

**UNDERSTANDING CURE WITH THE
SCANNING VIBRATING NEEDLE CUREMETER
(SCANNING VNC)**

(RTL/2844)

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CONTENTS

1. INTRODUCTION.....	1
2. MONITORING LIQUID POLYMER CURES	3
2.1 Elasticity and Modulus	3
2.2 Modulus and Cure.....	3
2.3 Fluid Flow and Viscosity	4
2.4 Oscillatory Measurements.....	5
2.5 Phase Angle (δ).....	8
2.6 Summary of Changes During Cure	15
2.7 Practical Cure Monitoring - The Rapra Scanning VNC	15
2.7.1 The Instrument.....	16
2.7.2 Amplitude Attenuation for the Scanning VNC	19
2.7.3 Resonance Frequency Effects	26
2.8 References.....	30
3. MONITORING THE CURE OF THERMOSET RESINS WITH THE SCANNING VNC.....	31
3.1 Polyurethanes.....	33
3.2 Polysulphides	35
3.3 Silicones.....	36
3.4 Epoxy Cures	36
3.5 Unsaturated Polyester Resins.....	37
3.6 Visible Light Cure	38
3.7 PVC Plastics.....	38
3.8 Polyurethane Foams	40
3.9 Cure Monitoring of Thin Films	45
3.10 Comparison of Fixed Frequency Monitoring and Scanning Frequency Monitoring.....	45
3.11 Assessment of Cured Rubbers	47
3.12 Summary.....	48
3.13 References.....	48
INDEX	49

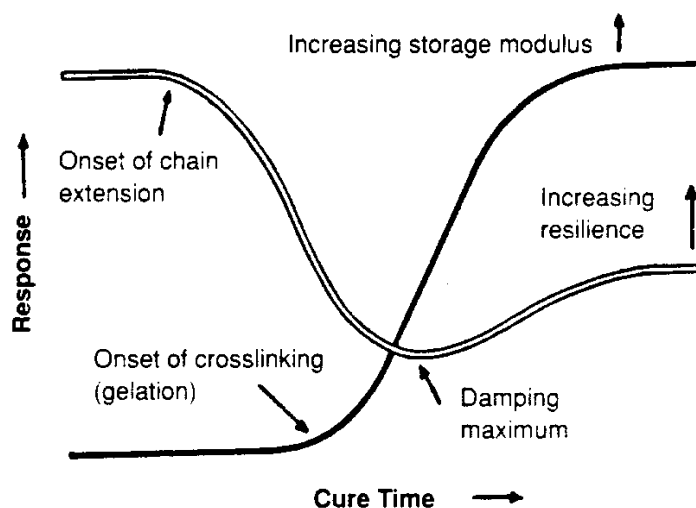
UNDERSTANDING CURE WITH THE SCANNING VIBRATING NEEDLE CUREMETER (SCANNING VNC)

1. INTRODUCTION

The Scanning Vibrating Needle Curemeter (SVNC) is a simple and robust instrument which is capable of providing a continuous profile of liquid polymer cures:

- for elastomeric systems up to the final stages of cure;
- for glassy systems, approaching the point of vitrification.

A continuous profile provides new levels of discrimination, releasing the technologist from the constraints of single point determinations. No longer need "gel point" be the sole focus of attention - a point in practical terms too long to define the working life of the uncured mix but too short to define demould time. Figure 1 shows the kind of



output obtained.

There are two continuous cure profiles giving complimentary information. What they mean with respect to the development of cure is discussed in more detail in Section 2 of this document.

Examples covering a diversity of cure profiles for cure systems are given Section 3.

All the examples are also provided as data files on the SVNC Program disk (Version 2.2) and can be displayed using the SVNC software - see "Operating Manual for the Scanning VNC" RTL/2843, Sections 5.5, 6.1.1.1 and 6.3 or "Description of a Demonstration Program for the Scanning Vibrating Needle Curemeter (Scanning VNC)" RTL/2846, Sections 4.1.1 and 4.2.

What is shown in Figure 1 are two outputs covering elastic (solid line) and damping responses. Together they show how fast cure is developing and what kind of product is obtained. They enable practical concepts of application time, work life, demould time, *etc.*, to be put into a coherent and recordable context.

In fact the standard software supplied with the SVNC allows for eighteen diagnostic points (including gel time) to be allocated for comparative purposes. Some can be selected entirely at the discretion of the user.

Reference to the "standard software" highlights a key feature of the SVNC in that it is a computer driven instrument - indeed the reader will soon realise it is only possible to operate this device in computer driven form. The sampling head is simple and robust - the sophistication is in the control. Yet developments in computers allow this control to be achieved with nothing more elaborate than a modern PC (386 or faster). Once the standard software is loaded, any IBM compatible PC of sufficient power can drive the SVNC. The control panel is even a display on the screen.

Integrating a computer into an instrument in this way obviates the need for a dedicated chart recorder - or for the storage and archiving of chart material. All recorded cure traces can be stored, and retrieved, as computer files. New data can be compared with old data directly on screen. Of course hard copies can be produced, as required, using conventional printers. Detail of the operation of the instrument are given in RTL/2843.

2. MONITORING LIQUID POLYMER CURES

During the cure of a liquid polymer, chain extension and crosslinking processes cause changes in the viscous and elastic properties of the polymer. Liquids which cure to solids are of major technological importance, providing structural materials (e.g. GRP), solid and foamed rubbers (e.g. PU, silicones), surface coatings and adhesives. Thus the reliable monitoring of these production processes is vital to effective process and product control, yet often little may be done bar a cursory single point determination (gel point). Whilst the technologist may recognise the importance of optimising application time, work life, etc., profiling cures has not reached the widespread acceptance that is seen in solid rubber processing.

The problem may reflect the major changes taking place with liquid polymer cures. These changes not only extend beyond the dynamic ranges of many measurement devices, they also challenge the technologist with respect to their understanding and rationalisation. Those seeking an up-to-date summary of network theory should consult Dusek¹ and the references listed therein.

However, familiarity with modern branching theory is not a pre-requisite to the understanding of liquid polymer cures, nor is access to expensive instrumentation a pre-requisite to monitoring them. This section explains in basic terms what changes are occurring during the cure and how the Scanning VNC can record them.

2.1 Elasticity and Modulus

A solid has a defined shape and an elastic solid is one which will revert to its original shape after any imposed distortion has been removed. The characteristic resistance to such distortion is the stiffness, or “modulus”, of the material.

Over the region where a solid displays ideal elastic behaviour, the resulting strain (γ) is directly proportional to the imposed stress (σ). Hence for example in simple shear

$$\sigma = G\gamma$$

where G is the shear modulus

2.2 Modulus and Cure

In rubbers, elastic behaviour results from a molecular architecture in which freely jointed chains are linked together at certain points (crosslinks). The restoring force against any imposed distortion arises from thermal motion and the drive to restore the equilibrium chain configuration. In the ideal elastic network where all molecular

segments can contribute to their restoring force (the so-called “Gaussian” condition), then shear modulus is directly proportional to crosslink density, *i.e.*

$$G = NkT$$

where N is the number of chains per unit vol.

K = Boltzmann’s constant

T = absolute temperature

Alternatively, if M_c is the molecular weight between crosslinks, then:

$$G = \rho RT/M_c$$

where ρ = material density

R = gas constant per mole

Although representative of an ideal case (freely-jointed chains, no network defects, etc.), the simplicity of the above relationship invites widespread use. Thus modulus is regarded as an index of “state of cure”; the cure being regarded as complete when the modulus has reached its maximum value and the faster that modulus increases, then the faster is the cure. Given the inherent difficulty of measuring M_c directly, such pragmatism is not unreasonable.

