

Draft ISO Standard for the determination of the transient extensional viscosity of polymer melts

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ABSTRACT

This document presents a proposal for a draft Standard for a method for determining the transient extensional viscosity of polymer melts. The document details the measurement of polymer melt specimens stretched uniaxially under conditions of constant strain rate and constant temperature.

The method is capable of measuring the transient extensional viscosity of polymer melts at Hencky strain rates typically in the range $0,01 \text{ s}^{-1}$ to 1 s^{-1} and Hencky strains up to approximately 4 and at temperatures up to approximately $250 \text{ }^{\circ}\text{C}$. It is suitable for measuring transient extensional viscosity values typically in the range from approximately 10^4 Pa.s to 10^7 Pa.s .

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on measurements related to the processability of materials

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CONTENTS

1. SCOPE	1
2. NORMATIVE REFERENCES	1
3. DEFINITIONS	1
3.1 GENERAL	1
3.2 HENCKY STRAIN	2
3.3 HENCKY STRAIN RATE	2
3.4 NET TENSILE STRESS	2
3.5 TENSILE STRESS GROWTH COEFFICIENT	2
3.6 TENSILE VISCOSITY	2
4. GENERAL PRINCIPLES	3
4.1 DESCRIPTION	3
5. APPARATUS	3
5.1 GENERAL DESCRIPTION	3
5.2 TEMPERATURE-CONTROLLED ENCLOSURE	5
5.3 TEMPERATURE MEASUREMENT AND CONTROL	5
5.4 STRAIN AND STRAIN RATE MEASUREMENT	6
5.5 FORCE MEASUREMENT	6
5.6 CALIBRATION	6
6. SAMPLING AND SPECIMEN PREPARATION	7
6.1 SAMPLING	7
6.2 SPECIMEN PREPARATION	7
6.3 SPECIMEN MOUNTING	8
7. PROCEDURE	8
7.1 SPECIMEN LOADING	8
7.2 PRE-CONDITIONING OF THE SPECIMEN	8
7.3 TESTING	8
8. ANALYSIS OF EXTENSIONAL MEASUREMENTS	9
8.1 TERMINOLOGY	9
8.2 GENERAL THEORY: ANALYSIS OF EXTENSIONAL FLOW	9
8.3 ANALYSIS: TYPE A	10
8.4 ANALYSIS: TYPE B	12
8.5 ANALYSIS: TYPE C	12
8.6 ANALYSIS: TYPE D	13
9. PRECISION	13

10. TEST REPORT 13

Annex A.1 15

 Uncertainties in transient extensional viscosity testing 15

 A1.1 Summary 15

 A1.2 Uncertainty analysis..... 15

Annex A.2 19

 Effect of viscous dissipation in the specimen during stretching on measurements 19

 A2.1 Summary 19

 A2.2 Analysis of viscous heating effect 19

Annex A3 20

 Bibliography 20

ACKNOWLEDGEMENT 20

Plastics - Determination of the transient extensional viscosity of polymer melts

SCOPE

This International Standard specifies the general principles of a method for determining the transient extensional viscosity of polymer melts. The procedure details the measurement of the polymer melt specimens stretched uniaxially under conditions of constant strain rate and constant temperature.

The method is capable of measuring the transient extensional viscosity of polymer melts at Hencky strain rates typically in the range $0,01 \text{ s}^{-1}$ to 1 s^{-1} and Hencky strains up to approximately 4 and at temperatures up to approximately $250 \text{ }^{\circ}\text{C}$ (see notes 1 and 2). It is suitable for measuring transient extensional viscosity values typically in the range from approximately $10^4 \text{ Pa}\cdot\text{s}$ to $10^7 \text{ Pa}\cdot\text{s}$ (see note 3).

NOTE 1: Hencky strains and strain rates are used (see clause 3).

NOTE 2: Values of strain, strain rate and temperature outside these limiting values may be attained.

NOTE 3: The operating limit of an instrument, in terms of the lowest transient extensional viscosity values that can be measured, is due to a combination of factors including the ability of the specimen to maintain its shape during testing and the resolution of the instrument.

2. NORMATIVE REFERENCES

The following Standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions 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 Standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 472: 1988, *Plastics - Vocabulary*.

3. DEFINITIONS

3.1 GENERAL

For the purposes of this International Standard, the definitions given in ISO 472 apply. In addition the definitions presented in subclauses 3.2 - 3.6 apply.

The definitions presented in subclauses 3.2 - 3.6 are given by Whorlow [1] for strains and strain rates, and by the Nomenclature Committee of the Society of Rheology for start-up flow in tensile uniaxial extension at constant Hencky strain rate [2].

3.2 HENCKY STRAIN

Hencky strain ε : also referred to as the natural or true strain. It is given by the natural logarithm of the elongation ratio

$$\varepsilon = \ln(\ell / \ell_o) \quad (1)$$

where ℓ is the specimen length and ℓ_o is the original specimen length.

It is dimensionless.

3.3 HENCKY STRAIN RATE

Hencky strain rate $\dot{\varepsilon}$: the rate of change of Hencky strain with time. It is given by

$$\dot{\varepsilon} = 1/\ell \times \partial \ell / \partial t. \quad (2)$$

where t is time. It is independent of the original specimen length ℓ_o .

It is expressed in reciprocal seconds.

3.4 NET TENSILE STRESS

Net tensile stress σ_E : in tensile uniaxial extension it is defined by

$$\sigma_E = \sigma_{11} - \sigma_{22} = \sigma_{11} - \sigma_{33} = \sigma_{zz} - \sigma_{rr} \quad (3)$$

where σ_{ii} is a stress tensor in either rectangular or axisymmetric co-ordinates. The tensile stress growth function is indicated by σ_E^+ where the $^+$ indicates start-up of flow.

