Application Note A1, Oct 2012

CureRod A

An oscillating rod rheometer/curemeter delivering continuous cure profiles by amplitude attenuation

- **For liquid polymer/resin cures – flexible, rigid or foamed**
- **Continuous profile gives a fingerprint of cure**
- **Accommodates a wide range of sample sizes**
- **Easy to operate with disposable sample cells**
- **Ambient or at temperatures up to 250°C**
- **Computer integrated for data storage & retrieval**

http://www.polymatrix.co.uk

Polymatrix

Polymatrix was formed in 2008 as a collaboration of two independent consultants with complementary expertise. One is a polymer physicist specialising in plastics and the other a polymer chemist specialising in elastomers. Both have a track record in test method development and, over their respective careers, they have mustered a total of 140 publications including three books.

With such differing backgrounds, it might be expected that their paths would rarely cross.

But this is not case, as problems are not so easily compartmentalised. Multi-disciplinary solutions are the rule rather than the exception, and Polymatrix was set up to explore the possibilities of closer collaboration. Polymatrix is not a consultancy. It is a company set up to explore new horizons and create products which break new ground. CureRod A is one such product – and the first to reach commercial production.

CureRod A (the “A” stands for amplitude) is the first curemeter for liquid polymer/resin systems designed from the outset to work with samples of different size, and therefore able to explore the effects of scale. It incorporates a number of innovations to achieve this, including magnetic sample location to avoid fixings with geometric constraints.

This Application Note provides an introduction to the instrument, covering the principles of operation and giving examples of output traces for a range of different materials.

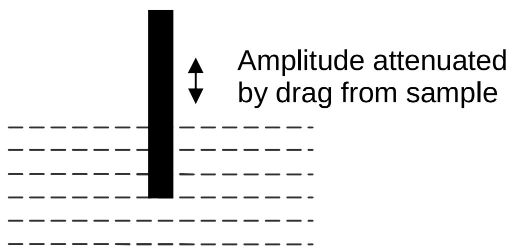
Bryan Willoughby and Mike Hough, the two principals of Polymatrix

Amplitude Attenuation

CureRod A is an oscillating rod rheometer/curemeter which tracks the changes in a curing liquid through amplitude attenuation of an embedded probe. The probe is a plain rod. It is not a paddle or plunger, it is not threaded or grooved – it is just a plain flat-ended rod cut to a suitable length. It must be rigid, but otherwise can be made of any material which will not interfere with the cure. It is intended to be cheap, basic and fully disposable.

The same philosophy applies to the sample holder, which an open vessel (cup or whatever) of any size that can be accommodated in the instrument. It can even be an open mould. Simple fixings allow the whole sample-rod assembly to be easily removed from the instrument at the end of cure. What is not required can be thrown away.

In operation, the instrument drives the rod in vertical oscillation. When immersed in the sample, the rod experiences drag in the same manner as any bluff object moving within a viscous medium. The greater the viscosity, then the greater the drag. If the peak thrust remains constant, then the amplitude will fall as the viscosity (drag) increases. This condition is achieved by using an electrodynamic vibrator driven at a constant (RMS) voltage.



This is not in any way groundbreaking, as vibrating reed devices, working on the principle of amplitude attenuation, have been used for years for in-line monitoring of viscosity in production sites. The absence of a defined shear field means that they will require reference calibration for absolute values of viscosity, but they remain both highly responsive and robust, and are the viscometers of choice for “difficult” samples such as gels or sludges.

More recently the principle has been applied to cure monitoring where changes can be tracked well into the later stages of cure [1,2]. Amplitude attenuation can detect the earliest stages of reaction and describe processability in a single trace that can be regarded as a fingerprint of cure.

This easily obtained instrumental output provides a continuous profile of cure which:

- proves highly sensitive to formulation and temperature variables,
- is far more discriminating than any single point measurement,
- removes subjectivity from cure rate assessment.

Operating Frequency

CureRod A takes the established capabilities of vibrating probe devices into a new frequency regime. Traditionally these instruments have operated at audio frequencies to stay on, or close to, the resonance condition. Resonance operation may carry advantages with respect to signal strength (e.g. less amplification), but it is also restrictive from an applications perspective. CureRod A exploits modern developments in electronics to deliver the required performance at well below audio frequencies. The instrument uses a precision waveform generator to deliver a high accuracy sine wave at 5 Hz.

The shift away from resonance therefore sets CureRod A apart from traditional vibrating probe devices. Whatever instrumental convenience may accrue from resonance operation, there is no fundamental requirement to do so. Indeed there is a major limitation if trying to explore the effects of scale. This is because the dynamic viscosity (responsible for the drag in oscillating systems) is frequency dependent and the resonance frequency depends on the vibrating mass. So,

(i) changing the sample size changes the resonance frequency, and
(ii) changing the monitoring frequency changes the viscous response.

