Polymatrix

Innovative Tools for Polymers

Technical Note April 2012

OSCILLATING ROD CUREMETER (ORC)

A simple and user-friendly tool for liquid cure monitoring

- For liquid polymer/resin cures - flexible, rigid or foamed
- Accommodates various sizes of sample
- Simple to operate with disposable sample cells
- Provides a continuous profile of cure
- Digital output for PC storage & retrieval
- Compatible with the latest PC operating systems

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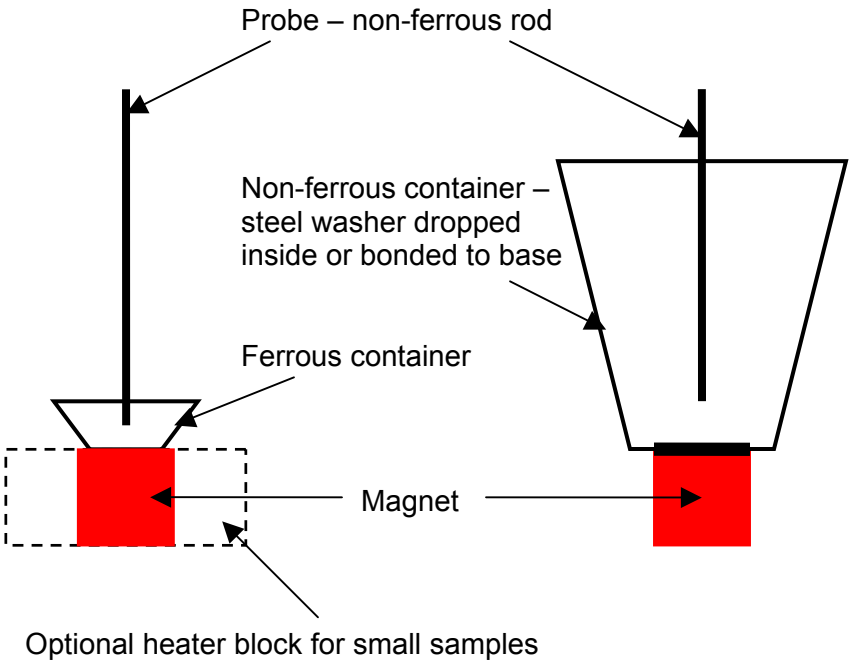
Oscillating Rod Curemeter

The Polymatrix Oscillating Rod Curemeter (ORC) tracks the progress of a curing liquid through amplitude attenuation of an embedded probe. The probe is a plain rod and is intended to be disposable. The sample is in an open vessel (cup, or whatever) of any size that can be accommodated in the instrument. Current designs can accommodate samples in containers as small as a (steel) bottle top or as big as a metre-cube cardboard box. Disposable sample configurations are a feature of the ORC.

Simplicity extends to the output which exploits the attenuation of vibration, at constant thrust, to translate changes in (dynamic complex) viscosity into amplitude measurements – i.e. an output simply in millimeters. This output scale has the same significance whatever the size of sample. As the sample cures, the amplitude falls. A second output is temperature, from a thermocouple which can record the exotherm within the sample – or just the ambient temperature.

This flexible approach allows for sample vessels that suit the user. These can be paper cups, plastic beakers or cardboard boxes. The sample vessel can even be a (steel) bottle top. The standard bottle top accommodates samples up to ca. 5 ml and is the recommended choice for heated samples. The optional heating block provides for sample temperatures up to 150°C.

The option for switching between different sample vessels is made possible by an ingenious magnetic location. Samples in ferrous containers (e.g. bottle tops, small cans) locate directly on the magnetic base. Samples in plastic beakers or paper cups can be simply located by dropping a steel washer inside. Alternatively a steel washer can be bonded to the underside – a method that works well for aluminium vessels.