It is expressed in pascals.

3.5 TENSILE STRESS GROWTH COEFFICIENT

Tensile stress growth coefficient η_E^+ : a transient extensional viscosity, it is the ratio of the net tensile stress to Hencky strain rate

$$\eta_E^+(t, \dot{\varepsilon}) = \sigma_E / \dot{\varepsilon} \quad (4)$$

where t is time, and $^+$ indicates start-up of flow. The above term is a transient term.

It is expressed in pascal seconds.

3.6 TENSILE VISCOSITY

Tensile viscosity, η_E : is defined by

$$\eta_E(t, \dot{\varepsilon}) = \lim_{t \rightarrow \infty} [\eta_E^+(t, \dot{\varepsilon})] \quad (5)$$

It is the limiting tensile stress growth coefficient value and represents an equilibrium

extensional viscosity if a steady value is achieved. However for materials that do not exhibit a steady state behaviour the use of an 'equilibrium extensional viscosity' such as this is not appropriate.

It is expressed in pascal seconds.

4. GENERAL PRINCIPLES

4.1 DESCRIPTION

In contrast to shear flow where reference is normally made only to steady shear flow behaviour, extensional flow behaviour is best described as being transient. In describing the transient behaviour of materials in extension at constant strain rate, they may exhibit either an unbounded stress growth behaviour in which the stress continually increases with increasing strain until the material fails, or the stress reaches a steady value with increasing strain thus yielding a tensile or equilibrium extensional viscosity. The latter occurs typically at large strains. An equilibrium extensional viscosity is thus dependent on strain rate but not on strain or time. Normally the extensional viscosity will vary as a function of both strain and strain rate as well as temperature.

In describing and modelling plastics processing the Hencky strain is preferred as the rate of strain of an element of fluid within a flow is then independent of its original length and is determined only from the velocity field of that element. It is thus a more suitable characteristic of the flow. Strain or strain rate are taken by default herein to imply Hencky values.

Stretching flow methods can be used to generate quantitatively accurate data on the extensional viscoelasticity of polymer melts. In carrying out extensional flow measurements there are four types of measurement that are normally made: constant strain rate, constant stress, constant force or constant speed. This method describes the first of these: constant strain rate. In this method the instantaneous value of strain rate is uniform throughout the specimen and the strain rate is held constant with time.

The basic principle behind stretching flow measurements is to subject a specimen to a tensile stretching deformation. By measurement of the force and deformation of the specimen the stresses and strains and hence strain rate can be determined.

5. APPARATUS

5.1 GENERAL DESCRIPTION

The measuring apparatus shall consist of one of the following Types, figure 1 - 4. These Types are defined to describe the various instrument configurations. The notation used in these figures is defined in subclause 8.1.

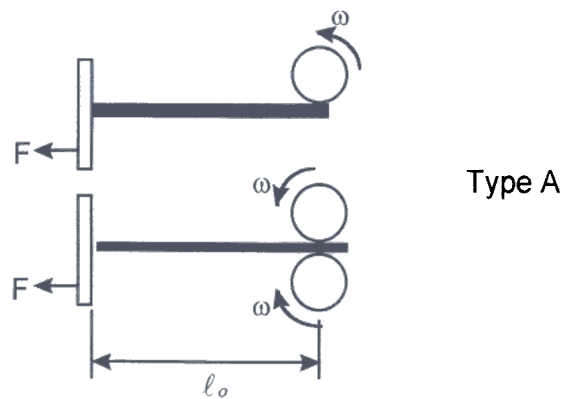


Figure 1: Schematic diagram of test instrument Type A

Type A: A single rotating clamp and a fixed clamp. The rotating clamp shall consist of either a single or a pair of rotating elements. The force exerted on the specimen is measured at the fixed end.

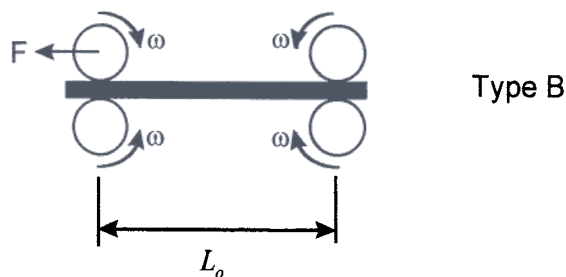


Figure 2: Schematic diagram of test instrument Type B

Type B: Two rotating clamps. Each clamp shall consist of either a single or a pair of rotating elements - only the pair arrangement is shown. The force exerted on the specimen is measured at one end.

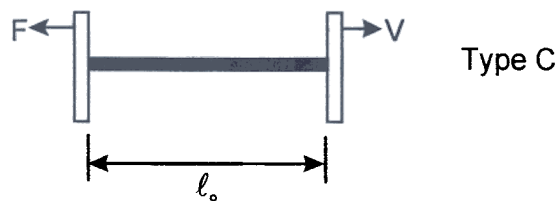


Figure 3: Schematic diagram of test instrument Type C

Type C: Single translating (non-rotating) clamp.

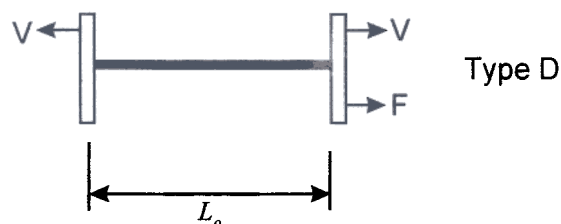


Figure 4: Schematic diagram of test instrument Type D

Type D: Two translating (non-rotating) clamps.

