SCHOTT
Instruments

Testing high polymers e.g. PETP or PBTP

Testing of polymers

Measurement problem

One of the major quality features of synthetic materials is the mean molecular weight of the polymer molecules. The molecular weight characterises the chain length of the molecules which has a decisive influence on the processing properties of a synthetic material.
The strain exerted on the plastic by the processing process may lead to changes in the polymer changes (as a rule a decay of the chains). Under certain circumstances the properties of the finished part might be changed to such an extend that it's no longer suitable for its intended purpose.
In the research and development of polymers new polymers are being developed and produced. In this process, too, the chain length of the polymer molecules is of essential importance as to the characterisation of the finished product.

This results in the following measurement tasks:

Polymer research and development

- Determination of the mean chain length or mean polymerisation degree of the polymer molecules
- Objectives:
  - Characterisation of the finished product
  - Optimisation of its chemical and physical properties
  - Rating of polymerisation installations
  - Determination of process parameters

Polymer chemistry (polymer production)

- Determination of the mean chain length or mean degree of polymerisation of the finished product (raw granules)
- Objectives:
  - Characterisation of the finished product
  - Quality assurance
  - Optimisation of the process parameters
  - Prevention of the production of spoiled batches

Polymer processing

- Characterisation of the properties and the capabilities of the starting material (raw granules)
- Objectives:
  - Rating of plants for polymer processing
  - Determination of optimum process parameters

- Determination of the chemical and physical properties of the finished part
- Objectives:
  - Quality assurance
  - Optimisation of the process parameters

Solution:

That determination of the chain length, processing properties and quality of a synthetic material is done in a form of viscosity measurement on solutions of the plastic in suitable solvents using capillary viscometers (solution viscometry). The following table will inform you about the solvents, viscometers, the application and the relevant standards.

Polymer	**Abbrev.**	**Solvent**	**Capillaries**	**DIN**
Polyamide	PA	Formic acid (90%) Sulphuric acid (96%) m-cresol	I, Micro Ic II, Micro IIc II	53 727 53 727 53 727
Polycarbonate	PC	Dichlormethane	Oc	7744, Part 2
Polyethylenterephthalate Polybuthylenterephthalate	PET PBT	Phenol / 1,2-dichloro benzene (1:1 patrs by weight) 2-chlorphenol m-Kresol Dichloro acetic acid	Ic Ic II II, Mikro IIc	53 728, Teil 3
Polyvinyl chloride	PVC	Cyclohexanone Tetrahyrofurane	I Ic	53 726
Polyethylene Polypropylene	PE PP	Decahydronaphthalene (Decalin)	I	53 728, Sheet 4
Polystyrol	PS	Toluoene o-Xylol 1,2-Dichlor benene	I I I	7741, Part 2
Polymethylmethacrylate	PMMA	Chloroform Acetophenone	Oc I	7745, Part 2
Cellulose acetate	CA	Dichlormethane/ Methanole (9:1 pert by volume)	Oc	53 7228, Sheet 1

Further information about viscometry you'll find in our brochure "Theory and practice of capillary viscometry".

The **viscosity number** (for a definition, please refer the following table) gives information about the processibility of plastic material. It plays a decisive role within a framework of quality control of the granules. In addition it's important to verify the viscosity number of the finished plastic part.

In most cases the indication of the viscosity number or of the **relative viscosity** (please refer the following table) is sufficient as a quality criterion of established plants. This requires the determination of the solvent and of the plastic solution (concentration mostly 0,5 g/100 ml).

Instead of the viscosity number the determination frequently involves the **K value after Fikentscher**.

The determination of the mean molecular weight of the polymer molecules is done via the **limiting viscosity number** (please refer the following table). It's of particular importance in the range of research and development of polymers and of procedures and installations for their production and processing. In addition it's an important feature as regards quality assurance in case of special applications, such as plastic recycling and the processing of recycled plastics.

To determine the limiting viscosity number polymer solutions of different concentrations are produced (so called dilute series). The limiting viscosity number results from extrapolation of the viscosity numbers to a concentration = 0.

Definition and description of the terms

Value	Description
η	dynamic viscosity
$\nu = \eta / \rho$	kinematic viscosity
$\eta_r = \eta / \eta_S$	relative viscosity, viscosity ratio
$(\eta - \eta_S) / \eta_S = \eta_r - 1$	relative viscosity change, spezific viscosity
$J_v = 1 / c \cdot (\eta - \eta_S) / \eta_S$	Staudinger function, viscosity number
$\mathrm{Ln}\,(\eta / \eta_S) / c$	inherent viscosity
$J_g = \lim\limits_{c \to 0} [1 / c \cdot (\eta - \eta_S) / \eta_S]$	Staudinger index, limiting viscosity number, intrinsic viscosity

Necessary basic equipment

The basic equipment should have an appropriate standard of a modern chemical laboratory.
That means, the bench top surface should be solvent resistant and should be ventilation equipped (exhaust cabine) for existing solvent evaporations, probably.

