Matériau Ingénierie GROUP

MI-Tech

Technical Presentation

P-Reactech

Conventional reactivity of thermoset compounds

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SUMMARY

Reactivity is, together with fluidity, moulding capacity and density, one of the main parameters to characterise a thermoset, whether it deals with BMC (Bulk Moulding Compound), SMC (Sheet Moulding Compound) or a variant of these products. Since these compounds are transformed under pressure and temperature, it appeared logical to test them at given pressure and temperature.

The **P-REACTECH** developed and distributed by fully fits the standard :

√ **ISO 12114 (1997) – Fibre reinforced plastics – Thermoset moulding Compositions and prepregs – Determination of hardening characteristics.**

This standard is particularly applied for test:

- from reception control
- from storage control
- from validation of batches closed to the deadline

This test does not need any particular training and can be easily integrated in the workshop (next to the press)

Principle of measurement

✓ SMC/BMC characteristics

SMC/BMC are glass/resin thermoset compounds (unsaturated polyester most of the time) ready for use. Therefore they are stabilized to allow perfect storage and the furthest possible deadline.

The hardening of these materials (from pasty state to solid state) is generally made under temperature and pressure. Like any thermoset compound, this change of state is followed by a heavy exotherm which is relevant from the state of the material.

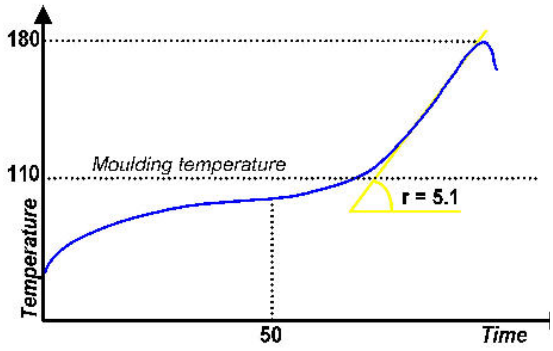


Figure 1 : sound material

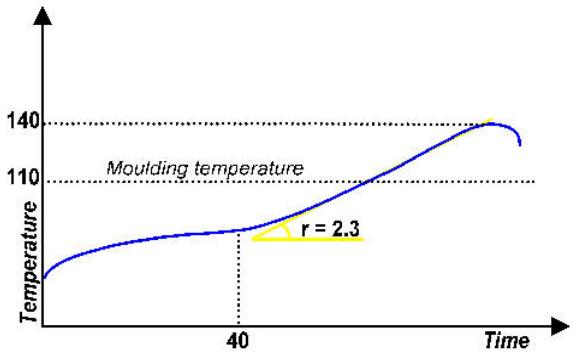


figure 2 :same aged material

An old material will experience :

- a slight decrease in its gelling time.
- a high decrease in its reactivity.
- a decrease also in its exotherm peak.

If the material becomes older, its gelling time will increase :