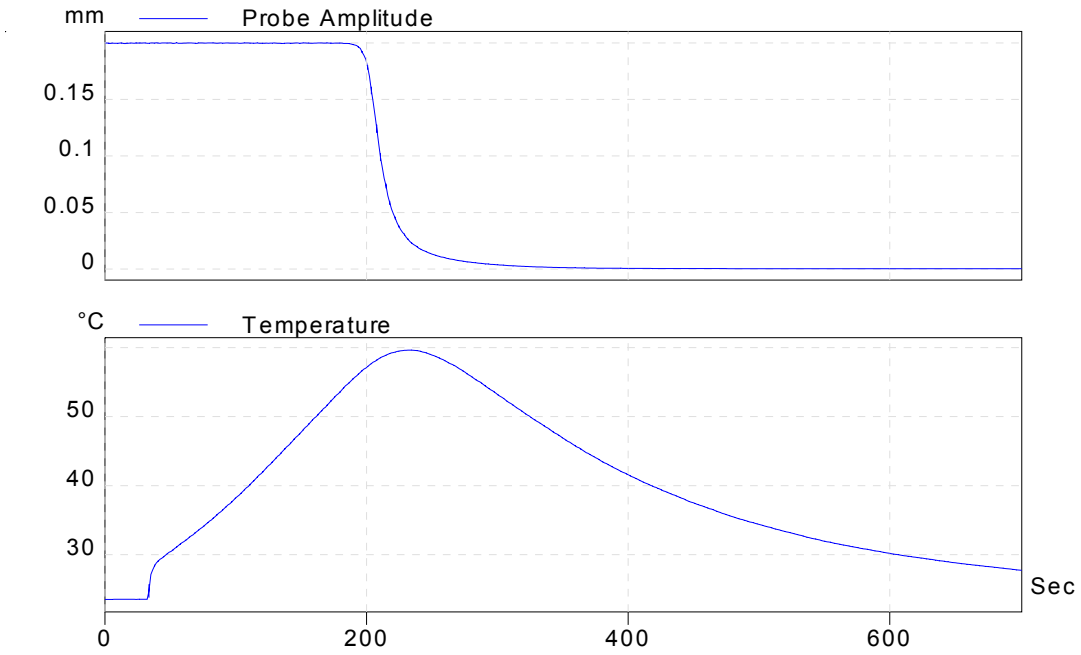


Of course, the probe itself must be non-magnetic. Brass is suitable, but is a heat sink. Carbon fibre rod (4 mm) works well in these sample configurations.

The rod includes a sleeve coupling, so that the lower (embedded) part can be disconnected once the test is complete. The cured sample/rod section can then be discarded - samples which set hard (e.g. epoxy) are no problem at all. This simple arrangement allows the sample to be removed after cure without any elaborate rise-and-fall on the vibrator assembly. In the ORC, the sophistication is on the inside - where the amplitude is tracked by a dedicated displacement transducer.

This displacement transducer removes other design constraints and allows the unit to move away from the resonance condition. Oscillating probe devices, widely used for in-line viscosity monitoring, commonly work at resonance where the back EMF gives a measure of amplitude. However, resonance operation introduces complications in a cure monitoring device (where the sample changes from liquid to solid), and is best avoided unless suitable compensation is applied. For simplicity, the ORC works well away from resonance.