The picture shows an AVSPro automatic sampler system for the determination of the solution viscometry on high polymers of SCHOTT Instruments GmbH in a suitable laboratory environment.

Necessary measuring equipment

ViscoSystem	Type: AVS 360, AVS 370 or AVS 470
Glass panelled thermostat	Type: CT 53/ CT 54
Flow through cooler	Type: CK 300
Thermometer	Type: VZ 7101 (for 25°C)
Measuring stand	Type: AVS/SK (PVDF)
PTFE tube cable combination	Type: VZ 5622
Overflow safety device	Type: VZ 6245 (AVS 360), VZ 8552 (AVS 370 or AVS 470)
Ubbelohde viscometer (standard version)	Type. 530 20 or suitable depending to the application
Micro-Ubbelohde viscometer	Type: 538 23 or suitable depending to the application
Software	Type: WinVisco 370
Data cable	Type: TZ 1599 (AVS 360), VZ 7116 (AVS 370)
as option:	half automatic discharging (Please request for a detailed offer)

Necessary laboratory equipment:

(order numbers according to SCHOTT laboratory glass catalogue)
Analytical balance (resolution min. 1 mg)
Magnetic stirrer and/or **shaker**
Water jet or another **vacuum pump** with connection to a filtering flask
Weighing glasses (no.: 24 210 ..)
Glass funnels, div. diameters (no.: 21 331 ..)
Spatula, forceps
Volumetric flask 50 ml, 100 ml (no.: 21 678 17, 21 678 24)
Filtering device (250 ml) with conical gasket (no.: 21 201 36, 29 202 27)
Filter crucibles 30 or 50 ml, e.g. porosity 2 (no.: 25 851 22, 25 851 32)
Screw cap flasks of glass 100 ml (no.: 21 801 24)
Pasteur pipets
div. **magnetic stirrer barrs (PTFE coated)**
pH paper
div. **beakers** (no.: 21 106 .. or 21 116 ..)
Waste container for acids

Necessary solvents:

concentrated sulfuric acid, m-kresol, Dichlorbenzene-phenol, Dichlore acidic acid (dep. on application)
(refer the table on page 3)
distilled or diionisized water
Acetone (p.a.) for drying the viscometers, quickly

The sample preparation never should be done without e.g. analytical balance, heatable magnetic stirrer or shaker.
The reason:
Only a very accurate sample concentration grants for reasonable measuring results!

Sample preparation:

In laboratory practice are two different styles of sample preparation usual, momentary.

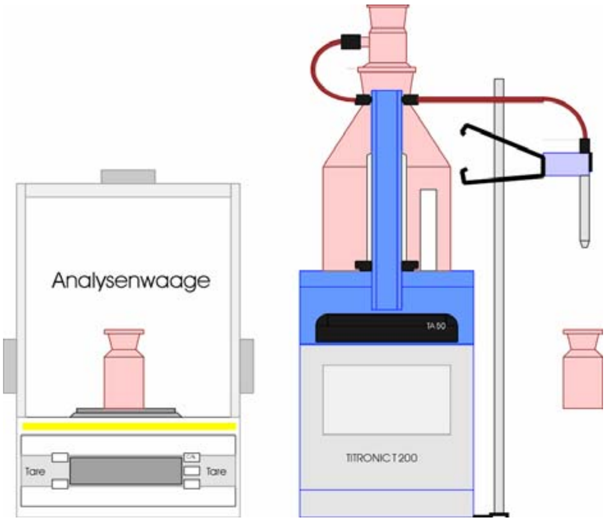
For example – Polyester (PETP / PBTP):

1. A sample (0,25 ± 0,002) g of PETP or PBTB should be weight in with an accuracy of 0.1 mg and filled on quantity in a volume flask of 50 ml. After this approx. 25 ml of solvent will be added until the polymer sample is completely diluted at approx. 80°C under warming up in a water bath or under shaking. Please remark that longer heating may cause a thermal reduction of the PETB or PBTB condition. A protection again too long dilution times it would be possible to use a thermal oil bath with higher temperature. Nevertheless, the combination between dilution time and dilution temperature is to check if there was reduction of the polymer structure, time by time.
   For arbitral reasons it seems recommended to make an agreement about dilution time and temperature.
   After cooling down the solution to approx. 20°C the volumetric flask will be filled up to the measuring mark with solvent which has the same temperature. The finished solution must be mixed by shaking.