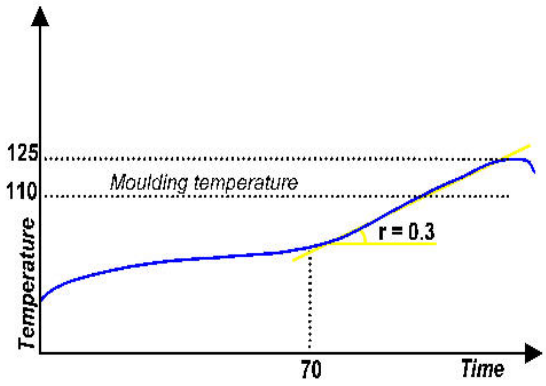


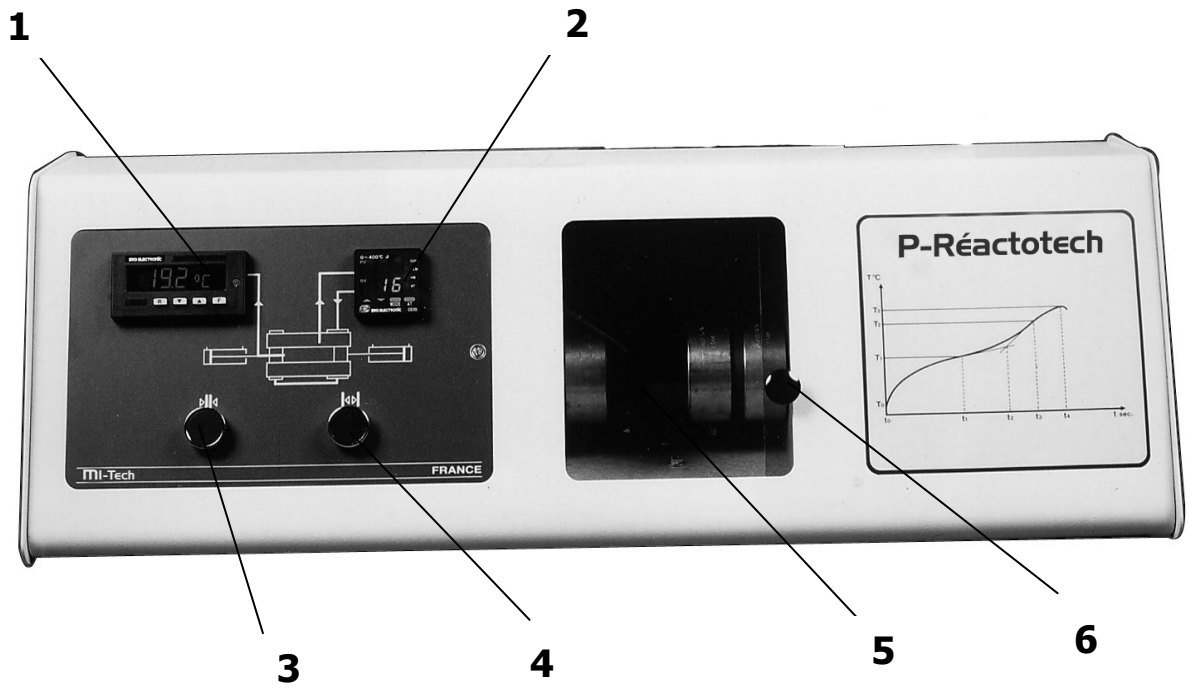
Figure 3 : characteristics of a material after a long period of time.

✓ The principle of measurement is therefore very simple :

It consists in continuously measuring under strictly defined conditions the exotherm occurring in a 6 cm≥ sample, heated at a referenced temperature (usually 140°C) and under a 10 bar pressure. A specific software performs the data acquisition, plots the curve and calculates the main remarkable points thus enabling statistical treatments on different samples from the same batch.

Description of the apparatus

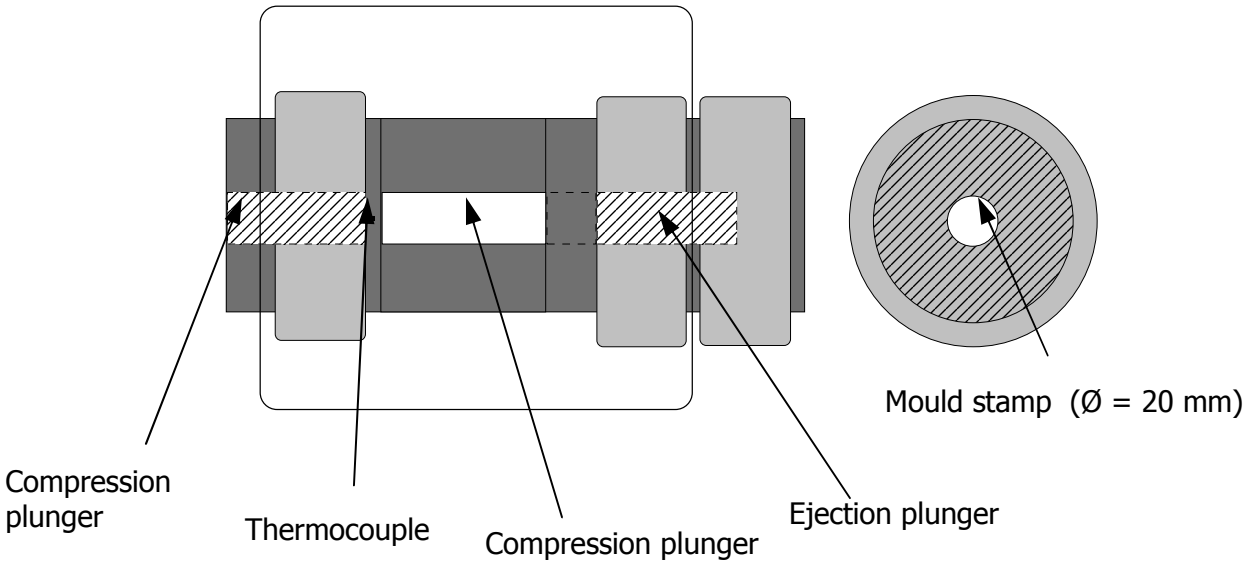
*Figure 4 : front view of the **P-REACTECH.***



① Display of the temperature inside the sample
② Regulation unit PID
③ Cycle Start button
④ Cycle Stop button
⑤ Heated mould
⑥ Safety door

The mould consists in a treated steel cylinder bored along its longitudinal axis by a 2.0 cm diameter hole. This mould is heated by heater bands which are thermoregulated by a PID regulation device. It is closed at the right end by an ejection plunger.

