DETERMINATION OF OXIDATION INDUCTION TIME AND TEMPERATURE BY DSC
Results of round robin tests

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Results obtained from three round robin tests, performed in 1998, 2000 and 2004, are summarized and presented. Oxidation Induction Time (OIT_{time}) and Oxidation Induction Temperature (OIT_{temp}) on six different grades of polyethylene were measured by DSC. The measured data were collected by Empa and evaluated using a robust statistical method concerning repeatability and reproducibility standard deviation.

The results of the tests indicate that the determination of OIT_{time} is associated with a high degree of uncertainty, especially for low OIT_{time} values. Thus, OIT_{temp} measurements could be a valuable alternative for testing less stabilized or non-stabilized polyolefin in particular. However, OIT_{temp} data reveal that the ability to distinguish between different polymer samples decreases drastically as OIT_{temp} values increase.

Introduction

The validation of measurements is a key problem of almost any analytical method [1]. One possibility to realize such a validation is to execute or participate in round robin tests [2]. Comparing data, generated from different laboratories on the same sample, afford a lot of valuable information regarding repeatability and reproducibility of the certain analytical method. In order to suppress biased behavior and to obtain a high independency in this field, round robin tests are often organized by neutral federal institutions like Empa (Swiss Federal Institute for materials testing and research), BAM (German Federal Institute for materials research) or DACH (German Accreditation for Chemistry).

The determination of oxidation induction time (OIT_{time}) and oxidation induction temperature (OIT_{temp}) are widely used methods in the thermal analysis of polymers [3, 4]. The aim of these measurements is to estimate the stability of polymeric materials under oxidative conditions. In particular it is used for polyolefin formulations intended to be used in water pipes or outdoor applications. Several international standards describe the methods and the operating sequence of OIT measurements [5]. The OIT_{time} method is most popular in this context and considerably work was done already to investigate the influ-

ence of different parameters on OIT_{time} data in detail [6–8]. Furthermore, the prediction of the lifetime of plastic products due to OIT_{time} measurements was attempted [9, 10]. Also approaches with chemiluminescence measurements were made to study polymer oxidation induction processes by radiation [11, 12], or even combine chemiluminescence with DSC to realize simultaneous measurements of heat flow and light emission [13].

The present work compares OIT_{time} and OIT_{temp} data obtained from three round robin test campaigns, where the participants uses the same samples for the OIT_{time} and the OIT_{temp} measurements. This should reveal, which of both methods is more precise and which method is more suitable for which measuring problem. Preliminary results on this topic have already been published by our group [14]. In this previous paper the principles and intentions of the round robin tests are described in detail. The meaning of terms like repeatability and reproducibility is discussed and a lot of statistic expressions are explained as well. Table 1 summarizes the most important statistical terms used in the following.

For the evaluation of the ring test data a robust statistic was used. Robust statistics are characterized by the fact that no outlier tests are applied. All data of the round robin test participants are consulted for the evaluation. During an iterative process the data re-

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Table 1 Important statistical terms and definitions used in the present publication

Expression	Abbreviation	Explanation
Repeatability conditions	–	Conditions where independent test resuts obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time
Reproducibility conditions	–	Conditions where test results obtained with the same method on identical test items in different laboratories by different operators using different equipment
Median value ('Hampel Schätzer')	x_{median}	Median value calculated by robust statistics from all mean values obtained from a fourfold determination from every participant
Repeatability standard deviation	s_r	The standard deviation of the test results obtained under repeatability conditions and calculated by robust statistics
Reproducibility standard deviation	s_R	The standard deviation of the test results obtained under reproducibility conditions and calculated by robust statistics

Table 2 Description of the materials used in the round robin tests

Sample	Material	Producer	Type/visual characterization
A	PE-HD	BASF AG	Lupolen 4261 A/ white powder
B	PE-LD	BASF AG	Lupolen 1852 H schw. 412/ black granules
C	PE-HD	BP Solvay	Eltex PLB 101/ black granules
D	PE-HD	Basell	Hostalen GM 5010/ black granules
E	PE-HD	DOW Plastics	BG 10050/ black granules
F	PE-HD	Hoechst	Hostalen CRP 100/ black granules

cords will be weighted depending on how far they are apart from the median value (x_{median}). The bigger the gap between the data and the calculated median value, the weaker the influence of this data on the expression of the round robin test becomes. Thus, the 'good data', close to x_{median} exert more influence on the result. The median value itself, called 'Hampel-Schätzer' is also calculated new after every iterative step. The exact mathematics, which is basic of all statistical calculations of our round robin tests, is described elsewhere [15].

