

Requirements for the testing of plastics receptacles

Guidelines for 6.1.5.2.7 and 6.5.6.3.6

Laboratory methods using samples for proving chemical compatibility of polyethylene in accordance with the definition in 6.1.5.2.6 and 6.5.6.3.5 with filling substances (substances, mixtures and preparations) as compared with the standard liquids according to 6.1.6.

Carrying out laboratory methods A to C described below will enable determination of the possible deterioration mechanisms on the material of the receptacle for the substances intended to be carried, as compared with the standard liquids in each case.

The deterioration mechanisms to be expected will determine the choice of test method.

The laboratory methods will establish

- softening through swelling (laboratory method A),
- formation of stress cracking (laboratory method B),
- reaction by oxidizing and molecular degradation (laboratory method C),

in the material of the receptacle, where these cannot already be determined on the basis of the formulation, and will in each case be compared with the appropriate standard liquids with similar effects.

Test samples of the same thickness within the tolerance limits indicated shall be used.

Laboratory method A

The increase in mass through swelling is determined using flat test samples from the receptacle material stored at 40°C in the substance intended to be carried and in the standard liquid to be compared.

The change in mass through swelling is determined by weighing the test samples before storage and if the test samples are not more than 2 mm, after a reaction period of 4 weeks, otherwise after a reaction time sufficient for the test samples to reach mass constancy.

In each case, the average value of 3 test samples shall be determined. Test samples shall only be used once.

Laboratory method B (pin insertion procedure)

1. Short description

The performance of a receptacle material made of high density polyethylene with respect to the substance intended to be carried and the appropriate standard liquid is tested using the pin impression test, to the extent that this performance can be influenced by the formation of stress cracking, with or without simultaneous swelling up to 4%.

For the test, the test samples are provided with a drilled hole and a notch, and undergo preliminary storage in the filling substance to be tested and in the appropriate standard liquid. After preliminary storage, a pin of a defined oversize is inserted into the drilled hole.

The test samples prepared thus are then stored in the filling substance to be tested and in the appropriate standard liquid and are removed after storage periods of different duration and tested for residual tensile strength (procedure 3.1) or for the length of time until the test samples crack (procedure 3.2).

By making comparative measurements with the standard liquids "wetting solution", "acetic acid", "normal butyl acetate/normal butyl acetate-saturated wetting solution" or "water" as the test substance, it can be determined whether the degree of deterioration caused by the filling substance to be tested is equal to, more than or less than that of the standard liquid.

2. Test samples

2.1 Form and dimensions

The form and dimensions of the test sample are shown in figure 1. The thickness of the sample should not vary by $\pm 15\%$ of the average value within a test series.

The filling substance to be tested and the appropriate standard liquid are part of the test procedure.

Figure 1

Extrusionsrichtung = direction of extrusion

Probekörper ohne Stift = test sample without pin

Mindestwanddicke: 2mm = minimum wall thickness: 2mm

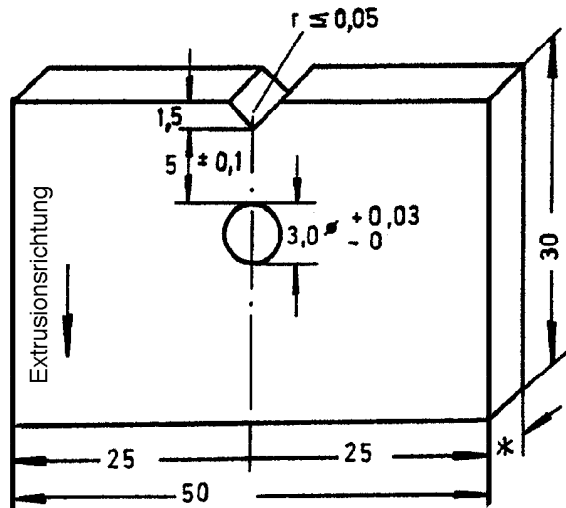


Abbildung 1
Probekörper ohne Stift

* Mindestwanddicke: 2mm

2.2 Manufacture

The test samples of a test series may be taken from receptacles of the same design type or from the same piece of an extruded semi-finished product.