Hence, if operating at resonance, it is impossible to explore the effects of scale under comparable monitoring conditions. Moreover, electing to work at a single frequency for a range of different sample sizes runs the risk of some being closer to resonance than others, if that frequency is in the audio region. Some may even come into resonance during the cure – to increase the amplitude at a point when it would normally be falling. It is perhaps not surprising that vibrating probe instruments can go to some lengths to hold the resonance condition.

CureRod A goes to similar lengths to avoid the resonance condition! The operational frequency of 5 Hz is well below resonance for this instrument configuration. In principle, the frequency could have been set even lower. But too low a frequency will compromise the ability to track very fast cures. A precision sine wave is also a key requirement – and, after a number of trials, a frequency of 5 Hz was found the most suitable. The instrument has proved more than a match for the most active systems and delivers a good signal-to-noise response throughout the cure.

For obvious reasons, the frequency is pre-set in the instrument and it not amenable to operator control.

By operating at a frequency well below resonance, the effects of scale can be properly explored. Since curing reactions are invariably exothermic – some more so than others – differing sample sizes give different temperature profiles and therefore different rates of cure. Having the ability to explore the effects of scale is critical to understanding the differences between laboratory and production regimes.

Thus CureRod A stands apart from other vibrating probe devices in that it:

- operates at a pre-set frequency well below resonance,
- is not limited to any one sample size,
- can explore the effect of scale and match lab data with production results.

The Instrument

CureRod A is an instrument designed from the outset to operate with a range of sample sizes. Clearly this capability cannot be compromised by the mechanics of sample location – in fact a radically new approach to this is required.

CureRod A breaks new ground in using magnetic sample location.

The concept is simple. A magnet sits in the base of the instrument (or on the heater block). If the sample is in an iron or mild steel container, such as a (paint) can, (food) tin or similar, then it will be held securely in place. If the sample is in a plastic beaker or paper cup, then it can be held in place by simply dropping a steel washer inside (Fig 1). Alternatively a steel washer can be bonded to the underside – a method that works well for aluminium vessels. A magnet is not the only option (user-specified fixings can be supplied on request), but it is the standard arrangement for CureRod A.

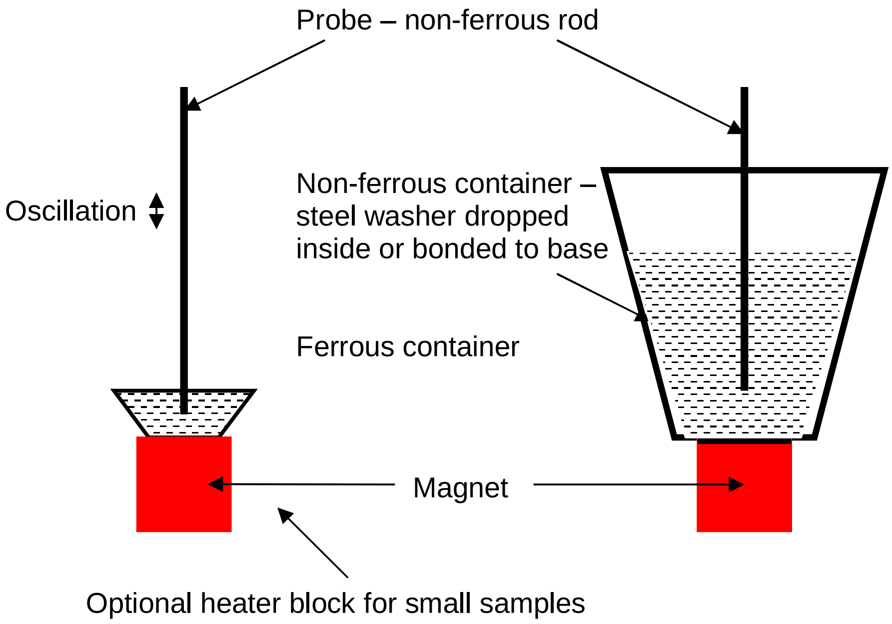


Figure 1 Schematic layout for samples in ferrous or non-ferrous containers

Of course, this means that the probe itself must be non-magnetic. Brass or aluminium are suitable, but are possible heat sinks. Carbon fibre rod works particularly well.

With this configuration, both rod and sample are completely disposable. The rod is in two-parts connected by a simple sleeve coupling. By loosening the coupling (at the end of testing), the lower (embedded) part can be disconnected and discarded. This combination of magnetic sample location together with a sleeve coupling on the rod avoids the need for any rise-and-fall mechanism on the vibrator assembly. Any vertical compliance in the vibrator mounting will impact on performance, and the simple arrangement adopted here avoids the compromises of more elaborate mechanisms.

