

A DIFFERENT ANGLE ON CURE MONITORING

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ABSTRACT

The options for cure monitoring may be limited to the choice of single-point (gel time) measurements, or continuous outputs which can sometimes conspire against simple rationalisation. This paper explores the middle ground – a simplified treatment of cure to generate a diagnostic profile based on degree of elasticity in the sample. A user-friendly instrument which can provide such a profile is described together with examples of its application to cast elastomers.

INTRODUCTION

Some form of monitoring is essential to a proper understanding and control of cure, but the choice of method is not always straightforward. On the one hand there are single point instruments (gel timers) which are easy to operate and understand but which offer only a limited insight into the process of cure. On the other hand there are continuous monitoring techniques which can reveal much about cure but which can require skill in interpretation. Indeed, they may often require high levels of specialization and present pitfalls for the unwary.

A case in point is where a parameter linked to molecular mobility is used to track the progress of cure. Such a parameter might be electrical (e.g. resistivity) or rheological (e.g. viscosity or modulus). The expectation is that such mobility will reduce with increasing cure, but molecular mobility is not only a function of cure. For example, molecular mobility depends on backbone type and on temperature, presenting difficulties when making comparisons between different polymer types and between cures at different temperatures.

A classic case is the initial fall in modulus in the rheometer trace for a traditional rubber vulcanization (Figure 1).

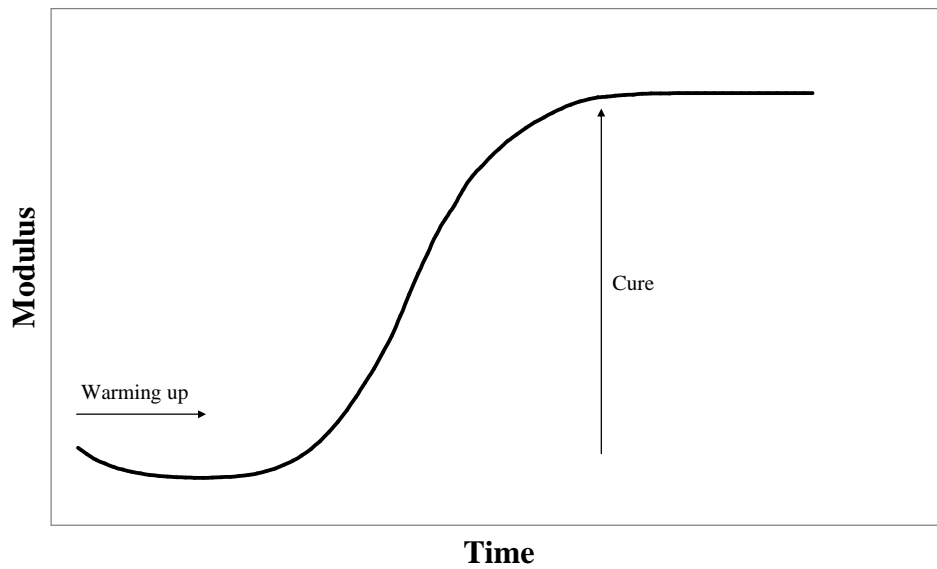


Figure 1 Typical rheometer trace for conventional rubber vulcanization

While this initial fall is clearly due to the effect of bringing the sample to the vulcanization temperature, it has not stopped technologists from assuming that no cure is occurring over this time and assigning an induction period to the vulcanization. Nor has it stopped rubber chemists from incorporating an induction step in their chemical reaction schemes.

No such induction step figures in established mechanisms for two-part polyurethane cures, yet this same effect can be seen in monitoring of an elevated temperature PU cure where a response linked to molecular mobility is being followed. For example, the dielectric constant of polymers can increase markedly with temperature. A typical elevated temperature cure of a PU elastomer may present a dielectric profile as shown in Figure 2.