2.3 Fluid Flow and Viscosity

The molecular weights of segments in a network may present a severe challenge to measurement, but molecular weight *per se* is not beyond the scope of nominally routine investigation. For molecules of finite length, molecular weight is capable of estimation by a variety of techniques. For liquid polymers, a growth in molecular weight is indicative of the onset of cure. This is reflected as an increase in viscosity, one theoretical treatment suggesting (for monodisperse polymers)

$$\eta \propto M^{3.5}$$

where η is the coefficient of viscosity.

Whilst viscosity itself is amenable to convenient, and continuous, monitoring, it should be recognised that the data obtained can give little insight into the processes of crosslinking. Viscosity is a property of a fluid, whilst molecular crosslinking is more commonly associated with solid materials.

A fluid will flow whenever a stress is applied and continue to flow for as long as that stress is in place. The resistance to flow is reflected in the rate of flow which results, and for an ideal (Newtonian) fluid the defining relationship is:

$$\tau = \eta \dot{\gamma}$$

where τ is shear stress

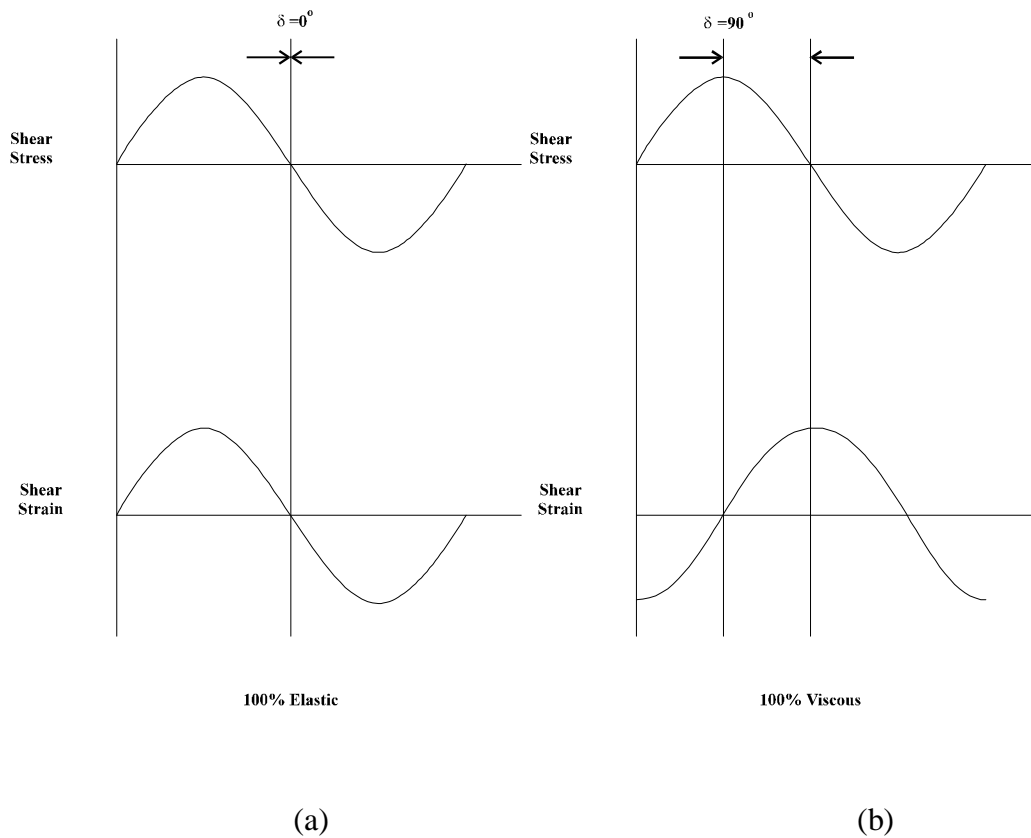
and $\dot{\gamma}$ is the resulting shear rate

Thus if the coefficient of viscosity (η) is low, less stress will be required to maintain a given shear rate, monitoring the torque required to achieve a given rotational shear rate being a common means of measuring η . What is obtained is a steady state coefficient, and this value must become infinite if and when the transition to a solid occurs.

This transition marks the point when a curing liquid is no longer capable of flow - i.e. the “gel point”. As an infinite value would be outside the measuring range of conventional steady state (e.g. rotational) instruments, continuous monitoring of steady state viscosity up to the gel point is not feasible.

2.4 Oscillatory Measurements

Figure 2: Stress and Strain Wave Relationship During Oscillation and Pure Elastic and Viscous Materials



For solid rubbers, the most commonly employed form of continuous cure monitoring is by an oscillatory or reciprocating technique. Thus instruments such as the Wallace-Shawbury Curometer and the Monsanto Rheometer have widespread familiarity.

The kind of information which can be obtained can be seen from the example of a sinusoidal oscillation. The dependencies of stress and strain with time are shown in Figure 2(a): for a purely elastic solid, the maximum strain occurs at the point of maximum stress and the dependencies of stress and strain with time are completely in phase.

However this situation will not apply if the medium is purely viscous. Here the maximum stress produces the maximum rate of strain, and the dependencies of stress and strain with time are 90° out of phase (see Figure 2(b)). Thus for a purely viscous material the strain lags the stress by 90°, the so-called phase angle (δ).

It follows that if a material is neither purely viscous nor purely elastic (i.e. visco-elastic), the sinusoidal stress and strain responses will not be in-phase, but the phase angle will be less than 90°. The sinusoidal strain will lag behind the applied stress; the stress (σ) and strain (γ) at any time t being given by the expressions

$$\mathbf{s} = \mathbf{s}_0 \sin(\omega t + \mathbf{c})$$

$$\mathbf{g} = \mathbf{g}_0 \sin \omega t$$

where ω is the frequency

The equation for σ can be re-written

$$\sigma = s_0 \sin \omega t \cos \mathbf{d} + s_0 \cos \omega t \sin \mathbf{d}$$

showing that the shear stress can be considered to consist of two parts: one which is in-phase with the strain (with an amplitude $s_0 \cos \mathbf{d}$) and the other which is 90° out-of-phase with the strain (with an amplitude $s_0 \sin \mathbf{d}$). The shear-stress/shear-strain relationship can thus be specified by a modulus G' in-phase with the shear strain and a modulus G'' 90° out-of-phase with the strain, *i.e.*

$$G' = \frac{s_0}{g_0} \cos \mathbf{d}$$

$$G'' = \frac{s_0}{g_0} \sin \mathbf{d}$$

The parameters s_0 and g_0 in the above expressions represent the amplitudes for the stress and strain waves, respectively. Thus if these, and the phase angle δ are determined experimentally, G' and G'' may be obtained.

