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Fibre-reinforced plastics — Thermosetting moulding compounds and prepregs — Determination of cure characteristics

*Plastiques renforcés de fibres — Compositions de moulage
thermodurcissables et préimprégnés — Détermination des caractéristiques
de durcissement*

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International Organization for Standardization
 Case postale 56 • CH-1211 Genève 20 • Switzerland
 Internet central@iso.ch
 X.400 c=ch; a=400net; p=iso; o=isocs; s=central

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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 12114 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 13, *Composites and reinforcement fibres*.

Introduction

The description of the cure characteristics of thermosetting moulding compounds is rather complex. Various parameters and properties like reactivity, temperature, pressure and shrinkage are of interest to the end user. Some of these parameters influence each other. For this reason, several test methods are necessary for quality control and to determine the effect of varying the proportion of any particular component in the formulation. The characteristics determined are selected to enable different moulding compounds and preregs to be compared and their shelf life assessed.

One important characteristic of thermosetting compounds is their reactivity, i.e. their ability to polymerize under the influence of a catalyst and/or heat. This reactivity can be evaluated by various methods. This International Standard gives two such methods:

- the first of which is a simple procedure which is limited to the determination of reactivity and shelf life by measuring the variation of temperature as a function of time under the conditions usually used in production;
- the second method is more sophisticated and gives information on the physical behaviour of the compound under simulated moulding conditions.

The description of the curing behaviour of a thermosetting compound is not possible by a single value. It is dependent on several parameters, like pressure, temperature and shrinkage, which influence each other. This interdependence must also be described. Such a description can be given by mathematical functions or expressed in terms of a set of curves for the various parameters, as in this International Standard. The curves for a particular compound are all shown in the same figure to enable the interdependence of the parameters concerned to be seen at a glance.

Fibre-reinforced plastics — Thermosetting moulding compounds and prepregs — Determination of cure characteristics

1 Scope

This International Standard specifies two methods for the determination of the cure characteristics of fibre-reinforced thermosetting moulding compounds and prepregs.

The characteristics measured are

- the heat generated by the exothermic reaction;
- the thermal expansion of the compound accompanying the rise in temperature;
- the shrinkage due to the curing reaction.

The methods specified are applicable to all compounds comprising thermosetting matrices reinforced with fibres. The major field of application is compounds based on unsaturated polyester resins.

Method I describes a test method to determine the reactivity of a thermosetting compound by a simple procedure. This method examines only the reactive behaviour of the matrix and its state of stabilization (one factor affecting the shelf life of the moulding compound).

Method II describes a test method which needs more sophisticated equipment, takes more time but provides additional detailed information about the physical behaviour of the compound under simulated practical moulding conditions. It produces a plate which can be used for further testing to determine properties of the moulded article.

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 editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 472:1988, *Plastics — Vocabulary*.

ISO 8605:1989, *Textile glass reinforced plastics — Sheet moulding compound (SMC) — Basis for a specification*.

ISO 8606:1990, *Plastics — Prepregs — Bulk moulding compound (BMC) and dough moulding compound (DMC) — Basis for a specification*.

3 Definitions

For the purposes of this International Standard, the definitions given in ISO 472, ISO 8605 and ISO 8606 apply, plus the following definitions:

3.1 reactivity: The reactivity of a thermosetting material is taken, by convention, as the maximum gradient, in degrees Celsius per second, of a plot of the temperature of the thermosetting material as a function of time during curing.

3.2 curing behaviour: The behaviour of a thermosetting material when moulded under commonly used moulding conditions, as described by the following set of parameters:

- cure time;
- thermal expansion;
- shrinkage due to the curing reaction;
- net shrinkage (reaction shrinkage less thermal expansion).

The values of these parameters will depend on the actual moulding conditions used.

3.3 elementary unit: The smallest normally commercially available entity of a given product. The description (form, dimensions, mass, etc.) of the elementary unit will normally be defined in the product specification. Elementary units may be supplied in the form of rolls or packages, for instance.

NOTE — For a given product, the dimensions, mass or volume of the elementary unit may change, as manufacturing techniques evolve, without necessarily causing any modification in the properties of the product or the way in which these properties vary within the elementary unit.