Disposable sample configurations thus are a feature of CureRod A. This flexible approach allows for sample vessels, and rods, that suit the user. For small-scale work, a standard 27 mm diameter (crown cap) bottle top (Fig 2) works well. It accommodates up to 4.0 ml of sample and is the recommended choice for heated samples. The optional heating block provides for sample temperatures up to 250°C.

Figure 2 Magnetic location of sample in crown cap

Crown caps are available from Polymatrix or from local home-brewing suppliers.

The optional heating block incorporates a sample well with a magnet in the base. The well is designed to accommodate a standard steel crown cap (Fig 3). The presence of the magnet also facilitates good thermal contact.

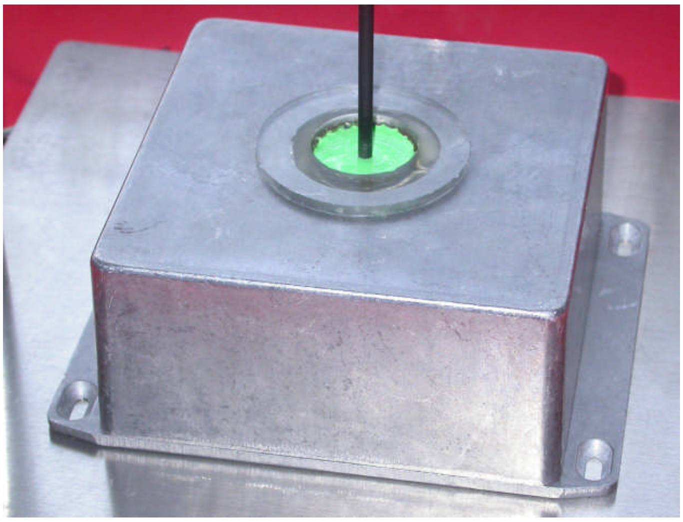


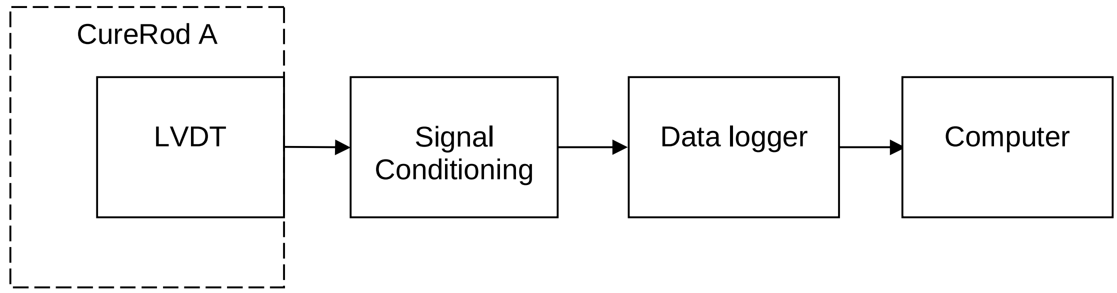
Figure 3 Optional heater box with the sample in place

Thus magnetic sample location brings in a host of advantages, including:

- easy insertion and removal of sample (even when hot),
- ability to accommodate different sample sizes,
- good thermal contact with heater block,
- fully disposable sample system.

Data Handling

The principal output of CureRod A is an amplitude detected using a Linear Voltage Displacement Transducer (LVDT). The LVDT output (voltage) undergoes signal conditioning prior to passing through a 24-bit data logger on its way to a PC or laptop.



The data logger supplied with CureRod A can collect an unlimited number of data points at pre-selected sampling rates at speeds as fast as one data point per second. It connects to the USB port on a PC or laptop, and is compatible with 32– and 64–bit editions of Windows XP (SP2 and above), Vista and Windows 7.

The data logger can process up to eight inputs simultaneously – two of which are used to derive the amplitude. The extra capacity can be exploited to record temperature (as an additional input on an optional thermocouple. Figure 7 (for water-blown foam) gives an example of a monitoring exercise with three simultaneous displays: amplitude (2 channels), temperature (one channel) and rise (one channel).

Thus, in principle, the data logger can support two such foam instruments (for three displays) or up to four instruments delivering amplitude only.

The data logger can be set up to repeat immediately and indefinitely. That means at the end of one file, it will open a second one, and so on. Ultimately the time limit for any test is determined by the priorities of the operator and the size of the available memory in the computer.

For example, if the sampling interval was set to 1s and the experiment was left to run for one year, then ~31.5million samples would be taken and that would consume ~171MB of memory – about the same as 100 medium quality photographs.

The data logger supplied with CureRod A is a PicoLog device from Pico Technology. The associated Pico Technology software displays the data on the computer screen as the test is running. A typical example of a real time display is presented in Figure 4.