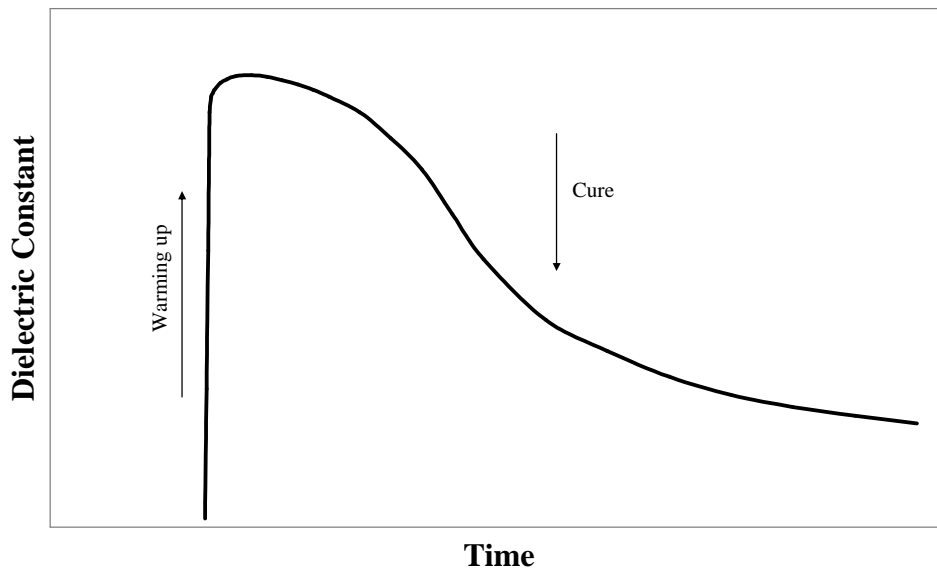


Figure 2 Typical dielectric profile for an elevated temp. PU elastomer cure

The opposing effects of heating up and cure, mean that the cure profile by dielectric constant takes the form of a peak. While undoubtedly a useful fingerprint of cure, it does not present a straightforward picture for the casual user. Indeed, if the cure is sufficiently active to develop a significant exotherm, then the heat generated has the potential to moderate the dielectric response due to cure. To the uninitiated, a faster cure may not be seen as such. As with the rheometer trace in Figure 1, there are pitfalls for the unwary.

The point to be made here is that a response which is not unique to the development of cure requires value judgements to be made on the data obtained. Is a particular feature in the response/time trace a direct consequence of the cure or not?

This is not an idle question, as, the more that is asked of the cure profile, then the more such value judgements come into play. Consider Figure 3 which presents actual data on a PU elastomer cure recorded as a dual output profile [1]. This cure was monitored at 40°C on a cone-and-plate rheometer (StressTech HR©) at a frequency of 1 Hz. The dynamic modulus is the response being tracked, but, in this case, it is resolved into its in-phase (storage) and out-of-phase (loss) components. For reference, the formulation was that of an MDI prepolymer reacted with a blend of difunctional and trifunctional polyether polyols.

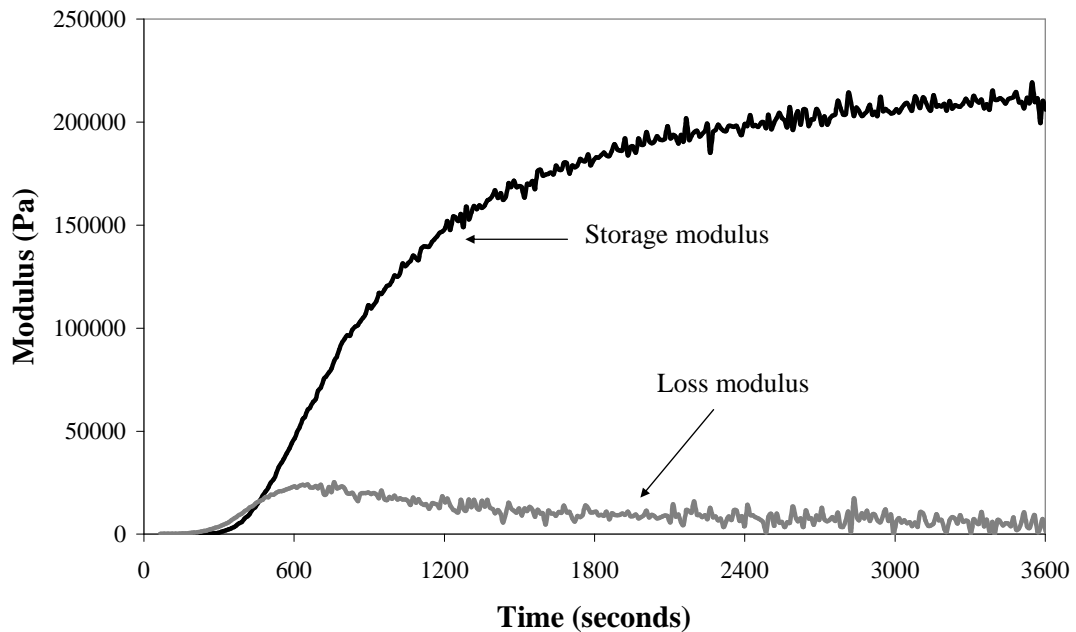


Figure 3 Oscillating rheometer trace for PU elastomer cure

Both traces have significance in the development of cure. For example, the crossover point at around 400 seconds is conventionally taken as the gel time. However the loss modulus passes through a maximum at around 600 seconds and then falls back in value with increasing cure time. Is this a real effect in cure or an artifact of some other change?

The fact is that it is indeed real, although recognizing its significance will require some understanding of network theory. Many cures pass through a maximum in the damping response as a consequence of the type of molecular network developed [2]. This behavior can be of diagnostic value in the cure profiling of both solid [3] and cellular PU [4], but this level of detail may be beyond the requirements of basic cure screening.

For the development technologist, the detail may prove indispensable, but for those in routine testing, a dual-output profile may be just one trace too many. But what is the alternative? Is there an option for continuous cure profiling which is simple and straightforward, even for the non-specialist? This paper seeks to answer that question.

BASIC REQUIREMENTS

Before seeking to answer the above questions, it will be useful to consider what would be required of a simple cure-profiling technique. At the most basic level, it might be that the technique should offer the operational simplicity of a gel timer with the ability to track the cure before and after gelation. If so, then this identifies one prime requirement – that the technique should uniquely identify the gel time. Gel time is a critically important

point in the cure – it represents the transition between liquid and solid character, otherwise known as the *no-flow condition*.