An alternative mathematical treatment uses complex representations of stress and strain, whereby:

$$\mathbf{s}^* = \mathbf{s}_0 e^{i(\omega t + \mathbf{d})}$$

$$\mathbf{g}^* = \mathbf{g}_0 e^{i\omega t}$$

The complex modulus G^* is given by:

$$G^* = \frac{\mathbf{s}^*}{\mathbf{g}^*} = \left(\frac{\mathbf{s}_0}{\mathbf{g}_0} \right) e^{i\mathbf{d}} = \left(\frac{\mathbf{s}_0}{\mathbf{g}_0} \right) (\cos \mathbf{d} + i \sin \mathbf{d})$$

Hence

$$G^* = G' + iG''$$

where G' is the in-phase or “storage” modulus

and G'' is the out-of-phase or “loss” modulus

Whereas the in-phase component relates to the elasticity in the material, the out-of-phase components relate to damping or viscous behaviour. Indeed, a complex viscosity can be derived from these values. Thus if the strain at any time t is given by:

$$\mathbf{g}^* = \mathbf{g}_0 e^{i\omega t}$$

Differentiating against time given:

$$\dot{\mathbf{g}}^* = i\omega \mathbf{g}_0 e^{i\omega t} = i\omega \mathbf{g}^*$$

$$G^* = \frac{\mathbf{s}^*}{\dot{\mathbf{g}}^*}$$

Thus if

$$\mathbf{h}^* = \frac{\mathbf{s}^*}{\dot{\mathbf{g}}^*} = \frac{G^*}{i\omega}$$

Hence two complementary expressions can be derived:

$$G^* = G' + iG''$$

$$\mathbf{h}^* = \mathbf{h}' - i\mathbf{h}''$$

$$\text{and } \mathbf{h}' = G'' / \omega \quad \mathbf{h}'' = G' / \omega$$

The dynamic viscosity coefficients are frequency-dependent parameters - at low frequencies \mathbf{h}' approaches the steady-state coefficient η , but its value remains finite even through gelation.

2.5 Phase Angle (δ)

The phase angle between stress and strain gives a measure of the damping in the system and its measurement provides the means by which these complex functions may be resolved, *i.e.*

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

Figure 3: Log(G') versus Time

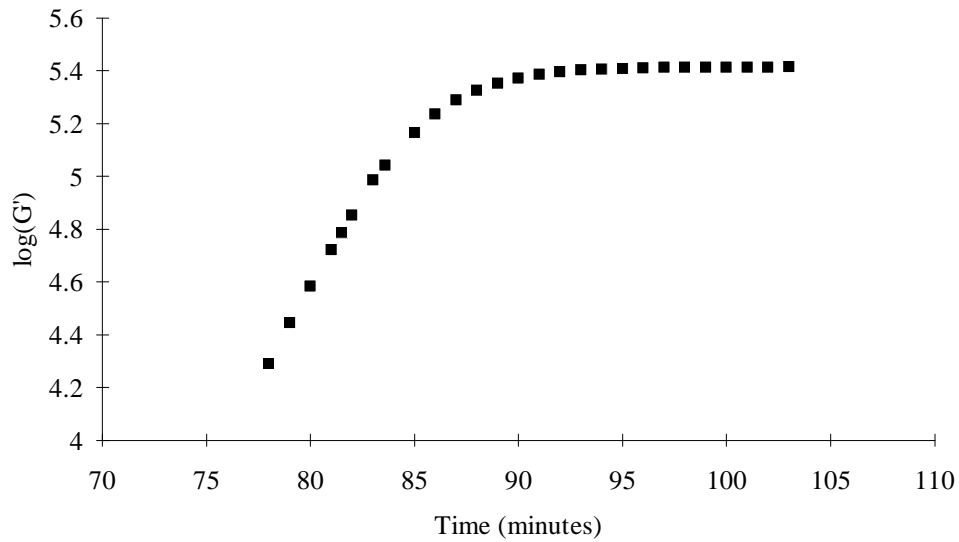


Figure 4: The "delta" Curves with different final values.

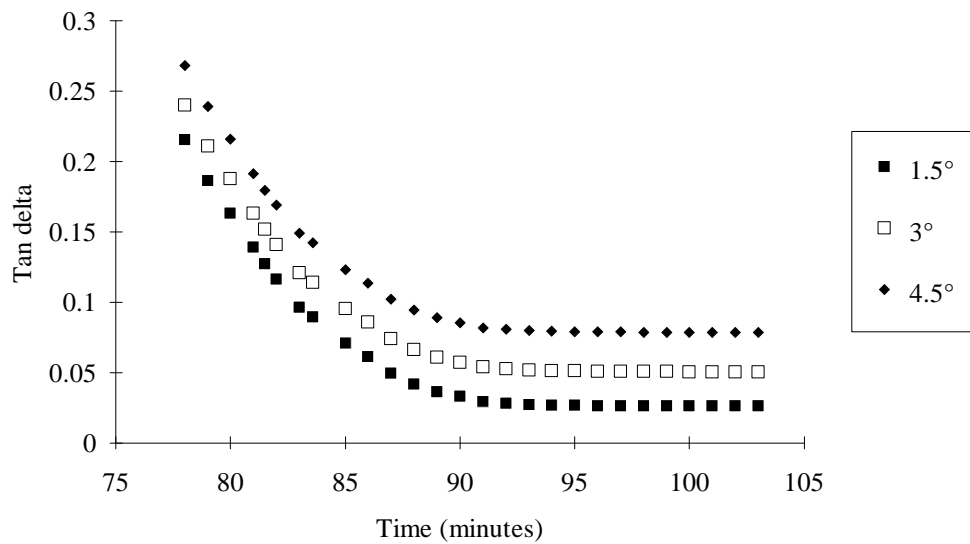
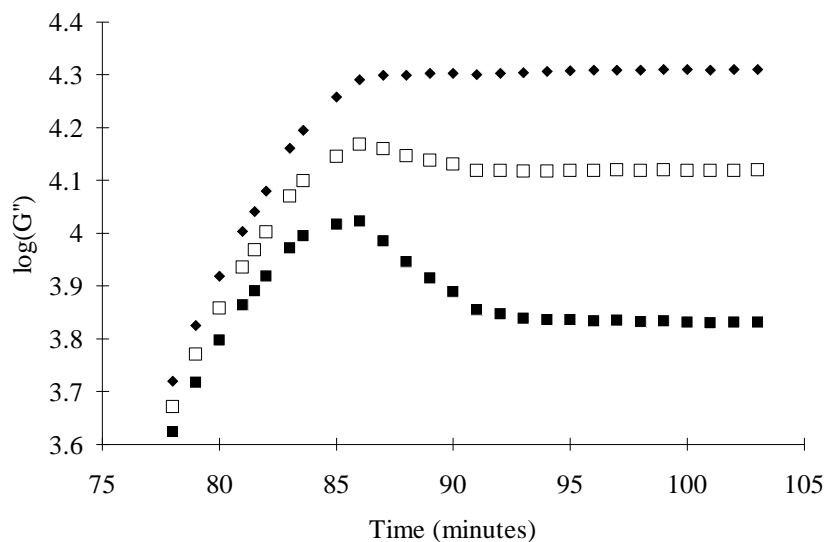


Figure 5: The $\log(G'')$ Curves with different final values.

Whilst the build-up of G' with time can give an indication of the increasing crosslink density, the development of elasticity should also be reflected in changes in δ . Thus if the change is from a viscous liquid through to an elastic solid, δ should reduce from near 90° to near zero. Not only does this give a complementary insight into the development of cure, it also provides a means of gel point determination. In this case the premise is simply that gelation occurs at the mid-point between viscous and elastic behaviour, *i.e.* when $\delta = 45^\circ$.

The traces are complementary in that they are monitoring different aspects of crosslinking; one (G') showing the build-up of crosslink density whilst the other (δ) gives an insight into the character of the network formed. A delta value which does not decay to zero indicates the level of residual damping and hence network imperfections.

