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Plastics — Determination of dynamic mechanical properties —

Part 10:
Complex shear viscosity using a parallel-plate oscillatory rheometer

Plastiques — Détermination des propriétés mécaniques dynamiques —

Partie 10: Viscosité complexe en cisaillement à l'aide d'un rhéomètre à oscillations à plateaux parallèles

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 6721-10 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 2, *Mechanical properties*.

Together with the other parts of ISO 6721, it cancels and replaces ISO 537:1989 and ISO 6721:1983, which have been technically revised.

ISO 6721 consists of the following parts, under the general title *Plastics — Determination of dynamic mechanical properties*:

— *Part 1: General principles*

— *Part 2: Torsion-pendulum method*

— *Part 3: Flexural vibration — Resonance-curve method*

— *Part 4: Tensile vibration — Non-resonance method*

— *Part 5: Flexural vibration — Non-resonance method*

— *Part 6: Shear vibration — Non-resonance method*

— *Part 7: Torsional vibration — Non-resonance method*

— *Part 8: Longitudinal and shear vibration — Wave-propagation method*

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
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- *Part 9: Tensile vibration — Sonic-pulse propagation method*
- *Part 10: Complex shear viscosity using a parallel-plate oscillatory rheometer*

Annex A of this part of ISO 6721 is for information only.

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Plastics — Determination of dynamic mechanical properties —

Part 10:
Complex shear viscosity using a parallel-plate oscillatory rheometer

1 SCOPE

This part of the International Standard ISO 6721 specifies the general principles of a method for determining the dynamic rheological properties of polymer melts at angular frequencies typically in the range 0,01 - 10 Hz by means of an oscillatory rheometer with a parallel plate test geometry. Frequencies outside this range can be used (see Note 1). The method is used to determine values of the dynamic rheological properties: complex shear viscosity η^*, dynamic shear viscosity η', the out-of-phase component of the complex shear viscosity η'', complex shear modulus G^*, shear loss modulus G'' and shear storage modulus G'. It is suitable for measuring complex shear viscosity values typically up to approximately 10 MPa.s (see Note 2).

[NOTE 1: The angular frequency range of measurement is limited by the specification of the measuring instrument and also by the response of the specimen. When testing using frequencies lower than 0,01 Hz the testing time can increase significantly as the time taken to obtain a single datum is proportional to the reciprocal of the test frequency. Consequently, when testing at low frequencies degradation or polymerisation of the specimen is more likely to occur and have an effect on the results. At high angular frequencies the specimen may distort or fracture at the edge consequently invalidating the test results.]

[NOTE 2: The range of complex shear viscosity values that can be measured is dependent on the specimen dimensions and also the specification of the measuring instrument. For a specimen of given dimensions the upper limit of the range is limited by the machine's torque capacity, angular displacement resolution and compliance. However, correction can be made for compliance effects.]

2 NORMATIVE REFERENCES

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 472: 1988, Plastics - Vocabulary.

ISO 6721-1: 1994, Plastics - Determination of dynamic mechanical properties - Part 1: General principles.

3 DEFINITIONS

For the purposes of this part of ISO 6721, the definitions given in ISO 6721-1:1994 and ISO 472: 1988 apply. In addition the following definitions apply:

3.1 controlled-strain mode: testing by applying a sinusoidal angular displacement of constant amplitude.

3.2 controlled-stress mode: testing by applying a sinusoidal torque of constant amplitude.

3.3 complex shear viscosity, η^*: The ratio of dynamic stress, given by $\sigma(t) = \sigma_0 \exp i\omega t$, and dynamic rate of strain $\dot{\gamma}(t)$, where the shear strain $\gamma(t)$ is given by $\gamma(t) = \gamma_0 \exp i(\omega t - \delta)$, of a viscoelastic material that is subjected to a sinusoidal vibration, where σ_0 and γ_0 are the amplitudes of the stress and strain cycles, ω the angular frequency, δ is the phase angle between the stress and strain and t is time.