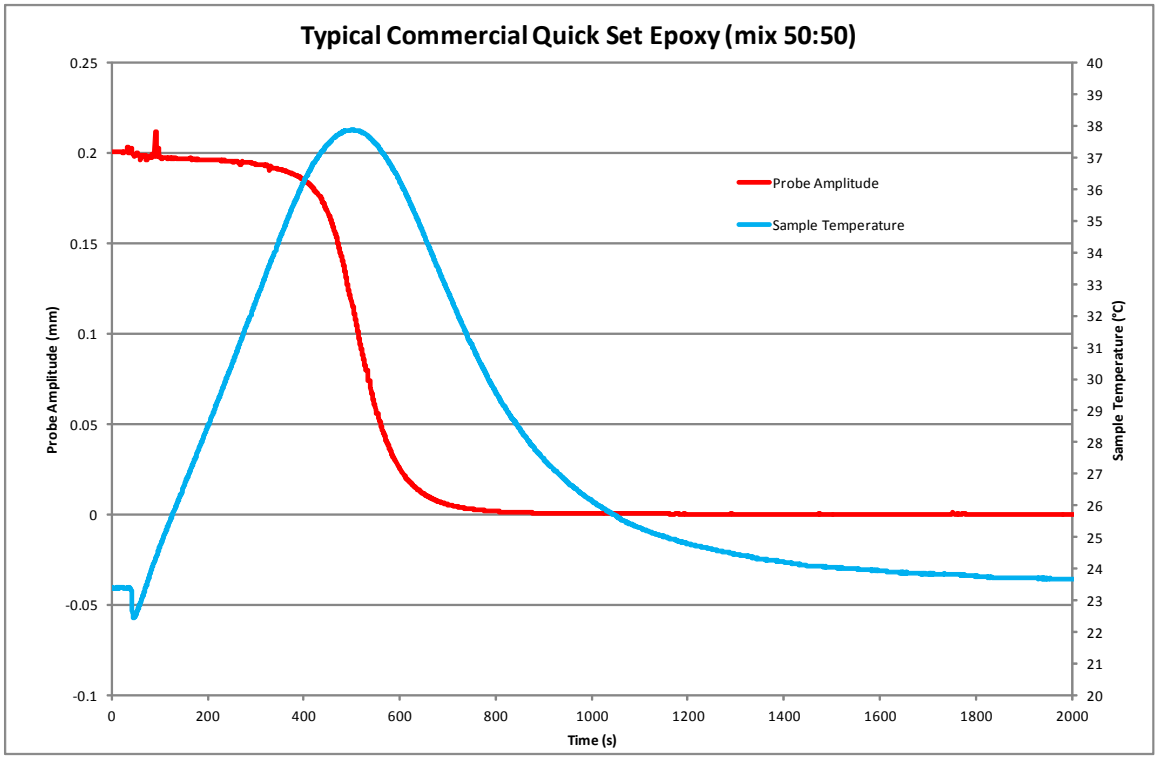
The operating frequency is 5 Hz and data acquisition is achieved using a Pico Technology data logger that simply plugs into the USB port on the PC or laptop. The supplied PicoLog data acquisition software both collects and displays the data as the test is running. A typical example of a real time display is presented in the Figure below.



It can collect up to 1 million samples (11.5 days sampling at 1Hz) and the data can be exported to spreadsheets and databases. It supports 32– and 64–bit editions of Windows XP (SP2 and above), Vista and Windows 7. It is also available in international language versions.