With regard to machining of test samples, the surface quality obtained by cutting with a saw is sufficient. Ridges that occur during manufacture should simply be removed from the surface which is later to be notched. The test samples shall be notched parallel to the direction of extrusion.

A hole with a diameter of 3 mm $^{+0,03}_{-0}$ is to be drilled into each test sample as shown in Figure 1.

The test sample shall then be provided with a V notch as shown in Figure 1, with a notch radius of ≤ 0.05 mm.

The distance between the bottom of the notch and the perimeter of the hole shall be 5 mm ± 0.1 mm.

2.3 Number of test samples

To determine the residual tensile strength in accordance with paragraph 3.2, 10 test samples per storage period shall be used. As a rule, at least 5 storage periods shall be used.

In order to determine the time required until the test samples crack in accordance with paragraph 3.3, a total of 15 samples is required.

2.4 Pins

See Figure 2 for the dimensions of the 4 mm thick pins.

Figure 2

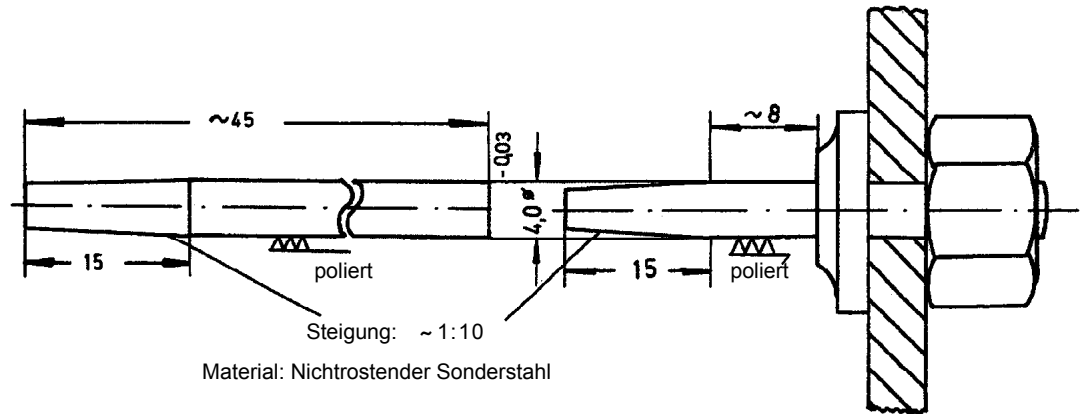
a: Pin to determine residual tensile strength

b: Pin to determine the standing time until the test sample cracks

poliert = polished

Steigung = gradient

Material: Nichtrostender Sonderstahl = Material: stainless (rust-resistant) steel



The preferred material for the pin is stainless steel (e.g. X 12 Cr Si 17).

For substances which can corrode this steel, glass pins shall be used.

3. Test procedure and evaluation

3.1 Preliminary storage of the samples

Before having the pin inserted, the test samples shall undergo preliminary storage for 21 days at $40^{\circ}\text{C} \pm 1^{\circ}\text{C}$ in the test liquids and standard liquids. For standard liquid c) in accordance with 6.1.6.1, preliminary storage shall be in n-butyl acetate.

3.2 Procedure to determine the residual tensile strength curve

3.2.1 Method

The pin in accordance with Figure 2a is inserted into the drilled hole in the test samples past the tapered part on to the cylindrical section.

The samples prepared thus are then immersed in storage receptacles filled with the respective test liquid, thermally conditioned to a temperature of 40°C , and then stored in an oven at $40^{\circ}\text{C} \pm 1^{\circ}\text{C}$. For standard liquid c), this test is carried out using wetting solution with the addition of 2% n-butyl acetate.

The period of time between inserting the pin into the test samples and continuing the storage in the test liquid must be uniformly selected and kept constant for a test series.