In each of these configurations the specimen is mounted between the clamps and is uniaxially stretched. The use of two sets of moving or rotating clamps results in a static point at the mid-point of the specimen. However, measurement of the force is then required through a moving clamp. The use of a single moving clamp allows the measurement of force through a static clamp but does not result in a static point at some position along the length of the specimen.

The force on the specimen shall be measured during the test. The strain and rate of strain of the specimen shall either be derived from the displacements and/or velocities of the clamp or clamps, or measured directly from the dimensions and/or local velocities of the specimen.

The requirements of the apparatus are that it shall permit the measurement or determination of the force, strain and rate of strain of a specimen subjected to a constant strain rate under isothermal conditions.

5.2 TEMPERATURE-CONTROLLED ENCLOSURE

Heating may be provided by the use of a silicone oil bath or forced gas (see note 1).

When heating using forced gas, a gas may be used in the environmental chamber surrounding the test specimen to provide the required test environment, for example nitrogen to provide an inert atmosphere.

For low viscosity materials it is essential to support the specimen during heat-up and testing to avoid it sagging under the influence of gravity.

The use of a silicone oil bath results in the specimen being supported by the silicone oil due to its buoyancy, particularly if the densities of the silicone oil and specimen are matched at the test temperature. If a forced gas oven is used then support of the sample can be obtained by providing a cushioning effect by the gas.

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

NOTE 1: The use of a silicone oil bath may permit more rapid heating of the specimen.

5.3 TEMPERATURE MEASUREMENT AND CONTROL

The uniformity of temperature along the specimen length is critical to the measurement of the transient extensional flow properties of polymer melts. Localised hot spots will result in excessive strain in those regions that may lead to premature failure, particularly for materials that do not exhibit a high degree of strain hardening.

The test temperature shall preferably be measured using a device that is mounted close to the specimen. Contact of the device with the specimen shall not be permitted. It is preferable to mount temperature sensors in at least two positions to monitor temperature uniformity.

The spatial temperature uniformity shall be to within $\pm 0,75$ °C.

The temporal temperature variation shall be within $\pm 1,0$ °C of the set temperature.

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

5.4 STRAIN AND STRAIN RATE MEASUREMENT

The strain and strain rate of the specimen shall be determined either from measurement of the displacements and/or velocities of the clamp or clamps, or measured directly from the dimensions and/or local velocities of the specimen (see note 1).

NOTE 1: The diameter of the specimen may be measured during the test by use of optical or cutting methods to derive strains and strain rates and to assess the uniformity of deformation. The cutting method results in the test being terminated once the cuts have been made and thus prevents data to failure from being obtained. Local velocities may be measured using optical methods.

Corrections for slippage of the specimen at the clamp or clamps may be applied, obtained through independent measurement of the strain of the specimen during testing through measurement its diameter or local velocities by other methods.

The apparatus shall have an accuracy of strain determination or measurement to within $\pm 3\%$ of the absolute value.

The apparatus shall have an accuracy of rate of strain determination or measurement to within $\pm 3\%$ of the absolute value.

5.5 FORCE MEASUREMENT

The force on the specimen shall be measured during the test by an appropriate means, for example a leaf spring arrangement (see note 1).

The resolution of the force measuring device should preferably be at least 0.001 N.

The apparatus shall have an accuracy of force measurement to within $\pm 2\%$ of the full scale value.

NOTE 1: Typical peak forces measured in testing of polyethylenes are estimated to be up to $\approx$ N for specimens approximately 3 mm in diameter.

5.6 CALIBRATION

The force, displacement, rate of displacement and temperature functions of the rheometer shall be calibrated periodically.

It is preferable that calibration shall be carried out at the test temperature as measurement of these functions, in particular that of force, may be temperature sensitive.

No traceable standard reference materials exist for checking the calibration of such instruments. Where a reference material is used for checking the instrument it is preferable that the transient extensional viscosity of the reference material and the dimensions of the specimen produced using it shall have values that are similar to those encountered or used during normal operation of the instrument.

6. SAMPLING AND SPECIMEN PREPARATION

6.1 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.

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

As the test specimens are typically small, being of the order of a few grams, it is essential that they are representative of the material being sampled. Repeat testing may be used to identify batch-to-batch or within-batch variation.

6.2 SPECIMEN PREPARATION

The specimen shall be either cylindrical or rectangular in cross section.

Test specimens in the form of a cylinders may be produced by extrusion, injection, transfer or compression moulding.

Test specimens in the form of a strips may be produced by extrusion, injection or compression moulding or by cutting from sheet.

The length to diameter ratio of cylindrical specimens should be at least 10 (see note 1).

NOTE 1: A length to diameter ratio of at least 10 is required to minimise end effects. However, a longer specimen will result in a reduction in the maximum strain rate that can be achieved. The magnitude of the end-errors can be assessed by using specimens of different length or diameter to produce different length to diameter aspect ratios. The effect on measured values can then be determined.

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

For cylindrical specimens the diameter of the test specimen shall be measured at at least three positions along its length and repeat after rotating the specimen by 90°. An average value for the diameter shall be calculated from these measurements.

For rectangular specimens the width and thickness shall be measured at at least three positions along its length. Calculate average values for the width W and thickness H shall be calculated from these measurements.

The cross sectional area of the specimen shall be calculated from these measurements.

The diameter or width and thickness of the specimen, as appropriate, shall each be determined to and uniform to within $\pm 2\%$ of their average value.