Examples of Cure Traces from the ORC

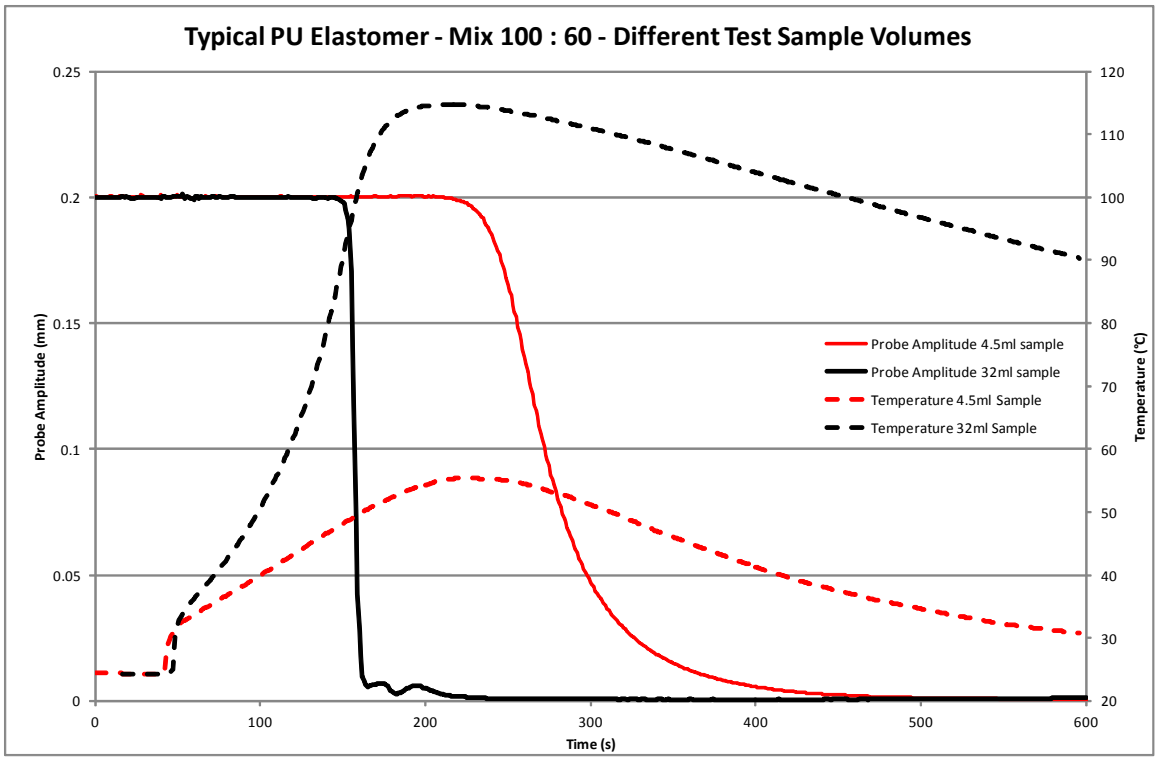
The system copes easily with samples which set hard. The traces below (Amplitude and Temperature) are for an epoxy resin in a bottle top. The time is taken from the start of mixing and the cure is virtually complete within 1000 seconds.