$G'' (= G' \tan \delta)$ is the loss modulus which reflects damping levels and plotting the respective increases of G' and G'' with time provides an alternative insight into the development of network density and character.

Figures 3 to 5 show something of how these cure traces may appear. All the traces have the same cure profile with respect to G' (Figure 3), this increasing with time to a value of around 250,000 Pa. Three different curves for delta are provided (Figure 4), each one levelling off at the same time as G' , but with the final values reaching 4.5° , 3.0° and 1.5° . Figure 5, showing only the later stages of the cure (*i.e.* from δ lower than ca. 15°), reveals different curing profiles for G'' .

The cure that leaves the highest level of residual damping ($\delta = 4.5^\circ$) shows G'' rise to a plateau at around 20,000 Pa. When δ drops to 2.5° , the plateau value of G'' is somewhat lower at around 13,500 Pa., but there are signs of an intermediate maximum value (at around 85 minutes) perhaps some 1,500 Pa. higher. The existence of an intermediate maximum is quite distinct in the third trace where δ drops to 1.5° . Here the maximum is reached perhaps a little earlier than before and at a lower level of 11,000 Pa. The residual plateau value is only 7,000 Pa.

These traces demonstrate pictorially what is in essence a mathematical expectation, namely that the product $G' \tan \delta$ will be numerically low when either G' or $\tan \delta$ are low - *i.e.* at the start and end of cures. Thus the intermediate values of G'' may be higher than either starting or finishing values.

Theoretical treatments may suggest that where a maximum in G'' occurs this will be shortly after gelation. Without recourse to the rigours of branching theory, an insight into what happens after gelation can be obtained by reference to a model system. The example considered here is for the creation of a simple trifunctional network, as might occur if a polyether triol were cured by simple addition of diisocyanate. However no specific system is intended to be represented by this example; the calculations being based on a simple linking of a single molecular type - a trifunctional molecule of 1500 molecular weight.

Figure 6 (a) and (b): Thirty Molecule Example

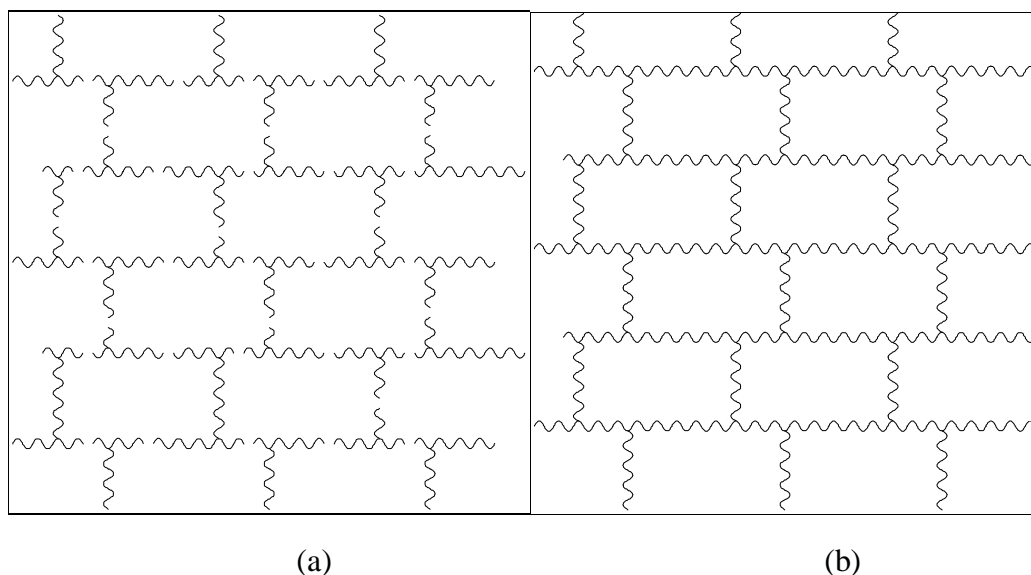
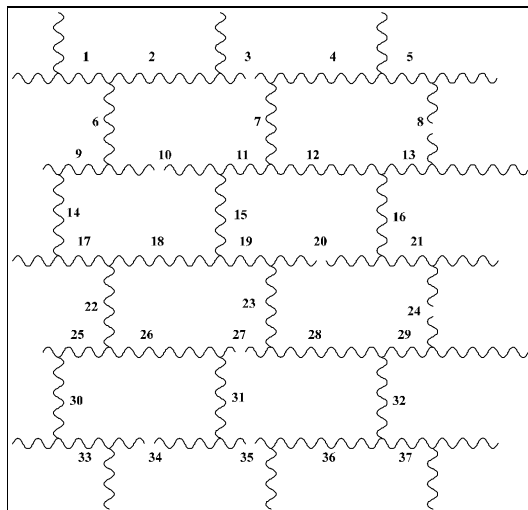


Figure 6 (c): Thirty Molecule Example

(c)

Consider the example of 30 such molecules arranged in a suitable manner for network formation (see Figure 6(a)). After the first bond has been formed there will remain 29 molecules. Hence after 29 bonds there will be only one molecule (MW 45,000) and the maximum molecular weight has been attained. The situation where all reactants have been linked together to form one complete molecule is representative of the gel point - in reality the point where the molecular weight becomes infinite.

The example under consideration shows what happens after gelation. The 30th bond made (first one after “gelation”) cannot raise the molecular weight any higher, but introduces one crosslink. The 31st bond gives a second crosslink, and so on. In the situation represented in the Figure 6(b), a total of 37 bonds have formed (74 chain ends reacted, 16 still free). A plot of MW and N (number of crosslinks) against bond number from 1 - 37 gives the type of plot which might be expected for viscosity (before gelation) and G' (after gelation).

What is happening within the crosslinked structure can be seen by assembling the network, step-by-step. Each link is assigned a number from 1 - 37 (left-to-right, top-to-bottom) and the bonds are assembled in random number order. The situation at the 29th bond is shown in Figure 6(c). The remaining eight bonds are filled in the numerical sequence: 35 (30th), 24 (31st), 8 (32nd), 34 (33rd), 10 (34th), 27 (35th), 20 (36th) and 3 (37th).

The build-up of molecular weight, both within the network and outside the networks can be seen in Table 1.

Table 1:

No. of Bonds Made	Av. Mol. Wt.	No. of X-links	MW in open chain	MW in network
0	1,500	0	1,500	-
1	1,550	0	1,550	-
10	2,250	0	2,250	-
20	4,500	0	4,500	-
25	9,000	0	9,000	-
26	11,250	0	11,250	-
27	15,000	0	15,000	-
28	22,500	0	22,500	-
29	45,000	0	45,000	0
30	45,000	1	35,000	10,000
31	45,000	2	28,000	17,000
32	45,000	3	23,000	22,000
33	45,000	4	19,000	26,000
34	45,000	5	15,000	30,000
35	45,000	6	14,000	31,000
36	45,000	7	13,000	32,000
37	45,000	8	10,000	35,000

It is clear from this the network is changing in character as it forms with the molecular weight within the network eventually exceeding that in free chains. If the respective proportions of material inside and outside the network reflects the level of damping in the system then it is perhaps not surprising that G'' continues to increase beyond the gel point.

However it might also be expected that in the final stages of network formation, especially when most of the material is combined within the network, then G'' must ultimately decrease. Under these circumstances, a maximum value for G'' will be seen.