6.3 SPECIMEN MOUNTING

Specimens may be either gripped by the clamps or attached using adhesive to studs that are then clamped into the instrument (see note 1).

NOTE 1: Attachment by a suitable high temperature epoxy adhesive has been found suitable. The ends of the specimen are first treated by passing them through a butane flame and then dipping them into concentrated sulphuric acid for 30 seconds. Care was taken to prevent any other part of the specimen, except that to be stuck, from being exposed to either the flame or the acid. The ends are dipped into the adhesive and then attached to the studs. The specimen and studs are then placed into an oven and the adhesive cured using a suitable time-temperature cycle. For the materials tested an epoxy adhesive (Ciba AV119) proved to be suitable, with a cure cycle of 100 °C for 1 hour. The specimens are then allowed to cool before handling.

7. PROCEDURE

7.1 SPECIMEN LOADING

Mount the specimen in place in the rheometer.

Measure the length of the specimen between the clamps to within 1% of its absolute value.

After mounting the specimen into the instrument, immerse the specimen into the silicone oil bath or environmental chamber. Where possible, allow the bath or chamber to be at the test temperature before inserting the specimen to reduce the time spent by the specimen reaching and equilibrating at the test temperature. Allow the specimen and apparatus to reach thermal equilibrium at the test temperature. This period of time is referred to as the equilibrating time (see note 1).

NOTE 1: The adequacy of the time allowed for the specimen to reach thermal equilibrium and the effects of the silicone oil, degradation and other time dependant phenomena on the specimen can be checked by varying the time for which the specimen is immersed in the oil bath or environmental chamber before testing. The effect on measured values can then be assessed.

A correction for thermal expansion of the specimen diameter during heating should be made (see note 3).

NOTE 3: For example, measurements of a HDPE indicate a 20% decrease in density on heating from 25 °C to 150 °C.

7.2 PRE-CONDITIONING OF THE SPECIMEN

The specimen may be pre-conditioned by applying a known strain prior to testing and allowing the induced stresses to relax to zero before commencing the test.

7.3 TESTING

Subject the specimen to a constant strain rate deformation until the specimen fails or up to a set strain value.

Record the force, clamp velocities, strain and strain rate data as functions of time, as appropriate.

Analyse the data using equations presented in clause 8 as appropriate. Corrections for effects such as machine compliance, end-effects, errors in strain and strain rate determination and thermal expansion of the specimen may be applied, as necessary.

It may be necessary to check for degradation or cross-linking, particularly when testing at low strain rates when the test duration is long (see note 1). Also check for premature fracture of the specimen or breakage or pull-out at the clamps.

NOTE 1: The effects of degradation, cross-linking and silicone oil on the specimen can be checked by varying the time for which the specimen is immersed in the oil bath or environmental chamber before and during testing. The effect on measured values can then be assessed.

8. ANALYSIS OF EXTENSIONAL MEASUREMENTS

8. TERMINOLOGY

v	-	effective velocity of separation of the ends of the specimen for rotating clamps, type A and B, m.s^{-1} .
V		velocity of separation of the ends of the specimen for non-rotating clamps, types C and D, m.s^{-1} .
ω		angular velocity of rotating clamp, rad.s^{-1} .
		rotating clamp radius, m
t		time, s
ℓ_o or L_o		original specimen length (dependent on Type), m
ℓ or L		specimen length at time t (dependent on Type), m
A_o		original specimen cross-sectional area, m^2
A		specimen cross-sectional area at time t , m^2
F		force, N
ε		Hencky strain (dimensionless)
$\dot{\varepsilon}$		Hencky strain rate, s^{-1}
σ_E		net tensile stress, Pa
η_E		tensile stress growth coefficient, Pa.s

8.2 GENERAL THEORY: ANALYSIS OF EXTENSIONAL FLOW

Rearranging the Hencky strain, equation (1), yields

$$\ell = \ell_o e^{(\varepsilon)} \quad (6)$$

where ℓ_o is the original specimen length, ℓ is specimen length at time t and ε is the Hencky strain. For constant Hencky strain rate $\dot{\varepsilon}$

$$\varepsilon = \dot{\varepsilon} t \quad (7)$$

where t is time. Thus

$$\ell = \ell_o e^{(\dot{\varepsilon} t)} \quad (8)$$

Assuming conservation of volume of the specimen then

$$\ell_o A_o = \ell A \quad (9)$$

where A_o is the original specimen cross sectional area and A is specimen cross sectional area at time t . The net tensile stress σ_E , expressed as the ratio of the force F applied to the specimen to the cross sectional area of the specimen, is given by

$$\sigma_E = \frac{F}{A}$$

and can thus be rewritten using equation (9) as

$$\sigma_E = \frac{F \ell}{A_o \ell_o}$$

Substitution for ℓ , using equation (8), yields

$$\sigma_E = \frac{F e^{(\dot{\varepsilon} t)}}{A_o}$$

Thus the tensile stress growth coefficient, the ratio of net tensile stress to Hencky strain rate, is given by

$$\eta_E = \frac{F e^{(\dot{\varepsilon} t)}}{A_o \dot{\varepsilon}}$$

8.3 ANALYSIS: TYPE A

For type A instruments the effective length of the specimen is equal to the separation between the fixed clamp and the point at which the specimen meets the rotating clamp at a tangent. It is indicated by ℓ_o in figure 1. The effective specimen length ℓ_o remains unchanged during the test as the specimen is wound onto the rotating clamp. The instantaneous velocity of separation of the effective ends of the specimen, v , is given by

$$v = \omega r$$

where ω is the angular velocity of the rotating clamp and r is the radius of the rotating clamp. The velocity can also be written as

$$v = \partial \ell / \partial t$$

Thus, by using the definition of Hencky strain rate

$$\dot{\epsilon} = 1/\ell \times \partial \ell / \partial t$$

the strain rate in the specimen is given by

$$\epsilon = \frac{\omega r}{\ell}$$

Thus for an instrument with one fixed clamp and a clamp that is rotating at constant angular velocity the strain rate is constant (see note 1).

