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Interlaboratory Tests on Polymers: Thermal Analysis*

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Several interlaboratory tests according to ISO 5725 (1994) on polymeric materials using thermal analysis are presented. The results, especially repeatability and reproducibility data, are discussed. Thermogravimetric analysis (TGA) was used for the determination of carbon black, ash and plasticizer content in polymeric compounds (thermoplastic and rubber materials). Additionally the determination of the vinyl acetate content in ethylene/vinyl acetate copolymers (E/VAc) was performed with TGA. The comparisons between TGA and standardized methods reveal that TGA can be an alternative, which is time effective and produces at least equal or even better results. Differential scanning calorimetry (DSC) was used for the determination of the crystallinity of thermoplastic materials (polyethylene and poly(ethylene terephthalate)), the curing of epoxy resins, and the oxidation induction time of polyolefins. All tests were conducted under industrial conditions. They are valuable for the validation of the test methods as there is only a limited number of validation data available.

Keywords: Interlaboratory tests; Repeatability; Reproducibility; Polymers; Plastics; Rubber; Thermal analysis; TGA; DSC

INTRODUCTION

The EMPA St. Gallen organizes periodically interlaboratory tests on polymeric materials. Participants are laboratories of the polymer industry and institutes, which work in the field of testing, research and development of polymeric materials. The present report summarizes

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results and findings using thermal analysis. These interlaboratory tests have been performed in three campaigns since 1993. An overview of the treated topics is shown in Figure 1.

The following features represent the philosophy of the presented interlaboratory tests:

- Interlaboratory tests produce data on the repeatability and reproducibility of measured results, which can also be used for the determination of the uncertainty of a measuring procedure. The uncertainty of measurement is mostly unknown for newly developed test methods. Available calculation methods ^[1] usually supply no representative uncertainty values produced under rough industrial conditions.
- Older standardized methods will be substituted by the development of new analytical methods. Interlaboratory tests contribute to the comparison of the validation of traditional and newly developed test methods.
- For the mutual acceptance of results of measurements the following aspects are considered during the planning and realization of interlaboratory tests: For the selection of methods and materials,

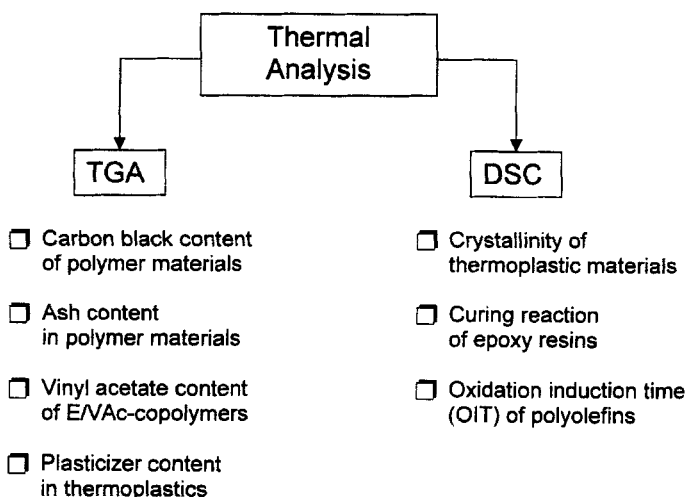


FIGURE 1 Systematic overview of the performed interlaboratory tests with polymeric materials using thermal analysis (TA).

cited results in the literature and in standards, discussions with experts and our own experiences are taken into account. Furthermore the data are produced under routine conditions to arrive at realistic values of reproducibility. Usually, two laboratories produce differing results although they use the same method. These findings lead sometimes to conflicts between partners (*i.e.*, supplier and customer). In such cases interlaboratory test data can help to interpret and assess the results and to change laboratory practice if required.

- Interlaboratory data lead sometimes to important improvements by adjusting or even changing processing parameters.
- The participants have the chance to test the reliability of their results (proficiency testing).

The interlaboratory tests of the EMPA St. Gallen in polymer analysis are part of an overall program in connection with the creation of an international measuring base. The aim is to improve the reproducibility of analytical results and, if possible, the traceability of these results on stated references, usually national or international measurement standards. Our future goal is to certify polymeric reference materials, reference materials that contain substances with well-defined content with known levels of uncertainty of measurement, which are determined by primary methods and/or round robin tests. These materials can then be used by laboratories as certified reference standards.

Thermal analysis (TA) is standard in polymer laboratories^[2, 3] and is frequently used for quality control of polymeric materials. Only few data about the uncertainty of TA measurement are available. The aim of this report is to publish and discuss some interlaboratory test data, which can help laboratories to validate frequently used thermoanalytical methods.

INTERLABORATORY TESTS ACCORDING TO ISO 5725 (1994)

ISO 5725 (1994)^[4] describes the procedure for interlaboratory tests. The requirements, equipment and instrumentation, the statistical

evaluation and the calculation of the relevant interlaboratory data are defined exactly.

Steps of an Interlaboratory Test

The described round robin tests were realized according to the following steps:

Definition and preparation of the interlaboratory test

- Definition of the test method, measuring parameters, number of single measurements (minimal 3)
- Selection of suitable materials
- Selection of interested participants (proposed minimum: 8)

Realization of the interlaboratory test

- Mailing of the test materials
- Testing and generation of test results

Evaluation of the results

- Compilation and statistical examination of the results (assessment of and decision about the way to handle inconsistent data, use of outlier test and/or robust evaluation procedures)
- Calculation of the characteristic interlaboratory data, the repeatability limit r , and the reproducibility limit R (see following section)
- Rating of the results and conclusions

Definition of Statistical Terms

The most important factors that produce deviations between single-measured results are the operator, the equipment and analytical instruments, calibration and environmental factors, such as temperature, humidity, light, *etc.* These factors are mathematically described by calculating the main characteristic interlaboratory results, the repeatability limit r and the reproducibility limit R . The source and the significance of these and other statistical terms used in interlaboratory tests are described in Table I.