2.6 Summary of Changes During Cure

The following scheme generalises the various stages that occur during the cure of a liquid polymer.

1. Viscosity increase.
2. Development of elasticity - (*e.g.* through entanglements) - end of work life.
3. Gelation (viscosity $\rightarrow \infty$) - no flow beyond this point
4. Crosslink density increases (G' increases) - rate of G' change equates to rate of cure.

5. Network flaws decrease - extra network content decreases, network content increases.
 - G'' reaches a maximum
 - G'' may then decrease as flaws disappear.
6. Crosslinking reaction ceases
 - G' reaches a maximum
 - G'' levels out.
7. Reversion?
 - G' starts to decrease
 - G'' starts to increase.

2.7 Practical Cure Monitoring - The Rapra Scanning VNC

Classical rheometers can give cure traces as above for a range of materials, but are not necessarily optimised for curing liquids. One limitation relates to the strict geometric requirements for the accurate determination of G' . The geometry which is imposed will be that which is required for the measurement range, and not necessarily that which is of interest to the technologist. The most active liquid curing systems will exploit their exothermic behaviour to some degree in their cures so that thin film studies may not be totally relevant. Such studies may characterise the system, but not necessarily its practical curing characteristics.

Furthermore, the “system” as such must be taken to the instrument, indeed it may have to be mixed in close proximity to the instrument if the true start of cure coincides with the start of mixing. Additionally it may be less than willing to leave the instrument if a strong adhesive cure results.

It follows from this that, if an instrument can be taken to the cure (rather than the other way around), practical benefit would result. A transportable robust instrument which poses no special geometric constraints on the sample would have remarkable versatility for the monitoring of liquid polymer cures. Thus rapidly curing liquids could be monitored in the thicker sections more representative of practice, or even in the mixing container itself. Without unnecessary geometric constraints, cures could be monitored within a container large enough to allow for expansion or even in applications related configurations.

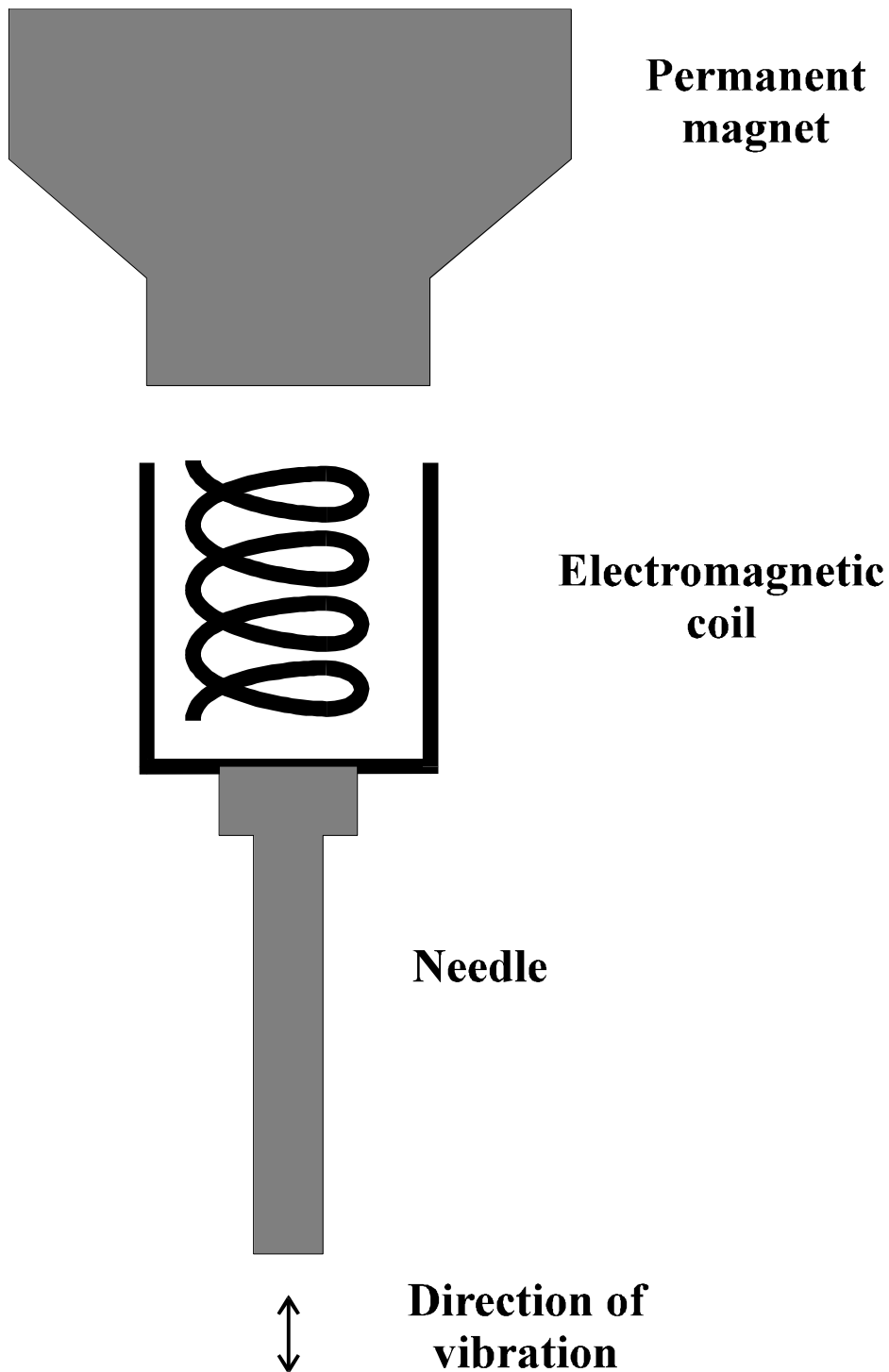
This is the rationale behind the development of the Rapra Vibrating Needle Curemeter (or VNC), an instrument which is robust and transportable to the sample. The only

special constraints are the need for access for the needle into the sample and the necessary mains electricity supply. The heart of the instrument is a simple electrically-driven vibrator and its power to resolve a cure comes from the manner of its integration to a PC. The computer both selects the frequency for oscillation and analyses the outputs. Thus, unlike a great many other instruments, the VNC does not work at a single fixed frequency. The fact that the instrument is scanning a range of frequencies gives it the name Scanning VNC.

2.7.1 The Instrument

The heart of the Scanning VNC is the vibrator itself. This contains a moving coil assembly located via flexible mountings close to one pole of a permanent magnet (Figure 7). The coil is energised by an AC current to produce a vibration of the same frequency as the oscillating current. This drive is provided by the Control Box of the instrument and the frequency of the AC signal is scanned over a range of frequencies.

Figure 7: Schematic Diagram for the Transducer and Needle of the Scanning VNC



Changes in the amplitude of vibration are detectable by changes in the back EMF in the electromagnetic coil. Thus by measuring this back EMF at different frequencies, the resonance characteristics of the system can be measured. These resonance

characteristics, in particular the resonance frequency and amplitude, are used to monitor the progress of cure.

2.7.2 Amplitude Attenuation for the Scanning VNC

The processes of cure will change the resonance characteristics of a vibrating probe (e.g. needle) penetrating that curing mix. How the resulting effects can be rationalised requires consideration of the whole system, then vibrator, the needle and the curing formulation.

