Comparison of Thermal Stability Measurement Processes for PVC

Quality Assurance. Thermal stability is one of the most important criteria for the processing and application of PVC. There are four different methods used to measure it. An interlaboratory test was carried out to compare different test equipment and their precision using systematically determined data.

A simple method of determining the thermal stability of polyvinylchloride (PVC) is to measure the amount of hydrogen chloride evolved as the polymer degrades. Such test methods have already been the subject of numerous investigations in the past [1, 2, 3], and the results of these form the basis of the method described in ISO 182/parts 1–4 [4]. Four different methods are used, which differ principally according to the way the amount of hydrogen chloride is indicated:

- In the Congo red test according to ISO 182-1, the time is measured until discoloration of an indicator paper that is mounted in a test tube above the sample to be tested, whereas in the three other methods described in ISO 182/parts 2–4, nitrogen is used as carrier. In these three methods, the amount of hydrogen chloride evolved is led into a liquid-filled measurement cell, which measures the concentration of the evolved HCl molecules.
- In the pH method (ISO 182-2), the gas mixture is directed into an NaCl solution at pH 6.0 and then the time is measured until the pH reaches 3.8.
- The conductivity test method (ISO 182-3) uses demineralised water as test medium, and continually measures its conductivity. When the conductivity has changed by 50 µS/cm, the hydrogen chloride concentration has been reached at which the sample has been thermally consumed.
- In the potentiometric method (part 4 of ISO 182), the Cl- concentration is determined potentiometrically in an aqueous electrolyte solution.

Translated from Kunststoffe 9/2003, pp. 131–134

Formulations

Blend	A	B	C
Acrylic modified S-PVC	100	100	100
Pb phosphite stabiliser	3	/	/
Calcium stearate	0.2	/	/
Lubricant (Pb stearate)	0.5	/	/
Lubricant (dicarboxylic acid ester)	0.5	0.5	0.5
Lubricant (wax)	0.1	0.1	0.1
Filler	5	5	5
Titanium dioxide	3	3	3
Ca/Zn stabiliser	/	3	1
Stabiliser proportion	**100 %**	**100 %**	**33 %**

Table 1. Composition of the tested mixtures

All the methods define the stability time as the time until a particular HCl concentration has been reached, while the induction time determines the value at which HCl evolution begins. This value can be determined as the tangential intersection or alternatively as the maximum of the second derivative of the conductivity curve.

There are no publications to date documenting the comparability of different test apparatus using systematically determined data. This article describes the performance and evaluation of an interlaboratory test based on ISO 5725-2 [5].

Preparation of the Specimens and Instrumentation of the Tests

To achieve a graduation of the induction and stability times, a standard window compound formulation, as well as Ca/Zn and Pb-stabilised blends with different amounts of stabiliser were prepared in a heating/cooling mixer (Table 1). These mixtures were plasticated in the laboratory extruder and processed into pellets about two millimetres in diameter and two millimetres in length (temperatures of the heating zones in the laboratory extruder: 160 °C, 165 °C, 175 °C and 180 °C die temperature). In preliminary tests, the samples showed very good reproducibility of the test results, with the advantage that there was no need for complicated sample preparation by comminution, screening etc.

The PC-controlled test instrument, PVC Thermomat 763 (manufacturer: Metrohm), with which the measurements are made in laboratories 01-03, consist of two individually heatable aluminium heating blocks with four test stations each (Fig. 1). The clear glass reaction vessels are inserted directly into the aluminium heating block. The stability and induction times are determined automatically by means of the evaluation software, with the indication time determined via the maximum in the second derivative of the measurement curve. The predetermined gas flow is set automatically via an internal controller. The nitrogen introduced