Materials and methods

Overall six different commercially available polyethylene grades were used for the ring test evaluations (see Table 2 for exact description of the materials). The materials are chosen regarding their different lev-

els of stabilization, in order to cover a wide measuring range. Altogether 14 (year 1998 and 2004) respectively 16 (year 2000) laboratories participated in the round robin tests. The test program was accurately prescribed for all participants for OIT_{time} measurements and OIT_{temp} measurement as well. The temperature of the isothermal oxidation phase for OIT_{time} was defined as 210°C.

The sequence of a standardized OIT_{time} measurement using the DSC method according to ISO 11357-6 (2002) is outlined in Fig. 1. After positioning an uncovered sample pan in a calibrated DSC oven (sample mass approximately 5–15 mg), nitrogen is subjected to the measuring cell. The DSC cell is heated rapidly (at least=20 K min^{-1}) to the temperature at which the OIT_{time} value should be determined. After reaching the required temperature for the first time, an isothermal step of 3 min follows. The end of this phase is indicated as t_1 in Fig. 1. At t_1 the atmosphere is switched to oxygen and the DSC-Oven is held at the same temperature until an exothermal signal (oxidation) can be recognized. The onset of this oxidation signal corresponds to a time t_2. The OIT_{time}
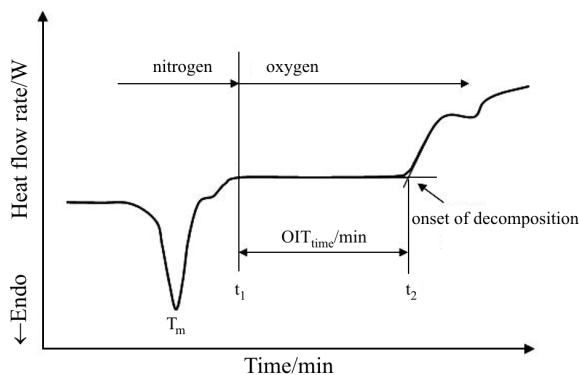
Fig. 1 Principle sequence of OIT_{time} measurements according to ISO 11357-6 (2002)

value can now be determined as the time between t_1 and t_2, as described in Fig. 1. Frequently however, the oxidation signal is less pronounced than indicated in Fig. 1, making the determination of a clearly defined onset temperature difficult. Finding a suitable measuring temperature for the isothermal phase often causes further difficulties with OIT_{time} measurements. If the temperature is too low there is a substantial increase of the duration of the measurement. And if the temperatures are too high, oxidation takes place immediately after the introduction of oxygen. The onset temperature of the decomposition signal (t_2) can no longer be determined.

The oxidation induction temperature (OIT_{temp}) is evaluated in accordance with Fig. 2. The sample is heated up continuously (i.e. 10°C min^{-1}) under a pure oxygen gas flow. A change of gases at a defined time, as stated under OIT_{time} measurement, isn't necessary. OIT_{temp} is determined as the onset of the decomposition signal results. OIT_{temp} is usually more clearly pronounced as the onset time t_2 in OIT_{time} measurements (t_2 is necessary for the determination of the OIT_{time} values). To give an overview, the essential characteristics of both methods (determination of OIT_{time} vs. OIT_{temp}) are summarized in Table 3. By comparing the statements in Table 3 it is obvious, that OIT_{temp} needs less effort in setting up the measurements and in the majority of cases it delivers clear defined onset points.

Results and discussion

The interlaboratory test data of the OIT_{time} and OIT_{temp} values are summarized in Table 4. From the data in Table 4, it is possible to establish that the repeatability and reproducibility of the OIT_{time} values depend on the order of magnitude of the median values of the samples. The lower the OIT_{time} median values, the greater the relative values (s_r relative, s_R relative) of the standard deviations. This correlation becomes obvious when the data of the ring tests are compared with data from other round robin
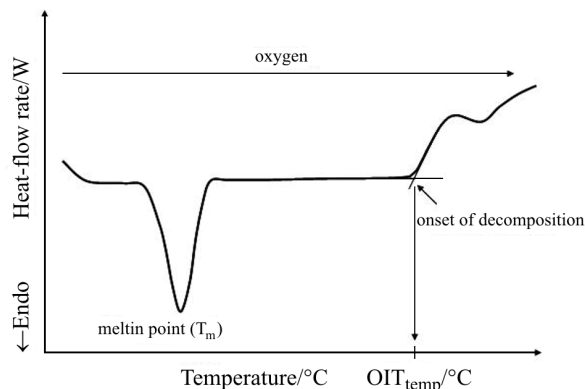
Table 3 Correlation and comparison of the two oxidation induction measuring principles