It is expressed in Pascal.seconds.

3.4 dynamic shear viscosity, η': The real part of the complex shear viscosity.

The dynamic shear viscosity is expressed in Pascal.seconds.

A torque measuring device shall be connected to one of the plates thus permitting measurement of the torque required to overcome the viscoelastic resistance of the specimen.

An angular displacement measuring device shall be fitted to the moving plate thus permitting determination of its angular displacement and angular frequency.

The apparatus shall have an accuracy of torque measurement to within ± 2% of the minimum torque amplitude used to determine the dynamic properties.

The apparatus shall have an accuracy of angular displacement measurement to within $\pm 20 \times 10^{-6}$ radians.

The apparatus shall have an accuracy of angular frequency measurement to within ± 2% of the absolute value.

5.2 Temperature-controlled enclosure

Heating may be provided by the use of forced gas, radio-frequency heating or other suitable means.

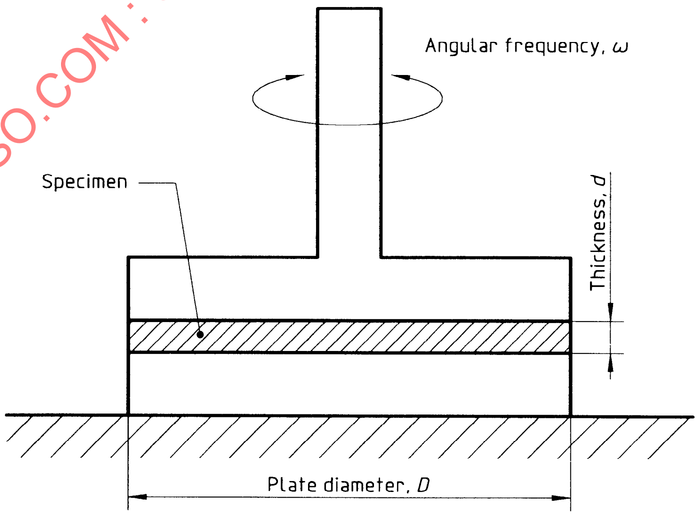

Figure 1 — Parallel-plate rheometer test geometry

3.5 out-of-phase component of the complex shear viscosity, η": The imaginary part of the complex shear viscosity.

The out-of-phase component of the complex shear viscosity is expressed in Pascal.seconds.

4 PRINCIPLES

The specimen shall be held between two concentric, circular, parallel plates, Figure 1. The thickness of the specimen shall be small compared with the diameter of the plates.

The specimen shall be subjected to either a sinusoidal torque or a sinusoidal angular displacement of constant angular frequency. These are referred to as `controlled-stress' or `controlled-strain' testing modes respectively. In using the controlled-stress mode the resultant displacement and the phase shift between the torque and displacement are measured. In using the controlled-strain mode the resultant torque and the phase shift between the displacement and torque are measured.

The complex shear modulus G*, shear storage modulus G', shear loss modulus G", the phase angle δ and the corresponding complex shear viscosity parameters (see clause 3) are determined from the torque and displacement functions and the specimen dimensions. In deriving these terms it is assumed that the specimen exhibits a linear viscoelastic response.

The mode of oscillation used is designated as oscillatory mode I (see ISO 6721-1:1994, clause 4).

5 APPARATUS

5.1 Measuring apparatus

The measuring apparatus shall consist of two concentric, rigid, circular parallel plates between which the specimen is placed, Figure 1. One of these plates shall be made to oscillate at a constant angular frequency while the other remains at rest.

The requirements of the apparatus are that it shall permit measurement of the amplitudes of the torque and angular displacement functions and the phase difference between these functions for a specimen subjected to either a sinusoidal torque or a sinusoidal displacement of constant angular frequency.

An environmental chamber surrounding the test geometry can be used to provide specific test environments, for example a nitrogen atmosphere.