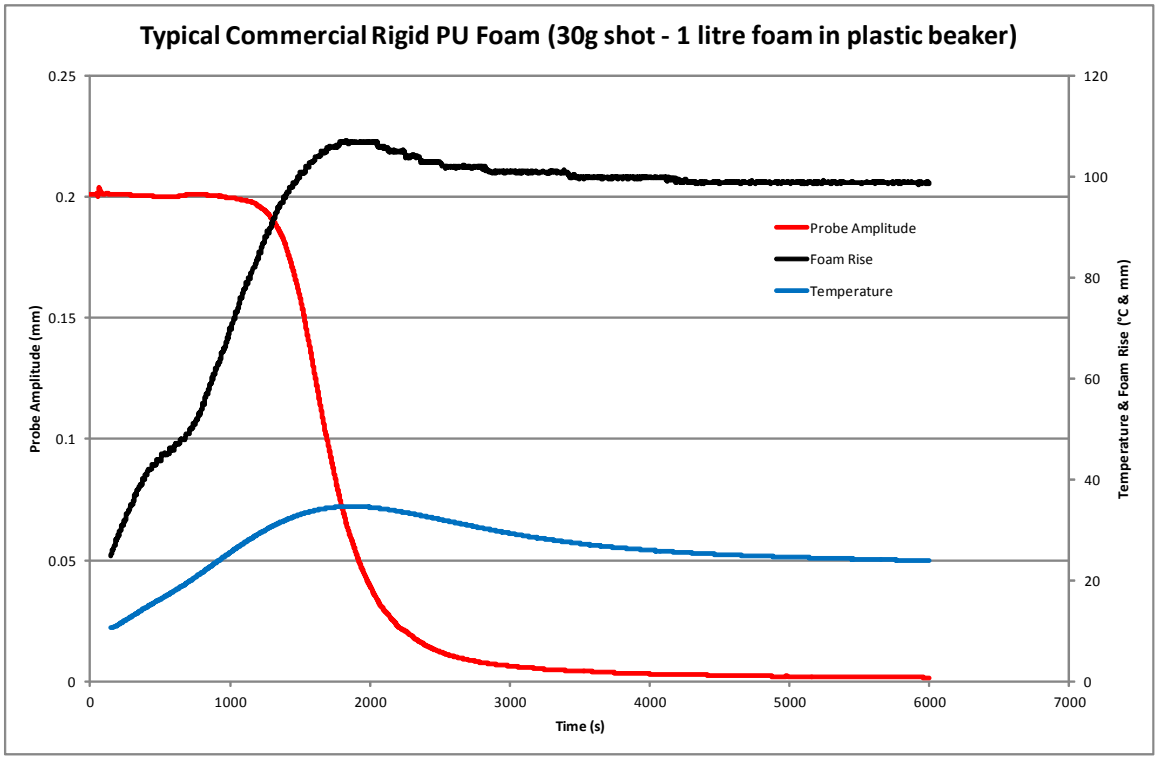


The standard output time scale is seconds (10,000 seconds equates to ca. 167 minutes or 2.75 hours). Of course, the data can be manipulated in commercial spreadsheet software to generate traces on any timescale and create combination plots for direct comparison between samples.

Sample size is critical to cure. It influences heat transfer and conserves the exotherm. Formulations developed in small-scale lab tests may well result in runaway reactions on the production scale. The first figure below gives traces for the same polyurethane elastomer formulation cured, from ambient temperature, in a bottle top (4.5 ml) and a plastic beaker (32 ml). In the small sample the exotherm barely reached 30°C, whereas that in the larger sample exceeded 100°C. Not surprisingly, the cure rates are very different.

Not only can the ORC cope with different sizes of sample, it can also cope with samples which change size during cure such as foaming systems. An optional (optical) distance sensor can be supplied with the instrument to record foam rise. The second figure below is for a rigid PU foam.


Typical PU Elastomer - Mix 100 : 60 - Different Test Sample Volumes
Probe Amplitude (mm)
Temperature (°C)
Time (s)
Probe Amplitude 4.5ml sample
Probe Amplitude 32ml sample
Temperature 4.5ml Sample
Temperature 32ml Sample
0.25
0.2
0.15
0.1
0.05
0
120
110
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600


Typical Commercial Rigid PU Foam (30g shot - 1 litre foam in plastic beaker)
Probe Amplitude (mm)
Temperature & Foam Rise (°C & mm)
Time (s)
Probe Amplitude
Foam Rise
Temperature
0.25
0.2
0.15
0.1
0.05
0
120
100
80
60
40
20
0
0
1000
2000
3000
4000
5000
6000
7000