4 Apparatus

4.1 Method I

4.1.1 Cylindrical metal mould, with an inside diameter of 20 mm, equipped with a heater and a temperature control system, and with a heated steel punch which fits inside the cylindrical mould (see figure 1).

4.1.2 Device for applying a minimum force of 15 daN to the punch (see figure 2).

4.1.3 Insulated thermocouple, diameter 1 mm, located at the centre of the bottom of the mould and rising 5 mm into the mould cavity. The thermocouple shall be insulated from the heated steel block by insulation having a thickness of > 2 mm.

4.1.4 Suitable recording system, for plotting a curve of temperature versus time.

4.1.5 Device for preparing moulding-compound test specimens (see figure 3).

4.1.6 Syringe, for measuring out paste specimens.

4.1.7 Balance, accurate to the nearest 0,1 g.

4.1.8 Brass bristle brush, to clean the mould.

4.2 Method II

4.2.1 Suitable press, capable of applying a moulding pressure of 100 bar \pm 3 %.

4.2.2 Shear edge mould, mounted in the press, with a cavity of surface area not less than 200 cm², heatable to 200 °C with an accuracy of 1 % (see figure 4). The mould shall be equipped with a pressure sensor and temperature sensor, mounted in the centre of the mould. For pressure measurements, piezoelectric sensors are normally used.

The temperature sensor shall be insulated from the mould to measure changes in temperature at the surface of the moulding compound with an accuracy of \pm 1 %.

Both sensors shall be flush with the surface of the mould cavity. A displacement sensor shall be fitted to the mould to measure mould lid travel of about 20 mm with a resolution of 0,01 mm.

NOTE — For practical reasons, it is recommended that the sensors be mounted at a maximum distance apart of 30 mm and equidistant from the axis of symmetry.

4.2.3 Recording equipment, connected to the sensors in the mould, to plot the variation with time of

- pressure (from 0 to 150 bar);
- displacement (from 0 to 20 mm);
- temperature (from 0 to 200 °C).

4.2.4 Calipers, for measuring the thickness of the moulded test specimen.

5 Sampling

For a sheet moulding compound, take a laboratory sample over the full width of the roll. Reduce the width by 5 cm on each side to avoid edge effects.

For a bulk moulding compound, take a laboratory sample from the centre of an elementary unit. When taking the laboratory sample, do not remove any protective sheet, and place the sample, immediately after taking it, in a suitable bag to avoid loss of volatile matter or absorption of moisture.

The laboratory sample shall be of a size sufficient to enable the required number of test specimens to be prepared (see 7.1).

6 Conditioning and test atmospheres

6.1 Conditioning

Condition the laboratory sample for a time sufficient to establish temperature equilibrium. The temperature of the laboratory sample immediately before the test specimens are taken shall not be less than 18 °C.

6.2 Test atmosphere

The atmosphere for testing shall be the same as that used for conditioning.

7 Test specimens

7.1 General

For both methods, take three specimens from the conditioned laboratory sample.

NOTE — The product specification or the person ordering the analyses may require that the determination be performed on additional specimens or at specific places in the elementary unit or laboratory sample.

7.2 Method I

For each test specimen, take $6 \text{ cm}^3 \pm 0,5 \text{ cm}^3$ of moulding material, giving a test specimen height in the range 1,75 cm to 2,10 cm. This quantity can be obtained by direct measurement of a given volume in the case of pastes and resins. For other moulding compounds, it is easier to weigh out a given mass, calculated from the density of the moulding compound.

7.2.1 Sheet moulding compound specimens

Stamp the required number of pieces of moulding compound with a blanking die punch of diameter $19 \text{ mm} \pm 1 \text{ mm}$. Cut all the pieces from the same sheet at intervals of about 10 cm. Remove the protective sheets and stack the pieces together to form test specimens.

7.2.2 Bulk moulding compound specimens

Shape the moulding compound using the device described in 4.1.5.

7.2.3 Paste specimens

Take $6 \text{ cm}^3 \pm 0,5 \text{ cm}^3$ of the paste or resin with the syringe (4.1.6).

7.3 Method II

The thickness of the moulded test specimen should preferably be the same as the thickness of the production moulding it is intended to represent. However, the thickness of the moulded specimen depends on the number of complete layers of the same size of a sheet moulding compound used and their individual thickness or, in the case a bulk moulding compound, the density of the compound under test.