It shall be checked that the chamber is not in contact with the specimen, plate geometries or their supports.

5.3 Temperature measurement and control

The test temperature shall preferably be measured using a device that is either in contact with or embedded in the fixed plate.

The test temperature shall be accurate to within ± 0,5 °C of the set temperature for set temperatures up to 200 °C ± 1,0 °C for temperatures in the range 200 °C - 300 °C, and ± 1,5 °C for temperatures above 300 °C.

The temperature measuring device shall have a resolution of 0,1 °C and shall be calibrated using a device accurate to within ± 0,1 °C.

5.4 Test geometry

The test geometry is defined by two concentric, circular parallel plates between which the specimen is held. The plates shall have a surface finish corresponding to a maximum roughness of $R_a = 0{,}25$ µm and shall have no visible imperfections.

The results may be dependent on the type of material that is used to form the surfaces of the plates. This can be identified by testing using plates of different surface materials.

The diameter of the plates D shall be determined to ± 0,01 mm and is typically in the range 20 - 50 mm.

The specimen thickness d is defined by the plate separation and shall be determined to ± 0,01 mm. It is recommended that the specimen thickness should lie in the range 0,5 - 3 mm and the ratio of plate diameter to specimen thickness should lie in the range 10 to 50 in order to minimize errors in the determination of properties. For low viscosity polymer liquids it may be necessary to employ dimensions outside these recommended ranges. The total variation in the plate separation due to non-parallelism of the plates shall be less than ± 0,01 mm. Variation in the plate separation during testing shall be less than ± 0,01 mm.

5.5 Calibration

The rheometer shall be calibrated periodically by measuring the torque, angular displacement and angular frequency response of the machine or by using reference liquids of known complex viscosity, in accordance with the instructions of the instrument manufacturer. It is preferable that the complex viscosity of reference liquids used for calibration shall have values in the same range as that of the specimens to be measured.

It is preferable that calibration shall be carried out at the test temperature.

6 SAMPLING

The sampling method, including any special methods of specimen preparation and introduction into the rheometer, shall be as specified in the relevant materials standard or otherwise by agreement.

As the test specimens are typically small, being of the order of 3 - 5 g, it is essential that they are representative of the material being sampled.

If samples or specimens are hygroscopic or contain volatile ingredients then they shall be stored to prevent or minimise any effects on viscosity. Drying of samples may be required prior to preparing test specimens.

The test specimens shall be in the form of a disc when produced by injection or compression moulding or by cutting from sheet. Alternatively they may be formed by placing pellets or liquid or molten polymer into the test geometry. The sample may be loaded in the molten state only if it is not sensitive to oxidation or loss of volatiles.

The specimen shall not contain any visible impurities or air bubbles. The specimen shall not show any obvious discolouration prior to or after testing.

7 PROCEDURE

7.1 Test temperature

Generally, because of the temperature dependence of viscosity, measurements for comparison purposes shall be carried out at the same temperature. Details shall be as specified in the relevant materials standard or otherwise by agreement.

7.2 Loading the test specimen

The specimen shall be loaded into the instrument in either its solid or molten state in accordance with clause 6. The specimen shall completely fill the gap between the two plates. Any excess material around the edges of the plates shall be removed before testing is commenced. Specimens may need to be slightly squeezed after trimming to promote good contact but precautions should then be taken to ensure that the specimen does not extend beyond the edges of the plate.

The specimen and plates shall then be allowed to reach thermal equilibrium at the test temperature. This period of time is referred to as the preheat time. For any particular instrument, test geometry, polymer type, sample thickness, loading procedure and test temperature the preheat time shall be determined by repeating the measurement but using a preheat time that is 10% greater (see Note 3). If there is no further change in the measured values of the complex shear modulus G*, shear storage modulus G' and shear loss modulus G" then the preheat time is sufficient for thermal equilibrium to have occurred.
[NOTE 3: This test can be incorporated into the time sweep test for thermal stability of the sample (see clause 7.5)]

When the instrument and specimen have reached the test temperature the specimen thickness d, which is equivalent to the plate separation, shall be determined (see subclause 5.4). This value for the specimen thickness shall be used for calculations.