Highly deviating single results, which are inconsistent with the rest of the normally distributed results, arise sometimes also under the best conditions and highly precise measurements. The two calculation

TABLE I Definitions of terms used in interlaboratory tests

	Repeatability conditions	Conditions where independent tests results are 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 are obtained with the same method on identical test items in different laboratories with different operators using different equipment
\bar{y}	General mean	Mean value of all the test results obtained by all the laboratories at a particular level of the experiment (indicated with y in ISO 5725 (1998))
s_r	Repeatability standard deviation	The standard deviation of test results obtained under repeatability conditions
s_R	Reproducibility standard deviation	The standard deviation of test results under reproducibility conditions
r	Repeatability limit	$r = 2.8 \times s_r$ The value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 95%
R	Reproducibility limit	$R = 2.8 \times s_R$ The value less than or equal to which the absolute difference between two test results obtained under reproducibility conditions may be expected to be with a probability of 95%
	Relative values	Relative deviations and characteristic interlaboratory data $[(s_r, s_R, r, R) \div \text{mean value } (y)] \times 100$ in %

approaches to handle inconsistent data are:

- (a) Outlier tests (according to ISO 5725 (1994), part 2^[4]): With outlier tests according to Dixon, Grubbs (to eliminate inhomogenities at the upper or lower ends of number files), and Cochran (to eliminate inhomogenities of variances), potential and statistical outliers can be found. One has to decide if the deviating result will be used for further evaluation. Normally statistical outliers are eliminated. The use of outlier tests can influence the quality of the interlaboratory data (*i.e.*, smaller r and R values).
- (b) Evaluation of the interlaboratory results by using robust statistics (according to ISO 5725 (1994), part 5^[4] or Schweizerisches Lebensmittelbuch, Kap. 60b, Anhang 3 (SLMB)): robust procedures use all results for the evaluation and show the following features:
 - Good efficiency on an ideal model (*i.e.*, normal distribution).
 - Small deviations from a model have only small effects on the values r and R .
 - Greater deviations do not lead to a breakdown of the model.

The principle of the procedure according to SLMB is as follows: "Good" (normal distributed) data are used for the calculation with a weight factor 1. However, "bad" results (large deviations from the mean) are handled with a weight factor lower than 1. The factor decreases with increasing deviation of a single result from "good" data. The determination of the factors of each result and the implementation of the factors in the calculation of the interlaboratory results is an iterative process.

For the calculation of the interlaboratory data in this paper, the conventional method using outlier tests (according to ISO 5725 (1994), part 2) or the method using robust statistics (according to SLMB) was used. The evaluation method is specified for each interlaboratory test.

Use of Interlaboratory Data

The benefit of interlaboratory data in daily laboratory routine is described in ISO 5725 (1994), part 6^[4] in detail. The following aspects relevant for the reported interlaboratory tests are:

- In the absence of one's own material or method-specific validation data, the interlaboratory data, especially s_r , can be used for an estimation of the uncertainty under the condition that the test method and the material are comparable to those in the interlaboratory test. Estimations of statistical deviations can also be calculated.^[1]
- Single measurements on one sample with regard to repeatability cannot be judged; two results are necessary. A duplicate determination with one method should be repeated, if the span range $(x_{\max} - x_{\min})$ of both single results exceeds the repeatability limit $r = 2.8 \times s_r$. With three results the following equation is valid: $(x_{\max} - x_{\min}) < 3.3 \times s_r$; with four results $(x_{\max} - x_{\min}) < 3.6 \times s_r$.
- If results of two laboratories with several measurements (n_1 and n_2) are available, the difference between the mean values \bar{x}_1 and \bar{x}_2 should not exceed the critical difference $CD_{0,95}$ (see Eq. (1)), otherwise the reason for the deviation could be in processing and/or material parameters.

$$(\bar{x}_1 - \bar{x}_2) \leq CD_{0.95} = \sqrt{R^2 - r^2 \left(1 - \frac{1}{2n_1} - \frac{1}{2n_2}\right)} \quad (1)$$

(for single measurements ($n_1 = n_2 = 1$) is valid: $CD_{0.95} = R$)

INTERLABORATORY TESTS WITH THERMAL ANALYSIS

Thermogravimetry (Thermogravimetric Analysis, TGA)

Thermogravimetry is mainly used for the determination of the composition of polymer compounds.^[2,3] Depending on the chemical composition, the percentage of volatile and low molecular chemicals (*i.e.*, plasticizer) and of the polymer itself, carbon black and thermally inert fillers can be determined easily. An example of a typical TGA curve of a compounded EPDM rubber is shown in Figure 2.

The chemistry of the ingredients of a polymeric material can drastically influence the thermal degradation of several components. The most known example is the carbonization of polymers with high contents of heteroatoms, like N, O, Cl, F, which can lead to higher results of measurement for the content of carbon black. For the quantification of each component, it is therefore necessary to know the possible influences in advance and to take them into account.

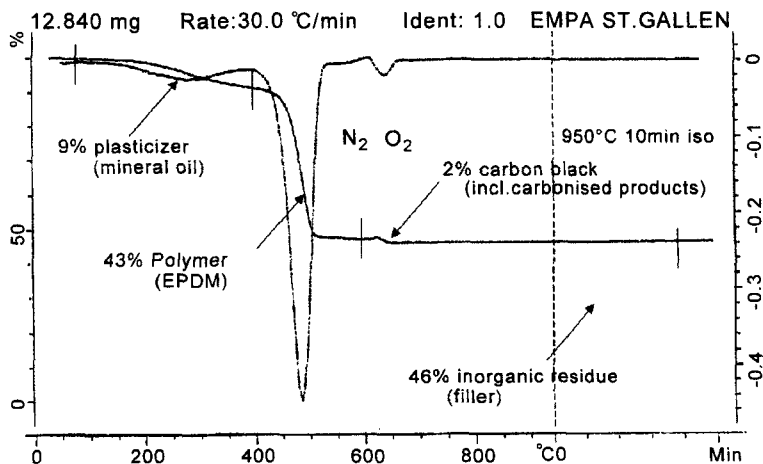


FIGURE 2 Typical TGA plot of a polymer material (gray EPDM rubber).