Figure 5 : large view of the mould.



On the left side of the mould is the compression plunger, equipped with a J Thermocouple (hot point at the mass) sticking out from 5 mm length and designed to apply a 10 bar pressure to the sample. Both plungers are controlled by an internal pneumatic automate.

Utilisation

✓ Operating a series of tests

The **P-REACTECH** is switched on and time is let to temperature to stabilize at desired temperature (usually at 140)2°C) which takes about 30 minutes.

A 6 ± 0.5 cm^3 sample is prepared, either by sampling (BMC) or by cutting (SMC).

Note : Since the volume of the sample is not easy to measure, it is more convenient to weigh the sample, while knowing the material's density.

Example : If $d_{material}$ = 1.8, and if W_{sample} = 11 g , then V_{sample} = 6.11 cm^3.

The software is easy to use. The fields are filled (name of supplier, batch number...).

It is possible to perform up to 10 tests per series and 676 series per batch of material.

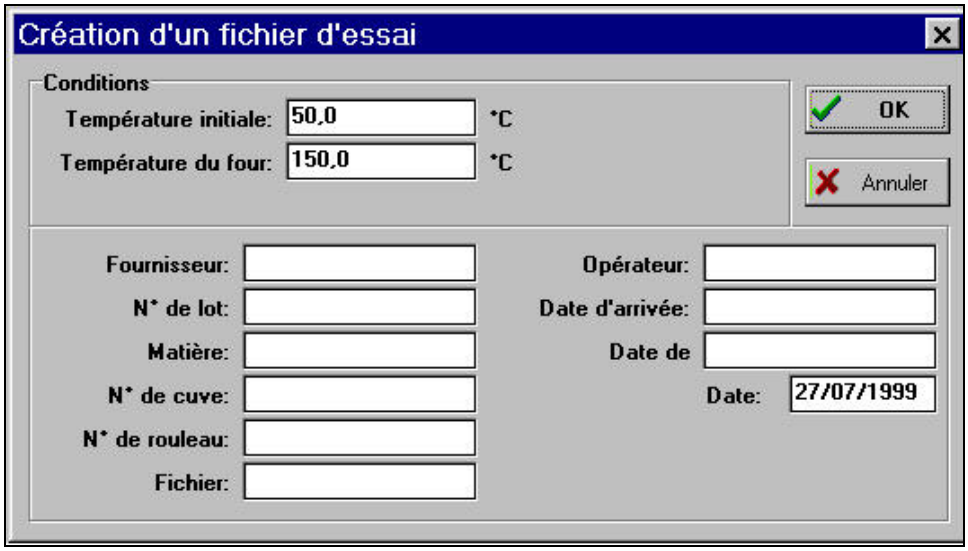


Figure 6 : example of acquisition window of v. 4.03 software.

A sample is introduced inside the mould, pressure system is launched by pressing on the start button, situated on the front part of the **P-REACTECH**. This action automatically launches the temperature acquisition. This acquisition automatically stops when, temperature comes back to 5°C below the exothermal peak.

The opening of the central door launches the opening of the oven and therefore the ejection of the polymerized sample.

✓ Results exploitation

The main points of the curve are computed according to **ISO 12-114** standard :