NOTE 1: The specimen length may change with force due to the compliance of the force transducer.

As the strain rate is constant the strain ϵ is determined as the integral of strain rate with respect to time t ,

$$\epsilon = \int_0^t \dot{\epsilon} dt$$

thus integrating equation (17) yields the strain

$$\epsilon = \frac{\omega r t}{\ell} \quad (19)$$

The cross-sectional area of the specimen at time t is determined from the original cross-sectional area of the specimen and its strain. Assuming conservation of volume on stretching, the net tensile stress is given, using equation (12), by

$$\sigma_E = \frac{F e^{\left(\frac{\omega r t}{\ell}\right)}}{A_o}$$

and the tensile stress growth coefficient, using equation (13), by

$$\eta_E = \frac{F \ell_o e^{\left(\frac{\omega r t}{\ell}\right)}}{A_o \omega r}$$

8.4 ANALYSIS: TYPE B

For the experimental configuration in which there are two sets of clamps rotating at the same angular speed ω (Type B, figure 2) then the analysis presented for type A is valid except that ℓ_o is equal to a half of the effective specimen length L_o . The effective specimen length L_o is defined as the distance between the points at which the specimen touches the clamps at a tangent, figure 2. Thus the strain is given by

$$\varepsilon = \frac{\omega r t}{\left(\frac{L_o}{2}\right)}$$

the net tensile stress by

$$\sigma_E = \frac{F e^{\left(\frac{\omega r t}{\left(\frac{L_o}{2}\right)}\right)}}{A_o}$$

and the tensile stress growth coefficient by

$$\eta_E = \frac{F \left(\frac{L_o}{2}\right) e^{\left(\frac{\omega r t}{\left(\frac{L_o}{2}\right)}\right)}}{A_o}$$

8.5 ANALYSIS: TYPE C

In the case of a single translating clamps (Type C) to obtain a constant strain rate $\dot{\varepsilon}$ then the relative velocity of the clamp V , where

$$V = \frac{\partial \ell}{\partial t}$$

is given, using equation (8), by

$$V = \ell_o \dot{\varepsilon} e^{(\dot{\varepsilon} t)}$$

where ℓ_o is the original specimen length. The strain ε is simply determined as the integral of strain rate with respect to time t and, as strain rate is constant, is given by

$$\varepsilon = \dot{\varepsilon} t$$

The net tensile stress is given by equation (12) as

$$\sigma_E = \frac{F e^{(\dot{\varepsilon} t)}}{A_o}$$

and the tensile stress growth coefficient is given by equation (13) as

$$\eta_E = \frac{F e^{(\dot{\epsilon} t)}}{A_o \dot{\epsilon}}$$

8.6 ANALYSIS: TYPE D

In the case of using two clamps moving with the same speed to obtain a constant strain rate $\dot{\epsilon}$ then the velocities of the clamps V , where

$$2V = \frac{\partial L}{\partial t}$$

is given, using equation (8), as

$$V = \frac{L_o \dot{\epsilon} e^{(\dot{\epsilon} t)}}{2}$$

where L_o is the original specimen length. The net tensile stress is given by equation (28) and the tensile stress growth coefficient by equation (29).

9. PRECISION

The results of an intercomparison of stretching methods made in 1998 [3] comprising 6 laboratories indicated that the variation in tensile stress growth coefficient values was estimated to be up to $\pm 60\%$. The variation in peak tensile stress growth coefficient values was up to $\pm 100\%$. A high density polyethylene that was stable at 190 °C for in excess of two hours was used as the intercomparison material. Samples of the material were provided to each of the participants who produced their own specimens. Measurements were made at 150 °C and 190 °C.

An analysis of the uncertainties of transient extensional viscosity measurements is presented in Annex A1.

An analysis of the effect of viscous heating on transient extensional viscosity measurements is presented in Annex A2.

10. TEST REPORT

The test report shall include the following information, as applicable:

- a) a reference to this Standard;
- 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 any pre-treatment of the material and preparation and loading of the specimen;
- g) reference to the instrument used;
- h) the set value for the test temperature in degrees Celsius;
- i) details of equilibrating time and any pre-conditioning of the specimen;
- j) duration of thermal stability in seconds;
- k) test duration in seconds;
- l) any of the following, presented as functions of strain, strain rate, temperature and time as required:

net tensile stress σ_E in Pa
tensile stress growth coefficient in Pascal.seconds;

- m) details of any corrections applied to the data;
- n) any visual observations of premature failure or degradation of the specimen;
- o) any test conditions that have been agreed on that deviate from this International Standard.

Annex A.1

(informative)

Uncertainties in transient extensional viscosity testing

A1.1 Summary

An analysis of the uncertainties in transient extensional viscosity measurements is presented. The equations can be used to calculate the uncertainties in the derived tensile stress growth coefficient values, given the uncertainties in each component of the measurement.

A1.2 Uncertainty analysis

The following uncertainty analysis is based on the use of a Type A extensional rheometer (figure 1) having a single rotating clamp and a fixed clamp for the measurement of force. Similar analyses can be carried out for other instrument configurations.