This section deals with the validation of thermogravimetric analysis. The first results have been described 1983 by Gross *et al.*^[5] using one of the first generation commercial equipment. Herein a standard deviation $S_{r,absolut} \leq 0.4\%$ under repeatability conditions was found for each weight loss step, working with a sample size of about 10 mg. Another challenge beside the validation work was to compare the efficiency of some TGA methods with conventional chemical procedures.

Carbon Black Content of Polymer Compounds

Carbon black is often used in plastics as UV stabilizer. The determination of the content of carbon black is fixed in some product standards^[6]. For efficient UV stabilization a minimal content of 2% is usual. Higher contents are applied for increasing the Young's modulus and tensile strength or electrical conductivity.

For the interlaboratory test, commercial polyolefin materials with carbon black contents of 2–3% were used as raw granules and as homogenized material by an additional extrusion step. Also vulcanized elastomers with contents over 30% were used. The chosen materials did not show any carbonization phenomena.

The participants were free to choose a suitable test method: a majority used TGA following ISO 9924-1 (1993)^[7] with sample sizes of about 10 mg. Some laboratories used a muffle furnace treatment following ASTM D 4218 (1996)^[8] with sample sizes of 1 to 2 g. The procedure was repeated five times for each material.

The evaluation of the interlaboratory test was carried out with application of the robust evaluation procedures according to SLMB. Table II summarizes the results.

The homogenization of the PE-LD material (sample CB-1 to CB-4) led to a massive reduction of the repeatability limit r (a factor of about 5) and the reproducibility limit R (a factor of ca. 2.5). With the TPE material (sample CB-5 and CB-6), no obvious reduction was observed. According to producers, the mixing process of PE raw material with carbon black is usually not efficient enough; a better homogeneity is reached by the second extrusion step to produce end products. For this reason, the determination of carbon black content in raw material for quality control purposes can lead to highly deviating and uncertain results; therefore it is possible to get results under 2%.

TABLE II Interlaboratory data of carbon black content of polymer materials

Code	Material ^a	Labs.	y [%]	r [%]	R [%]
CB-1	PE-LD	17	2.35	0.60	0.69
CB-2	CB-1, regranulated	12	2.34	0.10	0.30
CB-3	PE-LD	18	2.33	0.27	0.72
CB-4	CB-3, regranulated	12	2.29	0.07	0.32
CB-5	TPE based on EPM	13	2.84	0.18	0.81
CB-6	CB-5, regranulated	13	2.86	0.15	0.66
CB-7	IIR, vulcanized	17	41.78 ^b	0.40	2.15
CB-8	SBR/BR/NR-Blend, vulcanized	15	33.84 ^b	0.48	1.50

^aThe detailed composition of the materials is confidential. The following abbreviations are used: PE-LD = low-density polyethylene; TPE = thermoplastic elastomer; EPM = ethylene-propylene rubber; IIR = isobutene-isoprene rubber, butyl rubber; SBR = styrene-butadiene rubber; BR = butadiene rubber; NR = natural rubber.

^bConventional evaluation method with eliminated outliers.

As expected, the absolute repeatability is higher in materials with higher carbon black content (CB-7, CB-8), but relative values r_{rel} and R_{rel} are much lower. The r_{rel} is about 5% for low carbon black contents in homogenized polyolefins and about 2% for high-content (> 20%) materials.

Differences in results and measurement uncertainty between thermogravimetric methods and the muffle furnace treatments were not observed. Also effects of TGA equipment and of blank measurements could not be detected.

Ash Content in Polymer Compounds – Comparison of TGA with Standardized Methods

In polymeric compounds small amounts of thermal inert fillers (up to 1000°C) are applied as pigments (*i.e.*, TiO₂), higher contents are used as cheap fillers or for reinforcement (*i.e.*, some silicates). For the interlaboratory test two thermoplastic materials with about 3% TiO₂ and two cross-linked elastomers with approximately 45% fillers were used. Two methods were compared:

- Conventional determination of ash under air according to usual standards (*i.e.*, ISO 247 (1990),^[9] method A); sample size: grams
- Thermogravimetric method similar to ISO 9924-1 (1993);^[10] optimized for the determination of ash; sample size: 10–20 mg

The ash was produced in both methods at temperatures above 850°C. The procedure was repeated five times for each material. The evaluation of the interlaboratory test was carried out with the application of conventional evaluation procedures by eliminating statistical outliers. Table III and Figure 3 summarize the results.

TGA is as efficient and precise as conventional standardized methods for materials with high filler contents. For materials with small contents (about 3%), the conventional determination of ash is superior (factor of 5–10) to the TGA method with regard to the

TABLE III Interlaboratory data of ash content in polymer compounds

Code	Material ^a	Method	Labs	y [%]	r [%]	R [%]
ASH-1	EPDM, vulcanized	Ash	8	46.10	0.32	0.48
		TGA	10	46.01	0.49	1.53
ASH-2	NR, hard rubber	Ash	8	44.09	0.46	2.01
		TGA	11	44.50	0.62	1.48
ASH-3	PS, film for thermoforming	Ash	8	2.80	0.06	0.50
		TGA	10	2.64	0.84	2.44
ASH-4	PVC-P-film	Ash	8	2.83	0.08	0.19
		TGA	10	2.49	0.72	1.85

^a The detailed composition of the materials is confidential. The following abbreviations are used: EPDM = ethylene-propylene-diene rubber; NR = natural rubber, vulcanized with sulfur; PS = polystyrene; PVC-P = plasticized poly(vinyl chloride).