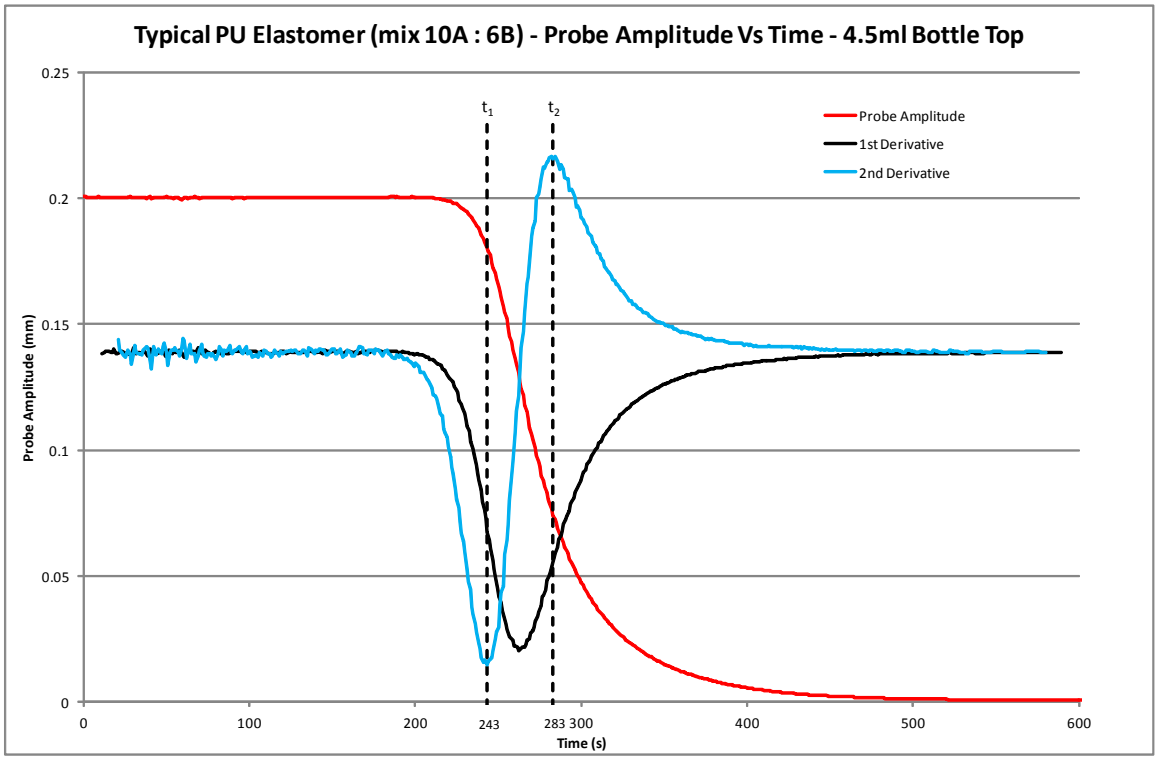
Catalyst Profiling

Organometallics (i.e. compounds containing a metal-carbon bond) are readily soluble in organic media and are widely used as curing catalysts. Bringing metals into play at the site of organic reactions gives full rein to their activity and selectivity, and organometallic catalysts can deliver high levels of process control and through-cure in polyurethane elastomers. Unfortunately these same organometallics can interact in living systems where their presence is far from welcome. Toxicity concerns can only mean that their days as catalysts are numbered.

There is no shortage of alternative catalysts for PU, but there are no direct substitutes for organometallics in performance terms. What alternatives work best for a specific system is usually a case of trial and error. Success depends on the ability to generate, store and retrieve diagnostic cure data, and the ORC is the ideal tool for this.

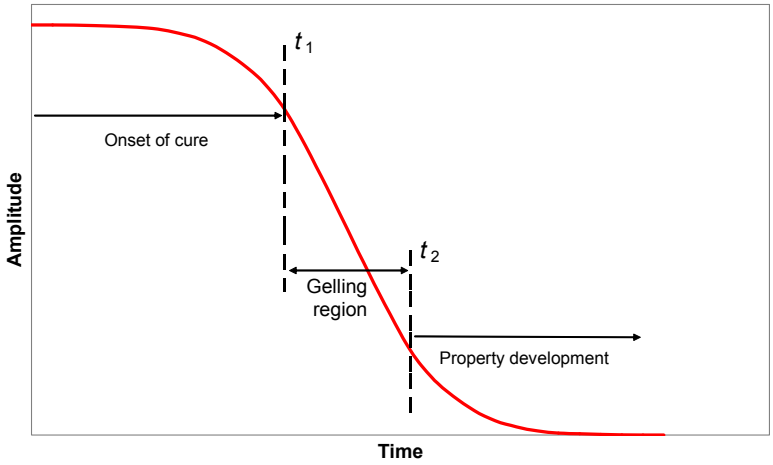
The continuous cure profile, in digital form, allows for easy comparison of different systems. Cure traces can be laid alongside one another to check for a match. Formulation effects will take on a visual significance – a powerful aid in system development.

But the traces also need cataloging if proper comparisons are to be made. This means assigning some diagnostic numbers to the output trace. The figure below shows the amplitude/time plot (red) for a PU elastomer cure alongside its first and second derivatives (black and blue, respectively). These derivative plots are easily generated in commercial spreadsheet software.



The black trace (1st derivative) shows a minimum at the point of maximum (downward) gradient on the amplitude/time trace. The blue trace (2nd derivative) shows both a minimum and a maximum – these corresponding to the points of maximum gradient on the black trace.

The minimum and maximum points on the 2nd derivative trace generate two diagnostic times, which roughly bracket the gelling region in the cure.