The transducer has been shown diagrammatically in Figure 7 and it may be recognised from this that perhaps the simplest model for such a system is a spring fixed at its upper end with a mass suspended beneath it. This layout is shown in Figure 8a where the spring has a stiffness constant k_0 . The equation of motion for this mass m is given in equations 1 and 2, and its integrated form (from equation 2) is given in equation 4. The substitution in equation 3 gives ω , the natural frequency of oscillation in radians per second.

$$m d^2 y / dt^2 + k_0 y = 0 \quad (1)$$

$$\text{or} \quad d^2 y / dt^2 + \omega^2 y = 0 \quad (2)$$

$$\text{where } \omega^2 = k_0 / m \quad (3)$$

$$y = y_0 \sin \omega t \quad (4)$$

Figure 8 (a) and (b): Spring and Damper Combinations

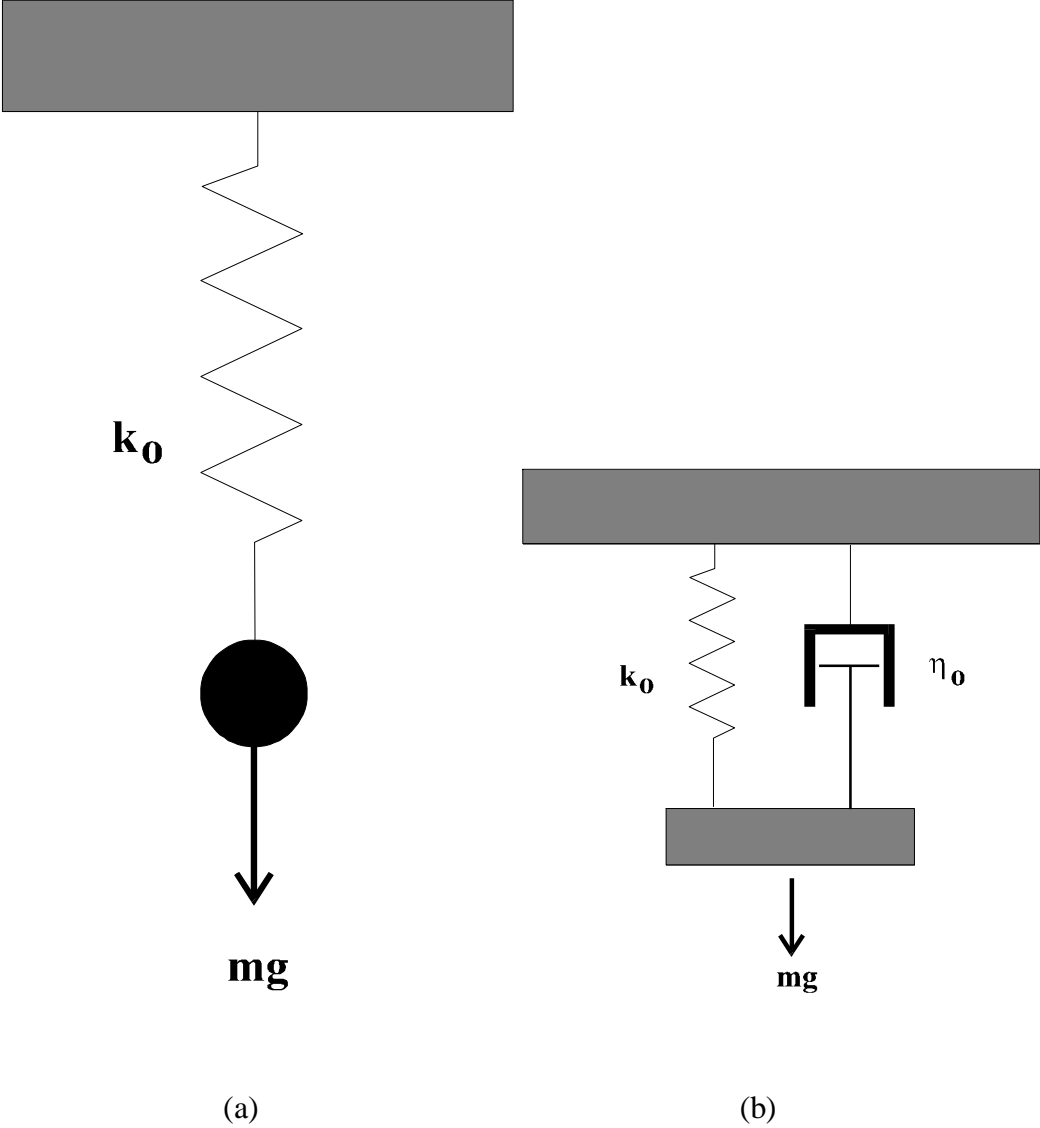
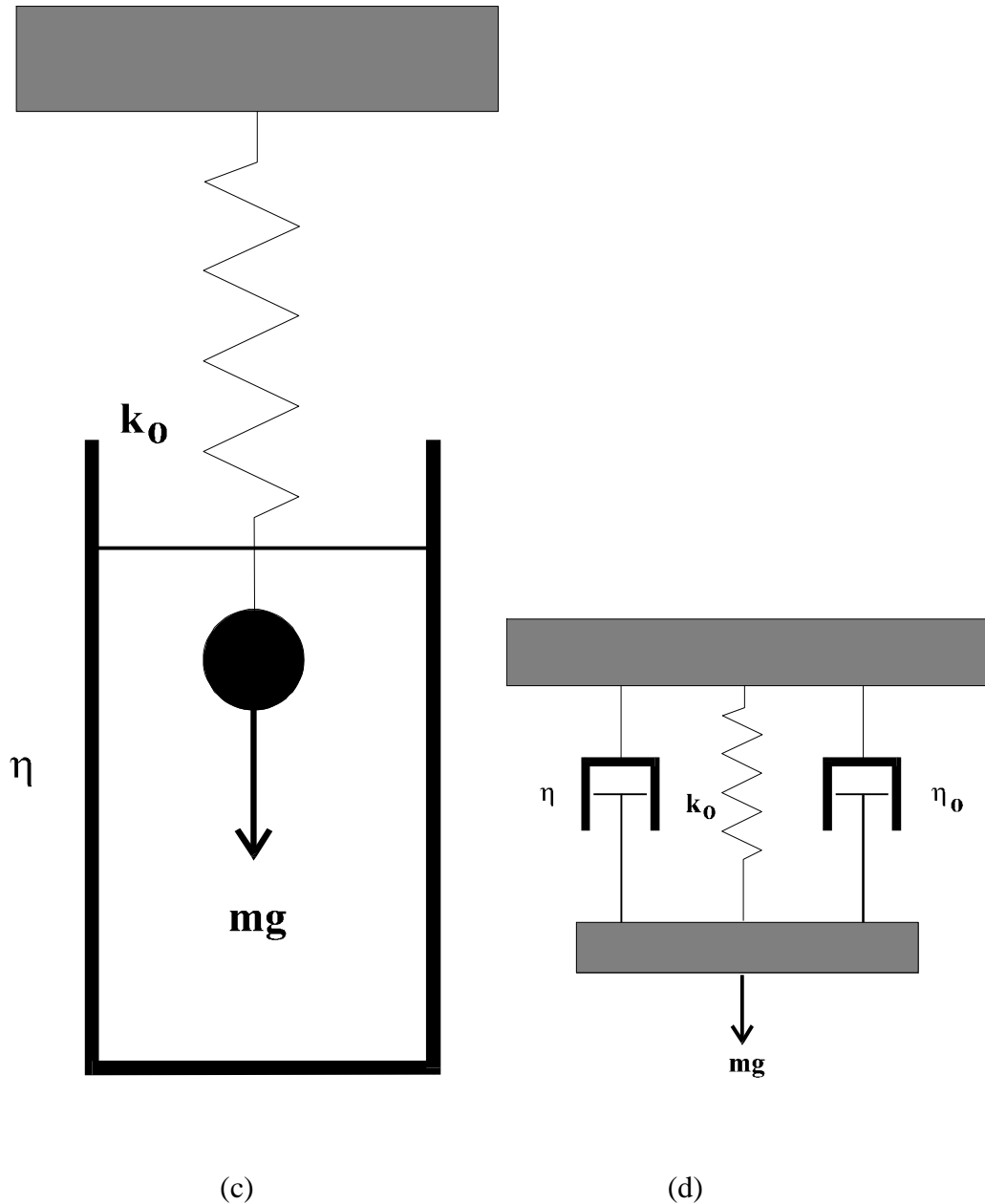


