Report

Reference Material

BAM-E028

Compound for curemeter (MDR)

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Coordinator: Dietmar Schulze
Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 7.5 „Technical Properties of Polymeric Materials "
Unter den Eichen 87
D-12205 Berlin
Phone: +49 30 8104 3340
Email: dietmar.schulze@bam.de

Summary

This report describes preparation, analysis and characterization of the reference material (RM) BAM-E028. This reference material is an unvulcanized rubber compound, available as a section of a compound sheet. It is intended to represent characteristic properties of an elastomer compound for the manufacture of a vulcanized rubber. It may be used to review and check the results of a corresponding testing device, i.e. a curemeter or moving die rheometer for rubber.
The following typical properties of an elastomer compound may be covered by this reference material:

property	Value [unit]	Range [unit][1)]
M_L	2.55 dNm	0.10 dNm
ts_1	0.69 min	0.06 min
ts_2	0.81 min	0.07 min
tc_{50}	1.43 min	0.14 min
tc_{90}	2.84 min	0.25 min
M_H	21.44 dNm	1.87 dNm

1) The range was determined with 79 values from the homogeneity studies and with 6-time steps (3 measurements each) from the stability studies.

According to the evaluation of an interlaboratory reproducibility study, significant deviations are to be expected (see section 5).
This report contains detailed information on the preparation of the RM as well as on investigations concerning homogeneity and stability as well as on the methods used for characterization.
From the results, guidelines for shipment, handling and use of the RM are inferred.

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1. Introduction

In rubber industry the properties of an unvulcanized compound for manufacturing of a cured rubber are characterized by means of specific rheometers, commonly termed curemeters or vulcameters. These devices are able to monitor and record a vulcanization isotherm and to determine the reaction kinetics of the curing or vulcanization process. For the measurement a sample of the material under investigation is subjected to a cyclic deformation with constant frequency and amplitude.
The properties of the reference material BAM-E028 are determined using a torsional rheometer as specified in ISO 6502, part 1 [1], and ISO 6502, part 3 [2]. In particular, an unsealed torsion-shear rotorless curemeter with biconical-die cavity was used, also known as Moving Die Rheometer (MDR).

In this device a shear strain is exerted on the test specimen of rubber compound in a pre-heated chamber. Two dies with a special surface pattern to maintain mechanical contact between die and specimen form this test chamber. Between these dies the torque is measured continuously. One die is exerting the shear strain of defined frequency and amplitude, the other is equipped with the torque sensor. The measured shear torque depends on the stiffness or shear modulus of the specimen. When a curing reaction sets-in (usually induced by the elevated temperature between the dies) the torque increases due the increasing crosslinking of the sample material. This process (vulcanization) is recorded as time-dependent torque signal up to an equilibrium value or until a maximum threshold is exceeded (ISO 6502, part 1). Alternatively, the curing may also be considered complete after a certain duration of time. Torque level as well as time period may strongly depend on the individual rubber compound and the chosen conditions of measurement.
From the recorded curve of the torque as a function of time, the following characteristic values can be determined (see Figure 1).

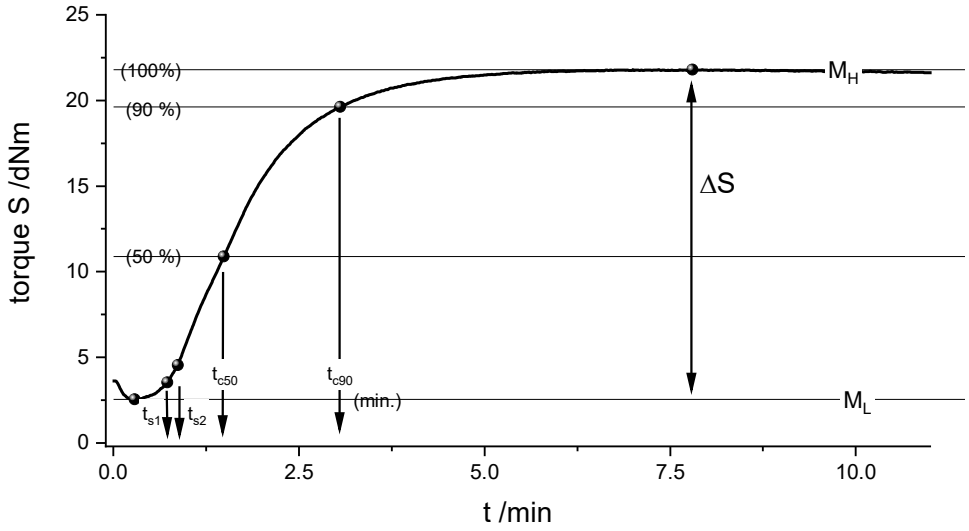

Figure 1: curemeter curve (schematic)

M_L		minimum torque
t_{s1}	-	Scorch time 1 (time to incipient cure)
t_{s2}		Scorch time 2 (time to incipient cure)
t_{c50}		time to 50% of full cure
t_{c90}		time to 90% of full cure
M_H		equilibrium torque (plateau)
DS		maximum change of torque

For the data presented in this report a torsional rheometer (MDR), with biconical-die cavity, according to ISO 6502, part 3, was used and the following measurement conditions were chosen:

- frequency: 1.66 Hz
- amplitude: 0.5 °
- temperature: 177 °C
- duartion of measuerement: 15 min
- specimen weight: ca. 5 g
- separation between die and specimen by commonly used separation foil (PET)

2. Candidate material and characterization study

For choosing a suitable rubber compound for the envisaged reference material several recipes based on different rubbers and different curing systems were evaluated. A compound based on SBR (Styrene-Butadiene-Rubber) was selected as best choice.