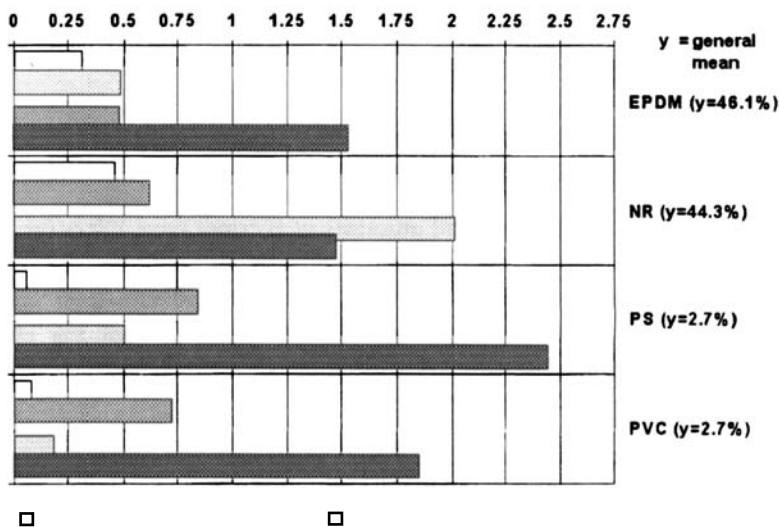


FIGURE 3 Diagram of the repeatability and reproducibility limits of the determination of the ash content in different polymer materials (EPDM, NR, PS and PVC).

uncertainty of measurement. In subsequent tests in the laboratories of EMPA, it was shown that the results of the filler content using TGA could not be improved by a subsequent thermoplastic reprocessing (extrusion) to reach a more homogeneous distribution of the fillers.

A lower ash content, as expected, was observed for ASH-1 (calculated: 47.3%, experimental: 46.1%), a higher content in ASH-2 (calculated: 43.7%, experimental: 44.3%). Deviations of expected values can occur under the following conditions (not a final list): (a) The material can explode and particles of fillers can be swept along with the pyrolytic smoke. A material loss is then expected. (b) Parts of the material can react with other components (*i.e.*, in ASH-2 metal oxide fillers react with surplus sulfur to form thermally inert metal sulfates or sulfides). Finally effects of TGA equipment and of blank measurements could not be detected.

Vinyl Acetate Content of E/VAc-copolymers – Comparison of TGA with Standardized Methods

The properties of ethylene–vinyl acetate copolymers (E/VAc) vary depending on the content of vinyl acetate: low content causes thermoplastic behavior, high content a viscoelastic behavior. Therefore the knowledge of the VAc content is of high relevance. The VAc content can be determined by different methods. Routine thermo-analytical methods (TGA, DSC) proved to be successful.^[11] In standards methods, like IR-spectrometry and titrimetry after hydrolysis or pyrolysis, are described. Also other methods can be used: nuclear magnetic resonance (NMR),^[12] CHO-elemental analysis, pyrolytic methods (*i.e.*, Pyr-GC-MS), and hyphenated methods (*i.e.*, TGA-MS,^[13] TGA-FTIR).^[14]

The participants were free to choose a suitable test method; a majority used TGA with the following parameters: sample size ca. 10 mg; temperature program 30°–600°C with 30°C/min; ≥ 50 mL nitrogen/min gas atmosphere. The evaluation of the TGA curve was done by the determination of the weight loss between 150° and 410°C, as shown in Figure 4. In this region, E/VAc decomposes mainly to acetic acid.^[15] The determination of the VAc content is done *via* a calibration with suitable reference materials (*i.e.*, E/VAc standards, Scientific Polymer Products Inc., New York. The specified contents of VAc vary for these products according to the supplier, to a 1% absolute maximum).

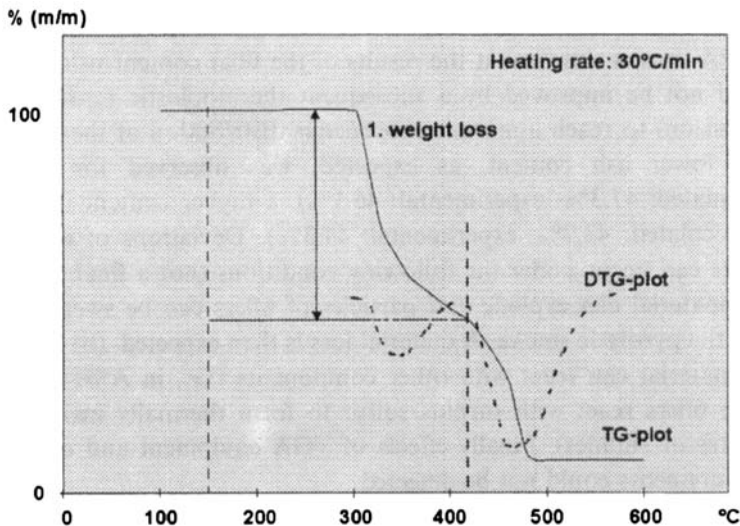


FIGURE 4 Schematic graph of a TGA plot used for the determination of the VAc content in E/VAc copolymers.

Beside TGA the following methods were used:

- standardised reference methods (hydrolysis and titration) according to ISO 8985 (1989).^[16]
- DSC, using the melting enthalpy after calibration with suitable standards.
- transmission-IR spectrometry according to ISO 8985 (1989),^[16] via the ratio of absorption intensities $\nu(\text{CH}_2)$ at 2678 cm^{-1} and $\nu(\text{CO})$ at 3460 cm^{-1} using $50\text{--}300\text{ }\mu\text{m}$ films, after calibration with suitable standards.

The chosen procedure was repeated five times for each material. Materials of commercial quality with VAc contents between $5\text{--}70\%$ were used. To reduce the influence of additives and/or cross-linking,^[17] the materials were neither compounded with any plasticizer, fire retardants ($\text{Al}(\text{OH})_3$) or fillers nor vulcanized (*i.e.*, with peroxides). Although different methods were used for the determination, the interlaboratory test was evaluated using the conventional method evaluation procedures by eliminating statistical outliers. Table IV summarizes the results.