It must also provide a continuous profile of cure over a diagnostically relevant region so that user-defined points can be assigned to the trace. For example, these can include:

- (i) pot life and work life before gelation,
- (ii) tack-free time or demold time after gelation.

Pot life, work life, gel time and tack-free time are of special relevance for those concerned with cast elastomer cures, while gel time and demold time are of particular importance for those involved with molded systems. Gel time is critical to both.

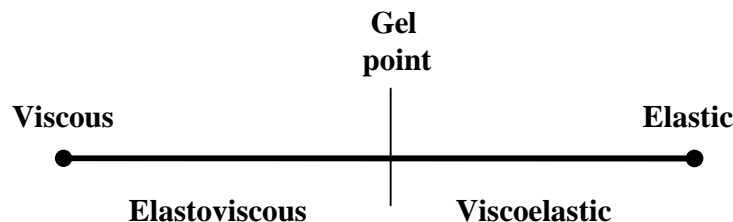
A further requirement is that the response should not be subject to other influences than cure. The interpretation should be straightforward – there should be no surprises (other than those of the cure). Thus the development and progress of cure should always cause the response to move in the same direction.

To meet these requirements requires a back-to-basics consideration of the nature of cure. It is a chemical process, but the specific reactions are not unique to cure. For example an isocyanate-alcohol reaction may give little or no cure at all if the requirements of functionality or stoichiometry are not met. Molecular mobility changes as a consequence of cure, but, as has been discussed earlier, such mobility is subject to other influences as well.

In chemical terms, cure is perceived as crosslinking. This process suppresses viscous flow and enhances elastic character. In its most basic terms, cure is the transition from viscous to elastic character. So is this how cure can be measured?

CURE AS DEGREE OF ELASTICITY

If cure is treated as the change from liquid (viscous) to solid (elastic) character, then the process of cure can be thought of as a continuous evolution in properties as set out below.



The degree of cure can be thought of as the extent of elasticity in the system at the stage of interest – i.e. extending from 0% in a purely viscous material to 100% in a purely

elastic material. Conceptually the gel point (the half-way-house in this change) would occupy the 50:50 position – i.e. at 50% elasticity.

A scale of this type is possible if the phase shift (in oscillation) is the diagnostic variable. In this context, the phase shift is that between stress and strain under sinusoidal oscillation. If the material has any viscous character, then the strain will fall out of phase with the stress (Fig 4).

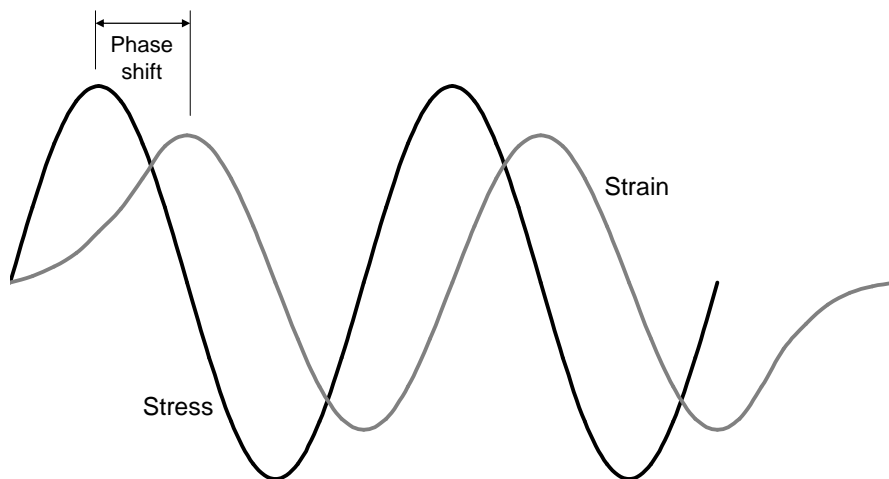


Figure 4 Phase shift in a sinusoidal oscillation

How this phase difference arises is set out in the Appendix. This shift is measured as the phase angle (δ). Phase angle is routinely measured in oscillating rheometry and provides the basis for the resolution of dynamic modulus (G^*) into its in-phase and (90°) out-of-phase components. This vectorial treatment gives the familiar storage modulus (G') and loss modulus (G'') as shown in Figure 5.

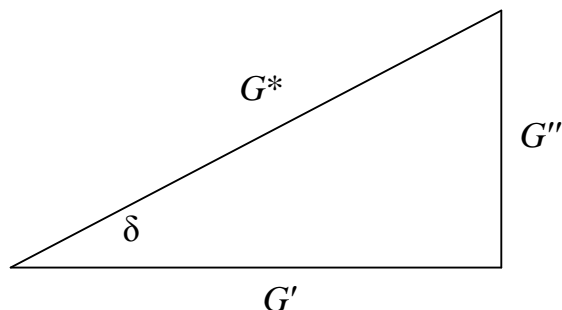


Figure 5 Vectorial resolution of modulus in sinusoidal deformation

It follows from Figure 5 that if $\delta = 0^\circ$, then $G' = G^*$ and G'' is zero - i.e. there is no mechanical loss (damping). Conversely, if $\delta = 90^\circ$, then $G'' = G^*$ and G' is zero - i.e. there is no energy storage and the system is entirely damping. Phase angle is uniquely diagnostic of the degree of elasticity in the system. The situation may be summarised as:

- for a purely viscous liquid, stress and strain are 90° out of phase, i.e. $\delta = 90^\circ$
- for an elastic solid, stress and strain are in phase, i.e. $\delta = 0^\circ$
- at intermediate states, $90 > \delta > 0^\circ$
- at the gel point, $\delta = 45^\circ$

For a curing system moving from a liquid to a solid, δ reduces over time. This offers the prospect of a linear scale of cure (elasticity) which has the gel point at the half-way stage. If δ is used to define cure, then the fractional degree of cure (α_t) at any time t is given by,

$$\alpha_t = (90 - \delta_t)/90 \quad (1)$$

where α_t is on a scale 0-1, and δ_t is phase angle at time t .

For percentage cure this expression becomes,

$$\% \text{ cure} = (90 - \delta_t)/0.9 \quad (2)$$

and the gel point is at 50% cure.

Absolute v Relative Scales of Cure

Equations 1 & 2, based on phase angle, give an absolute scale of cure - since the maximum possible range is predetermined (i.e. a range of 90°). This is not possible for a scale based on molecular mobility as there are no meaningful limits which apply in all cases. The practice here is to derive % cure in relative terms - e.g. for in-phase modulus as set out below,

$$\% \text{ cure} = 100(G'_t - G'_0)/(G'_\infty - G'_0) \quad (3)$$

where G'_0 is the storage modulus at the start of cure,
 G'_∞ the modulus at the end, and G'_t the modulus at time t .

Equation 3 gives a scale which is relative to the initial and final modulus values for *that* cure only. Indeed the scale is hostage to an accurate value of final modulus and the possible need to run the monitoring for extended times to obtain this. Furthermore, the percentage cure cannot be determined until this final value is obtained - i.e. % cure data is not accessible in real time.

Phase angle monitoring provides not only an absolute scale of cure, but also percentage cure in real time.

The example given in Figure 3 provides scope for comparing percentage cure based on phase angle (eqn. 2) and modulus (eqn. 3) for a curing polyurethane. The comparison is shown in Figure 6.

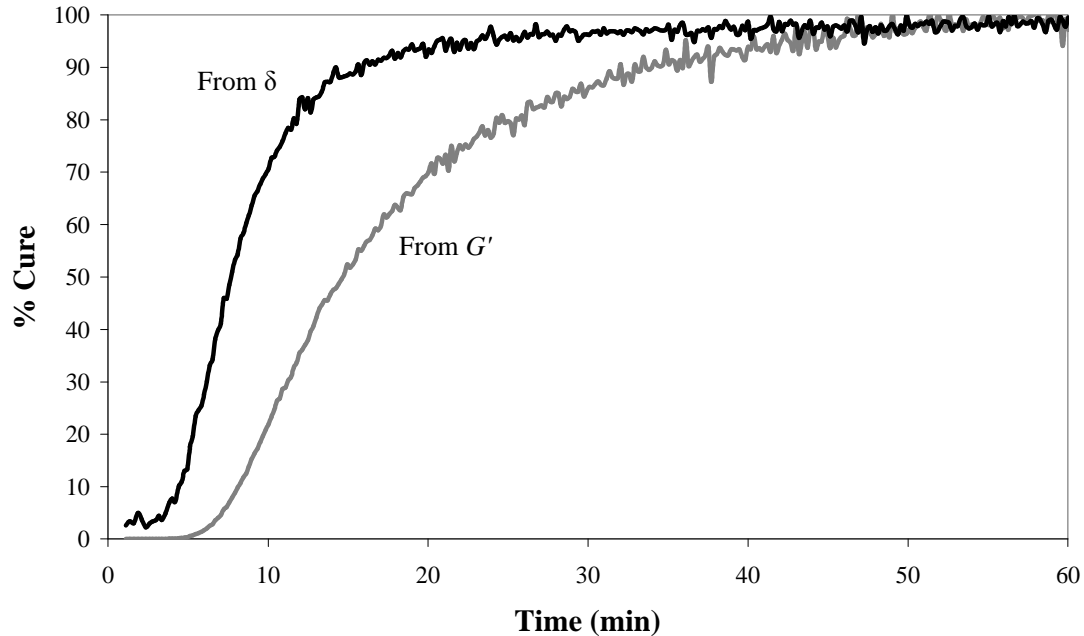


Figure 6 Percentage cure from eqns. 2 & 3 (blue) for a PU elastomer cure

One clear difference between these traces is the earlier response of the trace derived from phase angle. The gel time (at around 6 min 40 sec) occurs at less than 5% cure based on G' . A scale of cure based on G' would not therefore give useful discrimination of pre-gelation events like pot life or work life. The scale of cure based on δ offers a more practical scale for process control.

Thus a scale of cure based on phase angle is simple, rational and readily useful. Phase angle is routinely measured in oscillating rheometry, but unfortunately such instrumentation is expensive and requires specialist operation. Furthermore, materials which set in the sample cell are not always welcomed. Is there a simpler, cheaper and more robust option?