As the unvulcanized compound exhibits only a limited stability and storage life, for use as reference materials it has to be produced freshly again and again. (The time period for reliable use as RM and for being suitable for sale is addressed in section 4 below.) For the manufacture of the RM the quality management system of Division 7.5 BAM and the procedure for preparation and characterization described herein are applied.

As variations in the raw materials for manufacture have to be expected, the stated values for the RM may also slightly vary between lots. Nevertheless, the results concerning homogeneity and stability of the reference material BAM-E028 reported below are considered valid for all lots produced.

Generally, the evaluation of a freshly manufactured lot of the RM BAM-E028 is performed using a calibrated device (MDR) according to ISO 6502, part 3. The evaluation is performed at four points in time. The first measurement takes place after less than one day after manufacture of the compound. The subsequent measurements are due after one day, after 7 days and after 14 days. Each measurement has to be repeated three times. A median value for a certain property is then calculated based on all results (n=12) of these measurements and stated in the datasheet assigned to the lot of the reference material BAM-E028.

It should be noted that the date of property statement of BAM-E028 is therefore specified as 14 days after manufacture.

3. Evaluation of homogeneity

For the evaluation of the homogeneity of the reference material E028 a compound was produced according to the described procedure (section 2). The unvulcanized compound was sheeted out to a certain thickness and from this sheet several samples were taken for testing and characterization. Typically, a lot consists of about 4300 g of rubber compound. Samples for the curemeter (MDR) should have a similar volume and a mass of about 5 g and a diameter fitting into cavity of the test chamber (40 mm). Due to the uneven shape of the sheeted raw compound, there is an offcut. Overall, 91 samples were obtained for evaluation of the homogeneity which is more than 10 % of the complete amount of material. From the results of the 12 measurements (n=12) performed within the first 14 days after manufacture of this lot the median values of the characteristic properties were determined as specified in section 2. Within three weeks after manufacture, 79 additional measurements were performed. As a measure for the maximum scatter of each property the maximum deviation out of all values (n=91) with respect to the respective initial median value (from n=12) was taken.

characteristic property	*value [unit]*	*max. deviation [unit]*[1)]	*max deviation in %*
M_L	2.54 dNm	-0.10 dNm	-3.9 %
ts_1	0.73 min	-0.06 min	-8.2 %
ts_2	0.86 min	-0.07 min	-8.1 %
tc_{50}	1.61 min	-0.14 min	-8.7 %
tc_{90}	3.21 min	-0.25 min	-7.8 %
M_H	21.79 dNm	-0.62 dNm	-2.8 %

1) The maximal deviation range was determined from 79 values.

4. Evaluation of stability

For the evaluation of the stability of the reference material described another lot of the compound was produced according to the described procedure (section 2) and sheeted out. Parts of the sheet of this lot were stored at different temperatures for durations up to 372 days. The following temperatures were used and held constant over the respective period of time: 5 °C, 23 °C, 40 °C and 60 °C (Due to the greater changes induced at higher temperatures, the corresponding measurements were stopped earlier.)
For each temperature three samples were taken at different points in time and measured in the curemeter (MDR). Measurements were taken at a maximum of six points in time. At higher temperatures, correspondingly at fewer points in time.

In addition, the influence of packaging was addressed. Therefore, the compound stored at 5 °C and 23 °C was partly packaged in almost airtight pressure seal bags made from polyethylene.

The plots in figure 2 to 7 show the changes of the characteristic properties over time after storage under different conditions.

It has to be noted that the reference material BAM-E028 contains reactive ingredients and the key properties strongly depend on their actual residual reactivity when used. Although the curing is intended to start only at elevated temperatures and the actual test temperature is specified as 177 °C, significant changes under ambient or transport conditions cannot be excluded, even within comparatively short periods of time. Therefore, the shelf life and the time period of reliable application are limited. Duration and conditions of shipment, storage and application are to be considered critically.