TABLE IV Interlaboratory data of vinylacetate content of E/Vac copolymers

Code	VAc-content ^a	Labs ^b	y [%]	r [%]	R [%]	r _{rel} [%]	R _{rel} [%]
E/VAc-1	8 ± 2	7 (4)	8.41	0.66	2.59	7.8	30.8
E-VAc-1	8 ± 2	7 (1)	8.93	1.17	1.63	13.1	18.3
E-VAc-2	13 ± 2	7 (4)	12.7	1.07	2.55	8.4	20.8
E-VAc-3	28 ± 2	8 (4)	27.3	0.80	3.55	2.9	13.0
E-VAc-4	33 ± 2	8 (3)	32.6	1.32	3.60	4.0	11.0
E-VAc-4	33 ± 2	7 (1)	33.7	1.36	3.68	4.0	10.9
E-VAc-5	50 ± 3	7 (1)	48.7	1.16	6.02	2.4	12.4
E-VAc-6	70 ± 2	7 (1)	69.6	2.40	6.27	3.4	9.0

^a Declaration according the supplier.

^b In brackets: number of participants that used TGA.

All methods led to similar results: contents and standard deviations were comparable. The TGA method is an acceptable alternative to the other methods, even reference methods. The relative values of r and R decrease with increasing VAc content. For materials with less than 10% VAc content, only the reference method according to ISO 8985 (1989, § 3.1, reference method 1: hydrolysis and back-titration) led to smaller standard deviations than TGA and other methods.

Plasticizer Content in Thermoplastics – Comparison of Soxhlet Extraction with TGA-method

Plasticizer are often used for improving the flexibility or the impact strength of polymeric materials (*i.e.*, poly(vinyl chloride) (PVC), polyamide (PA) and elastomers). The plasticizer content is therefore a significant quality parameter. In the interlaboratory test two plasticized thermoplastics, a plasticized polyamide 12 (PA 12-P), plasticized with a sulfonamide and a plasticized poly(vinyl chloride) (PVC-P) plasticized with phthalic acid esters, were examined. The plasticizer content was determined by standardized Soxhlet extraction methods:

- PA 12-P: Extraction of the ground material with methanol for 16 h, drying the extract under vacuum at 40°C; following standards ISO 599 (1985),^[18] DIN 53738 (1983),^[19] ISO 6427 (1992).^[20]
- PVC-P: Extraction of the ground material or small cut film pieces with ethanol for 8 h minimum, drying the extract 2 h at 105°C; according to standards ISO 6427 (1992)^[20] or DIN 53738 (1983).^[19]

For each material the procedure was repeated four times. The evaluation of the interlaboratory test was carried out with the application of the robust evaluation procedures according to SLMB. Table V summarizes the results and shows a comparison with determinations of plasticizer by TGA.

The plasticizer content can also be determined with TGA by using suitable parameters of measurement. It is an essential requirement for a successful determination of plasticizer by TGA that there is no significant evaporation of plasticizer caused by the degradation of other components in the material. Thus it is possible to quantify monomeric plasticizers in PVC-P using a vacuum in the TGA furnace. However a determination of polymeric plasticizers ($M_w > 500$ to 10000) cannot be realized because the weight loss normally occurs in the same region as the polymer itself.^[21]

TGA can also be used for the determination of monomeric plasticizer in materials with known composition for quality control purposes, but it is highly recommended to validate the TGA method for each material. Future interlaboratory tests are in preparation to show the usefulness of TGA for plasticizer content determinations.

Differential Scanning Calorimetry (DSC)

DSC is an important method for the characterization of polymeric materials.^[2,3] The determination of calorimetric properties like melting point (T_m), crystallinity (C), glass-transition temperature (T_g) can be performed by DSC, as well as the determination of

TABLE V Interlaboratory data, of plasticizer content in thermoplastics with Soxhlet extraction in comparison with TGA-measurements, (%)

Material ^a	Labs	y [%]	r [%]	R [%]	TGA ^b	TGA ^c	TGA ^d
PA 12-P	13	13.86	0.38	1.84	13.41	13.77	12.40
PVC-P	10	36.92	0.27	1.87	— ^e	36.18	— ^e

^a The detailed composition of the materials is confidential. The following abbreviations are used: PA-P = with sulfonamide plasticized polyamide 12; PVC-P = plasticized poly(vinyl chloride).

^b TGA at 1 bar under N₂, 5°C/min, step between 50° and 300°C; (double determination; span range 0.0%).

^c TGA under vacuum, 5°C/min, step between 50° and 300°C (single measurement).

^d TGA at 1 bar under N₂, 20°C/min, step between 50° and 400°C (four-fold determination, standard deviation: 0.8%).

^e Disintegration of plasticizer is overlapped with the decomposition step of PVC (production of HCl).

exothermic and endothermic reactions (*i.e.*, oxidation stability and curing reactions).

For these kind of measurements unfortunately neither literature nor standards describe data for the uncertainty of measurements. The following results of the performed and reported interlaboratory tests give an overview of the quality and limitations of DSC measurements.

Crystallinity of Thermoplastic Materials

Thermoplastic materials usually consists of crystalline and amorphous domains. The amount and shape of crystals in the material depends on the chemical structure of the polymer, as well as on the thermal history of the material (rate of nuclei formation during the cooling process). The described interlaboratory test was performed with four different polyethylenes (PE) and one poly(ethylene terephthalate) (PET). Mainly raw materials (powder and granules) were used in the case of PE. Only in one special case a PE-film was used, which was additionally reprocessed by extrusion (well-defined cooling process) with the intention of obtaining a more homogeneous material.