The four steps of traditional sample preparation with volumetric flasks.

2. In the last time there are in use motor burettes for solvent dosing, more and more (see herefore our available T 110 *plus*).
   For this reason the sample will be weight into any sample bottle and the necessary volume of solvent will be dosed with the motor burette according to the weight.
   The advantage of this method is that here its possible to use a heatable magnetic stirrer or a thermal block for diluting the polymer.
   The advantage is clear!
   The uncomfortable and in parts dangerous manual handling of aggressive and sometimes corrosive solvents is missing nearly completely!
   For the further operation the validity is the same as described under 1..

The following graphic shows the most modern style of sample preparation.
With this style most of possible failure reasons will be eliminated in practice.
The weight data will be transferred from the analytical balance directly to a sample preparation system (intelligent burette or PC controlled system), directly.
The sample preparation system calculates the necessary volume of solvent for the polymer weight and eliminates failures (accurate sample concentration) for the sample preparation.
The reason:
The very time intensive and difficult weighting of the necessary polymer granules will be eliminated (it should be accurate to **1 mg** [**0,001 g**]).



Experiences out of the industrial practice confirm that using motor burettes minimises the possible failure of a incorrect or possible wrong solution concentration.

The following procedure description is authentic and advises as example.

Zweck

Diese Anweisung dient zur Bestimmung der konzentrationsbezogenen, relativen Viskositätsänderung von PBT und PET in einer verdünnten Lösung.

Geltungsbereich

Die Arbeitsanweisung gilt für die T... Electronics A.. GmbH, Standort D.......... Kunststoff-Labor ab dem Ausgabedatum und ersetzt die Arbeitsanweisung QA/A..-KSL-001-D/11-00, Ausgabedatum 04.02.2003.

Änderungsdienst

Zuständig ist der Leiter des Kunststofflabors.

Probennahme

Polymerspritzgussteile

Siehe Arbeitsanweisung zur fertigungsbegleitenden Prüfung an Polymerspritzgussteilen und Polymerrohstoffen AA / QA 6.003 / 18-04.

Polymerrohstoffe

Siehe Arbeitsanweisung zur fertigungsbegleitenden Prüfung an Polymerspritzgussteilen und Polymerrohstoffen AA / QA 6.003 / 18-04 und Arbeitsanweisung zur Prüfung von Polymerwerkstoffen des Wareneinganges AA / QA 6.002 / 18-04.

Prüfgeräte

- 50 ml Erlenmeyerkolben mit NS 19 Vollglas Schliffstopfen
- Rührmagnet (20mm) mit PTFE Überzug
- Heizplatte mit Magnetrührer
- Dosiergerät z.B. Fortuna Optifix 3 - 30 ml
- Laborzentrifuge mit ca. 80 ml Zentrifugengläser
- Durchsichtthermostat mit Wasserfüllung und Kontrollthermometer
- Ubbelohde-Kapillarviskosimeter mit Kapillare Ic bzw. Ia
- Automatischer Viskositätsmessplatz AVS 360 und Messstativ AVS/S, Fa. SCHOTT
- Glasfiltertiegel Porosität 1 D2
- Analysenwaage, Messgenauigkeit 0,0001 g
- Auswerteeinheit (PC)
- Auswertprogramm WinVisco, Ausgabedatum 05.02.2003.

Prüfmittel

Lösungsmittel

Mischung aus 50 Gew. % Phenol und 50 Gew. % 1,2 - Dichlorbenzol (zur Extraktionsanalyse) z.B. von Fa. Baker Bestellnummer.: 7227;

Die Mischung ist in braunen, gut verschließbaren Glasflaschen bei 18 - 28 °C aufzubewahren. Nach längerem Stehen Flaschen gut schütteln.
Bei tiefen Temperaturen kann Phenol auskristallisieren; durch Erwärmen im Wasserbad kann das Phenol wieder in Lösung gebracht werden.

Durchführung

Blindwertermittlung

Von jeder neu geöffneten Flasche Lösungsmittel ist mit jeder eingesetzten Kapillare der Lösungsmittelblindwert bei den geltenden Temperaturen zu ermitteln.
Ca. 16 ml des Lösungsmittels mittels Dosiergerät in das saubere, trockene Kapillarviskosimeter einfüllen (Füllhöhe siehe Abb. Seite 6). Anschließend die Kapillare in das Messstativ einklemmen und überprüfen ob die Badtemperatur der geforderten Temperatur entspricht. Anschließend den Schlauch mit rotem Gummihut auf Rohr Nr. 2 und den Schlauch mit schwarzem Gummihut auf Rohr Nr. 1 stecken (siehe Abb. Seite 6).
Anschließend starten des Messplatzes mittels Auswertprogramm WinVisco 1.1 D.
Vorgehensweise und Einprogrammierung der einzelnen Prüfparameter siehe Handbuch (Hardcopy) Hilfsprogramm WinVisco 1.1 D.