The storage periods for determining the time and test liquid related formation of stress cracking shall be selected such that a clear differentiation can be demonstrated between the residual tensile strength curves of the standard liquids tested and the filling substances to be classified with sufficient certainty.

After being removed from the storage receptacle, the pins shall immediately be removed from the test samples and any residual test liquid shall be cleaned off.

After being cooled to room temperature, the test samples shall be split parallel to the notched side through the middle of the drilled hole using a saw cut. Only the notched parts of the test samples shall be used for further testing.

These notched test samples shall then, no later than 8 hours after being removed from the test liquid, be subjected in a tensile testing machine to a uniaxial tensile stress, at a test speed (speed of the moving clamp) of 20 mm/min, until they break. The maximum strength shall be determined. The tensile test shall be carried out at room temperature ($23^{\circ}\text{C} \pm 2^{\circ}\text{C}$) in accordance with ISO/R 527.

3.2.2 Evaluation

The evaluation to determine the effect of the test liquid comprises calculation of the maximum tensile strength of the pre-stored test sample parts without the pin as the zero value, and the maximum tensile strength of the sample after the storage periods t_y where $y \geq 5$ (days). After converting these maximum tensile strength values at t_y into %, compared to the zero value, these values are plotted on a graph as in Figure 3.

A comparison with the corresponding residual tensile strength curves from measurements using the standard liquids "wetting solution" or "acetic acid" or "n-butyl acetate/n-butyl acetate-saturated wetting solution" or "water" then shows whether the filling substance tested has a stronger, weaker or no effect on the same receptacle material (see Figure 3).

Figure 3

Spannungsrißprüfung (Stifteindrückmethode) = stress cracking test (pin impression method)

Füllgut = filling substance

Standardflüssigkeit = standard liquid

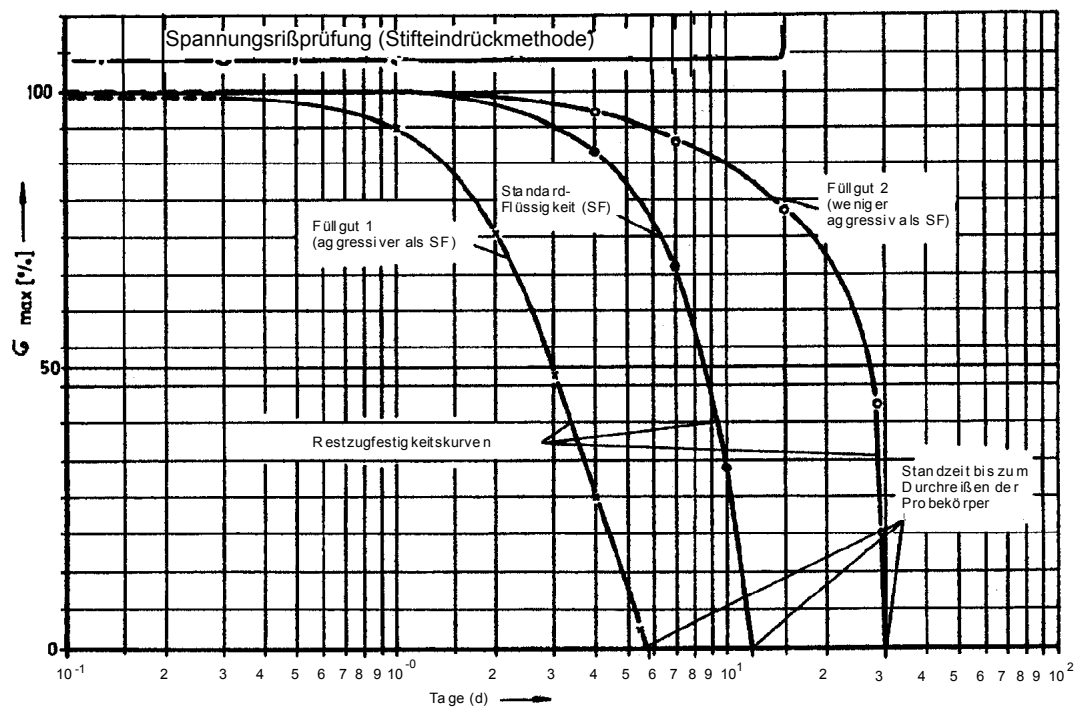
Aggressiver = more aggressive

Weniger aggressiv als = less aggressive than

Restzugfestigkeitskurven = residual tensile strength curves

Standzeit bis zum Durchreißen der Probekörper = time until the test samples crack