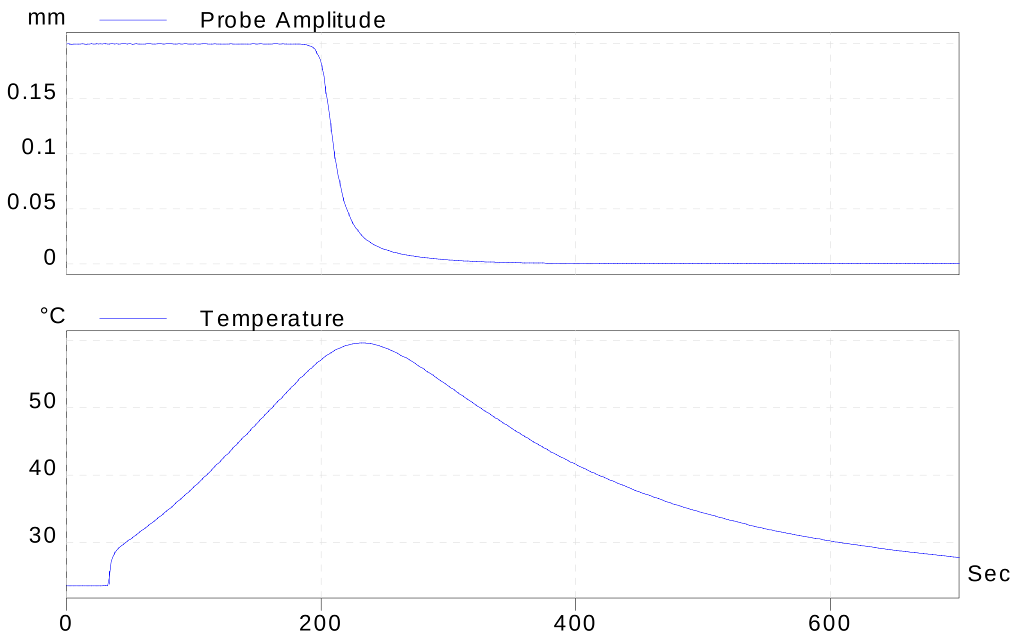


Figure 4 Real-time display on the PicoLog data logger

Of course the presence of the computer means that the output can be exported to spreadsheets and databases for a host of alternative display formats. Data can be:

- stored and retrieved as required,
- replotted in different formats,
- overlaid for detailed comparison.

The examples shown later in this Application Note will demonstrate these capabilities.

Operational Variables

CureRod A runs at a pre-set frequency (5 Hz) and therefore this is not amenable to operator adjustment.

The variables under control of the operator are therefore:

(i) sample size
(ii) rod type and diameter
(iii) rod position in the sample
(iv) starting amplitude

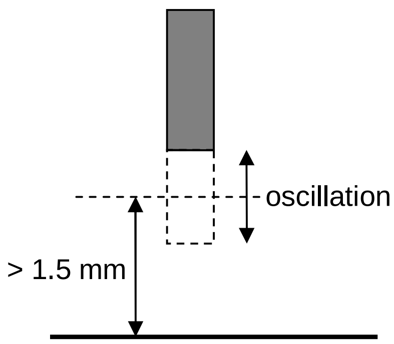
The instrument is intentionally designed to allow a range of sample sizes. The limitations are practical – i.e. the upper limit is whatever will fit in the instrument. Unless specified otherwise, the instrument will be supplied with dimensions able to accommodate sample holders ~300 x 200 x 200mm. Larger frame sizes can be supplied on request.

There is a lower limit on sample size, as there must be adequate clearance beneath the rod to accommodate the oscillation. CureRod A is not recommended for thin films.

Of course sample size influences heat transfer, and this affects the generation and dissipation of any exotherm and also the rate of heat input from external sources. Thermal history will change if sample size changes. This has been taken into account in the design of the (optional) heater block for CureRod A – which is configured to work with small samples of a standard size. The arrangement shown in Figure 3 accommodates samples in the 27 mm diameter steel crown cap (up to 4 ml).

Rod diameter is another possible variable although there are lower limits to what is practical. Very thin rods may bend in use, and the stiffest of common materials (e.g. ferrous metals) may be barred on magnetic grounds. Normally 3 mm (⅛") would be considered the minimum suitable diameter, and the standard instrument is supplied with a (sleeve) coupling able to accept 4 mm rods. Other couplings can be supplied on request.

Metal rods can function as a heat sink and influence the rate of cure. The recommended rod is 4 mm diameter carbon fibre.



For an immersed rod, diameter has a greater effect on the drag than length of immersion (i.e. pressure drag dominates over skin friction). Proximity to the base can become important, and pressure drag increases markedly when the clearance is low.

To avoid excessive depth sensitivity, the clearance beneath the probe should be at least 1.5 mm. For maximum reproducibility, the probe position and starting amplitude should always be the same.

Signal to Noise

For tracking any system which is potentially capable of rapid change, a stable output is critical. Achieving a good signal-to-noise response was a prime requirement in the development of CureRod A. A number of factors (electrical, mechanical) were addressed in optimising performance, and a typical output amplified to show the residual noise levels is presented in Figure 5.