Using equation (21), i.e.

$$\eta_E^\tau = \frac{F \ell_o e^{\left(\frac{\omega r}{\ell_o}\right)}}{A_o \omega r} \quad (\text{A1.1})$$

but rewritten for convenience, using equation (19), as

$$\eta_E = \frac{F \ell_o e^{(\epsilon)}}{A_o \omega r} \quad (\text{A1.2})$$

then the uncertainty in the tensile stress growth coefficient is given by

$$\left[\frac{\eta_E^+}{\eta_E^-} \right]^2 = \left(\frac{F}{F} \right)^2 + \left(\frac{\ell_o}{\ell_o} \right)^2 + \left(\frac{A_o}{A_o} \right)^2 + \left(\frac{\omega}{\omega} \right)^2 + \left(\frac{r}{r} \right)^2 + \left(\frac{u(e^{(\epsilon)})}{e^{(\epsilon)}} \right)^2 \quad (\text{A1.3})$$

where the underscore indicates the uncertainty in the parameter and $u(e^{(\epsilon)})$ indicates the uncertainty in the expression $e^{(\epsilon)}$. The ratio of the uncertainty in the parameter to the value of the parameter is the fractional uncertainty in that parameter.

Assuming

$$u(e^{(\epsilon)}) = e^{\epsilon + \delta\epsilon} - e^{\epsilon} \quad (\text{A1.4})$$

where $\delta\epsilon$ is the uncertainty in the strain ϵ then

$$\frac{u(e^{(\epsilon)})}{e^{(\epsilon)}} = e^{\delta\epsilon} - 1 \quad (\text{A1.5})$$

As

$$\varepsilon = \frac{\omega r t}{\ell_o} \quad (\text{A1.6})$$

(equation (19)) then the fractional uncertainty in the strain is given by

$$\left(\frac{\delta\varepsilon}{\varepsilon}\right)^2 = \left(\frac{\omega}{\omega}\right)^2 + \left(\frac{r}{r}\right)^2 + \left(\frac{t}{t}\right)^2 + \left(\frac{\ell_o}{\ell_o}\right)^2 \quad (\text{A1.7})$$

and thus the uncertainty in the strain is given by

$$\delta\varepsilon = \left[\left(\frac{\omega}{\omega}\right)^2 + \left(\frac{r}{r}\right)^2 + \left(\frac{t}{t}\right)^2 + \left(\frac{\ell_o}{\ell_o}\right)^2 \right]^{1/2} \times \frac{\omega r t}{\ell_o} \quad (\text{A1.8})$$

Thus equation (A1.5) can be rewritten, using equation (A1.8), as

$$\frac{\ln(e^\varepsilon)}{e^\varepsilon} = (e^{\delta\varepsilon} - 1)^2 \quad (\text{A1.9})$$

$$= \left[e^{\left\{ \left[\left(\frac{\omega}{\omega}\right)^2 + \left(\frac{r}{r}\right)^2 + \left(\frac{t}{t}\right)^2 + \left(\frac{\ell_o}{\ell_o}\right)^2 \right]^{1/2} \times \frac{\omega r t}{\ell_o} \right\}} - 1 \right]^2 \quad (\text{A1.10})$$

Thus the uncertainty in the tensile stress growth coefficient values is given, using equations (A1.3) and (A1.10), by

$$\left[\frac{\eta_E^+}{\eta_E^-} \right]^2 = \left(\frac{F}{F}\right)^2 + \left(\frac{\ell_o}{\ell_o}\right)^2 + \left(\frac{A_o}{A_o}\right)^2 + \left(\frac{\omega}{\omega}\right)^2 + \left(\frac{r}{r}\right)^2 + \left[e^{\left\{ \left[\left(\frac{\omega}{\omega}\right)^2 + \left(\frac{r}{r}\right)^2 + \left(\frac{t}{t}\right)^2 + \left(\frac{\ell_o}{\ell_o}\right)^2 \right]^{1/2} \times \frac{\omega r t}{\ell_o} \right\}} - 1 \right]^2 \quad (\text{A1.11})$$

The values of these terms, except for the force terms, are relatively easy to determine. The difficulty with the force terms is that the force decreases considerably at high strain values and thus the fractional uncertainty of the force will increase significantly as the test progresses. To estimate the effect of its contribution to the overall uncertainty in the determination of the tensile stress growth coefficient values then further analysis, presented below, is required.

The force supported by the specimen during testing is given by

$$F = \sigma A \quad (\text{A1.12})$$

and the net tensile stress by

$$\sigma = \eta_E^+ \dot{\varepsilon} \quad (\text{A1.13})$$

Thus the force

$$F = \eta_E^+ \dot{\epsilon} A \quad (\text{A1.14})$$

or, using equations (8), (9) and (17), by

$$F = \eta_E^+ \dot{\epsilon} A_o e^{\left(\frac{-\alpha \epsilon}{\epsilon_o}\right)} \quad (\text{A1.15})$$

Assuming the behaviour, figure 5, then the equation of a straight line fit to the data is of the form

$$\log(\eta_E^+) = m \log(t) + \log(\eta_{E,o}^+) \quad (\text{A1.16})$$

where $\eta_E^+ = \eta_{E,o}^+$ at $t = 1$ s and $\eta_{E,o}^+$ and m are constants. Equation (A1.16) can be rewritten as

$$\eta_E^+ = \eta_{E,o}^+ t^m \quad (\text{A1.17})$$

The force over the test duration is thus approximated by

$$F = \eta_{E,o}^+ t^m \dot{\epsilon} A_o e^{\left(\frac{-\alpha \epsilon}{\epsilon_o}\right)} \quad (\text{A1.18})$$

where $\dot{\epsilon}$ is given by equation (17). Values of $\eta_{E,o}^+ = 2.4 \times 10^5$ Pa.s and $m = 0.6$, were estimated for a HDPE at 150 °C, figure 5 (NPL ref. HGH [4]). The force F can thus be determined as a function of time and, assuming that all strain rate data fall on the same master curve (figure 5), also as a function of strain if one ignores any additional strain hardening. Thus the fractional uncertainty in the force F , given the decreasing magnitude of F at high strains, can be more accurately determined.

