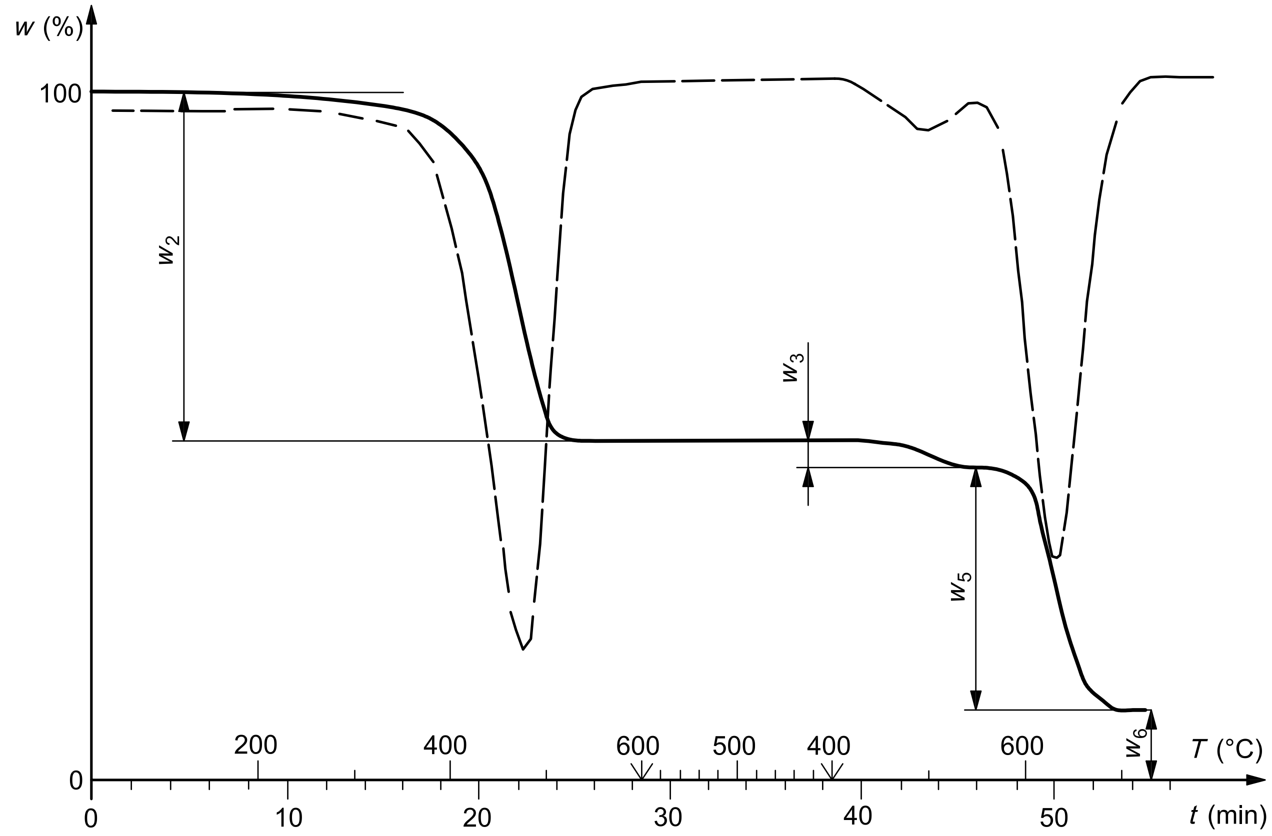
Figure B.2 — Example of a rubber with a hydrocarbon backbone



Key

t	time
T	temperature
w	mass fraction (content)
w_2	content lost due to pyrolysable part of polymer(s)
w_5	content lost due to combustion of carbon black
w_6	content of mineral fillers and metallic salts
w_7	content lost due to mineral filler decomposition
w_8	mineral residue yield at 800 °C or 850 °C under air