Data of the individual laboratories

		Sample							
		Standard formulation		Blend A		Blend B		Blend C	
		IT [min]	ST [min]	IT [min]	ST [min]	IT [min]	ST [min]	IT [min]	ST [min]
Lab. 01 n=8	Average:	71.63	73.43	52.95	56.10	34.05	37.58	14.70	18.60
	Abs. STD:	1.34	1.32	0.77	0.72	0.53	0.55	0.45	0.64
Lab. 02 n=8	Average:	71.03	73.58	55.65	59.10	36.00	40.35	16.43	20.33
	Abs. STD:	1.06	1.06	0.89	1.06	0.32	0.28	0.31	0.38
Lab. 03 n=8	Average:	71.40	73.65	53.85	57.90	36.08	40.13	16.20	20.25
	Abs. STD:	2.38	2.26	1.15	1.06	1.13	1.45	0.79	0.77
Lab. 04 n=8	Average:	71.21	74.85	53.46	57.71	34.61	39.51	14.10	18.21
	Abs. STD:	2.11	1.63	1.52	1.49	0.36	0.49	0.45	0.37

Abs. STD: Absolute standard deviations of the 8 repeat measurements

Table 2. Results of the laboratories participating in the interlaboratory test, original test data can be found at www.kunststoffe.de/A005

into the reaction vessel is not preheated. The temperature of the two heating blocks is corrected by means of calibrated, external temperature sensors such that the desired target temperature is reached in the reaction vessel. The cell constants of the conductivity test cells are automatically determined by means of a conductivity standard and stored in the software.

The measurements from laboratory 04 were carried out with a test apparatus according to DIN 53381 part 1, method B [6], also described in ISO 182-3 [4].

Procedure for the Individual Tests

- In the measurement in the PVC Thermomat 763, specimens of 0.5 ±0.025 g were weighed into the cold reaction vessels. In addition, 60 ml water was placed in the test vessels to absorb the hydrochloric acid. As soon as the equipment had reached the test temperature of 200 °C, the reaction vessels were placed in the apparatus, the tubes were connected and the measurements started. Nitrogen was used as carrier gas. The apparatus controlled the preset gas flow rate at seven litres per hour, as well as automatically determining the stability time (conductivity change by 50 µS/cm) and the induction time. Eight determinations were made per specimen.
- In the determination in the test apparatus according to DIN 53381-1, 0.5 ±0.025 g of the comminuted specimen (edge length approx. two millimetres) was filled into the cold test tube, and the test tube was closed with a rubber stopper with gas inlet and outlet pipes. Then, 60 ml deionised water with a conductivity of more than 5 µS/cm was poured into the conductivity test cell; the tubes were connected and the nitrogen flow was set at 7.0 ±0.5 l/h. The test tube was immersed in the thermostatic bath at 200 °C ±0.1 °C, and the chart recorder was started. The test determined the stability time (change of conductivity by 50 µS/cm) and the induction time. The induction time was evaluated graphically from the tangential intersections of both branches of the recorded conductivity curve.

Evaluation

Sample	Parameter	L	N	NAP (%)	$\bar{\bar{x}}$	SR	VR (%)	SI	VI (%)
Standard formulation	Induction time	4	31	3.1[1]	71.1	1.43	2.0	1.47	2.1
	Stability time	4	31	3.1[1]	73.7	1.47	2.0	1.31	1.8
Blend A	Induction time	4	32	0.0	54.0	1.57	2.9	1.12	2.1
	Stability time	4	32	0.0	57.7	1.62	2.8	1.12	1.9
Blend B	Induction time	4	32	0.0	35.2	1.19	3.4	0.67	1.9
	Stability time	4	32	0.0	39.4	1.48	3.8	0.83	2.1
Blend C	Induction time	4	32	0.0	15.4	1.24	8.2	0.53	3.5
	Stability time	4	31	3.1[1]	19.4	1.17	6.0	0.55	2.9

L = Number of laboratories after elimination of mavericks
N = Number of analysis results after elimination of mavericks
NAP = Percentage of mavericks
$\bar{\bar{x}}$ = Total mean value of all maverick-free analytical values in interlaboratory test