Importantly, these two diagnostic times (t_1 and t_2 in the above figure), put numbers to the shape of these traces and provide useful performance indeces. Two such examples are a Delay Index and a Rate Index,

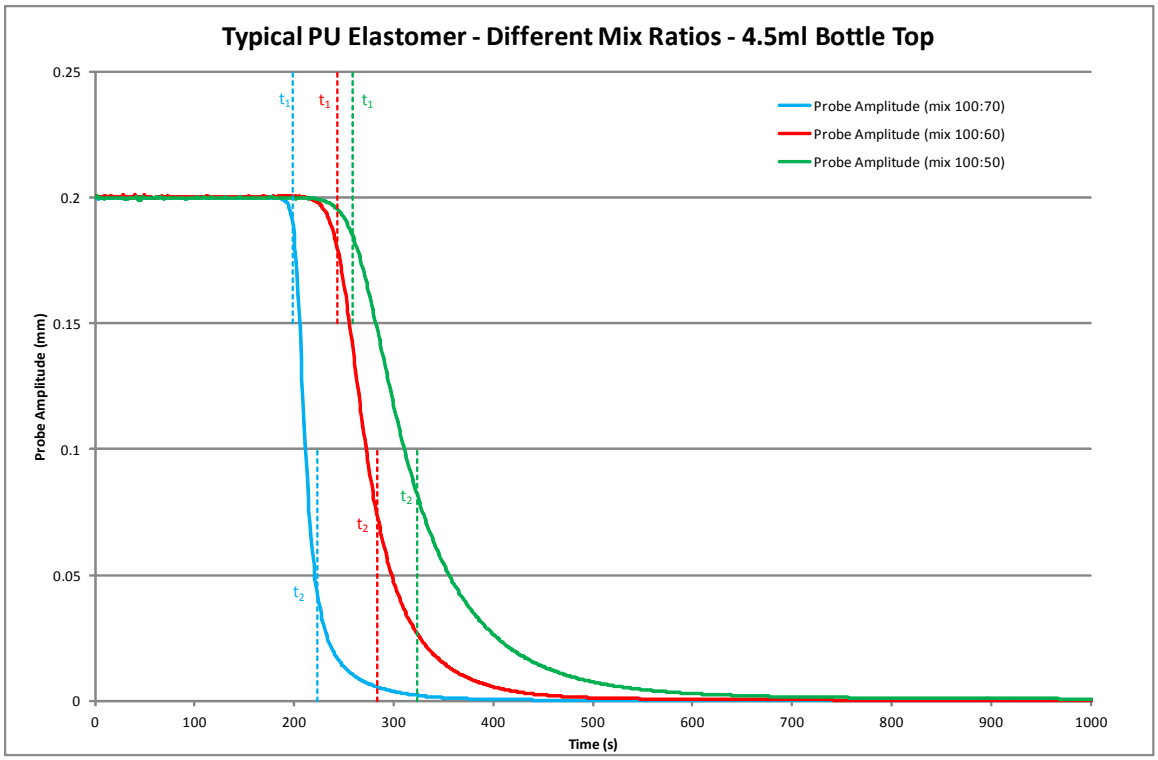
$$\text{Delay Index} = t_1/t_2$$

where the higher the value of t_1/t_2, the greater the level of delay in cure.

$$\text{Rate Index} = (A_1 - A_2)/(t_2 - t_1)$$

where A_1 is the amplitude at t_1 and A_2 the amplitude at t_2.

The cure traces for a PU elastomer formulation at three different mix ratios are shown in the figure below.



The corresponding values for t_1, t_2, Delay Index and Rate Index for each of these three cures are given in the Table below

			Delay Index			Rate Index (μm/s)
Mix Ratio	t_1 (s)	t_2 (s)	t_1/t_2	A_1 (μm)	A_2 (μm)	$(A_1-A_2)/(t_2-t_1)$
100/50	259	324	0.799	186.4	81.6	1.6
100/60	243	283	0.859	180.2	74.1	2.7
100/70	199	223	0.892	189.0	44.0	6.0