It will therefore not always be possible with a sheet moulding compound to produce a moulded specimen with the same thickness as the production moulding.

7.3.1 Sheet moulding compound specimens

Stack the required number of complete layers together. For rectangular moulds, the specimen shall cover the full width of the mould. The minimum length of the specimen shall be mould length minus 10 mm (or minus 10 % to a maximum of 20 mm).

7.3.2 Bulk moulding compound specimens

Spread the required mass of material as evenly as possible in the mould cavity.

8 Procedure

If test conditions are specified in the material specification, these conditions shall be used whenever possible.

8.1 Method I

Switch on the heating and recording systems.

Allow the apparatus to warm up until the thermocouple indicator shows a stable temperature (this will normally take about 2 h).

During this time, leave the punch inside the mould cavity. For normal testing, the temperature of the inside wall of the mould shall be $140\text{ °C} \pm 2\text{ °C}$. In certain circumstances, however, other temperatures may be required. If so, they shall be agreed between the interested parties and shall be stated in the test report.

Prepare a test specimen in accordance with clause 7 and immediately place it in the mould, close the mould and load it to 15 daN, or more if necessary. (In most cases, a force of 15 daN is sufficient to compact the moulding material. If the material is not sufficiently compacted, however, as evidenced by areas of porosity or voids, the force shall be increased. The force used shall be stated in the test report.)

Stop the recording system when the temperature curve has reached the maximum point and the temperature has started to decrease.

Open the mould and remove the moulded test specimen.

Clean the mould cavity and the punch, close the mould and wait until the temperature is not varying by more than 2 °C before moulding the next specimen.

8.2 Method II

Choose and record the test conditions.

Adjust the controls on the apparatus accordingly.

Prepare a test specimen in accordance with clause 7.

Start the recording system and place the test specimen in the mould cavity and close the mould within 10 s.

NOTE — It is recommended that sheet moulding compound specimens be bent into a curve to facilitate loading.

Allow the traces from each sensor to be recorded. When the readings of all the sensors are stable again, stop the recording system, open the mould and remove the moulded specimen.

If examination of the moulded specimen shows evidence of porosity, reduce the charge length and repeat the test to eliminate porosity.

NOTE — The test procedure described permits only limited flow of the moulding compound (see 7.3.1). This particular procedure has been chosen to minimize the effect of friction during moulding, which usually causes an unknown rise in the temperature of the moulding compound. As a consequence, degassing may not be as complete as under usual moulding conditions. This will have to be borne in mind if specimens for further testing are to be cut from the moulding produced by this procedure.

9 Expression of results

9.1 Method I

Determine, from the curve recorded (see figure 5), the following parameters:

- The reactivity, which corresponds to the maximum value of the temperature gradient, in degrees Celsius per second. It is given by the tangent to the curve at the second point of inflection of the curve.
- The time to onset of polymerization, which is defined as the time between the beginning of measurement (i.e. the point when the temperature reaches 50 °C) and the time when polymerization begins, which is indicated by the first point of inflection of the curve (t_1 in figure 5).
- The temperature of onset of polymerization, which is the temperature corresponding to the first point of inflection (T_1 in figure 5).
- The time to maximum temperature, which is the time between the beginning of measurement and the point when the temperature reaches its maximum value (t_2 in figure 5).
- The maximum temperature (T_2 in figure 5).

9.2 Method II

Determine, from the curves recorded (see figure 6), the following data:

- The zero point in the time axis (the starting point or "zero" time, which is taken as the point when the mould cavity pressure has reached 10 bar.
- The cure time from the temperature (CT), which is the time taken for the test specimen to reach its maximum temperature (point 1 on the temperature vs. time trace in figure 6). The time is measured from the zero point on the time axis.
- The moulding temperature: After passing through its maximum (point 1), the temperature of the test specimen approaches equilibrium with that of the mould (section 2 of the temperature vs. time trace in figure 6). This steady-state temperature is defined as the moulding temperature.
- The onset of thermal expansion (DS 3), which is the lowest point of travel of the mould lid (point 3 on the displacement vs. time trace in figure 6) and indicates the point at which the test specimen has spread out sideways to just fill the mould and is beginning to expand upwards. Record the values of the displacement and time at this point.