SR = Comparative standard deviation
VR = Comparative variation coefficient in %
SI = Repeat standard deviation
VI = Repeat variation coefficient in %

[1] Type 1 mavericks: strongly deviant individual value from a laboratory

Table 3. Evaluation of the interlaboratory test according to ISO 5725-2

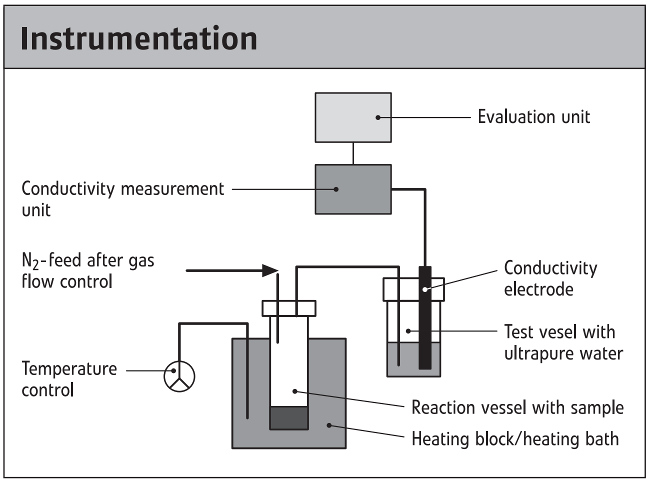

Fig. 1. Schematic set-up of the test apparatus

Results and Evaluation acc. to ISO 5725-2

As expected from the formulations given above, at 200 °C, the thermal stabilities decreased in the order from standard formulation to blend A, B and C. The conductivity/time curves (Fig. 2) were typical of Ca/Zn and Pb-stabilised blends and could be readily evaluated. Since the manual tangential method and automatic evaluation via the second derivative supplied virtually identical values for determining the induction time, the automatically determined induction times were quoted.

Table 2 shows the data from the individual laboratories as induction time (IT) and stability time (ST) in minutes. The mean values and standard deviations are given for the respective laboratory without a check for mavericks. The times from Table 2 were evaluated according to ISO 5725-2 [5] by eliminating deviant individual values from a laboratory by means of the Grubbs test. The induction time and stability time data for the standard formulation and stability time values for blend C were therefore not taken into account in computing the overall mean value and the scattering. Type 3 mavericks resulting from too great a standard deviation in a laboratory operating according to the Cochran test were not eliminated, since the results of all laboratories lay within the range of one to four percent determined from practical experience.

Discussion of the Results

The test results generally lead to the conclusion that consistent results can be achieved for the DHC test acc. to ISO 182-3 carried out in different laboratories and with different test apparatus. An important prerequisite for this is experience with the equipment and a knowledge of the influencing parameters that can lead to deviations. The most important parameter for the thermal stability time is the measurement temperature [7] itself: a deviation of only one degree Celsius changes both the stability time and the induction time by about eight percent. It is therefore necessary to calibrate the temperature at the individual test stations. A further important parameter is the sample size precisely specified in the different standards [7, 8].

The evaluation of the test data and their statistics shows that shorter test times increase the scattering of the results (Table 3). To allow work with longer test times, materials with results below 30 min. should therefore be tested at lower temperatures. On the other hand, to reduce the test times for thermally stable samples with test times over 90 min. to a practically useful order, these tests should be carried out at higher temperatures. The test data can be converted to different temperatures by means of a previously determined Arrhenius factor.

In the above-described method, the results show an absolute scattering of about one minute. For comparing the absolute test data, which were determined with different apparatus, the "dead time" should be taken into account. This value can be determined by re-testing a sample that has already been thermally stressed. The thermal stability time thus obtained corresponds to the time required for complete heating of the sample and for transfer of the hydrochloric acid produced to a test vessel. In the Congo red test (ISO 182-1), the dead time is about one minute; in the case of PVC Thermomat 763, the measurement was carried out at 200 °C and a nitrogen flow rate of seven litres per hour for about eight minutes.