7.3 Pre-conditioning of the test specimen

The test specimen may be pre-conditioned by applying an equilibrium time (zero shear at the test temperature for a specified period of time) and/or by pre-shearing prior to testing.

7.4 Test mode: controlled-stress or controlled-strain

Measurements are made using instruments either in a controlled-strain mode or in a controlled-stress mode.

In using the controlled-strain mode a sinusoidal displacement of constant amplitude is applied and the resultant sinusoidal torque function and the phase shift between the torque and displacement functions are determined.

In using the controlled-stress mode a sinusoidal torque of constant amplitude is applied and the resultant sinusoidal displacement function and the phase shift between the torque and displacement functions are determined.

Measurement of the dynamic rheological properties of specimens in accordance with this standard is restricted to the linear viscoelastic region of behaviour. Linear viscoelastic behaviour is defined, for the purpose herein, as that for which the viscosity or modulus is independent of the applied stress or strain. This assumption is necessary for the analysis of experimental data to be undertaken. It is therefore necessary that the amplitude of oscillation in the controlled-stress or controlled-strain modes shall be set such that the deformation of the specimen occurs within the linear viscoelastic region.

For procedures to determine the limit of the linear viscoelastic behaviour of the specimen see subclauses 7.6.1 - 7.6.3.

7.5 Time sweep - Determination of the duration of thermal stability of a sample

Prior to testing a sample it shall be necessary to carry out a time sweep at the test temperature to determine its thermal stability. The time sweep shall be made using the same test geometry and similar conditions of frequency and torque or angular displacement that are to be used in subsequent testing. It may be necessary to carry out time sweep measurements at more than one frequency (see Note 4). The duration of thermal stability is defined as the time taken from the start of the test to that at which any of the measured values of G^*, G' or G'' have changed from their initial value by 5% (see Note 5). It shall be specified as a time at a given temperature and angular frequency, for example 500 seconds at 250 °C and 1 rad/s. Subsequent measurements of new specimens of that sample at that temperature shall be completed in a time less than the duration of thermal stability.

[NOTE 4: Degradation effects on rheological properties are normally most easily identifiable when testing using low frequencies of oscillation.]

[NOTE 5: It may be necessary to discard initial spurious results when determining the initial modulus values.]

For some materials it may not be possible to obtain the desired results within the duration of thermal stability due to rapid degradation or crosslinking of the sample. In such cases the test report shall state the percentage change in modulus values occurring over the duration of the test, the value having been determined from the time sweep results.

7.6 Determination of the linear viscoelastic region of behaviour

7.6.1 Strain sweep - Determination of the linear viscoelastic region of behaviour using a controlled strain mode instrument

In using the controlled strain mode, the maximum permissible amplitude of oscillation shall be determined by performing a strain sweep. The strain sweep shall be made using the same test geometry and similar frequencies to those that are to be used in subsequent testing. It may be necessary to carry out strain sweep measurements at more than one frequency to check the frequency response of the limit of linear viscoelastic behaviour. The specimen shall be tested by increasing the amplitude of oscillation over a range of values, preferably commencing with a specimen strain evaluated at the edge of the plate of not more than 1%.

Values of the complex shear modulus G*, shear storage modulus G' and shear loss modulus G" as functions of the amplitude of oscillation shall be used to determine the maximum amplitude of oscillation for measurement within the linear viscoelastic region.

The maximum value of applied strain to be used in testing shall be not greater than the lowest value of strain at which a deviation of 5% occurred in any of the values of parameters G*, G' or G" from that of their values in the linear viscoelastic region. Where it is not possible to determine properties within the linear viscoelastic region, this shall be recorded in the test report (see Note 6).