NOTE — Expansion and shrinkage as described in this International Standard are displacements in the test specimen thickness direction. They should not be confused with expansion and shrinkage in the plane of the specimen.

- The maximum expansion (DS 4), which is the displacement of the mould lid at the maximum in the displacement vs. time trace (point 4 in figure 6), i.e. the point at which shrinkage becomes the dominant factor. Record the values of displacement and time at this point.
- The specific thermal expansion (liquid phase) (STE), which is calculated, as a percentage, from the equation

$$\text{STE} = \frac{\text{DS 4} - \text{DS 3}}{\text{DS 3}} \times 100$$

where

DS 3 is the lowest point of travel of the mould lid;

DS 4 is the maximum expansion.

- g) The end of shrinkage (DS 5), which is the displacement of the mould lid at the end of curing (section 5 of the displacement vs. time trace in figure 6). Record this value, which corresponds to the final thickness of the moulded test specimen.
- h) The reaction shrinkage (RS), which is calculated, as a percentage, from the equation

$$RS = \frac{DS 4 - DS 5}{DS 5} \times 100$$

where

DS 4 is the maximum expansion;

DS 5 is the final thickness of the moulded specimen.

- i) The net shrinkage (NS), which comprises the reaction shrinkage due to the curing reaction less thermal expansion. Calculate the net shrinkage NS, expressed as a percentage, from the equation

$$NS = \frac{DS 3 - DS 5}{DS 5} \times 100$$

where

DS 3 and DS 5 are as defined above.

- j) The moulding pressure (MP): The beginning of the pressure vs. time trace shows a phase of constant pressure (section 6 of the trace in figure 6). Record this value as the moulding pressure.
- k) The cure time from the pressure trace (CP), which is the time taken during curing for the local pressure in the cavity, as given by the pressure vs. time trace, to reach minimum or a constant, low value caused by local shrinkage effects (point 7 on the pressure vs. time trace in figure 6).

10 Precision

The precision of this method is not known because interlaboratory data are not available. When interlaboratory data are obtained, a precision statement will be added at the following revision.

11 Test report

The test report shall include at least the following information:

- a) a full description and identification of the moulding compound tested;
- b) a full description of the procedures used for sampling and for the preparation of the test specimens;
- c) the test conditions used;
- d) each individual result, their average value and the standard deviation:
 - 1) for method I
 - (i) the reactivity, expressed in degrees Celsius per second,
 - (ii) the time to onset of polymerization, expressed in seconds,
 - (iii) the temperature of onset of polymerization, expressed in degrees Celsius,
 - (iv) the time to maximum temperature, expressed in seconds,
 - (v) the maximum temperature, expressed in degrees Celsius;

- 2) for method II
 - (i) the thickness of the moulded test specimen, expressed in millimetres, at the moulding temperature,
 - (ii) the moulding pressure, expressed in bars,
 - (iii) the moulding temperature, expressed in degrees Celsius,
 - (iv) the cure time from the temperature trace, expressed in seconds,
 - (v) the cure time from the pressure trace, expressed in seconds,
 - (vi) the specific thermal expansion, expressed as a percentage,
 - (vii) the reaction shrinkage, expressed as a percentage,
 - (viii) the net shrinkage, expressed as a percentage;
- e) any procedural details not mentioned in the standard that may have affected the results.