Thus, given the values of the parameters and the uncertainties in each of the parameters, for example table A1, the uncertainty in the derived tensile stress growth coefficient values can be calculated. In the case presented (table A1) the tensile stress growth coefficient values are plotted, figure 6, along with uncertainty limits derived using equation (A1.11). The example illustrates the significant increase in measurement uncertainties at high strains due to the increase in the uncertainty in the measurement of force resulting from the significant reduction in the cross-sectional area of the specimen. Uncertainties were estimated to be between $\pm 5\%$ and $\pm 10\%$ for strains in the range 0.03 to 2.4, $\pm 20\%$ at a strain of 3.6, $\pm 50\%$ at a strain of 4.8 and $\pm 100\%$ at a strain of 5.6.

Table A1: Example values and uncertainties in the extensional testing parameters.

Parameter	Units	Fractional uncertainty	Value	Uncertainty
Force, F	N	variable, 0.02 at full scale	variable, 0.85 max	0.017
Initial length, ℓ_o	m	0.01	0.1	0.003
Initial area, A_o	m ²	0.04	7.1×10^{-6}	2.9×10^{-7}
Angular speed, ω	rad.s ⁻¹	0.02	5	0.1
Clamp radius, r	m	0.0005	0.02	0.0001
Time, t	s	0.01*	variable*	-*

Notes: $\eta_{E,o}^+ = 2.4 \times 10^5$ Pa.s and $m = 0.6$ estimated for an HDPE at 150 °C (figure 5).

* only potentially significant at very short times.

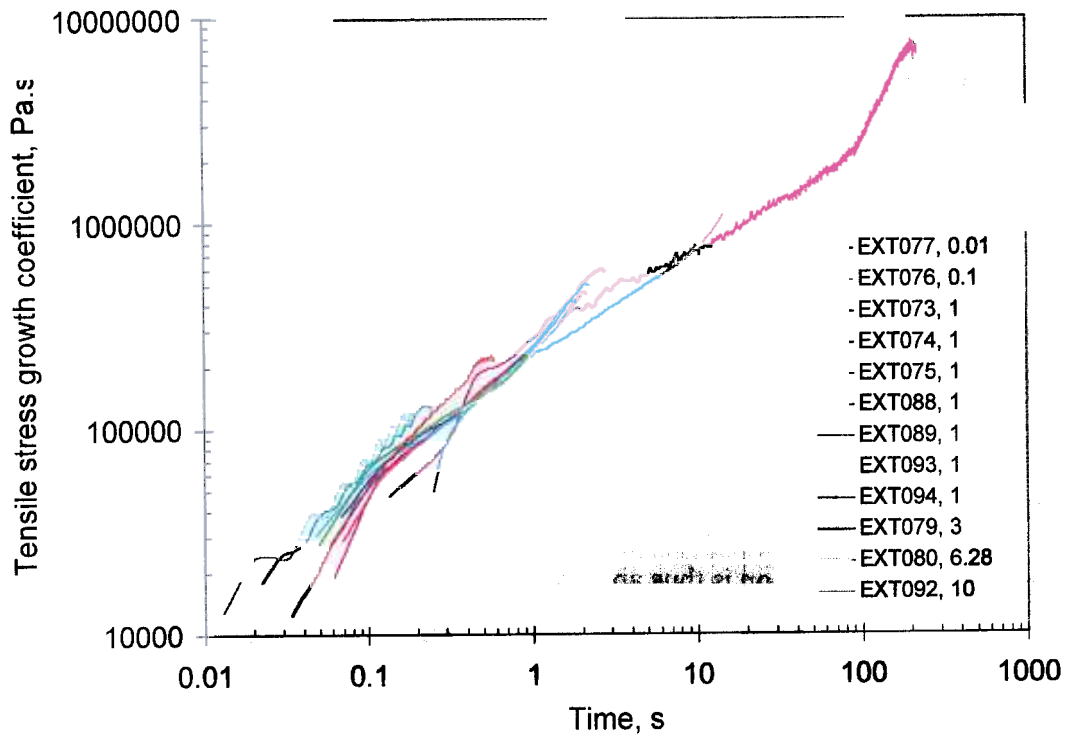


Figure 5: Effect of strain rate from 0.01 s^{-1} to 10 s^{-1} on tensile stress growth behaviour of a HDPE at 150 °C [4].