THE NEW INSTRUMENT

Any device for measuring compliance in a sample presents a challenge as it is essential to ensure that the compliance is in designed elements of the device and not in unintentional components. Not surprisingly, rheometers for polymers are substantial devices. However, the expense is not in their bulk but in their precision and instrumental sophistication. A notable feature of these devices is the requirement to measure the

forces transmitted through samples of defined geometry often at exceptionally low levels of shear. These demands arise from the need to determine reliable values of dynamic modulus and viscosity.

While the *designed compliance* requirement is universal, other demands may be relaxed somewhat if modulus or viscosity are not required outputs. Thus a curemeter measuring only phase angle (a *Phase-Shift Curemeter*) does not need all the elements of high performance rheometers. Indeed, a quite simple device is possible. Figure 7 presents a schematic layout of such a device.

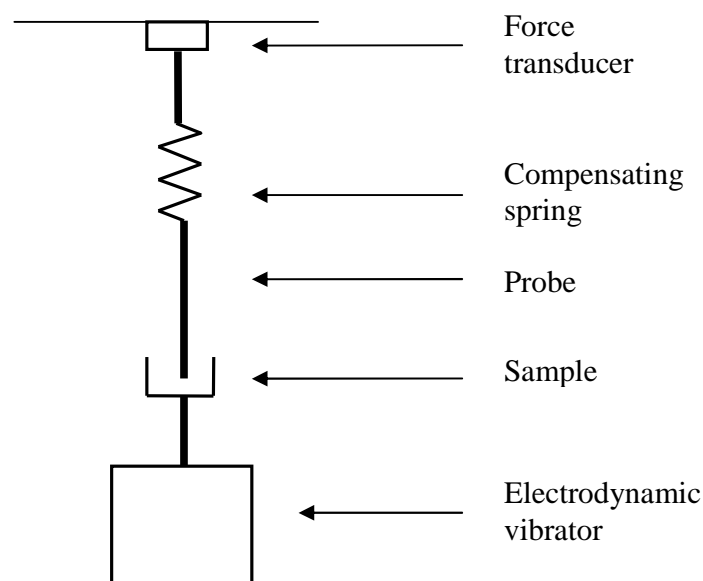


Figure 7 Schematic layout of a Phase-Shift Curemeter

The basic operational principle is that a sample in a cup mounted on a vibrator is caused to oscillate in a vertical plane and the motion is sensed by the force exerted on a probe embedded in the sample. The changing force on the probe is compared with the driving signal to the vibrator and any phase shift is recorded. Ideally the probe should not move at all, although this is impossible as the response to force must be as a displacement - however miniscule. To minimize any displacement, the sensing elements must be as stiff as is practical.

However, some compliance is essential to protect the force transducer if the sample sets hard. For this reason a compensating spring is mounted between the probe and the transducer. The optimized configuration should give a reasonably accurate phase angle measurement while enabling an epoxy to cure without damage. The unit described here is shown in Plate 1.



Plate 1 Prototype Phase-Shift Curemeter

For any sample with the potential to set hard, the sample cup and probe assembly must be disposable. Clearly this assembly must be inexpensive and readily demountable. In the Phase-Shift Curemeter, a magnet locates the sample cup. A small steel cup in the form of a (beer) bottle top provides a cheap and readily available sample holder. A close-up of this arrangement is shown in Plates 2a and 2b.

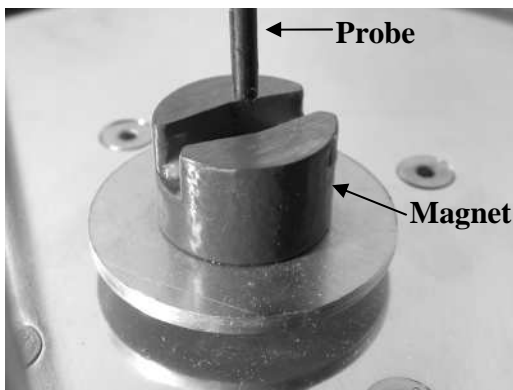


Plate 2a Magnet & probe tip

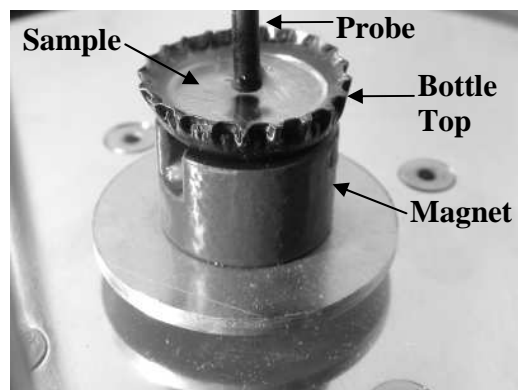


Plate 2b Assembly with bottle top & sample

Alternatively, paper or plastic cups can be used if a steel washer is dropped inside first. This arrangement is shown in Plate 3.