Probe / Probenvorbehandlung

Bei Granulaten findet keine Vorbehandlung statt. Es werden die vorliegenden Granulatkörner zur Bestimmung eingesetzt. Formteile werden mittels Seitenschneider (entspr. DIN 53733) auf Granulatgröße zerkleinert.
Es wird immer aus den einzelnen Musterschüssen bzw. eines Musters ein Blend des als kritisch eingestuften Bereiches gebildet. Kritische Bereiche sind bei Muster aus laufender Produktion oder Neuabmusterungen:
Filmscharniere, Rasthaken, ggf. dünne Wandungen, oder Bereiche bei denen es bereits zu Reklamationen kam.
Bei Reklamationsmuster: Reklamationsbereiche;

Probenvorbereitung / Durchführung der Messung

Intrinsic viscosity

200 mg (+/- 20 mg) des ungefüllten Polymers bzw. eine solche Menge der Zuschlagstoffe enthaltenen Probe, das sie 200 mg Polymer enthält, in den 50 ml Erlenmeyerkolben einwiegen.
20 ml Lösungsmittel zudosieren, Rührmagnet zugeben, Kolben verschließen mittels NS Stopfen und auf dem 140 °C (+/-10) warmen Magnetrührer stellen. Die Probe unter ständigem Rühren lösen.
Sobald das Polymer vollständig gelöst ist (Lösezeit: 20 - 40 Minuten) den Kolben sofort vom Magnetrührer nehmen und im kalten Wasser auf RT abkühlen.
Die Lösung – wenn erforderlich – durch Zentrifugieren von Glasfasern oder anderen Additiven trennen, durch einen 1 D2 Glasfiltertiegel in die saubere, trockene Kapillare filtrieren.
Anschließend die Kapillare in das Messstativ einklemmen und wie unter 8.1 beschrieben ans AVS 360 anschließen und den Messvorgang starten.

Viskositätszahl

100 mg (+/- 0,1 mg) des ungefüllten Polymers bzw. eine solche Menge der Zuschlagstoffe enthaltenen Probe, das sie 100 mg Polymer enthält, in den 50 ml Erlenmeyerkolben einwiegen.
Weitere Vorgehensweise siehe 8.3.1 → 20 ml Lösungsmittel......

Messung

Start der Messungen erfolgt über die Auswerteinheit unter dem Auswertprogramm WinVisco 1.1 D (siehe Punkt 8.1).

Messwerte

Anzahl der Messungen Blindwertbestimmung:
je Kapillare 8 Messungen, maximale Abweichung der Durchflusszeiten $\leq$ 0,2 %

Von jeder Probe ist eine Einfachbestimmung durchzuführen.
Je Probe sind 3 Messungen durchzuführen, maximale Abweichung der Durchflusszeiten $\leq$ 0,2 %

Berechnung

Die Berechnung der einzelnen Lösungsviskositäten erfolgt automatisch mittels Auswertprogramm WinVisco 1.1. D

Es liegen folgende Berechnungen zu Grunde:

Ermittlung der Rel. Viskosität (µrel)

Division der korrigierten Durchflusszeiten der Probenlösung durch die korrigierte Durchflusszeit des Lösungsmittels (= Blindwert) ergibt die Rel. Viskosität (Hagenbachkorrektur erfolgt automatisch durch WinVisco 1.1 D).

Ermittlung der Viskositätszahl (VZ) in ml/g

(Ermittelte Rel. Viskosität - 1) x 200 = VZ

Ermittlung der intrinsic viscosity (i.v.) in dl/g

Zur Ermittlung der intrinsic viscosity gilt die Billmeyer-Gleichung:

1,725 x Log (Rel. Viskosität) + 0,25 x (Rel. Viskosität – 1) = (i.v.) x c

Konzentration c = Einwaage (g) x (100 - % Korrekturfaktor Polymer) /
dl Lösungsmittel x 100 %

Korrekturfaktor Polymer siehe Punkt 11

Dokumentation der Analysen

Analysenprotokoll

Siehe Handbuch (Hardcopy) Hilfsprogramm WinVisco 1.1 D → Bericht

Analysenwerte

Dokumentation der Analysenwerte der einzelnen Prüfungen zur fertigungsbegleitenden Prüfung an Polymerspritzgussteilen und Polymerrohstoffen siehe Arbeitsanweisung AA / QA 6.003 / 18-04.
Dokumentation der Analysenwerte zur Prüfung von Polymerwerkstoffen im Wareneingang siehe Arbeitsanweisung AA / QA 6.002 / 18-04.