Features	Method	
	OIT_{time}	OIT_{temp}
Standardized	yes [5]	no (except Finland and Sweden)
Measuring principle	static	dynamic
Preliminary tests	yes (evaluation of a suitable measuring temperature)	no
Gas change	yes (possible source of error)	no
Onset of oxidation signal	partially difficult to recognize and to analyse	mostly expressed very well and clear analyzable

tests (Table 5). From the data in Table 5, it is possible to see, as a tendency, what influence the OIT_{time} median values exert on the s_r- and s_R-results. The lower the OIT_{time} values, the greater the relative standard deviation becomes. This could be seen with the relative reproducibility standard deviation (s_R relative) in particular. Even a border line within the range of 10 to 20 min seems to be present, below which the s_R values rise significantly (relative reproducibility standard deviations greater than 60%!). Evaluations of OIT_{time} values of samples with very low stabilizer amounts (OIT_{time} lower than 15 min) must therefore be regarded as critical. One possibility to improve the precision of OIT_{time} in that case could be, to lower the isothermal temperature in order to increase t_2 to a time region above 20 min. The key data of the interlaboratory test obtained from the evaluation of the OIT_{temp} values are summarized in Table 4. The standard deviations (s_r, s_R) of the temperature values in Table 4 seem to be reasonable because they have a similar order of magnitude as those found in other round robin tests, where temperatures was evaluated by means of DSC measurements [16, 17].

In the case of temperature measurements, it is quite clear that calculated relative values (s_r relative and s_R relative) strongly depend on the temperature scale used. For instance, if absolute temperatures (Kelvin scale) are used in our round robin tests, the relative standard deviation would become smaller. Another proposal could be to define the melting point of every material as the zero point of the respective OIT_{temp} measurement. In this case the relative standard deviations would increase substantially. In our interlaboratory test, we decided to use temperatures corresponding to the centigrade scale, because it is quite common in DSC measurements. Therefore, all further discussions and comparisons of relative temperature data refer to °C.

Fig. 2 Principle sequence of OIT_{temp} measurements

Table 4 Summary of the results of OIT_{time} and OIT_{temp} measurements on samples A–F

Method	Value	Samples					
		A	B	C	D	E	F
OIT$_{time}$	x_{median}/min	3.1	18.9	22.4	25.7	37.3	62.3
	s_r/min	0.2	0.3	0.6	0.8	0.8	0.6
	s_r relative*/%	6.5	1.6	2.7	3.1	2.2	1.0
	s_R/min	2.2	2.1	3.6	3.5	6.7	10.8
	s_R relative*/%	70.1	11.1	16.1	13.6	18.0	17.3
OIT$_{temp}$	x_{median}/°C	217.1	241.1	243.1	243.8	248.3	253.6
	s_r/°C	0.8	0.3	0.3	0.3	0.3	0.5
	s_r relative*/%	0.4	0.1	0.1	0.1	0.1	0.2
	s_R/°C	4.5	2.1	1.9	1.8	2.6	4.2
	s_R relative*/%	2.1	0.9	0.8	0.7	1.0	1.7

*$s_{r,R}$ relative/%=$(s_{r,R}\cdot 100)/x_{median}$

Table 5 Comparison of relative standard deviations (s_r relative and s_R relative) of OIT_{time} data from own (Empa) and foreign round robin tests (described in the mentioned standards)

	Material	Number of participants	OIT$_{time}$	
			x_{median}/min	s_R relative/%
Empa 1998 (sample A)[a]	PE-HD	14	3.1	70.1
Öfi 2000[b]	PE-HD	13	3.7	62.2
Öfi 2000[b]	PE-HD	12	9.3	64.1
Empa 1998 (sample B)[a]	PE-LD	14	18.9	11.1
Empa 2004 (sample C)[a]	PE-HD	14	22.4	16.1
ASTM D 3895[c]	PE-LD	11	23.4	20.1
ISO 11357-6[d]	PE-LD	—[d]	24.0	17.9
Empa 2004 (sample D)[a]	PE-HD	14	25.7	13.6
Empa 2000 (sample E)[a]	PE-HD	16	36.9	17.6
Empa 2000 (sample F)[a]	PE-HD	16	62.4	15.3
ASTM D 3895[c]	PE-LD	11	79.9	18.9
ISO/CD 11357-6[d]	PE-LD	—[d]	83.4	20.9
ASTM D 3895[c]	PE-LLD	11	119	14.0
ISO 11357-6[d]	PE-LLD	—[d]	120	12.2
ISO 11357-6[d]	PE-HD	—[d]	163	13.3
ASTM D 3895[c]	PE-HD	11	166	14.5