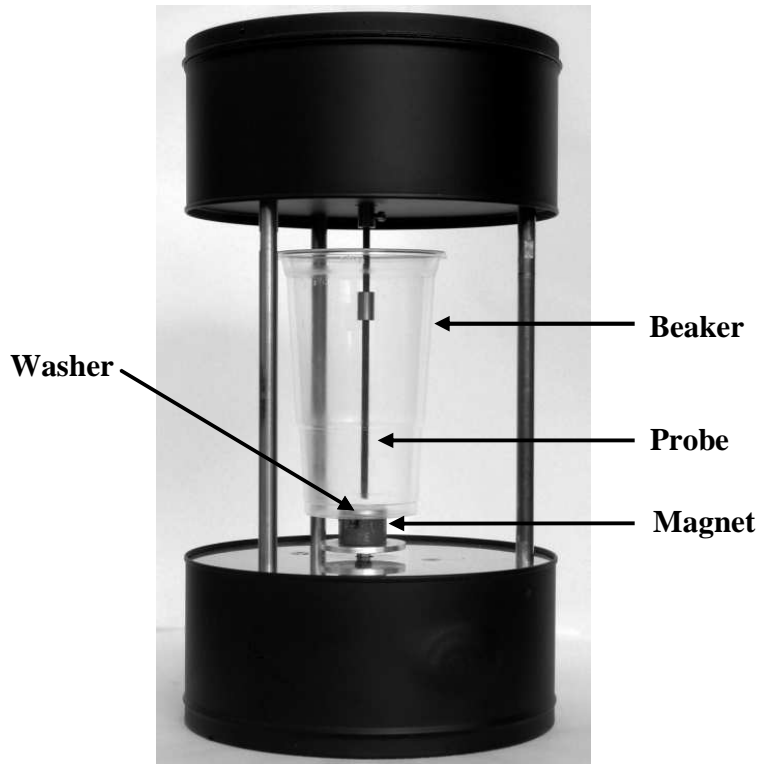


Plate 3 Plastic beaker retained by a steel washer dropped inside it

The prototype has successfully monitored an epoxy cure while giving good phase-angle data on reference liquids. For example, the measured phase angle on a (viscosity standard) silicone fluid in the Newtonian region was within 2° of the theoretical 90° value. The availability of such standard fluids allows for routine calibration of the unit.

Operating Frequency

The reference above to a fluid *in the Newtonian region* introduces the question of operating frequency. As far as polymers are concerned, they cannot be simply categorized as either viscous (Newtonian) or viscoelastic (non-Newtonian). They can show both characteristics depending on the applied frequency. The higher that frequency, the more likely is elastic character seen. Thus, to observe purely viscous behavior, the polymer must be of an appropriate type and in the right molecular weight range – and subjected to a suitably low vibrational frequency.

This raises issues with respect to the appropriate frequency for testing in oscillation rheometry. The ASTM method for cure monitoring by dynamic methods (D4473-03)

simply advises in favor of the low frequencies for more definitive cure-behavior monitoring and sets an advisory upper limit of 1.5 Hz [5]. Of course very low frequencies will limit the ability to track rapid cures and it is recognized that selection of the frequency for cure monitoring will ultimately be a compromise [6]. Such considerations led to a choice of 0.5 Hz for the Rubber Process Analyzer when used in vulcanization monitoring [6, 7].

Even lower frequencies were tried (e.g. down to 2 or 3 cycles per min) in some of the earliest rubber curemeters. For the trials of the Phase-Shift Curemeter reported here, the operating frequencies were 0.33 and 0.5 Hz (20 & 30 cycles per min).

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For these studies, the sample chamber was a bottle top and the probe was simply a length of (stiff) rod. Given its proximity to a strong magnet, the rod must be made of non-magnetic material – for example, aluminium, brass or CFRP. In the studies reported here, 4 mm diameter CFRP rod was used.

Figure 8 shows the percentage cure versus time at ambient temperature for the cure of a 75 Shore A elastomer based on an MDI prepolymer. The sample cup was a bottle top and the cures were monitored at either 0.33 or 0.5 Hz.