[NOTE 6: For some materials the linear viscoelastic region is confined to very small strains such that errors in measurements prevent the reliable determination of properties for this strain region.]

7.6.2 Stress sweep - Determination of the linear viscoelastic region of behaviour using a controlled stress mode instrument

In using the controlled stress mode the range of the linear viscoelastic behaviour of the melt shall be determined by performing a stress sweep. The stress sweep shall be made using the same test geometry and similar frequencies to those that are to be used in subsequent testing. It may be necessary to carry out stress sweep measurements at more than one frequency to check the frequency response of the limit of linear viscoelastic behaviour. The specimen shall be tested by increasing the amplitude of torque over a range of values, preferably commencing with a torque resulting in a specimen strain, evaluated at the edge of the plate, of not more than 1%.

Values of the complex shear modulus G*, shear storage modulus G' and shear loss modulus G" as functions of the amplitude of torque shall be used to determine the maximum amplitude of torque to be used for measurement within the linear viscoelastic region.

The maximum value of applied torque to be used in testing shall be not greater than the lowest value of torque at which a deviation of 5% occurred in the any of the values of the parameters G*, G' or G" from that of their values in the linear viscoelastic region. Where it is not possible to determine properties within the linear viscoelastic region, this shall be recorded in the test report (see Note 6).

7.6.3 Confirmation of linear viscoelastic behaviour

A further check may be carried out to confirm that measurements have been made within the linear viscoelastic region of behaviour. Assuming such a behaviour, then for an applied sinusoidal displacement or torque the resultant output of torque or displacement, respectively, shall also be sinusoidal. A non-sinusoidal output function indicates that the behaviour is non-linear. In such cases the assumptions made in the analysis of the experimental data are not valid and consequently the determined values of moduli and viscosities are incorrect. Where such checks have been made they shall be reported in the test report.

7.7 Frequency sweep

When carrying out a frequency sweep on a specimen it is necessary to check for degradation, particularly when testing at low frequencies, and for distortion or fracture of the specimen at high frequencies.

Changes in the specimen due, for example, to degradation, cross-linking or melt fracture can affect the test results. The effect of such changes can be identified by repeating, at the end of a test, the conditions used at the start of the test on the same specimen and then comparing the results.

If distortion of the specimen at the edges of the plates occurs, commonly known as melt fracture, then those measurements shall be invalid. However, results that were obtained prior to distortion of the specimen remain valid.

7.8 Temperature sweep

When carrying out a temperature sweep from a low to a high temperature it is necessary to ensure that good physical contact has been made between the specimen and the plates, preferably by melting the specimen between the plates prior to testing and cooling to the starting temperature as necessary.

When performing temperature sweeps consideration should be given to the application of a correction for the change in dimensions of the fixture through thermal expansion. Some systems make this correction in software, using a linear expansion coefficient for the fixture.

Also see subclause 7.7 concerning warnings related to degradation and distortion of the specimen.

8 EXPRESSION OF THE RESULTS

8.1 Nomenclature

D - plate diameter, expressed in metres;
d - plate separation, expressed in metres;
T - torque, expressed in Newton.metres;
θ - angular displacement, expressed in radians;
ω - angular frequency (of oscillation), expressed in radians per second;
σ - shear stress, expressed in Pascals;
γ - shear strain, expressed as a dimensionless number;
G' - shear storage modulus, expressed in Pascals;
G'' - shear loss modulus, expressed in Pascals;
G^* - complex shear modulus, expressed in Pascals;
η' - dynamic shear viscosity, expressed in Pascal.seconds;
η'' - out-of-phase component of the complex shear viscosity, expressed in Pascal.seconds;
η^* - complex shear viscosity, expressed in Pascal.seconds;
δ - phase shift or loss angle, expressed in radians;
t - time, expressed in seconds.