The determination of crystallinity was performed according to DIN 53765 (1994).^[22] The following parameters for measurement were: sample size: 5–10 mg; temperature program: $\leq 25^\circ - 200^\circ\text{C}$, $10^\circ\text{C}/\text{min}$; $\geq 20\text{ mL}$ nitrogen/min gas atmosphere. The crystallinity was determined *via* the melting enthalpy (ΔH_{melt}) according to Figure 5 (ΔH_{melt} is the integral of the region between the measured curve and the baseline; baseline is the linear connection between T_{onset} and T_{end}). The values for complete (100%) crystallinity were given in the literature^[23] (290 J/g for PE; 140 J/g for PET). The crystallinity in percent (%) was calculated according to Eq. (2):

$$C[\%] = \left(\frac{\Delta H_{\text{melt}}}{\Delta H_{\text{literature}}} \right) \times 100 \quad (2)$$

For each material, five single measurements were performed. The evaluation of the interlaboratory test was carried out with the application of conventional statistical procedures by eliminating statistical outliers. Table VI shows the most relevant results found in the interlaboratory test.

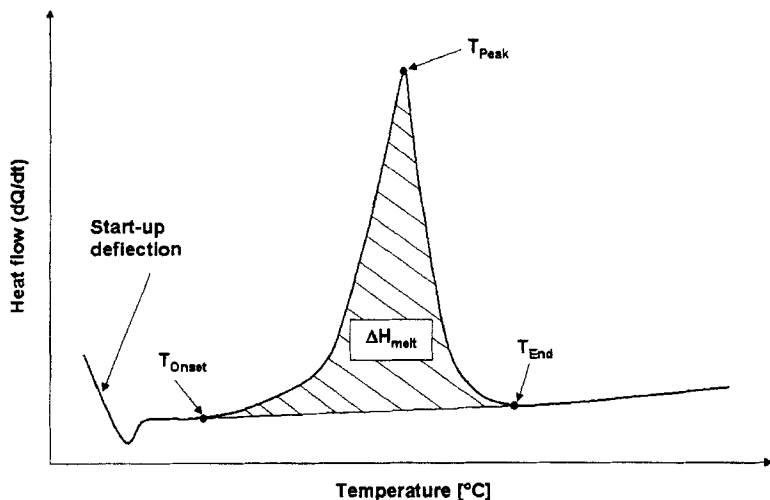


FIGURE 5 DSC plot for the determination of the crystallinity of thermoplastic polymers.

TABLE VI Interlaboratory data of the crystallinity (%) and melting point (T_{peak}) measurements of thermoplastic materials

Material ^a and code	Type	Labs	Crystallinity [%]					T_{peak} [°C]		
			y^b [%]	r [%]	R [%]	r_{rel} [%]	R_{rel} [%]	y [°C]	r [°C]	R [°C]
PE-LD-1	raw granules	6	41.2	2.7	3.8	6.6	9.2	—	—	—
PE-LD-2	extruded film of PE-LD-1	6	41.9	2.7	4.4	6.4	10.5	—	—	—
PE-HD-1	powder	8	60.8	2.8	8.2	4.6	13.5	—	—	—
PE-HD-2	powder	14	57.5	4.0	14.4	7.0	25.0	130.6	1.4	3.3
PE-HD-3	granules	9	66.6	6.0	9.7	9.0	14.6	—	—	—
PE-HD-4	granules	13	61.6	5.6	11.1	9.1	18.0	134.8	3.4	5.5
PET-1	pellets, annealed ^c	14	40.6	3.2	12.4	7.9	30.5	238.7	4.0	5.0

^a The detailed composition of the materials is confidential. The following abbreviations are used: PE-LD = low-density polyethylene; PE-HD = high-density polyethylene, PET = poly(ethylene terephthalate).

^b $\Delta H_{literature} = 290 \text{ J/g}$ for LDPE and HDPE, 140 J/g for PET. [2]

^c In the melting area of PET often a double peak at 238°C (main peak) and 262°C (partially as a shoulder) were observed. This indicates thermal pretreatment of the material at about 250°C (thermal memory effect). This effect is frequently visible with PET raw material; after the polycondensation reaction of the monomers a post-condensation step at temperatures of about 250°C is usually performed to increase the molecular weight of the PET.

As a whole, the results of crystallinity were rather disappointing. Even at sufficiently high heat of fusion values ($H_{literature}(\text{PET}) = 140 \text{ J/g}$), the DSC gave only a rough estimate of the degree of crystallinity.

Some measurements show that higher starting temperatures for integration (T_{onset}) led to lower heat of fusion values and, as a consequence, to lower crystallinities. Especially for PE samples, starting temperatures around 25°C led to the problem, since the starting deflection affects the exact positioning of T_{onset} . This problem causes significant variations in crystallinity results that had to be eliminated as statistical outliers. Because DIN 53765 (1994) defines no clear criteria for T_{onset} , it is especially recommended for measurements under repeatability and reproducibility conditions, to define start and onset temperatures in advance or to set it as low as possible (i.e., for PE: $T_{\text{onset}} \approx 0^\circ\text{C}$, $T_{\text{start}} = (T_{\text{onset}} - 50^\circ\text{C}) \approx -50^\circ\text{C}$).

Differences for r and R values between the raw material (PE-LD-1) and its homogenized counterpart (PE-LD-2) were not significant.

Besides crystallinity, the maximum of the heat of fusion intensities (T_{peak}) were also determined in some special cases. These data are also summarized in Table VI.

Curing Reaction of Epoxy Adhesives

The curing process of adhesives based on epoxy resins is related to a chemical reaction that can be monitored by DSC. Four different commercial adhesives were used. Samples ADH-1 and -2 were one-component adhesives based on epoxy resins. The others samples ADH-3 and -4 were two-component types based on epoxy resins. They were mixed just before measurement to ensure well-defined starting conditions. The procedure to monitor the curing reaction was performed following DIN 53765 (1994).^[22] This standard describes, besides other parameters, the temperature maximum (T_{peak}) and heat of fusion (ΔH_{fusion}) that can be used to characterize curing reactions. ΔH_{fusion} is the integral of the region between the measured curve and the baseline. The following parameters were used for the measurements: sample size 5–10 mg; temperature program: 20°–300°C, 10°C/min; ≥ 20 ml nitrogen/min gas atmosphere. All materials were measured five times by every participant. The evaluation of the interlaboratory test was carried out with the application of the robust evaluation procedures according to SLMB. Table VII summarizes the most relevant data found in this interlaboratory test.