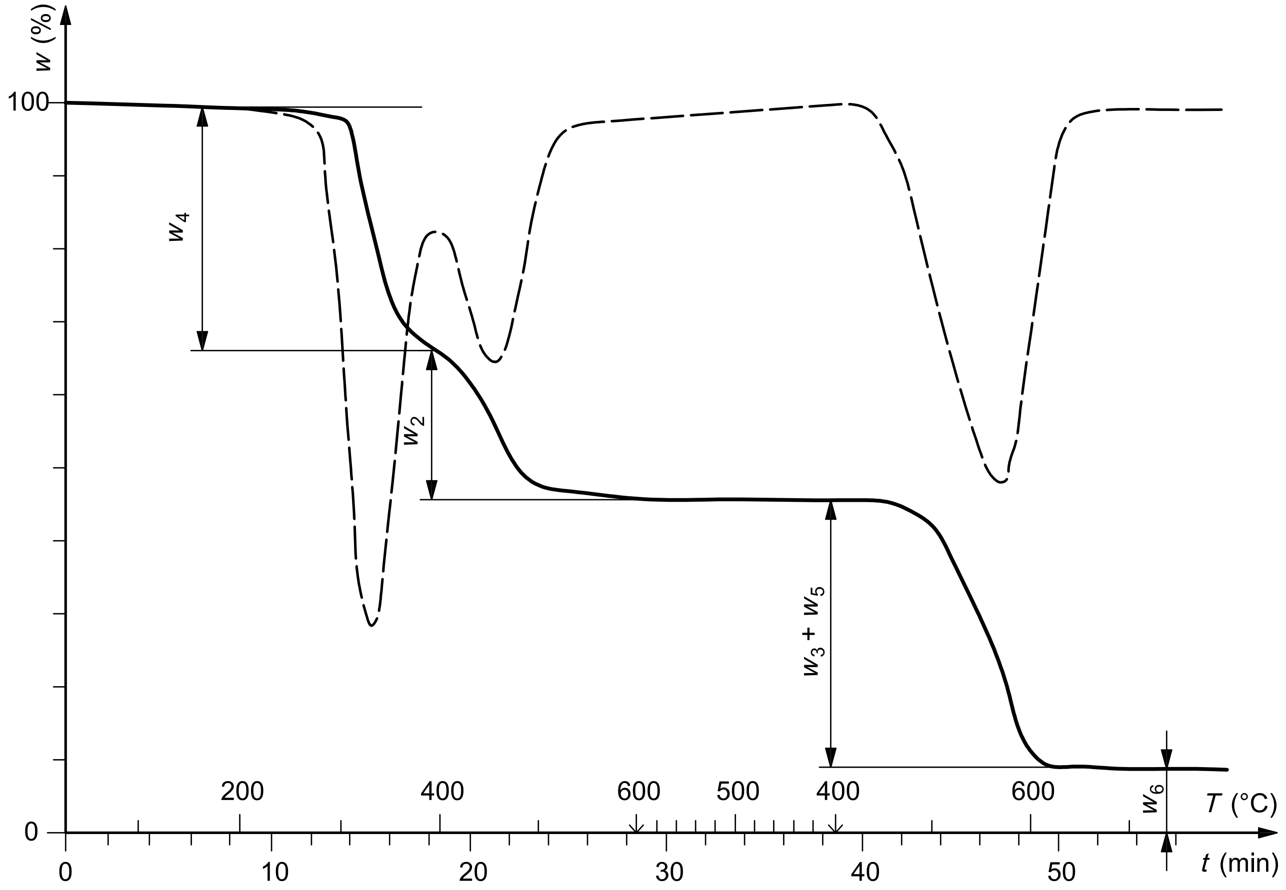
Figure B.3 — Example of a rubber with a hydrocarbon backbone, containing calcium carbonate



Key

t	time
T	temperature
w	mass fraction (content)
w_2	content lost due to pyrolysable part of polymer(s)
w_3	content lost due to combustion of any carbonaceous residues
w_5	content lost due to combustion of carbon black
w_6	content of mineral fillers and metallic salts

Figure B.4 — Example of a rubber with a backbone containing hydrocarbon and nitrogen



Key

t	time
T	temperature
w	mass fraction (content)
w_2	content lost due to pyrolysable part of polymer(s)
w_3	content lost due to combustion of any carbonaceous residues
w_4	content lost due to driving off any halogenated volatile fragments
w_5	content lost due to combustion of carbon black
w_6	content of mineral fillers and metallic salts

Figure B.5 — Example of a rubber with a halogenated hydrocarbon backbone

Annex C
(informative)

Precision

C.1 General

Precision was evaluated by an interlaboratory test programme (ITP) conducted in 2006 in accordance with ISO/TR 9272:2005[2]. See ISO/TR 9272:2005[2] for details of terminology, analysis procedures, and the expression of precision.