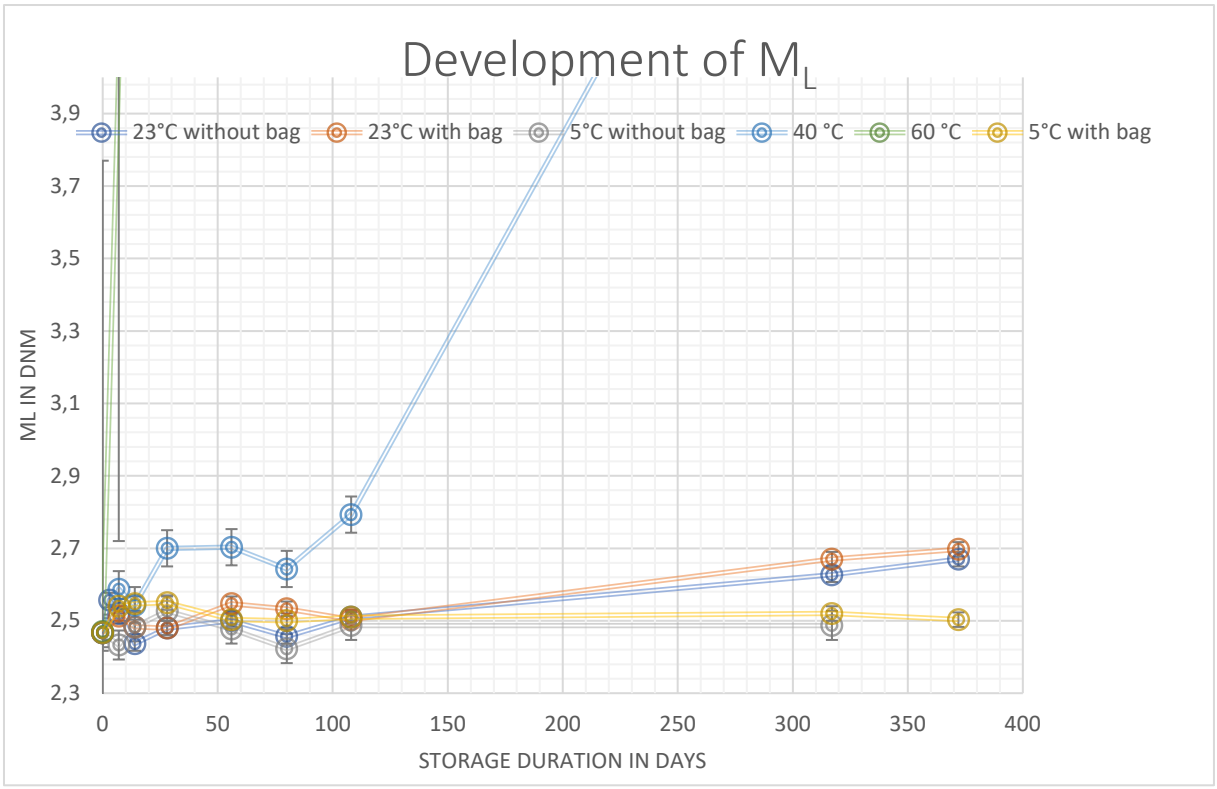

Figure 2: development of the minimum torque M_L under different storage conditions