TABLE VII Interlaboratory data of the maximum peak temperature and enthalpy of the adhesive curing reaction

Code ^a	Labs	Temperature max. (T_{peak})			Reaction enthalpy (ΔH_R)		
		y [$^{\circ}$ C]	r [$^{\circ}$ C]	R [$^{\circ}$ C]	y [J/g]	r [J/g]	R [J/g]
ADH-1	13	199.8	2.5	5.3	43.0	4.4	6.8
ADH-2	13	197.5	1.5	2.8	118.0	6.4	10.9
ADH-3	7	104.7	2.9	6.8	331.7	35.6	79.2
ADH-4	8	113.5	2.7	3.8	192.0	22.2	46.1

^aThe detailed composition of the materials is confidential. The following abbreviations are used: ADH-1 and ADH-2 are adhesives based on one-component epoxy resins; ADH-3 and ADH-4 are adhesives based on two-component epoxy resins.

Temperature (T_{peak}) The repeatability limit (r) is equal for all samples and ranges between 1.5 $^{\circ}$ and 3.0 $^{\circ}$ C. The values for the reproducibility limit (R) are also in the same area for all samples and ranges between 2.87 $^{\circ}$ and 6.8 $^{\circ}$ C (see Tab. VII). These values are to a great extent independent from the absolute temperature (about 200 $^{\circ}$ C for the one-component adhesives and about 110 $^{\circ}$ C for the others). These r - and R -values cover the same range as the corresponding peak temperature values T_{peak} in the section on crystallinity of thermoplastic materials (details see Tab. VI). The correspondence of these two round-robin tests regarding repeatability- and reproducibility limits suggests, that these values are characteristic and specific for the DSC method.

Heat of Fusion ($\Delta H_{reaction}$) The statistical evaluation of heat of fusion data is summarized in Table VII. Contrary to the temperature data (T_{peak}), a clear discrepancy between the one- and the two-component adhesives can be observed. The r - and R -values for samples ADH-3 and ADH-4 are significantly higher than those for ADH-1 and ADH-2. However, the general problem with user-defined baselines for an adequate integration of the curing enthalpy occurs again (see also in the section on crystallinity of thermoplastic materials). Nevertheless, the influence of the curing reaction, which starts at room temperature, is obvious and leads to an increase of the reproducibility limit R . The uncertainty of the measurement increases mainly because of the time between the weighing of the sample before the measurement and the start of the DSC-measurement which can vary for each sample.

Oxidation Induction Time (OIT) of Polyolefins

The oxidation induction time (OIT) is a relative measurement of the resistance of plastic materials at a given temperature in the presence of oxygen (or air). The OIT-measurement is well established, mainly for quality assurance, as a rapid test for the evaluation of the oxidation behavior of polyolefins respectively for the effectiveness of additives (antioxidants).^[24, 25, 29–31] The effect of different parameters of measurement on the precision of the results was also evaluated.^[26, 27] and there were trials to correlate OIT and life-time prediction of polyolefin pipes.^[28]

The OIT interlaboratory test was carried out in accordance with EN 728 (1997).^[29] The participants used the following measuring parameters: heating of samples from 50° to 210°C with a rate of 20°C/min under nitrogen; exactly 3 min after reaching the temperature of 210°C the gas stream was switched from nitrogen to oxygen and the time was measured until oxidation took place (onset of decomposition curve, see Fig. 6). For testing materials, two commercial polyethylene types (PE-HD, PE-LD), usually used for blow-and injection molding were selected. To create measurable effects on a short-time scale, low-level stabilized materials were used. The evaluation of the

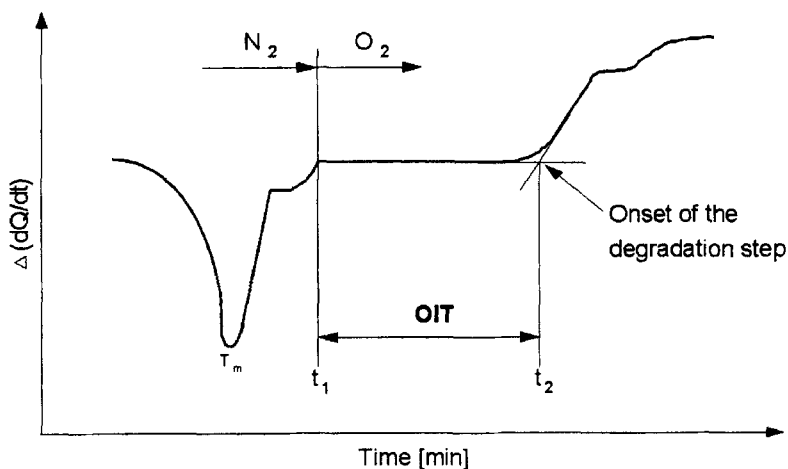


FIGURE 6 Schematic DSC plot for the determination of the oxidation induction time (OIT) of polyolefins.

interlaboratory test was carried out with the application of the robust evaluation procedures according to SLMB. Table VIII summarizes the most important data from the OIT interlaboratory test and compares them with already published data (ASTM D 3895^[30], ISO/CD 11357-6^[31]).

The data in Table VIII reveal that the repeatability and reproducibility limit for OIT measurements depends strongly on the magnitude of the actual OIT value. The smaller the general mean value (y) (y differs in the range between 3 min and 3 h depending on stabilization), the higher the value for relative repeatability (r_{rel}) and relative reproducibility limit (R_{rel}). For the extreme case of a very low-stabilized material PE-HD ($y = 3.4$ min) the relative reproducibility limit (R_{rel}) is above 100%.