Dimensions in millimetres

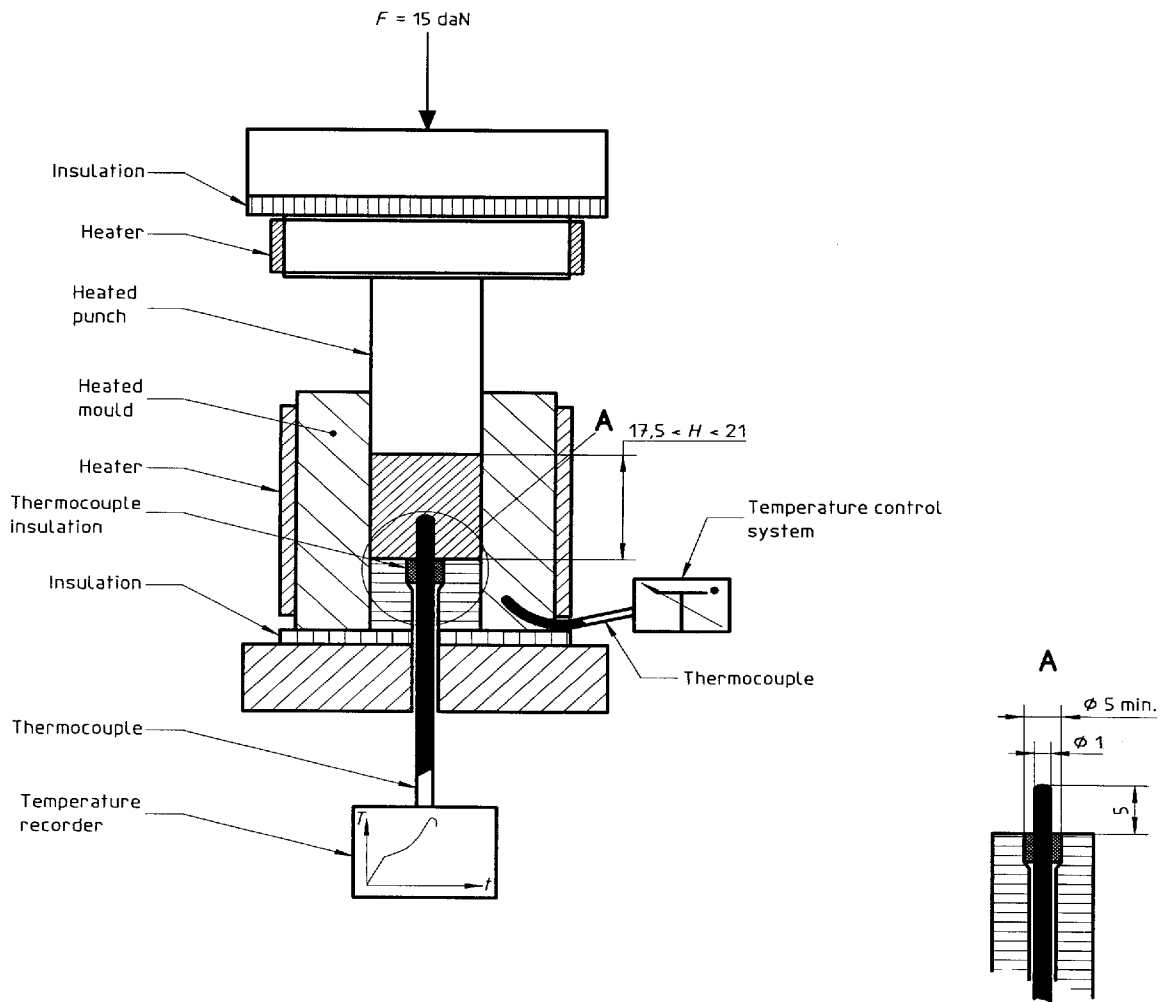


Figure 1 — Principle of apparatus (4.1.1)