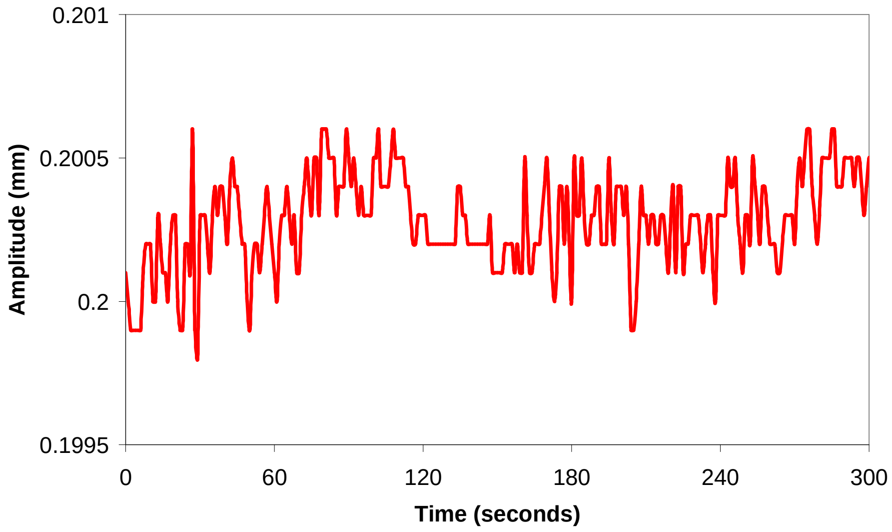


Figure 5 Signal to noise in N15000 silicone fluid at 0.20 mm amplitude (pk to pk)

The scale on the left shows that the level of noise is in the region of 0.5 µm at 0.20 mm amplitude. This exceptionally low level of noise is a considerable aid to data analysis.

It is perhaps worth a mention that eliminating secondary mechanical vibrations played a significant part in delivering this level of performance. Hence operatives are advised not to put them back! Physical disturbance (tapping the bench, etc.) can generate spikes on the output trace. Getting the best out of the instrument is just simple housekeeping. CureRod A will run perfectly well on any stable surface, provided this is free of external vibrations. No dedicated vibration isolation is required – Figure 5 was generated on an open bench.

The Amplitude Cure Profile

As has already been stated, the amplitude (responding to viscous drag) falls progressively with increasing cure. This response provides a continuous profile of cure.

The following examples (Figs 6-9) show the amplitude profiles for a section of different cures. All were produced using data exported (from the Pico software) into Excel.

Figure 6 shows the probe amplitude and sample temperature for a range of different systems. Included here are: epoxy, polyurethane, silicone and unsaturated polyester. It is perhaps remarkable to see such a compilation, as the systems differ in so many ways (generating products from soft elastomers to hard plastics and by step- or chain-reactions). It is a testament to the instrument that none presented any problems in monitoring. All were recorded in crown caps held in place only by a magnet