[a]Empa round robin test; evaluation according DIN 38402-45 with robust statistics, [b]round robin test performed by the Austrian Plastic Institute (Öfi); evaluation according ISO 5725-2 with consideration of outliers, [c]round robin tests performed by ASTM (1991); evaluation according ASTM E 691, [d]evaluation according ASTM E 691; not specified regarding the number of participants

Comparison of OIT$_{time}$ and OIT$_{temp}$ data

Table 4 summarizes the median values, standard deviations (s_r, s_R) and relative standard deviations (s_r relative, s_R relative) of the six PE samples and the two oxidation induction methods. By comparing the relative standard deviations (s_r relative and s_R relative) of OIT$_{time}$ and OIT$_{temp}$ data it can be seen that the dynamic measurement (OIT$_{temp}$) is connected with significantly smaller relative standard deviations than the static OIT$_{time}$ method. This could lead to the interpretation, that OIT$_{temp}$ measurements are always more reproducible than OIT$_{time}$ tests and should be preferred anyway. Additionally, also the set up of OIT$_{temp}$ measurements is even less complex.

However if one compares the absolute values, then it is noticeable that in the case of OIT$_{temp}$ measurements the differentiability between individual samples decreases significantly with rising temperature. This correlation is shown clearly in Fig. 3. The six round
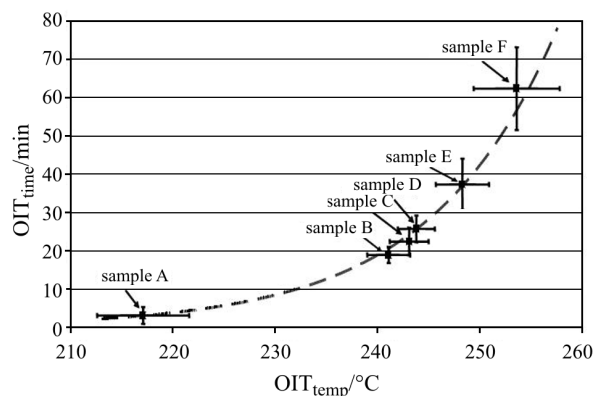
Fig. 3 X,Y-pair of OIT_{time}/OIT_{temp} values (symbol:■) of the six round robin test samples with the corresponding reproducibility standard deviation (s_R) as uncertainty bars

robin test samples are plotted here in an OIT_{time}/OIT_{temp} diagram with the median values as x,y values (symbol: ■) and the reproducibility standard deviations (s_R) as uncertainty bars. It can be clearly noticed that due to the exponential character of the oxidative decomposition of plastics with respect to temperature (dotted line in Fig. 3), OIT_{temp} values above approx. 240°C lead to an accumulation of the measured OIT_{temp} values. This finally leads to an overlay of the error bars concerning abscissa (overlapping region in Fig. 3). Thus, the differentiation between samples no longer exists in the case of the OIT_{temp} values, despite very small relative standard deviations (e.g. sample 5 and sample 6 may give the same OIT_{temp} result although they behave different in the oxidation process). In contrast to that, it is possible to distinguish the samples by way of the OIT_{time} values (ordinate axis), despite high relative standard deviations.

Conclusions

The present report indicates what repeatability and reproducibility standard deviations must be taken into account when oxidation induction time (OIT_{time}) or temperature (OIT_{temp}) measurements are performed using DSC. The data from this OIT ring tests demonstrate that the determination of the oxidation induction time (OIT_{time}) shows a substantial variation in the measured values, particularly for very low OIT_{time} values. Here, only a reduction of the temperature of the isothermal phase ($T<210°C$) or a reduction of the oxygen content in the measuring chamber could increase the differentiability of similar samples. The high values for repeatability and reproducibility standard deviations also show that the significance of OIT_{time} measurements, e.g. with regard to quality control or lifetime predictions of polyolefin parts, must be considered as

rather critically. Particularly for very low OIT_{time} values (polyolefin with none or low stabilization) the dynamic procedure for the determination of the oxidation induction temperature (OIT_{temp}) seems to be a valuable alternative. But, the OIT_{temp} data show clearly that differentiation between individual samples decrease rapidly as OIT_{temp} values increase.

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