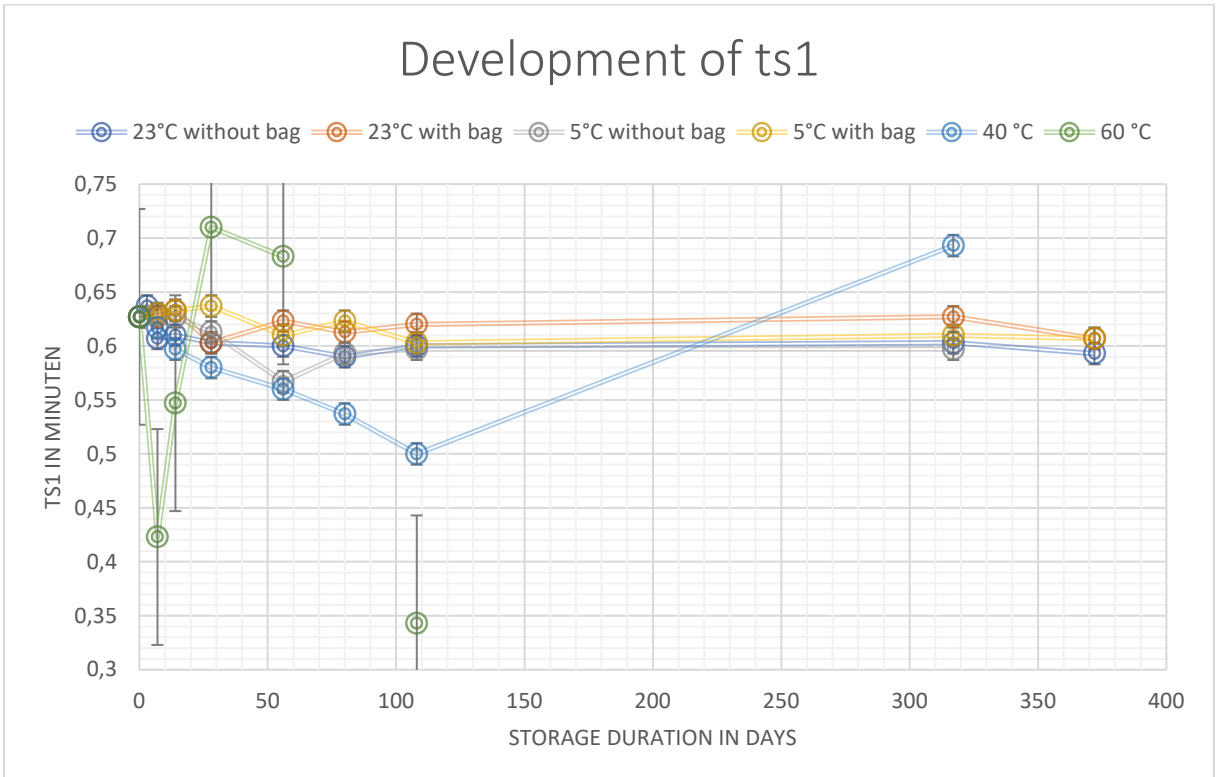

Figure 3: development of the minimum scorch time ts_1 under different storage conditions