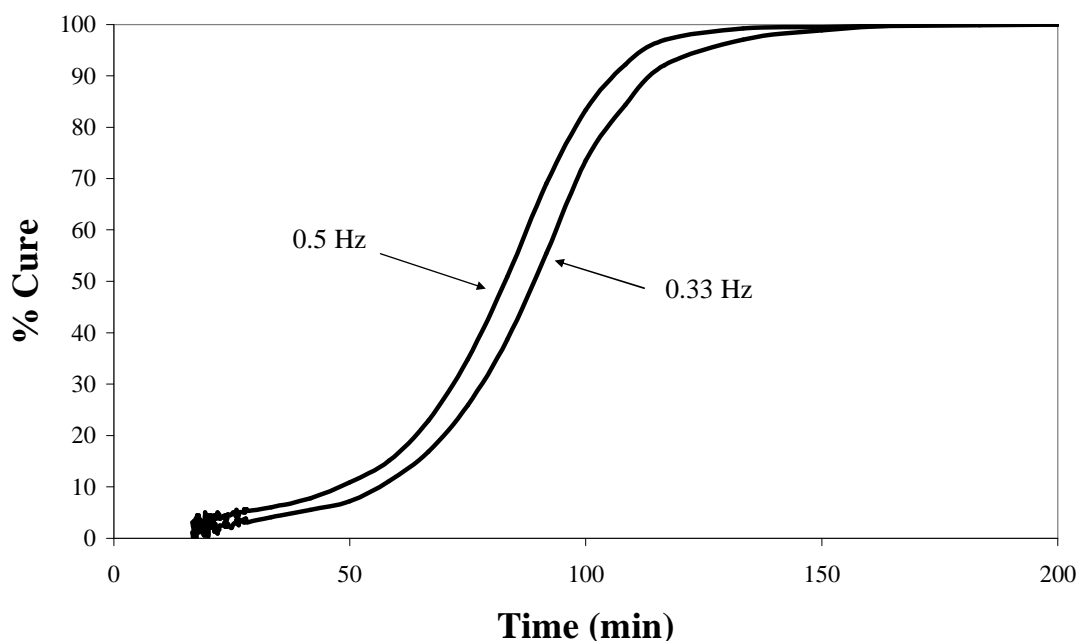


Figure 8 Percentage cure versus time for PU elastomer at 0.33 and 0.5 Hz

Although the frequencies are quite close, there is still a difference between the traces. This may reflect, in part, batch-to-batch variability in two hand-mixed samples, although the trend is consistent with the effect of frequency on elasticity response – i.e. the higher the frequency, the more elastic the sample. Thus the higher the monitoring frequency, the faster the apparent cure. The ASTM guidance on frequency is therefore not surprising.

One consequence is two slightly difference gel times: 83 min at 0.5 Hz and 89 min at 0.33 Hz.

This highlights the importance of running with a single operating frequency when making comparisons of system or process variables.

The force on the probe is lowest at the lowest viscosities and some noise is evident at the earliest stages of the cure. The origin of this noise is being investigated.

Elevated Temperature Cures

Elevated temperatures present a special challenge in any cure monitoring. Ensuring that the whole sample is at the required temperature places constraints on sample size and the method of heating. A thin film with heating on both faces is one solution.

While this is the approach of the rubber rheometers, it is not practical for hard-setting samples unless a completely disposable sample chamber is used. This is possible, but it is neither simple nor cheap.

The use of a bottle top for the sample ensures that the size is suitably small and provides a container of good thermal conductivity. The exposed sample surface may be problematic – but not if the sample is placed in an oven. The Phase-Shift Curemeter described here is designed to be used in an oven for elevated temperature cures. In this case, the whole instrument (not the control box) is placed in an oven and allowed to reach the required temperature before the sample is added.

In the same manner, the instrument may be placed in a freezer or refrigerator for sub-ambient cures.

Figure 9 shows the cure of the 75 Shore A PU elastomer in an 80°C oven monitored at 0.33 Hz. This is the same formulation as used in the ambient temperature cures and the much faster cure is evident by comparison with Figure 8. At 80°C, the gel time is only 5 minutes and 15 seconds.

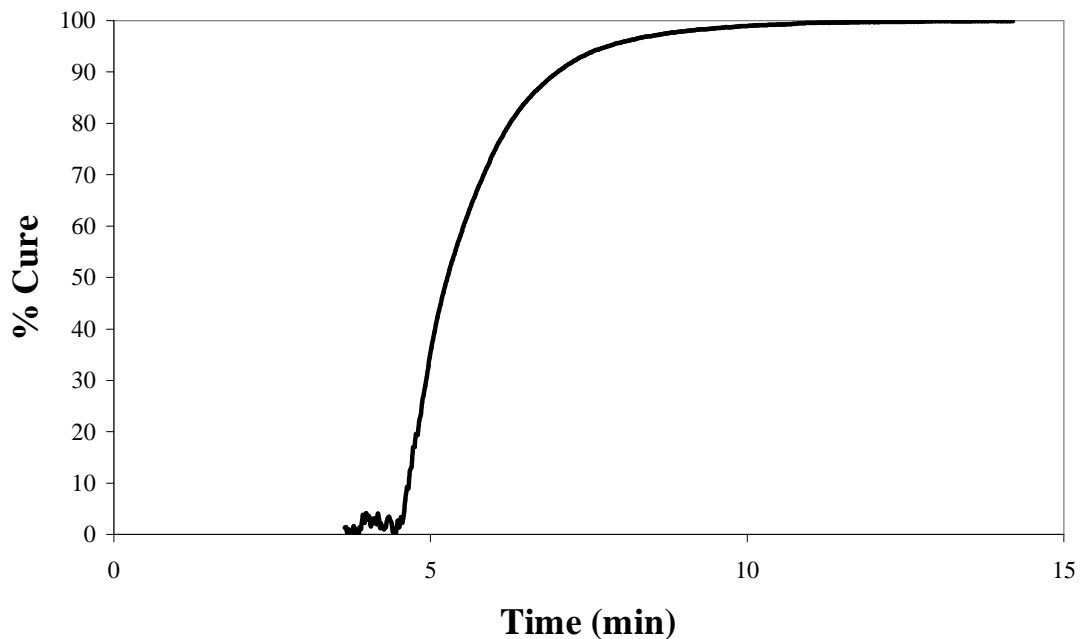


Figure 9 Percentage cure versus time for PU elastomer at 80°C (0.33 Hz)

CONCLUSIONS

The process of cure is neither easy to understand nor easy to monitor. It is tempting to turn to a gel timer for simple single-point measure, but this is not the only option if simplicity is the requirement. This paper explores the progress of cure as the development of elasticity in the sample, and shows how this provides a scale of cure which is simple, rational and practically useful.