Not only was OIT measured on the test samples, but also a dynamical version of OIT was performed. This method was also the objective of interlaboratory tests^[32] and is a standardized procedure.^[33] The procedure is as follows: the sample is placed in an open pan and heated continuously under oxygen (or air) until decomposition takes place. As a result, the so-called oxidation-induction-temperature (OIT*) is determined as the onset of the decomposition signal (see Fig. 7).

The participants used the following measuring parameters: heating from 30° to 300°C with a rate of 10°C/min under O₂. The evaluation

TABLE VIII Interlaboratory data OIT values [min] of polyolefins, compared to values mentioned in standards

	<i>Material</i>	<i>Labs</i>	<i>y [min]</i>	<i>r [min]</i>	<i>R [min]</i>	<i>r_{rel} [%]</i>	<i>R_{rel} [%]</i>
EMPA ^c	PE-HD	15	3.4	1.7	6.0	50.0	176.5
	PE-LD	16	18.8	3.2	5.7	17.0	30.3
ASTM D 3895 ^a	PE-LD	11	23.4	8.6	13.2	36.8	56.4
	PE-LD	11	79.9	25.6	42.4	32.0	53.1
	PE-LLD	11	119.0	22.0	46.4	18.5	39.0
	PE-HD	11	166.0	22.9	67.3	13.8	40.5
ISO/CD 11357-6 ^b	PE-LD	^b	24.0	8.0	12.2	33.3	50.8
	PE-LD	^b	83.4	25.7	48.8	30.8	58.5
	PE-LLD	^b	120.0	21.9	40.8	18.3	34.0
	PE-HD	^b	163.0	23.2	60.9	14.2	37.4

^a Interlaboratory test 1991, evaluation according ASTM E 691.

^b No statement regarding method and number of participants.

^c The detailed composition of the materials is confidential. The following abbreviations are used: PE-LD = low-density polyethylene; PE-LLD = linear low-density polyethylene; PE-HD = high-density polyethylene.

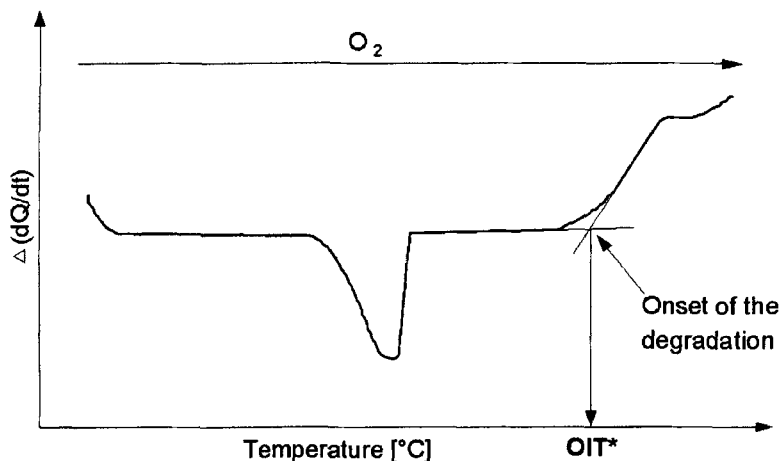


FIGURE 7 Schematic DSC plot for the determination of the oxidation induction temperature (OIT*) of polyolefins.

of the interlaboratory test was carried out with the application of robust evaluation procedures according to SLMB. Table IX summarizes the results. For comparison reasons of OIT* with OIT, both rows on the right side of Table IX show the appropriate data of the OIT measurement (see also Tab. VIII).

Although the relative data r_{rel} and R_{rel} for OIT and OIT* measurements are not based on general mean values with the same physical units, it is obvious that the dynamic process, especially in case of PE-HD, leads to results with an essentially higher reproducibility. This result is in accordance with Koski and Saarela^[32]

As already mentioned, the data of OIT, measured according to the static method, showed a considerable uncertainty of measurement. The very high values for r and R , especially for short OIT values

TABLE IX Interlaboratory test of OIT* values (°C) of polyolefins, comparison of the relative repeatability and reproducibility limit for OIT* and OIT

Material	Labs	OIT* (EMPA)					OIT (EMPA) ^a	
		y [°C]	r [°C]	R [°C]	r_{rel} [%]	R_{rel} [%]	r_{rel} [%]	R_{rel} [%]
PE-HD	14	217.3	6.7	11.1	3.1	5.1	50.0	176.5
PE-HD	14	241.5	1.9	6.1	0.8	2.5	17.0	30.3

^a see Table VIII.

(low-stabilized polyolefin materials), reveal that the benefit of these measurements, with regard to quality control or life-time prediction for polyolefin component parts, should be rated very low. For this reason, the dynamical OIT* method seems to be an interesting alternative, especially in the case of low-stabilized materials. Actual tests even suggests a higher selectivity (similar stabilized materials can be better distinguished) of OIT* measurements as compared to OIT. This hypothesis will be verified in future interlaboratory tests.

CONCLUSION

Generally, the analytical characterization of plastic materials with optimized thermogravimetric methods often gives results and uncertainties of measurement of the same magnitude as more work-intensive wet-chemical methods.

The interlaboratory test for the determination of carbon black content revealed an inhomogeneous distribution in commercial raw polyolefins with 2–3% carbon black. Thus for quality control purposes the material should be reprocessed (additional mixing during extrusion) to obtain more realistic contents with smaller uncertainties of measurement.

The precision of TGA measurements is sufficient and comparable with respect to the magnitude with standardised methods.

The statistical determination of OIT values according EN 728 has a considerable uncertainty of measurement. Especially for low OIT values (low-stabilized plastic materials), the dynamic method (OIT*) seems to be an attractive alternative and is easier to perform.

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