Tage = days



3.3 Procedure to determine the time until the test samples crack

3.3.1 Method

15 pins are fully inserted into 15 individual upright test samples in accordance with diagram 2b, which are then placed into a glass tube thermally conditioned to 40°C and filled with the test liquid.

The test temperature is kept constant $\pm 1^\circ\text{C}$. The cracking of the test samples on each pin is ascertained by visual observation. Experience shows that the crack always grows from the base of the notch to the surface of the pin.

3.3.2 Evaluation

The elapsed time T_{SF} with the standard liquid until 8 samples have cracked is decisive for the assessment. It is not necessary to wait for any further cracks to form.

The evaluation is carried out by comparing with the number of samples that cracked using the filling substance. There shall be no more than 8 samples that crack during the time T_{SF} .

3.4 Comment

For this test procedure, the test parameters "storage temperature" and "distance between the bottom of the notch and perimeter of the hole" were selected in such a way that in corresponding tests with the standard liquids "wetting solution", "acetic acid" and "normal butyl acetate/normal butyl acetate-saturated wetting solution", meaningful results in the context of this test procedure can be obtained within an overall test duration of about 28 days. In this case, a high molecular mass polyethylene with a density of $\sim 0.952 \text{ g/cm}^3$ and a Melt Flow Rate (MFR 190°C/21.6 kg load) of $\sim 2.0 \text{ g/10 min}$ was taken as a basis.

As the conclusion of this test procedure should always be a relative conclusion, it is also possible to modify the relative values of the test parameters above in order to reduce the period required for the test. This information must be specified in the test report.

4. Criteria for a satisfactory test result

4.1 The test result according to laboratory method A shall not exceed 1% increase in mass through swelling if standard liquid a), "wetting solution" or standard liquid b), "acetic acid" is to be used for making a comparison.

The test result according to laboratory method A with the filling substance being tested shall not exceed the increase in mass through swelling obtained with normal butyl acetate (about 4%) if standard liquid c), "normal butyl acetate/normal butyl acetate-saturated wetting solution" is to be used for making a comparison.

4.2 The test result according to laboratory method B shall yield the same or a longer standing time for the filling substance than that for the standard liquids used for the comparison.

Laboratory method C

In order to assess whether the filling substance poses a potential risk of oxidation or molecular degradation for a receptacle material made of high density polyethylene in accordance with 6.1.5.2.6 and 6.5.6.3.5 respectively, the Melt Flow Rate (MFR 190°C/21.6 kg load in accordance with ISO 1133 – Condition 7) of test samples with a thickness range equivalent to the design type, shall be determined before and after storage of these samples in the filling substance to be assessed.

By storing geometrically identical samples in the standard liquid "55% nitric acid" in accordance with 6.1.6.1 (e) and by means of melt flow rate data, it shall be ascertained whether the degree of degradation caused by the filling substance to the material of the receptacle is less, equal or greater.

Samples shall be stored at 40°C until it is possible to make a final assessment, up to a maximum of 42 days.

If the filling substance to be approved produces swelling with an increase in mass of $\geq 1\%$ in accordance with laboratory method A, in order not to affect the result of the measurement, the sample shall be "post-dried" whilst simultaneously checking the mass before the melt flow rate is measured, e.g. by storage in a vacuum drying cabinet at 50°C until mass constancy is reached, as a rule for not more than 7 days.

Criterion for a satisfactory test result:

The increase in the melt flow rate of the receptacle material caused by the filling substance to be approved shall not be greater than the change caused by the standard liquid "55% nitric acid", including a tolerance limit of 15% necessitated by the test method.