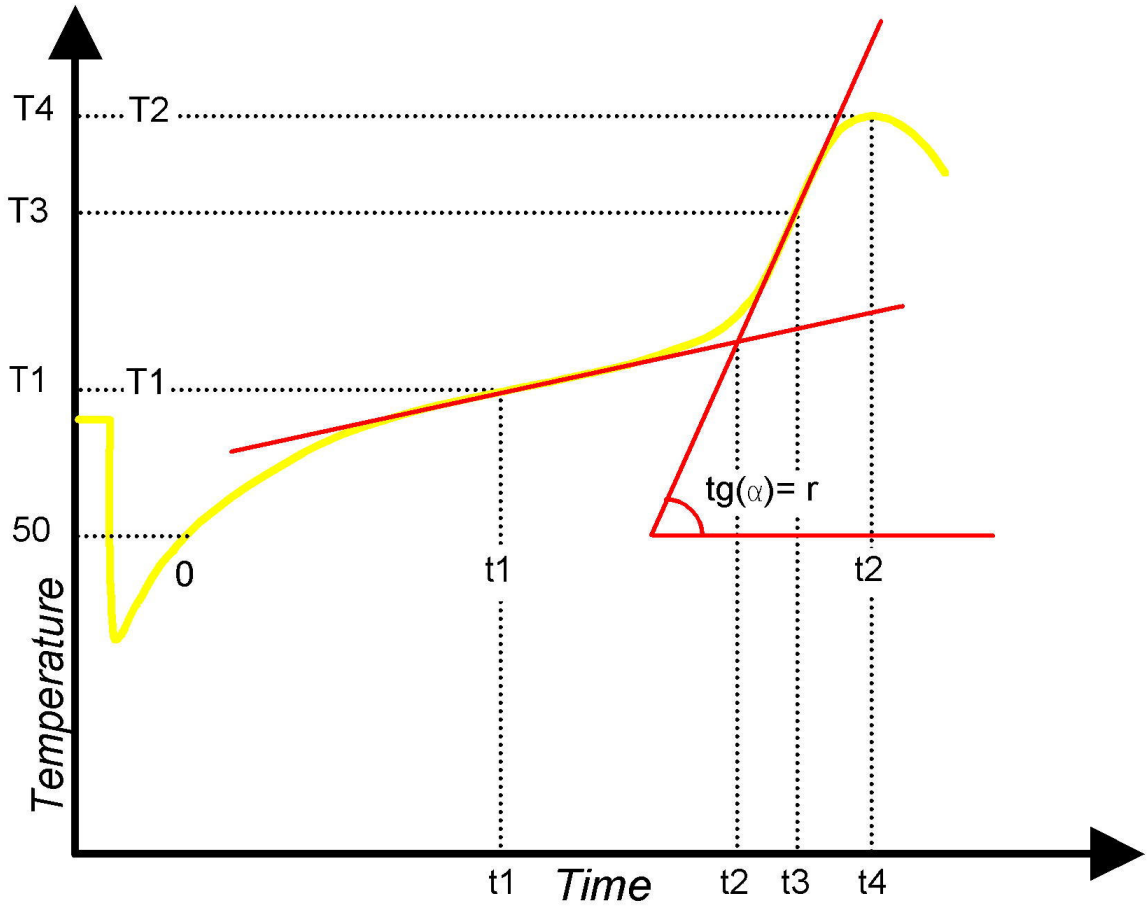


*Figure 7 : Standard example of a curve with **P-REACTECH** as well as the chain points that we can get.*

Legend :

50°C	Starting point of measurement (determined by standard) from which the different other points will de calculated.
t1 (s), T1(°C)	Initiation time of decomposition.
r(°C.s^{-1})	Conventional reactivity, that is to say maximum peak in temperature.
t2(s)	Gel time.
t3(s), T3(°C)	Maximum reactivity.
t4(s), T4(°C)	Exothermal peak.

Notes :

1- The dot (t4,T4) is noted (t2,T2) by the standard (norm).

2- The added dots (t2,T2) and t3 have not been requested by the standard but they remain important for a better knowledge of the material.

For each series of dots, a chart of results is printed and the mean (average) values and standard deviations are computed :

	Initiation		Reactivity				Peak	
Number	**t1**	**T1**	**t2**	**T2**	**t3**	**r**	**t4**	**T4**
1	112	85	122	131	164	3.6	187	165
2	113	87	121	133	163	3.5	185	164
3	111	86	124	130	167	3.7	188	166
4	114	84	123	133	166	3.6	185	164
5	115	89	120	132	163	3.6	184	167
6	113	86	125	132	167	3.4	187	167
7	112	88	124	134	166	3.5	185	169
8	115	87	127	131	168	3.5	189	168
9	*125*	*90*	*130*	*140*	*195*	*3.9*	*195*	*175*
Average	113.1	86.5	123.25	132	165.5	3.55	186.25	166.25
St. deviation	1.45	1.6	1.75	1.12	1.62	0.09	1.75	1.83
	s	°C	s	°C	s	°C/s	s	°C

Figure 8 : example of a statistical chart with P-Reactech v4.03 software.

✓ **Some useful notions.**

What is a gel time*?*

A gel time (noted as "tg") has no particularly fixed definition, even if it represents a very defined transition ; the change from liquid state to solid state.

Therefore it becomes necessary, as well as for the viscosity, to perfectly describe the method that has been used for determining the gel time.

According to the "zoom" and the orientation, which allow us to study this change from liquid to irreversible solid state, we shall not find at all the same gel times.

In the same way, it is difficult to use the same method for very reactive materials (such as unsaturated polyester) or "light" reactive materials (such as polyurethane), loaded or non-loaded materials.