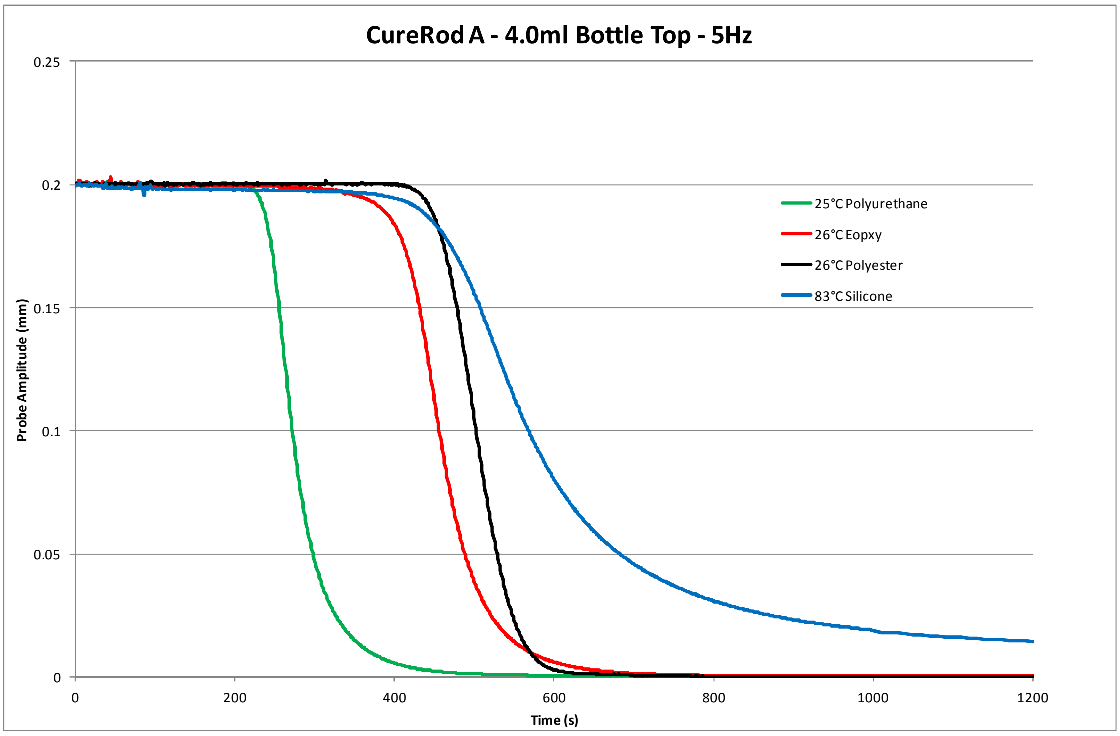


Figure 6 Amplitude profiles for epoxy, polyurethane, silicone and unsaturated polyester cures

The magnetic sample location can be seen to work well. The epoxy and unsaturated polyester both set solid, which means the rod is brought to a standstill (i.e. amplitude zero). The noise levels do not change – the whole system locks solid and the magnet holds firm.

Yet there are no difficulties with sample removal. Once the rod is split (at the sleeve coupling), the sample and the embedded rod can be easily slid away from the magnet. The whole sample-rod assembly is designed to be completely disposable, so a firmly embedded rod is no problem.

CureRod A is designed to accept samples of different sizes – and can even accept a sample that changes size during cure. Figure 7 shows the cure profiles for a rigid (water blown) PU foam, in this case for a 30 g sample in a large plastic beaker and expanding to about a litre of product. This is still recorded using magnetic location. A steel washer was dropped into the base of the beaker (Fig 1) to hold the beaker in place. The arrangement worked well – this was a rigid foam and the system set solid.

For this polyurethane foam monitoring, the instrument was equipped with an optical distance sensor (non-standard) to record the rise. Thus three simultaneous profiles of cure are recorded: amplitude, temperature and rise.

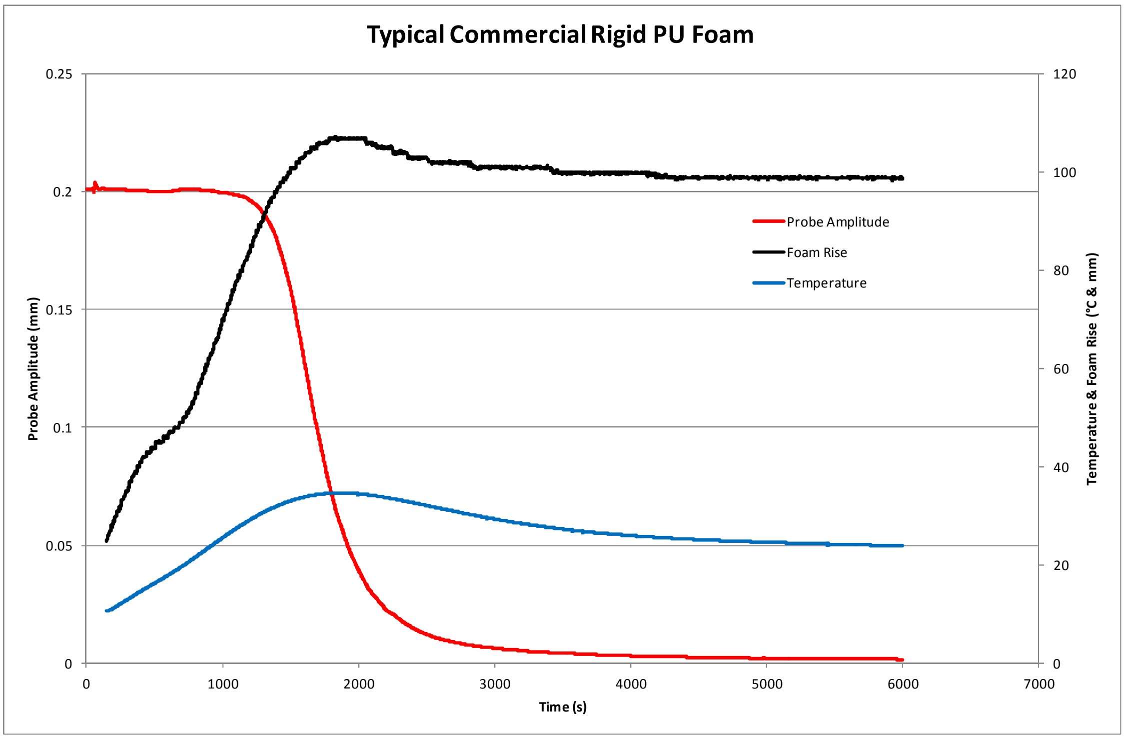


Figure 7 Amplitude, rise and temperature profiles for water-blown rigid PU foam

Effect of Scale and Temperature

CureRod A was designed from the outset to provide the freedom to explore different sample sizes. The output signal should not be affected by sample mass and length of rod immersion has only a limited effect on the response. Thus provided the same diameter rod is used in each case, and that close proximity with the base is avoided (>1.5 mm clearance), then any differences in amplitude profile should purely reflect any differences in cure.