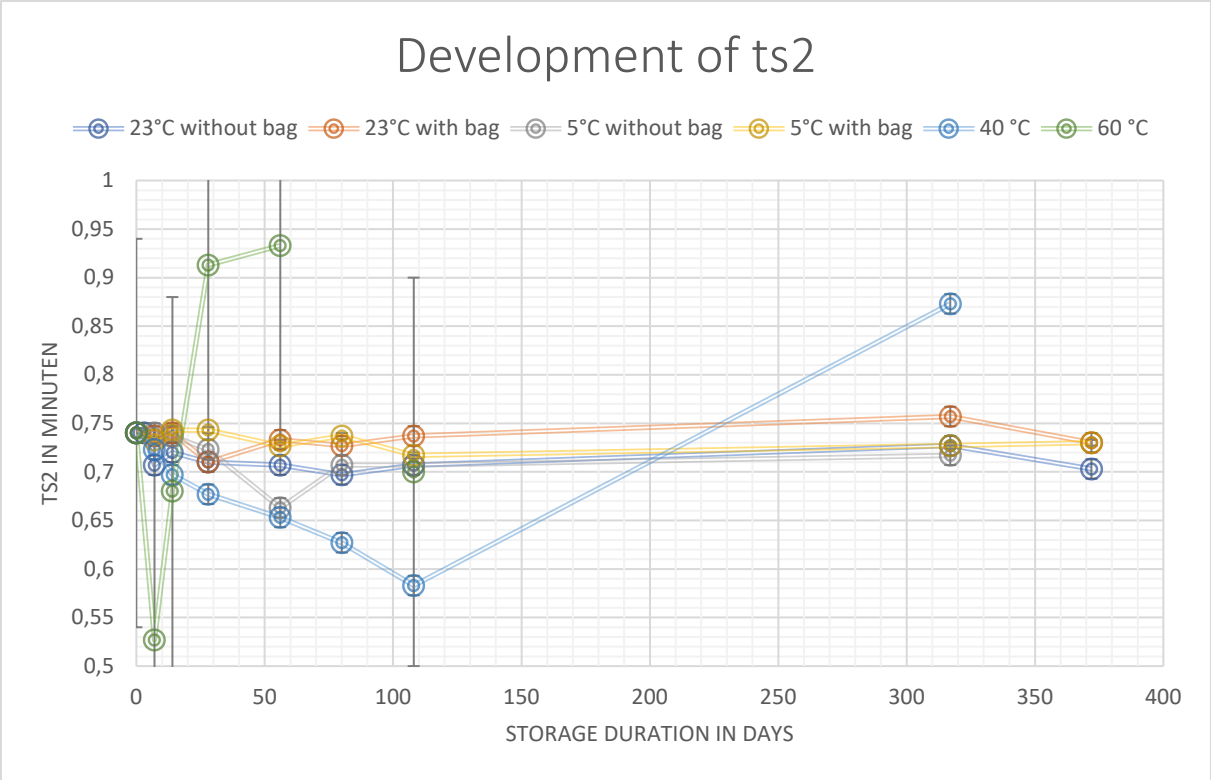

Figure 4: development of the scorch time ts_2 under different storage conditions

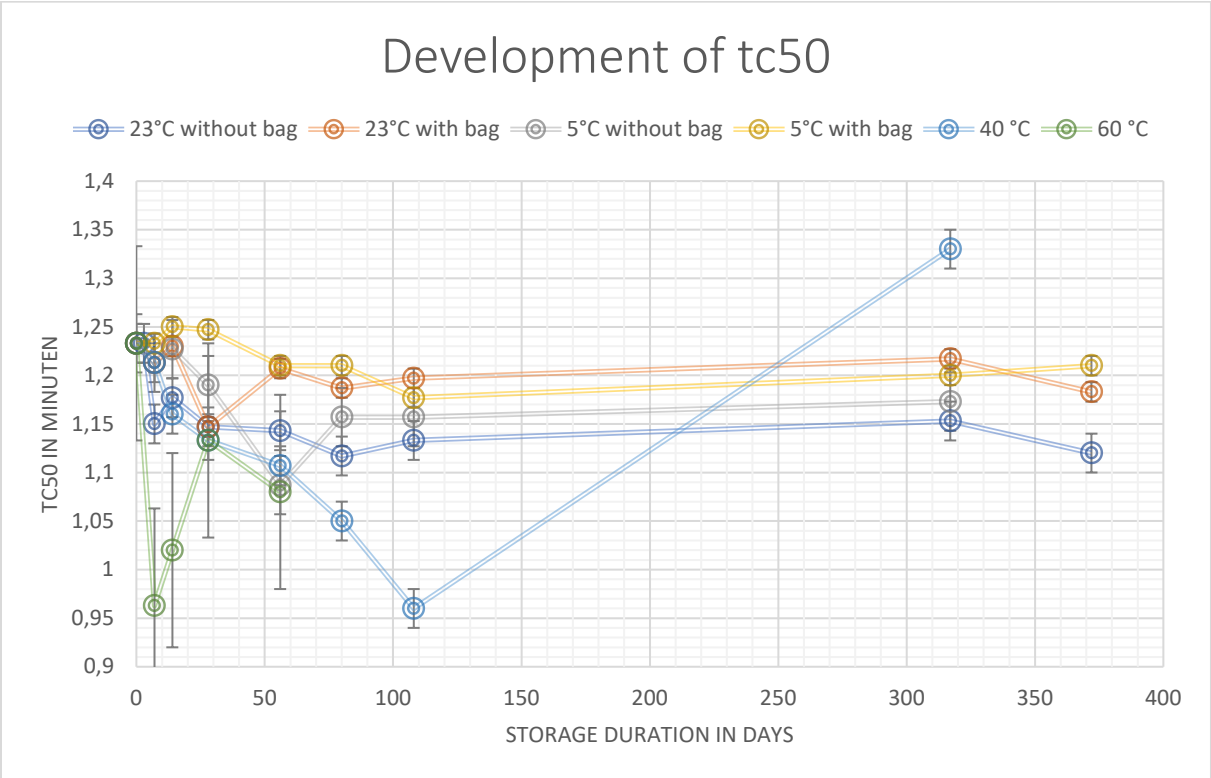

Figure 5: development of the time to 50 % of full cure tc_{50} under different storage conditions

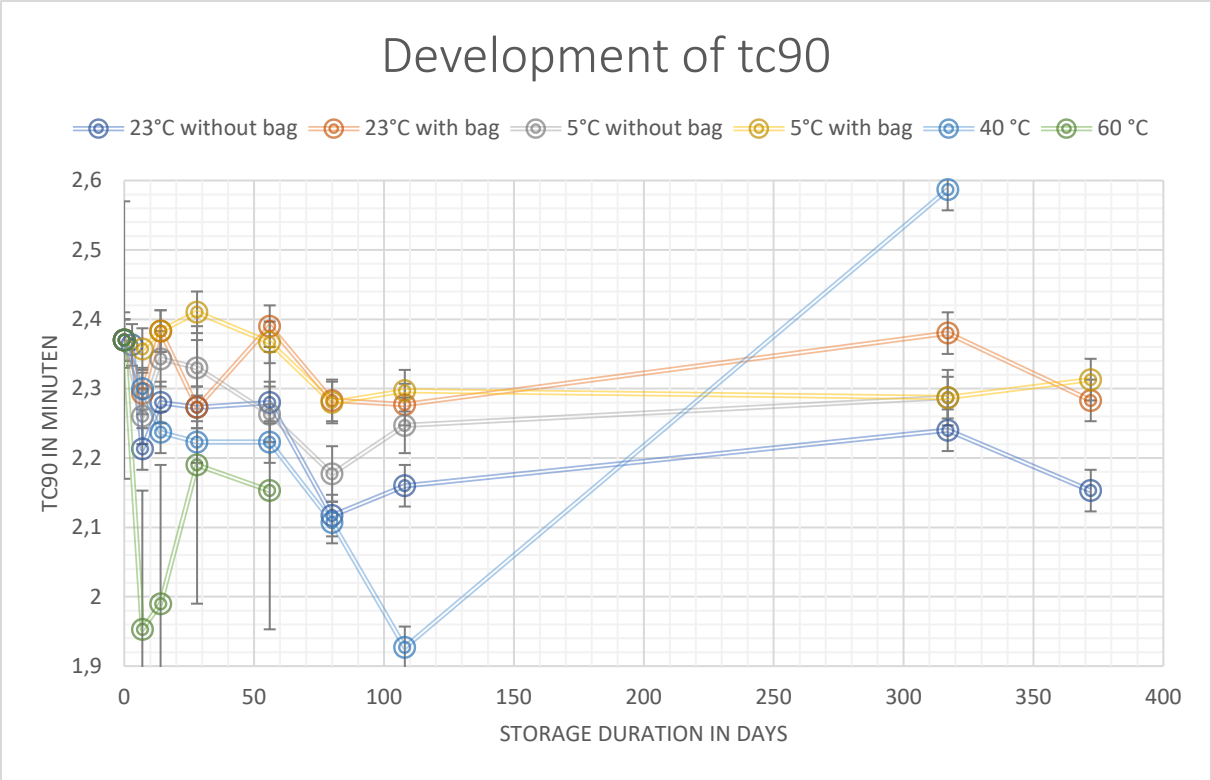

Figure 6: development of the time to 90 % of full cure tc_{90} under different storage conditions