Here are some examples for defining the gel time we have encountered :

- ☞ theoretical : time of appearance of the first three-dimensional network which covers all the space. This theoretical definition is hardly fit to serve as instrument.
- ☞ scientific : time of appearance of the first insoluble. This definition relies on the fact that a thermoset is reticulated and therefore that it can not be transformed in solution. Here again, it is difficult to perfectly perform tests (continuous sampling + changing into solution + G.P.C*. for example !).
- ☞ usual : ▪ time of doubling or tripling of the initial or minimum viscosity (mastics, loaded resins-.) See figure 9 ▪ Method of the tangents on the consistency evolution (reactive resins) - cf. figure 10 ▪ Change towards 50 Pa.s (unsaturated polyesters) ▪ Change to a determined consistency value. **These two last methods are empirical and therefore to be avoided**.
- ☞ particular : ▪ t2 of thermal reactivity (unsaturated polyester. S.M.C., B.M.C., etc) ▪ tg δ = 1 (viscoelasticity).

There are many other definitions but they do not represent the whole range of materials.

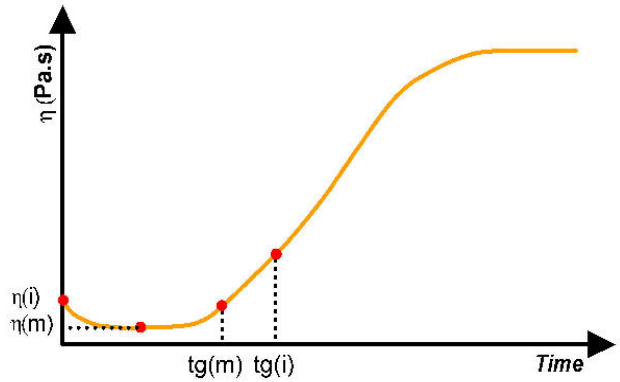


Figure 9 : Viscosity x2 or x3 (or x n)

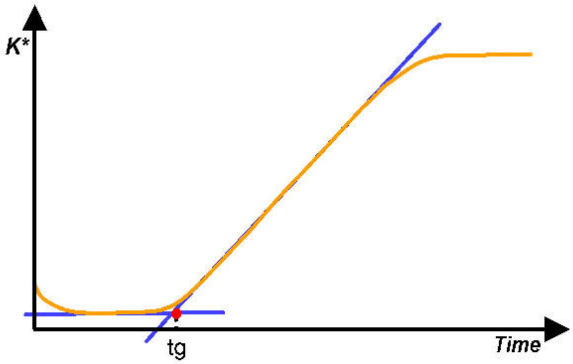


Figure 10 : K represents viscosity in a liquid state, consistency in « paste » state and its rigidity in solid state.*

What does thermal reactivity mean ?

There are two kinds of reactivity :

- conventional thermal reactivity, noted as $\mathbf{R_C}$, - Increase in number of degrees through time unit ($°C.s^{-1}$).

- physical reactivity, noted $\mathbf{R_P}$ Increase in number of "chemical links" through time unit.

When R_C or R_P highly increase, the system is said "more reactive" and generally it is followed lay a decrease in gel time (not systematically) and above ail by an increase in shrinkage and internal restraint in the sample.

On the contrary, if R_C or R_P are weak, moulding cadences will be weak arid to a certain degree the system may not have enough exotherm in order to "self-launching", entertain a good reticulation of tire material, etc.

* **G.P.C.** → chromatography in gaseous state.

Features

✓ Dimensions

- Overall dimensions (depth x width x height) : 230 x 800 x 270 mm.
- Net weight : 22 Kg.

✓ Connections

- Power : single phased 220 V,±10%, 50 Hz.
- Pneumatic : Dry air, not lubricated.
- Inlet pressure : P= 5 bars minimum.
- Computer : PC 286 minimum + printer.

✓ Metrological features

- Heating temperature :
  - Setting point : 0 to 200°C maximum.
  - Automatic regulation : P.I.D., ± 2 ° C.
  - Resolution : 1°C.
- Sample measured temperature :
  - Thermocouple : J, ∅ 1mm. Hot weld connected to the ground.
  - Range of measurement : 0 to 250°C.
- Visualization of temperature :
  - Numeric display : 4 digits.
  - Resolution : ± 1°C.
- Sample dimensions :
  - Length : 16 to 25 mm.
  - Diameter : 20 mm.
  - Volume : 6 ± 0.5 cm^3.

Specifications of our apparatuses are given for Information but can be changed far improvement without notice

Contacts

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