Figure 8 below shows the effect of scale on a typical PU elastomer cure. There are three cures, all the same formulation and all monitored using a 4 mm carbon fibre rod. All three were tested in plastic beakers (with steel washers added for magnetic location) and the sample loadings were: 25, 50 and 100 ml. All the cures started at ambient temperature and both the probe and thermocouple were located close to the geometric centre of each sample.

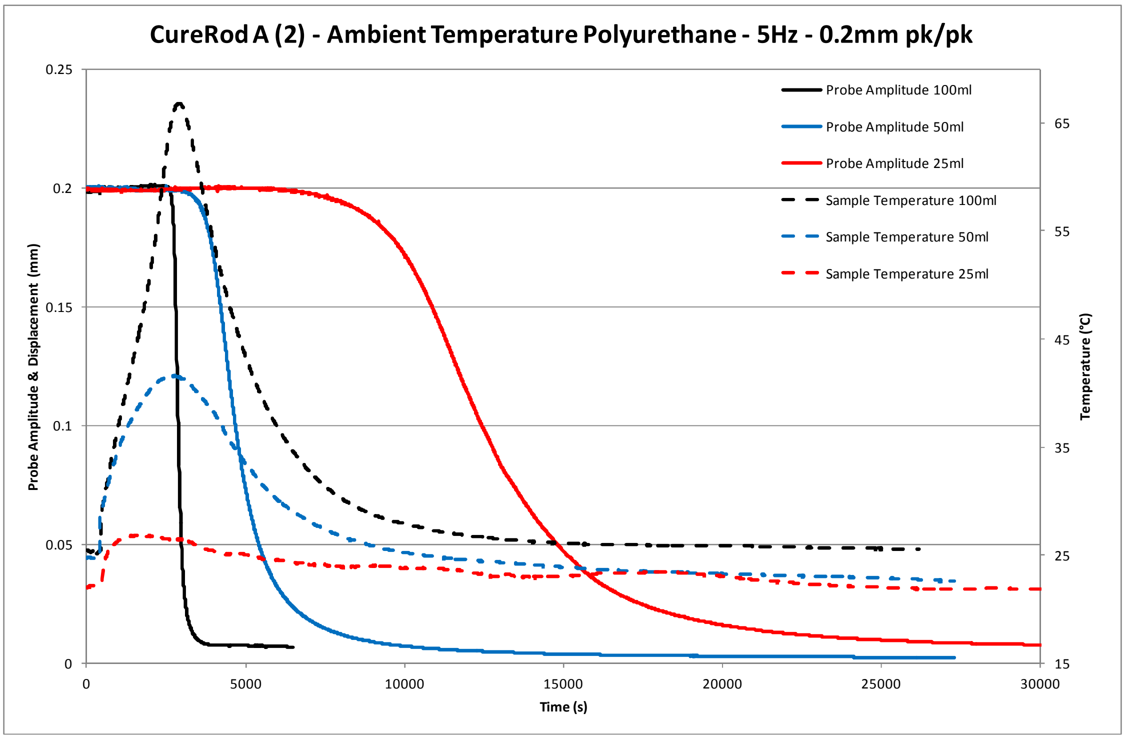


Figure 8 Amplitude & temperature profiles for three different amounts of PU

The effect of scale is quite striking – the larger the sample here, the (much) faster the cure. The cure in the 100 ml sample is virtually complete within an hour, whilst that in the 25 ml sample had barely started in twice that time. The difference is down to temperature, as can be seen in the figure. The exotherm in the 100 ml sample generates a peak temperature of over 65°C whereas that in the 25 ml sample managed an uplift of barely 5°C.

Of course the effect of temperature on cure (or any chemical reaction) is quite marked. This can be seen in Figure 9, where the same silicone elastomer formulation was heated to different temperatures – all in the (4 ml) bottle cap. The time is taken from when the sample was introduced into the (hot) bottle cap.

The cure rates vary enormously, from minutes to hours. All were recorded without changing the sampling rate at the data-logger (1 Hz). Even the longest of these cures (48 hours for the 26°C) presents no problems here. It is not always easy to predict the duration of a cure, and a capability to record over extended cure times is an important feature of CureRod A.