Frequently occurring errors when using glass capillary viscometers

Error symptom	**Error causes**	**Possible error elimination**
Syst. measurement error: Flow time too **large** with short flow times	After-flow error, Hagenbach correction too small	Experimental determination of the Hagenbach correction using substances having a similar viscosity and a surface tension as the measurement product
Syst. measurement error: Flow time too **small** with short flow times	After-flow error, Hagenbach correction too large	As above, better: Choose a viscometer with a smaller capillary diameter
Syst. measurement error: Flow time too **small** with (Ostwald-, Cannon-Fenske- or BS/IP/RF tube reverse flow viscometer)	Substance quantity filled in too small	Empty, clean and refill viscometer
Syst. measurement error: Flow time too **long** (Ostwald-, Cannon-Fenske- or BS/IP/RF tube reverse flow viscometer)	Substance quantity filled in was too big	as above
Syst. measurement error: Flow time too **small** with short flow times (Ubbelohde viscometer)	Disturbance of the suspended level	Select viscometer with a smaller capillary diameter
Syst. measurement error: Flow time too **short**	Temperature of the bath liquid too high	Check temperature; if necessary, readjust the thermostat
Syst. measurement error: Flow time too **long**	Contamination in the capillary	Empty and clean viscometer; repeat the measurement
	Temperature of the bath liquid too low	Check temperature; if necessary, readjust the thermostat
Drift of the flow times	Drift of the bath temperature	Protect the thermostat from direct radiation exposure; if necessary replace the thermostat
	Temperature adjustment of the measuring substance not completed	Continue temperature adjustment until the time values are stabil
	Evaporation of a high volatile component; reaction of the product being analysed with the air	Apply pressing operation mode

Error symtom	**Error causes**	**Possible error elimination**
Increased stochastic scattering of the measurement value	Contamination in the viscometer	Empty and clean viscometer; Repeat measurement
	Contamination in the sample solution	Empty and clean viscometer; repeat measurement with fresh filtrated sample; use probably a filter with smaller porosity
	Air bubbles in the viscometer	In case calf pure matters with chemical and physical heat resistance, drive out bubbles by shorter increase of temperature
	Air bubbles in the viscometer	Clean and empty viscometer; during refilling, ensure absence of bubbles
Excessive stochastic scattering occurring during measurements using optoelectric barriers (Possibility of total malfunction)	Contamination of the optical sensors	Remove the measuring stand out of the thermostatic bath; clean optical system using nondenatured alcohol on a soft cloth
	Errors triggered by the optoelectric barriers as a result of the formation of bubbles, foam or liquid lamellae	Use a TC Ubbelodde-, Ostwald- or Cannon-Fenske-Routine viscometer
Excessive stochastic scattering occurring during automatic measurements using TC viscometers (possibility of total malfunction)	Incrustation of the sensors (in case of thermally instable media)	Transparent media: use optical detection Opaque media: Use reverse flow viscometer
	Wear and tear of the sensors	Replace viscometer
Increased stochastic scattering in the case of short flow times (Ubbelohde viscometer)	Beginning deformation of the suspended level	Select a viscometer with a smaller capillary diameter
Periodically fluctuating flow times	Heating up or cooling down phases of the thermostat is too long	Set the heating and cooling of the thermostat in such a manner that at least two complete cycles are completed during one viscosity measurement cycle
	No timely stability of the bath liquid temperature (defective thermostat)	Replace the thermostat
Malfunction caused by air bubbles during the sucking-in process of the liquid into the delivery vessel	Substance quantity filled in was too small	Ubbelohde viscometer: fill up the measurement substance Others: empty and clean viscometer, repeat measurement

Source of supply for standards:

You may download the given standards in this description at Beuth publishing
Over the internet.

The internet address is as follows:

www2.beuth.de

Source material: DIN 51 562, Part 1 – 4
DIN 53 727;
DIN 53 728, Part 3
DIN 53 733;
ASTM D 445
ASTM D 446
ISO 3105
ISO 3106
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div. documentation of O. Hofbeck

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If you want to get more information about our laboratory program, please visit our webside or order our laboratory catalogue. You’ll find detailed descriptions about our viscometry-, titration-, pH-electrodes and pH-measuring instruments and accessories.

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