The parameter to be monitored is phase angle and this can be achieved without resorting to exotic instrumentation. A straightforward and user-friendly instrument is described which can track the changing phase angle during the process of cure. It uses an inexpensive disposable sample cell and the instrument can be placed in an oven (or freezer) for non-ambient cure monitoring.

Importantly a scale of cure based on phase angle put gelation into its proper context. The gel point is the half-way house between liquid and solid and this occurs at 50% cure on a phase-angle scale.

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APPENDIX

Phase Difference under Sinusoidal Oscillation

The phase angle of interest here is that between stress and strain in an oscillating system.

How this phase difference arises can be seen from the basic relationships between stress and strain for elastic and viscous systems. For a purely elastic material, stress is proportional to strain,

$$\sigma = G\gamma$$

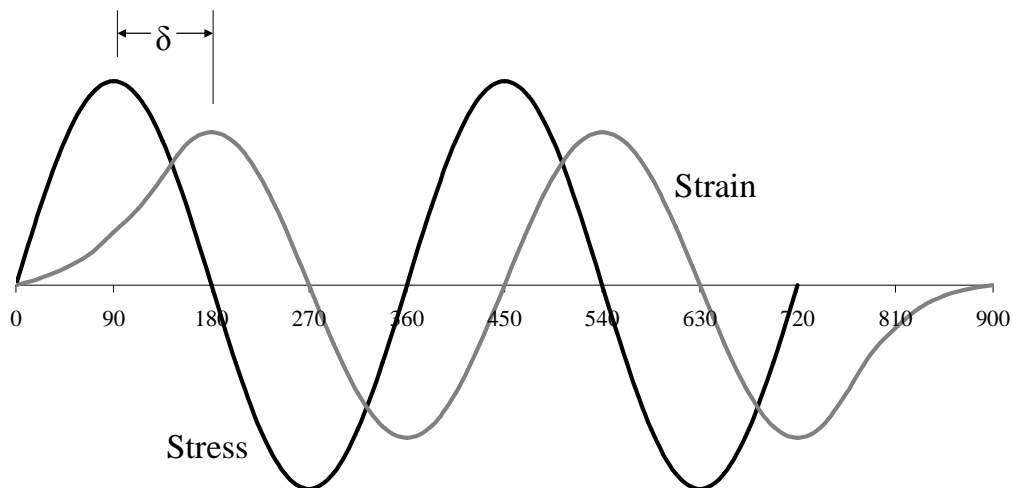
where σ is the applied stress, γ the resultant strain and G the elastic modulus.

However, for a purely viscous material, stress is proportional to the rate of strain,

$$\sigma = \eta d\gamma/dt$$

where η is the coefficient of viscosity.

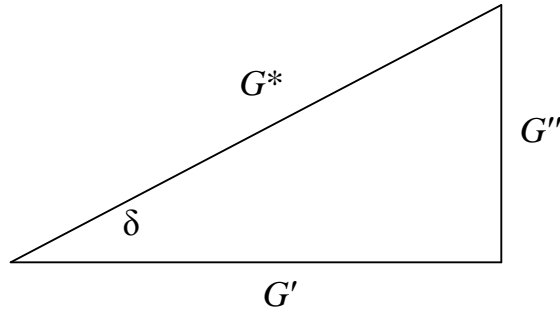
In a sinusoidal vibration, the maximum and minimum values are displaced from the maximum and minimum rates of change. Thus for a purely viscous liquid, the strain lags the stress by 90° .



For a purely viscous system, the maximum stress correlates with the maximum rate of strain so that the maximum on the stress trace corresponds with the maximum slope on the strain trace.

For a purely elastic material, stress and strain are completely in phase (i.e. the phase difference is 0°). For a material of intermediate character, stress and strain are out of phase, and the phase difference (*phase angle*), will lie between zero and 90° .

For a given value of phase angle (δ), the ratio between stress and strain can be resolved into in-phase and (90°) out-of-phase components. This vectoral treatment gives the familiar storage modulus (G') and loss modulus (G'') as shown below.



In this treatment, the phase angle is given by,

$$\tan \delta = G''/G'$$

Which gives the gel time (i.e. $G'' = G'$) when $\tan \delta$ equals unity and δ is 45° .

Thus for a scale of cure based on phase angle, the gelation is the mid-point of the cure. Such a scale can be equated to the development of elasticity in the sample. This provides the basis for a rational scale of cure which assigns a defined value to the gel point.

The phase angle decreases during cure, and the degree of cure at any time t , α_t , can be expressed as,

$$\alpha_t = (\delta_0 - \delta_t)/(\delta_0 - \delta_\infty)$$

At zero cure, the phase angle (δ_0) is 90° and at full cure it (δ_∞) is zero, hence substitutions can be made in eqn 10 to give,

$$\alpha_t = (90 - \delta_t)/90$$

Or in percentage terms,

$$\% \text{ cure} = (90 - \delta_t)/0.9$$

These final two expressions no longer include δ_0 or δ_∞ and thus the degree of cure can be obtained at any time without reference to initial or final values of the specific system under study. This places degree of cure on an absolute footing with a capability to assign values in real time.