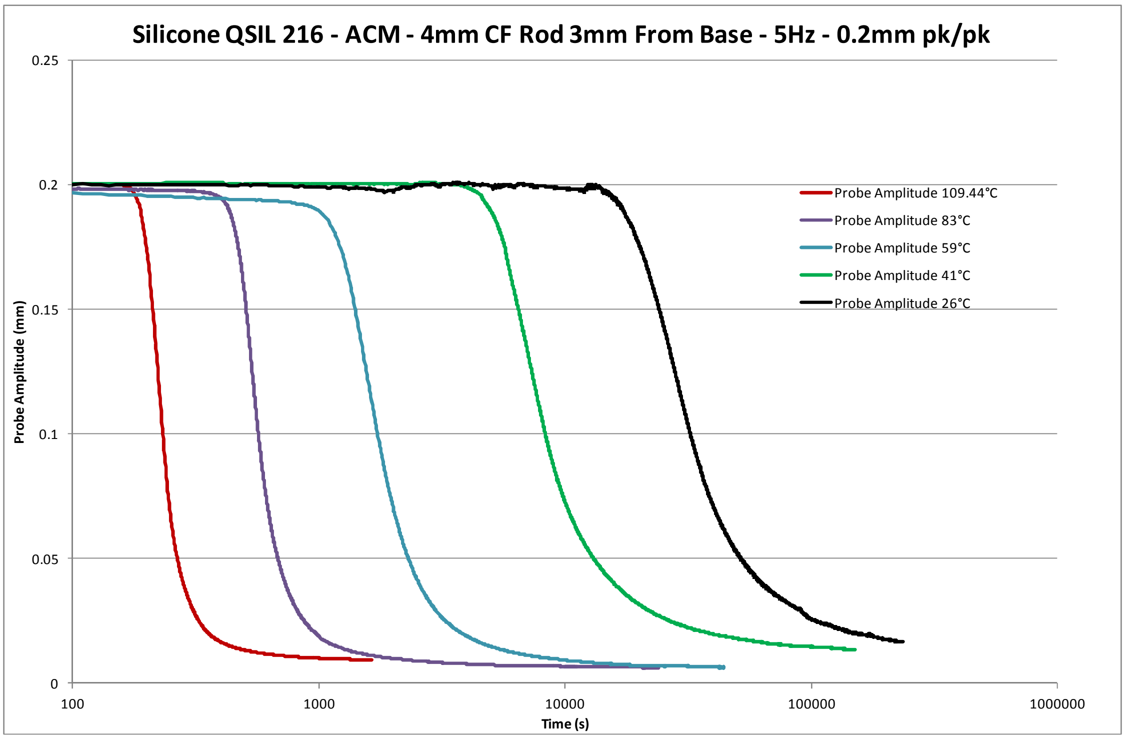


Figure 9 Amplitude profiles for silicone cures at different temperatures

These cures were all obtained on separate occasions, and the usual facilities for data storage and retrieval mean that the data can be brought together for collective analysis. Here the opportunity is taken to convert to a log time scale so that the whole range of cures can be recorded on a single graph.

It is the facility to lay traces alongside one another in this way which is especially advantageous. Differences are all the clearer when visual comparisons can be made. This is a routine capability when the instrument is computer compatible. In these few examples, three of the figures contained multiple amplitude profiles.

CureRod A opens the door to a host of different comparisons, allowing the exploration of ingredient, formulation, scale or temperature effects. Indeed, scale proves to be a most important effect. Thus two supposedly identical cures may differ enormously in rate, since:

- they may share the same formulation,
- but they may not share the same thermal history.

The effect of scale is the effect of exotherm temperature.

Summary

CureRod A works to established principles and tracks a curing liquid by monitoring the damping of an (oscillating) embedded rod.

- It delivers a continuous cure profile which is a fingerprint of cure.

It delivers low noise outputs, in real time, which can be exported to spreadsheets and databases so that the profiles:

- can be stored and retrieved as required,
- replotted in different formats,
- overlaid for detailed comparison.

CureRod A breaks new ground in the simplicity of the sample system

- It uses a plain rod in an open vessel – completely disposable.

It works at a fixed frequency well below resonance to eliminate sample mass effects and

- It uses magnetic sample location free from the limitations of mechanical fixings.

CureRod A can accommodate:

- liquids which cure to elastomers (soft or hard) or set completely solid,
- systems which cure in minutes, hours or even days,
- formulations which foam.

A design requirement from the outset was a capability to work with different sizes of sample. This brief has been achieved and the results are a revelation.

- Scale has a huge effect on cure.
- The effect of scale is the effect of temperature.

References

1. B G Willoughby, K W Scott and D Hands, “Cure Rationalisation using a Vibrating Needle Curemeter”, presented at the RAPRA International Conference “Flow and Cure of Polymers - Measurement and Control”, Moat House Hotel, Telford, March 22-23, 1990.

2. E A Sheard and B G Willoughby, *Adhesives Age*, 1997, **40(3)**, 44-49.