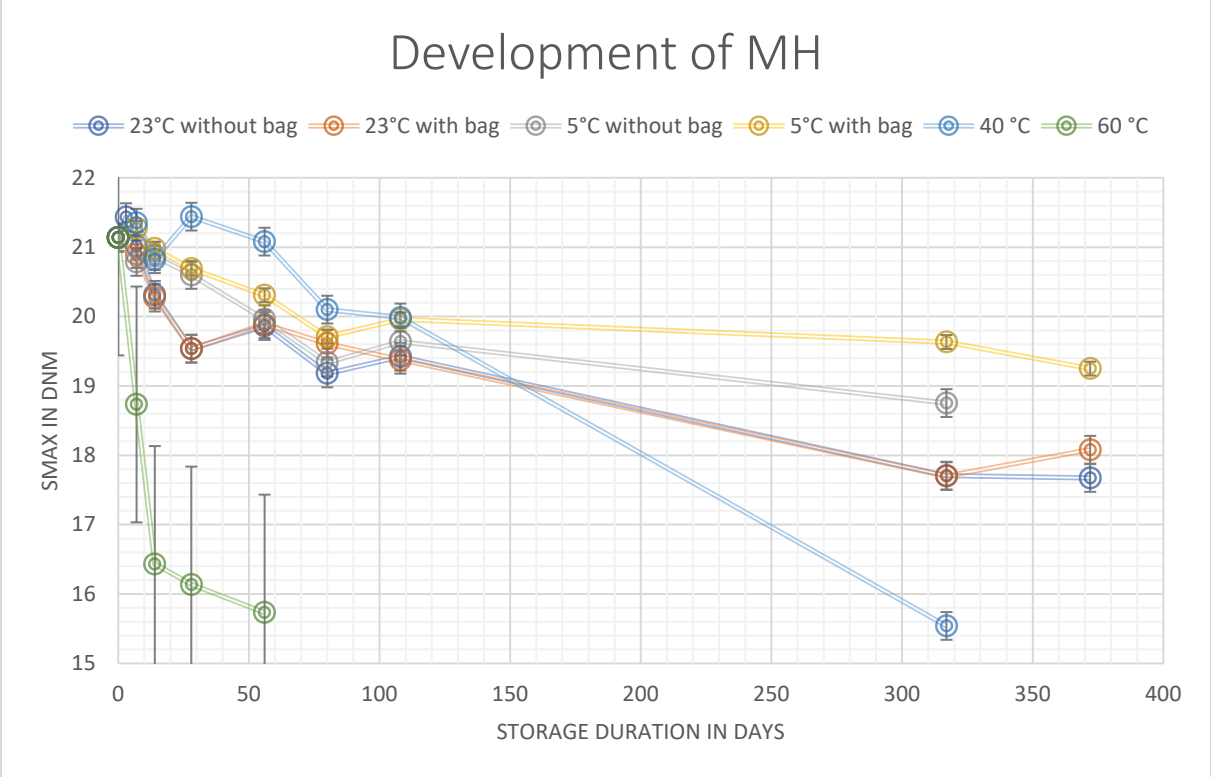

Figure 7: development of the maximum torque M_H under different storage conditions

The reference point (t=0) in these plots is determined as specified in section 2 (n=12) within 14 days after manufacture, i.e. the initial median value stated for this RM. As a measure for stability for this lot for each property the median of three values measured at the corresponding time step was compared to the respective median value (t=0 from n=12). Out of all time-dependent median values within the duration of the investigation (up to 372 days) the maximum deviation to the reference point was taken.

Results of lot for the evaluation of stability at 5 °C with pressure seal bag

characteristic property	*value [unit]*	*deviation after 28 days [unit]*	*deviation after 56 days [unit]*	*deviation after 80 days [unit]*	*deviation after 108 days [unit]*
M_L	2.54 dNm	0.01	-0.04	-0.03	-0.03
ts_1	0.63 min	0.01	-0.02	-0.01	-0.03
ts_2	0.74 min	<0.01	-0.01	<-0.01	-0.02
tc_{50}	1.24 min	0.01	-0.03	-0.03	-0.06
tc_{90}	2.36 min	0.05	0.01	-0.08	-0.06
M_H	21.12 dNm	-0.43	-0.81	-1.41	-1.16
characteristic property	*deviation after 317 days [unit]*	*deviation after 372 days [unit]*	*max. deviation [unit]* 1)	*max. deviation in %*	
M_L	-0.02	-0.04	-0.04 dNm	-1.6 %	
ts_1	-0.02	-0.02	-0.03 min	-4.3 %	
ts_2	-0.01	-0.01	-0.02 min	-3.1 %	
tc_{50}	-0.04	-0.03	-0.06 min	-5.1 %	
tc_{90}	-0.07	-0.05	-0.08 min	-3.4 %	
M_H	-1.49	-1.87	-1.87 dNm	-8.9 %	