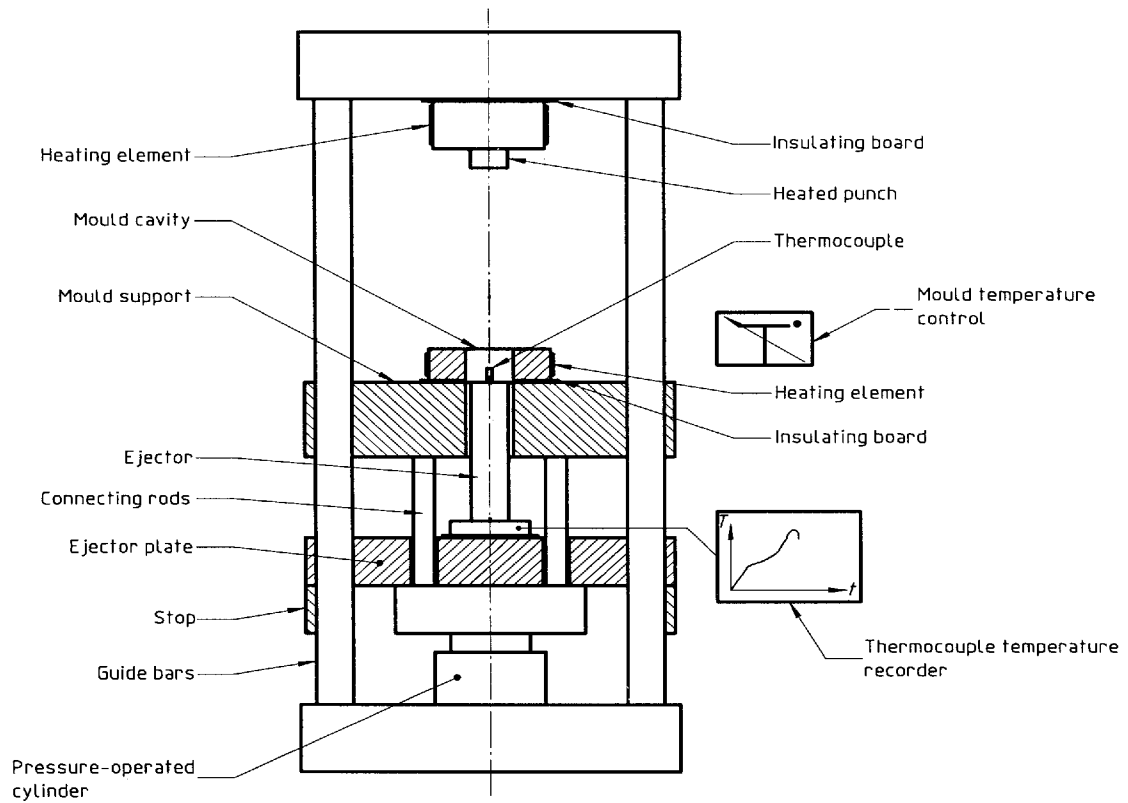


Figure 2 — Principle of apparatus (4.1.2)

Dimensions in millimetres

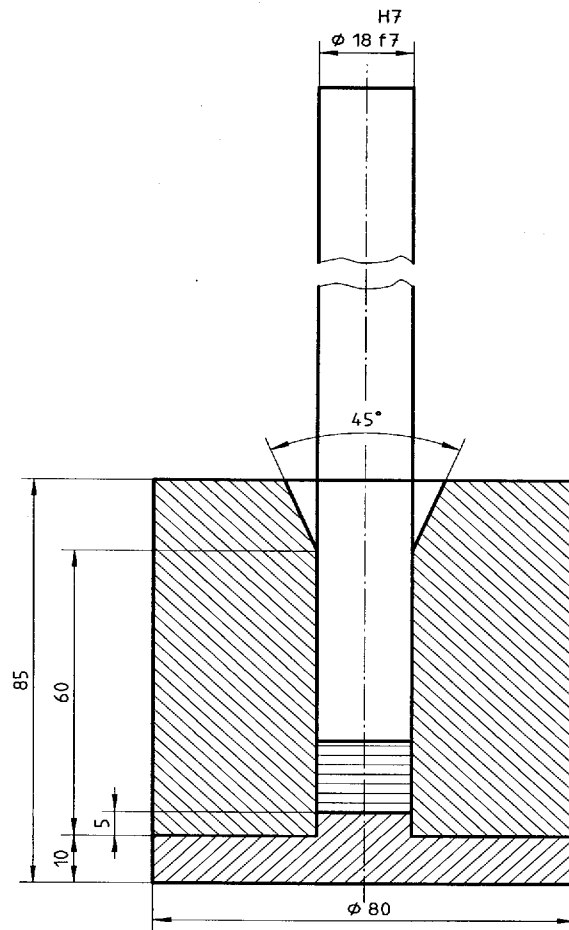


Figure 3 — Example of apparatus for the preparation of specimens from bulk products