8.2 Calculation of complex shear modulus and complex shear viscosity terms

For a linear viscoelastic fluid subjected to an applied harmonic stress $\sigma(t)$ where

$$\sigma(t) = \sigma_0 \exp i\omega t$$

resulting in an harmonic strain $\gamma(t)$ given by

$$\gamma(t) = \gamma_0 \exp i(\omega t - \delta)$$

where σ_0 and γ_0 are the amplitudes of the stress and strain respectively, ω the angular frequency and δ is the phase shift or loss angle between the stress and strain functions, the following quantities are defined:

shear storage modulus	$G' = \sigma_0 \cos\delta/\gamma_0$
shear loss modulus	$G'' = \sigma_0 \sin\delta/\gamma_0$
complex shear modulus	$G^* = G' + iG''$
dynamic shear viscosity	$\eta' = G''/\omega$
out-of-phase component of the complex shear viscosity	$\eta'' = G'/\omega$
complex shear viscosity	$\eta^* = \eta' - i\eta''$

where i is defined by $i = \sqrt{-1}$. Furthermore, it can be shown that

$$G^* = i\omega\eta^*$$

For forced oscillation of a parallel plate geometry and assuming a linear viscoelastic response of the specimen the equation of motion governing the flow is given by

$$T_o = (\pi D^4/32d)\,[G'(\omega) + iG''(\omega)]\,\theta_o \exp(-i\delta)$$

where T_o is the torque amplitude and θ_o is the amplitude of the angular displacement. This equation assumes that the inertia and compliance terms are small. The errors associated with these assumptions are generally small when testing polymer melts, particularly when using low angular frequencies of oscillation and when the stiffness of the specimen is low compared with that of the machine (see Note 7).

[NOTE 7. Corrections for the inertia and compliance terms are proposed by various authors, for example Marin (1), Walters (2) and Whorlow (3).]

Thus, for a given angular frequency, the shear storage modulus G' and shear loss modulus G'' are given by

$$G' = 32\,d\,T_o \cos(\delta)\ /\ \theta_o \pi D^4$$

and

$$G'' = 32\,d\,T_o \sin(\delta)\ /\ \theta_o \pi D^4$$

The phase shift δ is determined experimentally.

From the relations between the shear moduli and viscosities presented above the following equations can be derived.

$$\eta' = 32\,d\,T_o \sin(\delta)\ /\ \omega\theta_o \pi D^4$$

and

$$\eta'' = 32\,d\,T_o \cos(\delta)\ /\ \omega\theta_o \pi D^4$$

For an angular displacement θ the strain γ in the specimen at the edge of the plate is given by

$$\gamma = \theta D\ /\ 2d$$

Generally, commercial instruments use software to determine the values of the complex shear modulus and its real and imaginary components from the raw data. The method by which they obtain and analyze the raw data of torque and amplitude and the phase shift between the sinusoidal torque and amplitude functions may vary. Also, the implementation of corrections for inertia and compliance effects, if applied, may vary. Specification of these procedures is currently outside the scope of this standard. Where procedures differs fundamentally from that presented herein, the basis on which the instrument determines modulus and viscosity values shall be stated in the test report.

9 PRECISION

The precision of this test method is not known because inter-laboratory data are not available. When inter-laboratory data are obtained a precision statement will be added with the next revision.

10 TEST REPORT

The test report shall include the following information:

a) a reference to this part of ISO 6721;

b) test reference number;

c) the date of the test

d) operator identification;

e) all details necessary for identification of the material tested;

f) details of preparation and loading of the specimen between the plates;

g) a description of the rheometer measuring system used, including the plate diameter, plate separation and the material that forms the plate surface;

h) the set value for the test temperature in degrees Celsius;

i) the preheating time in seconds;

j) details of equilibrating time and any pre-shear conditioning;

k) duration of thermal stability in seconds;

l) test duration in seconds;