The thermal stability time of a sample, that is to say the time until a particular end point has been reached, is usually quoted as the result. In the case of the conductivity test method, the thermal stability time corresponds to the time after which the conductivity in the test cell has risen by 50 µS/cm. The induction time, i. e. the time until the deflection in the conductivity curve is not taken into account. This is because the curves were still recorded with line chart recorders until a few years ago, and then had to be elaborately evaluated by means of tangents drawn with ruler and pencil. With computerised test equipment, it is no longer a problem to form a second derivative from a series of measurements and read the induction time at the curve maximum. As the tabulated results show, both results show virtually identical precision.

There are advantages in considering the induction time as a measure of the thermal stability instead of the stability time. The evolution of HCl molecules only starts when the stabiliser in the material has been used up. While the time for evolution of a particular quantity of HCl depends both on the weight of the sample and the volume flow rate of the carrier gas, these parameters do not affect the evaluation of the induction time. Other factors, such as volume and temperature of the absorption solution have only a small effect on the induction time, so that possible sources of error on the test temperature can be restricted. In the quotation of the stability time, all these parameters must be maintained as precisely as possible, since even slight deviations affect the curve gradient.

Conclusions

This work shows that the determination of the thermal stability times by the conductivity test method provides comparable results even with different test apparatus. The prerequisite for this is not the apparatus proposed in ISO 182-3, but proper performance of the test measurement. It is primarily important to exactly maintain the sample test temperature. It is also important to use a defined test sample size and maintain the volume flow rate and purity of the carrier gas. A specification of alternative test equipment should be incorporated into ISO 182-3.

The induction time is a more robust test value than the stability time. It is therefore urgently necessary to describe in ISO 182-3 how the induction time is determined. The important temperature calibration should therefore be described in detail in the standards. It is not crucial which DHC method is used, but how it is used. In practice, however, the following arguments militate in favour of conductivity detection, with its direct proportionality to the HCl evolved:

- Greater sensitivity than the logarithmically dependent pH.
- No calibration and maintenance of the pH electrodes necessary.
- Water as a simple absorption agent, no pH adjustment necessary.
- Simple, automatic recording and evaluation of the conductivity/time curves.

The latest findings and technical developments should by all means be taken into account in the next amendment of ISO 182. Also the method described in the standard should be verified by means of comparative data from interlaboratory tests. The fact that this can be donescientifically is demonstrated by the independently performed interlaboratory test. ■

THE AUTHORS

KARL-HEINZ HAMSEN, born in 1954, is Manager Technical Service Dispersion Resin at Vestolit GmbH & Co. KG, Marl/Germany.

RALF JAKSCH, born in 1961, is Laboratory Manager in the Technical Service Dispersion Resin at Vestolit.

THOMAS KOLB, born in 1974, is Product Specialist for Ion Chromatography and Stability Measurements at Deutsche Metrohm GmbH & Co. KG., Filderstadt/Germany.

JOCHEN SCHÄFER, born in 1957, is Division Manager for Marketing and Sales at Deutsche Metrohm.

DIETER MARKS, born in 1954, is Head of the Plastics Pilot Plant at Cognis Deutschland GmbH Werk Neynaber Chemie GmbH, Loxstedt/Germany.

JENS SITTEL, born in 1972, is Laboratory Manager of the Plastics Pilot Plant at Cognis Deutschland GmbH Werk Neynaber Chemie GmbH.

DR. ANTON ZAHN, born in 1953, is Analytical Department Manager at SKZ - TeConA GmbH, Würzburg/Germany.

Title photo. In the test-tube test, the time is measured until discoloration of an indicator paper mounted above the sample in a test tube

Fig. 2. Thermal stability test: Typical conductivity-time curves at 200 °C, tested with the Thermomat 763
Induktionszeit = Induction time; Stabilitätszeit = Stability time; Mischung = Blend; Standard-Rezeptur = Standard formulation