Dimensions in millimetres

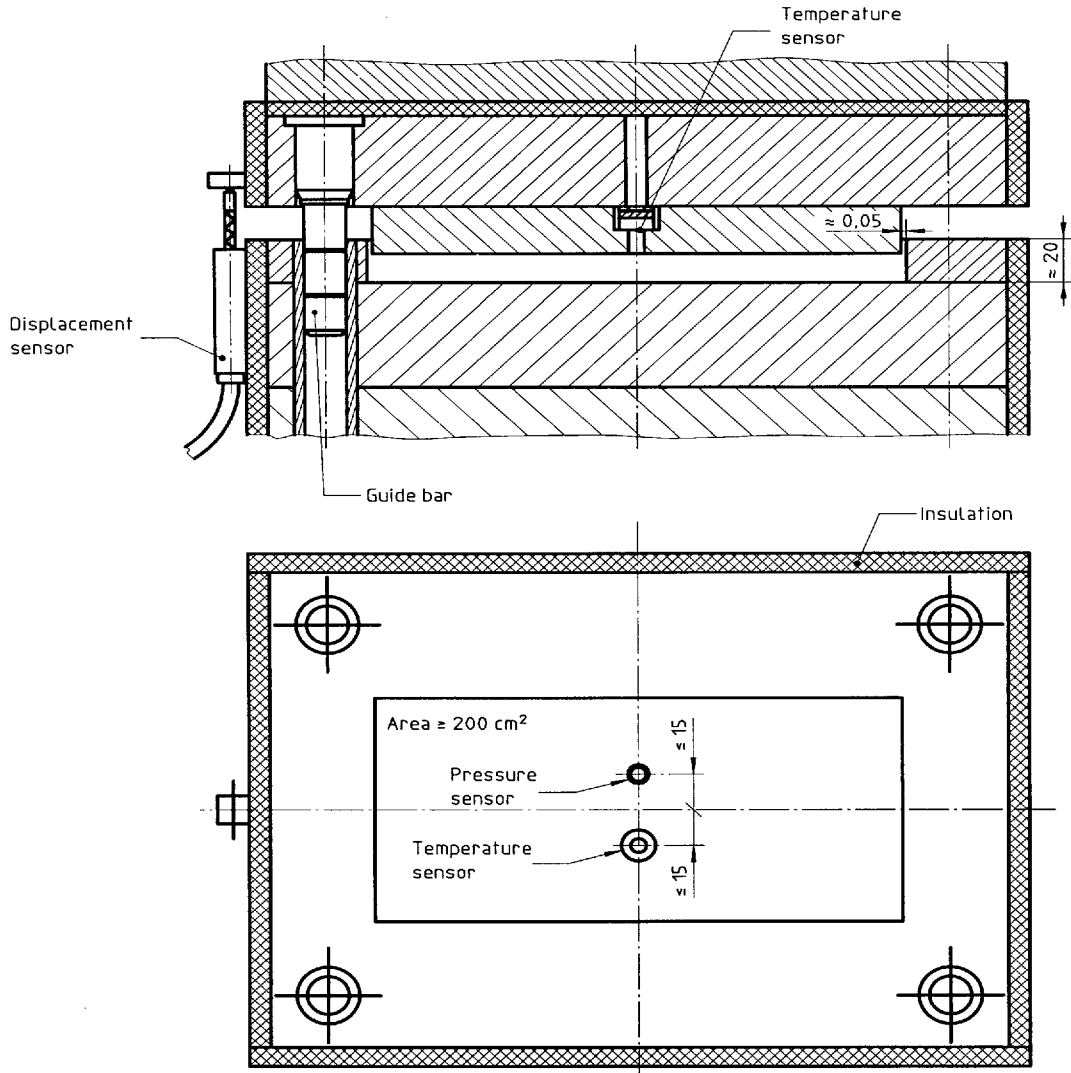


Figure 4 — Shear edge mould

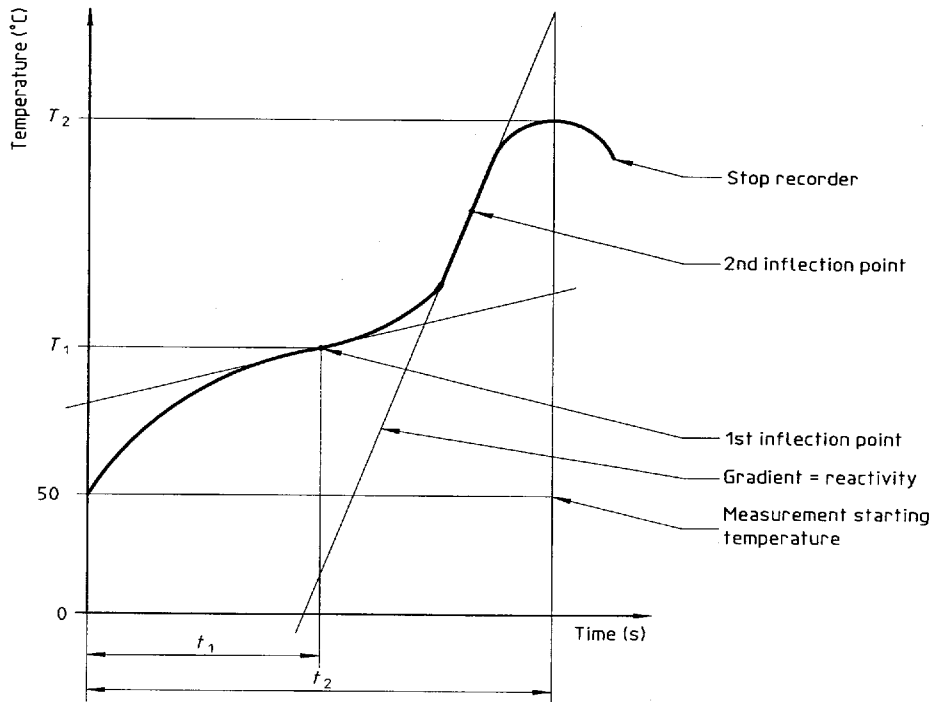


Figure 5 — Typical reactivity curve

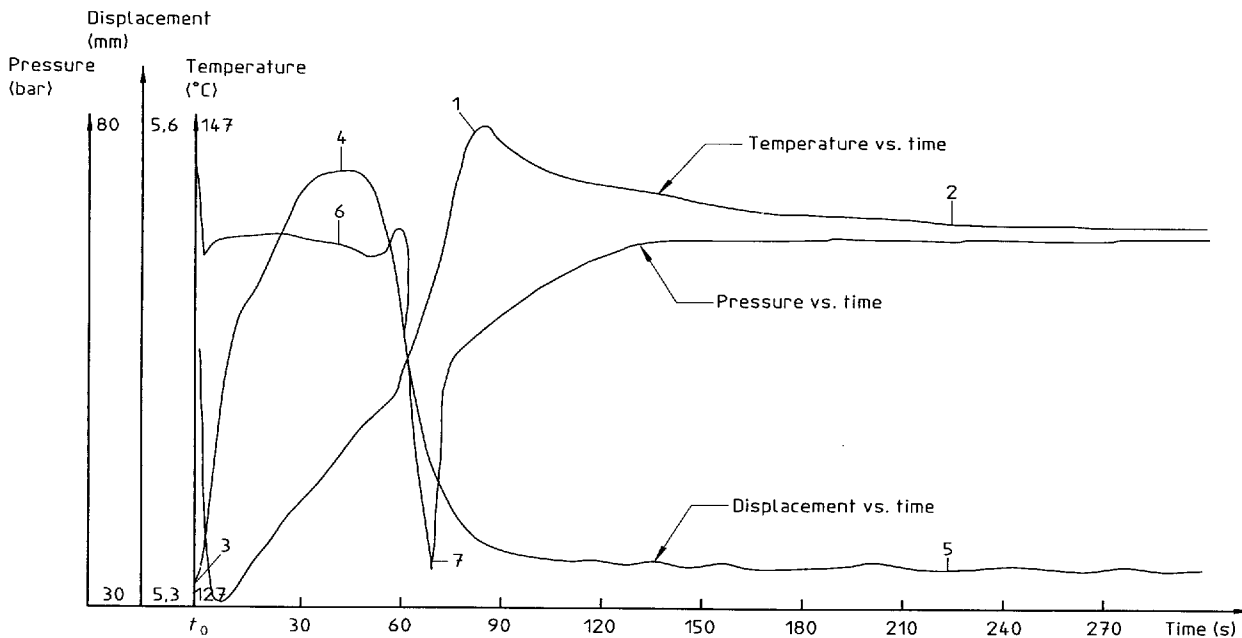


Figure 6 — Typical set of traces obtained by method II

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Descriptors: plastics, reinforced plastics, thermosetting resins, moulding materials, ingredients, preregs, tests, determination, characteristics, hardening, test equipment.

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