Results of lot for the evaluation of stability at 5 °C without pressure seal bag

characteristic property	*value [unit]*	*max. deviation [unit]* 1)	*max. deviation in %*
M_L	2.47 dNm	0.06 dNm	2.3 %
ts_1	0.63 min	-0.06 min	-10.0 %
ts_2	0.74 min	-0.08 min	-10.4 %
tc_{50}	1.23 min	-0.14 min	-11.6 %
tc_{90}	2.34 min	-0.16 min	-7.0 %
M_H	20.88 dNm	-2.13 dNm	-10.2 %

Results of lot for the evaluation of stability at 23 °C with pressure seal bag

characteristic property	*value [unit]*	*max. deviation [unit]* 1)	*max. deviation in %*
M_L	2.49 dNm	0.06 dNm	2.3 %
ts_1	0.63 min	-0.02 min	-3.7 %
ts_2	0.74 min	-0.02 min	-2.3 %
tc_{50}	1.23 min	-0.05 min	-3.8 %
tc_{90}	2.34 min	-0.07 min	-2.9 %
M_H	20.91 dNm	-2.83 dNm	-13.5 %

Results of lot for the evaluation of stability at 23 °C without pressure seal bag

characteristic property	*value [unit]*	*max. deviation [unit]* 1)	*max. deviation in %*
M_L	2.49 dNm	0.18 dNm	7.2 %
ts_1	0.62 min	-0.03 min	-4.4 %
ts_2	0.73 min	-0.02 min	-3.0 %
tc_{50}	1.21 min	-0.09 min	-7.1 %
tc_{90}	2.33 min	-0.17 min	-7.4 %
M_H	21.07 dNm	-3.40 dNm	-16.1 %

1) Considering 6 points in time at which the median of 3 measurements was taken.

A change of the characteristic properties of 10 % was reached at a storage temperature of 40 °C already after ca. 30 days. Therefore, an enduring temperature of 40 °C has to be avoided but is also not to be expected under usual conditions. Thus, the appropriate shipment at ambient conditions seems feasible. Nevertheless, the shipment of the RM has to be realized by expeditious means.
To ensure appropriate transport conditions during shipment to the customer, every delivery will be equipped with a thermometer strip recording at least the maximum temperature. In case that the delivery encountered a temperature of 40 °C or higher the respective RM BAM-E028 should not be used.
Cool storage at 5 °C in a bag on producer’s and customer’s side is mandatory.

To account for the limited stability of the compound the usability of the RM BAM-E028 after dispatch is specified as six months. Not later than six months after production, the batch is no longer used for shipment to customers.
To continuously validate this maximum shelf life of one year, every lot of the RM is continuously monitored with respect to the relevant properties within one year after manufacture based on retained samples.

5. Results from the interlaboratory comparison

In ISO 6502, part 3, for the method and the device referred in this report results of an interlaboratory test program (ITP) are cited. As our laboratory also took part in this interlaboratory comparison test (with success), the respective precision results for the biconical curemeters are given in the table below.
For the results of biconical curemeters (MDR), after outlier's deletion, the total number of labs represents a significant population for a pertinent statistical data analysis.

The symbols used in Table is defined as follows:
Sr is the within laboratory standard deviation
SR is the between laboratories standard deviation
r is the repeatability (in measurement units)
(r) is the repeatability (in percent on measured value)
R is the reproducibility (in measurement units)
(R) is the reproducibility (in percent on measured value)

		Intralaboratory			**Interlaboratory**		
tc_{10}	**Avg [min]**	**Sr**	**r**	**(r)**	**SR**	**R**	**(R)**
L	4.83	0.195	0.55	11.4	0.355	1.01	20.8
M	4.70	0.146	0.41	8.8	0.256	0.72	15.4
H	4.74	0.086	0.24	5.1	0.268	0.76	16.0
tc_{50}	**Avg [min]**	**Sr**	**r**	**(r)**	**SR**	**R**	**(R)**
L	7.14	0.360	1.02	14.3	0.488	1.38	19.3
M	6.98	0.280	0.79	11.3	0.368	1.04	14.9
H	7.05	0.246	0.70	9.9	0.451	1.28	18.1
tc_{90}	**Avg [min]**	**Sr**	**r**	**(r)**	**SR**	**R**	**(R)**
L	10.89	0.434	1.23	11.3	0.680	1.92	17.7
M	10.41	0.373	1.06	10.2	0.482	1.36	13.1
H	10.47	0.371	1.05	10.0	0.634	1.80	17.1
M_L	**Avg [dNm]**	**Sr**	**r**	**(r)**	**SR**	**R**	**(R)**
L	1.61	0.011	0.03	2.0	0.059	0.17	10.3
M	2.25	0.023	0.07	2.9	0.054	0.15	6.8
H	3.27	0.026	0.07	2.3	0.074	0.21	6.4
M_H	**Avg [dNm]**	**Sr**	**r**	**(r)**	**SR**	**R**	**(R)**
L	16.17	0.215	0.61	3.8	0.534	1.51	9.3
M	21.00	0.200	0.57	2.7	0.740	2.09	10.0
H	25.50	0.255	0.72	2.8	1.099	3.11	12.2