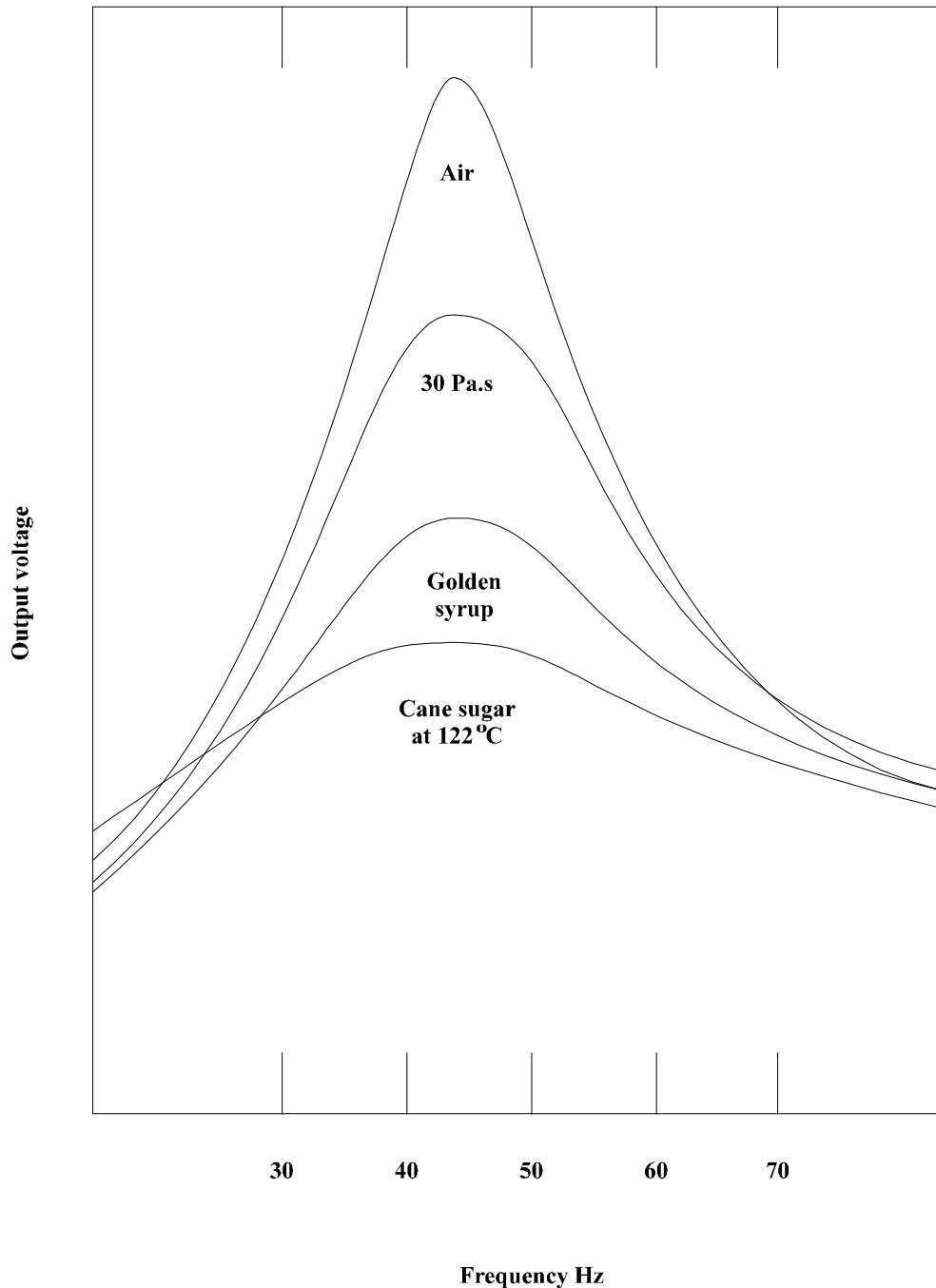
Figure 8 (c) and (d): Spring and Damper Combinations

In free vibration, a system as described by this model vibrates at its natural frequency ($\omega = \sqrt{k_0/m}$). However in forced vibration, such a system is capable of oscillating at any frequency as determined by the frequency of the periodic force. This is the case for the electrodynamic transducer of the Scanning VNC where the vibration frequency is that of the AC signal which energises the coil. However when the driving frequency equals that of the natural frequency of the system the condition of resonance is obtained. This effect is readily seen with the Scanning VNC which with the standard vibrator and probe/needle gives a resonance peak (in air) at around 85 Hz.

In reality there will be some internal friction in the vibrator and a damping term should be included in equations (1) and (2). The system is then represented by a spring and dash pot in parallel, as in Figure 8b.

This model is not representative of the situation when the vibration is being restrained by an additional viscous element, as is the case when the VNC needle is in contact with a fluid. Figure 8c shows a modification to the first model to accommodate this, the mass on the spring being immersed in a damping medium. This damping medium represents the sample being monitored, the container for which should not itself be free to vibrate. Thus the top and bottom of this system are both fixed in space with only the central part free to vibrate. Thus the layout in Figure 8c is equivalent to that in Figure 8d, the arrangement with the spring and dampers in parallel.

The effect of damping for forced vibrations is to reduce the amplitude. Figure 9 shows this effect for the VNC at resonance in four different fluids: air, silicone oil, golden syrup and molten sucrose (cane sugar). The amplitude at resonance as measured by the back EMF is significantly reduced as the viscosity increases to around 200 Pa.s in the case of the cane sugar melt.