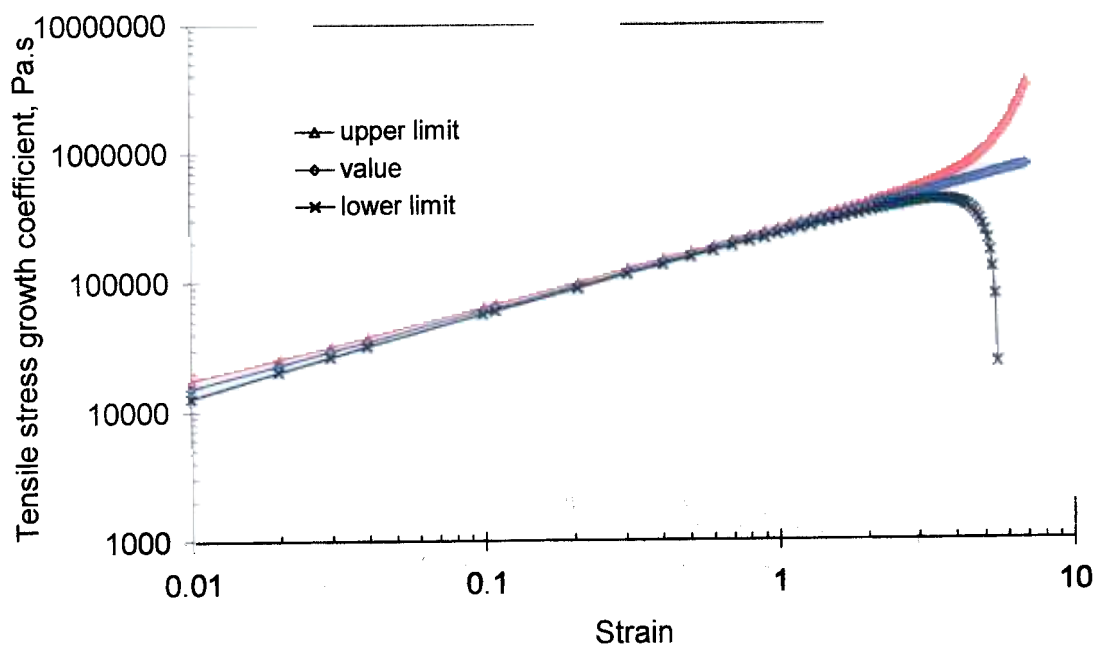


Figure 6: Analysis of uncertainties in tensile stress growth coefficient values yielding upper and lower bands, based on a HDPE at 150 °C and 1 s^{-1} [4].

Annex A.2

(informative)

Effect of viscous dissipation in the specimen during stretching on measurements

A2.1 Summary

Viscous heating of the specimen due to the work done in stretching, often a source of significant experimental error in shear flow testing, has been estimated on the basis of data for a HDPE at 150 °C and a Hencky strain rate of 1 s⁻¹ [4].

A2.2 Analysis of viscous heating effect

It is assumed, for the purposes of this analysis, that the force F exerted on the specimen for the duration of the test is constant and is equal to the maximum force exerted on the specimen. Furthermore the specimen is of initial length ℓ_o , initial radius R_o and undergoes a strain ε in a Type 3 configuration (figure 3). The final specimen length is given (equation (6)) by

$$\ell = \ell_o e^\varepsilon \quad (\text{A2.1})$$

Thus the mechanical work done on the specimen W_F is given by

$$W_F = (\ell_o e^\varepsilon - \ell_o) F \quad (\text{A2.2})$$

The work done per unit volume of the specimen w_F is thus

$$w_F = \frac{(\ell_o e^\varepsilon - \ell_o) F}{\pi R_o^2 \ell_o} \quad (\text{A2.3})$$

Assuming the thermal behaviour

$$w_\theta = \rho C_p \Delta\theta \quad (\text{A2.4})$$

where w_θ is the work done per unit volume to heat the melt, ρ is the density, C_p is the specific heat capacity and $\Delta\theta$ is the temperature rise in the specimen, and given the energy balance

$$w_F = w_\theta \quad (\text{A2.5})$$

then

$$\Delta\theta = \frac{(\ell_o e^\varepsilon - \ell_o) F}{(\rho C_p) \pi R_o^2 \ell_o} \quad (\text{A2.6})$$

Using the values obtained for a HDPE at 150 °C and 1 s⁻¹ (NPL ref HGH000 [4]):

$$F = 1 \text{ N}$$

$$\ell_o = 0.1 \text{ m}$$

$$R_o = 1.5 \times 10^{-3} \text{ m}$$

$$\varepsilon = 3$$

$$\rho = 900 \text{ kg/m}^3$$

$$C_p = 2300 \text{ J/(kg.K)}$$

then the temperature rise $\Delta\theta$ is estimated to be $\approx 1.3^\circ\text{C}$.

This estimate assumes that the force was constant over the duration of the test, that all the energy was dissipated as heat and that no heat was dissipated from the specimen. These assumptions will all result in a larger calculated temperature rise than actual. For example, although the peak force was approximately 1 N the average force would have been lower. Also, no account of the energy stored elastically in the specimen or heat dissipated from the specimen was made. All of these factors would result in a reduction of the calculated temperature increase. For a HDPE (NPL ref. HGH000 [4]) the shear flow temperature dependence was estimated to be less than $1\text{ }^\circ\text{C}$. As the dissipation would be evenly distributed through the specimen the effect on measurements is considered to be negligible.

For other materials and testing conditions the temperature rise may not be so insignificant. A more accurate calculation of the temperature rise can be carried out by summing the work done, i.e. force x displacement for increments in specimen length, over the test duration using the force and length equations, equations (A1.18) and (A2.1) respectively.

Annex A3

(informative)

Bibliography

- [1] Rheological Techniques, R.W. Whorlow, Ellis Horwood, London, 1992.
- [2] Dealy, J.M., J. Rheology 39(1) January/February 1995, pp.253-265.
- [3] Intercomparison of extensional flow characterisation techniques for polymer melts: tensile stretching and converging flow methods, Rides, M., Allen, C.R.G. and Chakravorty, S., NPL Report CMMT(A)171, April 1999, National Physical Laboratory, UK.
- [4] Extensional flow properties of polymer melts using stretching flow methods, Measurement Good Practice Guide No. 18, Rides, M. and Allen, C.R.G., May 1999, National Physical Laboratory, UK.

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