Number of laboratories p= 22
number of materials q= 3
number of replicates n= 2

Table: Precision data determined for biconical curemeters from interlaboratory comparison test (ITP, cited also in ISO 6502, part 3)

For the further statistical evaluation of the reference material BAM-E028 typical values for the between-laboratory reproducibility (R) (in percent on measured value) obtained in this interlaboratory test were taken as good estimate. The dynamic stresses in this interlaboratory test were the same as those used to characterize RM BAM-E028. As in this interlaboratory test the characteristic properties ts1 and ts2 were not covered, tc10 was chosen (as it is next to ts1 and ts2 in the temporal sequence in the curing curve).

Typical properties of an elastomer compound in relation to between-laboratory reproducibility (R)

characteristic property	Value [unit]	(R) from interlaboratory comparison test *[%]*	*Possible deviation [unit]*
M_L	2.55 dNm	8 %	0.2 dNm
ts_1	0.69 min	17 %	0.1 min
ts_2	0.81 min	17 %	0.1 min
tc_{50}	1.43 min	17 %	0.2 min
tc_{90}	2.84 min	16 %	0.5 min
M_H	21.44 dNm	11 %	2.4 dNm

It is planned to organize an interlaboratory comparison test with the reference material BAM-E028 to improve the significance of the statistical data for the actual material.

6. Calculation of uncertainty

From the results of the evaluation of homogeneity (section 3) and stability (section 4) a maximum range for the respective property values is determined.

The resulting, estimated uncertainties are summarized in the table below:

property	a [unit]	b [unit]
M_L	0.10 dNm *	0.04 dNm
ts_1	0.06 min *	0.03 min
ts_2	0.07 min *	0.02 min
tc_{50}	0.14 min *	0.06 min
tc_{90}	0.25 min *	0.08 min
M_H	0.62 dNm	1.87 dNm *

a – maximum deviation (w/ unit) from homogeneity evaluation
b - maximum deviation (w/ unit) from stability evaluation
(5 °C, w/ pressure seal bag)

The respective maximum range of deviation is marked with an *.

The possible deviations determined from the interlaboratory comparison test are based on a different statistical basis. Therefore, these results were not directly included in the determination of the uncertainty.

7. Information on the proper use of BAM-E028

7.1 Shelf life

From the stability study reasonable shelf life at 5 °C could be estimated. A very conservative estimate for the stability is 12 months from the date of property statement. The validity of this estimate will be maintained by post-certification stability monitoring after property statement. Therefore, the document of property statement will be valid until further notice for six months beginning with the dispatch of the material from BAM. Not later than six months after production, the batch is no longer used for shipment customers.

7.2 Transport, storage, use

The stability of the RM allows dispatching the material at ambient temperature. On receiving, it is to be stored at 5 °C in a pressure seal bag. Before withdrawing a subsample, the pack must have reached ambient temperature. The conditions for using the RM BAM-E028 are already described in the introduction to the report. In addition, the instructions of the manufacturer of the test device apply.

Thereafter, the pack must be closed tightly and stored at 5 °C again in a pressure seal bag.

7.3 Safety instructions

Information on safe handling can be found in the available safety data sheet.

It is strongly recommended to handle and dispose of the reference material in accordance with the guidelines for materials legally in force at the site of end use and disposal.

7.4 Legal notice

Neither the Bundesanstalt für Materialforschung und -prüfung (BAM) nor any person acting on their behalf make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document may not infringe privately owned rights, or assume any liability with respect to the use of, or damages resulting from the use of any information, material, apparatus, method or process disclosed in this document.

8. Information on the RM and its purchase

Reference material BAM-E028 is supplied by
Bundesanstalt für Materialforschung und -prüfung (BAM)
Division 7.5 „Technical Properties of Polymeric Materials "
Unter den Eichen 87
D-12205 Berlin
Phone +49 (0)30 - 8104 3230
Email: crm-elastomer@bam.de
Internet: www.webshop.bam.de

Each Reference material will be distributed together with a detailed datasheet containing the values and their uncertainties of all accepted data sets.
Information on reference materials (RM) and certified reference materials (CRM) can be obtained from BAM, www.bam.de.

9. References

[1] ISO 6502-1:2018-07, Rubber - Measurement of vulcanization characteristics using curemeters - Part 1: Introduction

[2] ISO 6502-3:2018-07, Rubber - Measurement of vulcanization characteristics using curemeters - Part 3: Rotorless curemeter