Interlaboratory tests for the three “phase” components listed in Table C.1 were conducted on compounds using three polymers; CR and NBR, where the analysis components were total polymer, carbon black and mineral residue and VMQ where two major components were evaluated, namely organic content and mineral residue. A total of 17 laboratories participated in the ITP and test results were obtained on a day 1 – day 2 basis with 7 days between the day measurements. A test result is a single measurement of any component. ISO 9272:2005[2], option 1 outlier deletion was adopted for each analysis. The programme as conducted evaluates type 1 precision based on test results with samples ready for test upon arrival in each laboratory. The precision results for all component types are given in Table C.1.

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.

General statements for the use of the precision results are cited in Clauses C.2 to C.5. These are given in terms of both the absolute precision, r or R, and also for relative precision, (r) and (R).

Table C.1 — Precision for interlaboratory test programme

			Within lab			**Between labs**			
Material	**Phase**	**Mean**	**Standard deviation**[a]	**Repeatability**[a]	**Repeatability as percentage of mean**	**Standard deviation**[a]	**Reproducibility**[a]	**Reproducibility as percentage of mean**	**Number of labs after deleting outliers**
	%		s_r	r	(r)	s_R	R	(R)	
CR	Total polymer	41,0	0,20	0,56	1,36	0,90	2,52	6,15	15
	Carbon black	55,8	0,28	0,77	1,38	1,24	3,48	6,23	16
	Mineral salts	2,8	0,11	0,32	11,2	0,55	1,53	53,9	12
NBR	Total polymer	59,1	0,23	0,64	1,09	0,33	0,93	1,57	14
	Carbon black	37,7	0,22	0,63	1,66	0,34	0,94	2,50	15
	Mineral salts	3,1	0,063	0,176	5,61	0,28	0,77	24,7	11
VMQ	Organic content	45,7	0,17	0,46	1,01	0,40	1,11	2,42	12
	Ash content	54,2	0,17	0,47	0,97	0,41	1,16	2,13	12

[a] In measurement units.

C.2 Repeatability

The repeatability, or local domain precision, for each of the test properties has been established for each material or polymer by the values found in Table A.1. Two individual test results (obtained by the proper use of this part of ISO 9924) that differ by more than the tabulated values for r, in measurement units and (r), as a percentage, shall be considered as suspect, i.e. to have come from different populations. Such a decision suggests that some appropriate investigative action be taken.

C.3 Reproducibility

The reproducibility, or global domain precision, for each of the phases has been established for each material or polymer by the values found in Table A.1. Two individual test results obtained in different laboratories (by the proper use of this part of ISO 9924) that differ by more than the tabulated values for R, in measurement units, and (R), as a percentage, shall be considered as suspect, i.e. to have come from different populations. Such a decision suggests that some appropriate investigative action be taken.

C.4 Analysis comments

The relative repeatability, (r), for both ITPs is good, in the range 1 % to 2 % for total polymer and carbon black. The relative reproducibility, (R), for both ITPs is also good, in the range 2 % to 7 % for total polymer and carbon black. The residue and mineral salts content for CR and NBR has poorer precision (higher values), (r) ranges from 6 % to 11 % and (R) ranges from 25 % to 55 %. For VMQ, the mineral residue content measurements gave an (r) of approximately 1 % and (R) values in the range 2 % to 3 %, both quite good. This better precision is due to the higher residue level (average) compared to the low values for mineral salts in the 2 % to 3 % average range.

C.5 Bias

Bias is the difference between a measured average test result and a reference or true value for the measurement in question. Reference values do not exist for this test method and therefore bias cannot be evaluated.

Bibliography

[1] ISO 1629, *Rubber and latices — Nomenclature*

[2] ISO/TR 9272:2005, *Rubber and rubber products — Determination of precision for test method standards*

ICS 83.060

Price based on 16 pages