Figure 9: Scanning VNC resonance Peaks for Different Damping Media

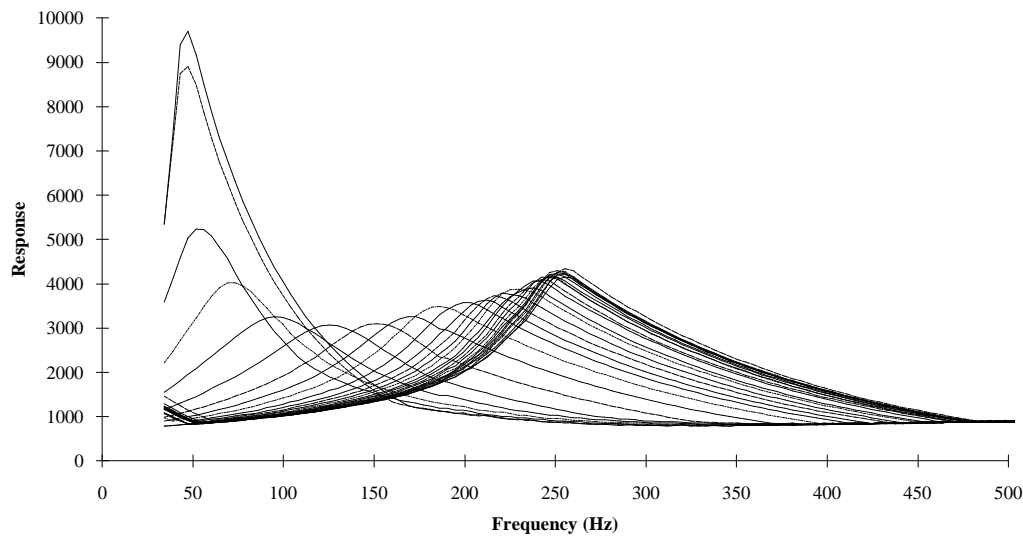
Interestingly the position of the resonance peak with respect to frequency changes very little, the top three traces in Figure 9 all having their maxima at 43-45 Hz. This is in accord with the expectations of such a system, the frequency at maximum amplitude showing little dependence on viscosity except at very high viscosities (refs. 2 and 3). The anticipated shift at very high viscosities is to reduced frequencies of resonance (the shift of the peak for cane sugar to around 40 Hz may be a reflection of this). (The

resonance frequencies are lower than usually obtained as the transducer used here was not the standard transducer.)

2.7.3 Resonance Frequency Effects

Gel time is an important parameter of the cure of liquid polymers and a useful cure-monitoring device should be capable of recognising it. How this can be achieved with the Scanning VNC may be appreciated by reference to the resonance peaks shown in Figure 10 measured during the cure of a polyurethane elastomer.

Figure 10: Typical Resonance Peaks for the Cure of a PU

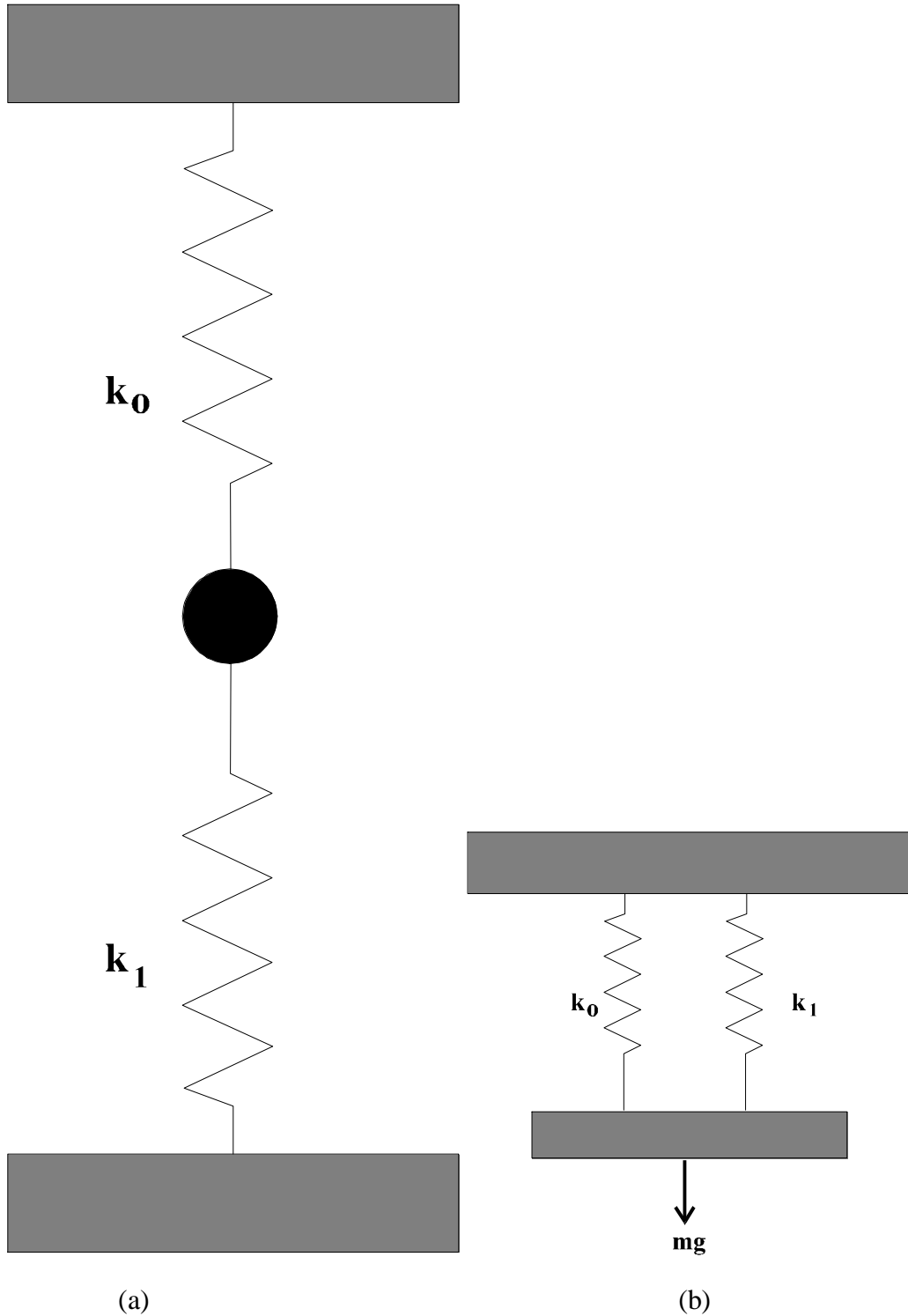


What is evident is that the frequency of the resonance maximum is increasing, a feature not observed in studies of purely viscous damping (*e.g.* see Figure 9). The reasons for this may be appreciated by reference again to an elastic model.

The change in resonance frequency for a model system can be illustrated with respect to the simplest of these, based on undamped springs as in Figure 8a. The introduction of a second spring beneath the vibrating mass is shown in the arrangement in Figure 11a where the second spring has a stiffness constant k_1 . If both springs act both in extension and compression then the model is analogous to that in Figure 11b for which the equation of motion of the mass m is given by equation 5. It follows from this that the natural frequency for free vibration is given by the expression in equation 6.

$$m d^2 y / dt^2 + (k_0 + k_1) = 0 \quad (5)$$

$$(k_0 + k_1) / m = \omega^2 \quad (6)$$

Figure 11: Combination of Two Springs

Thus it follows that the addition of a second elastic element increases the natural vibrational frequency and consequently the frequency of resonance for forced vibrations. Since a shift to higher frequencies has not been associated with viscous changes (*e.g.* see Figures 8 and 9 and discussion thereof), it may be inferred that the

observation of such a shift is diagnostic of additional elasticity in the vibrating system. The initial development of elasticity during cure, indicated by an increase in the resonance frequency, gives a close approximation to the gel point.

2.8 References

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2. Morrision R.B., Concise Physics, Arnold, London, 1962, pp. 15-17.
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3. MONITORING THE CURE OF THERMOSET RESINS WITH THE SCANNING VNC

During the cure of a liquid polymer two processes are caused by the chemical reaction used to effect the cure:

- 1) Chain Extension; and
- 2) Crosslinking.

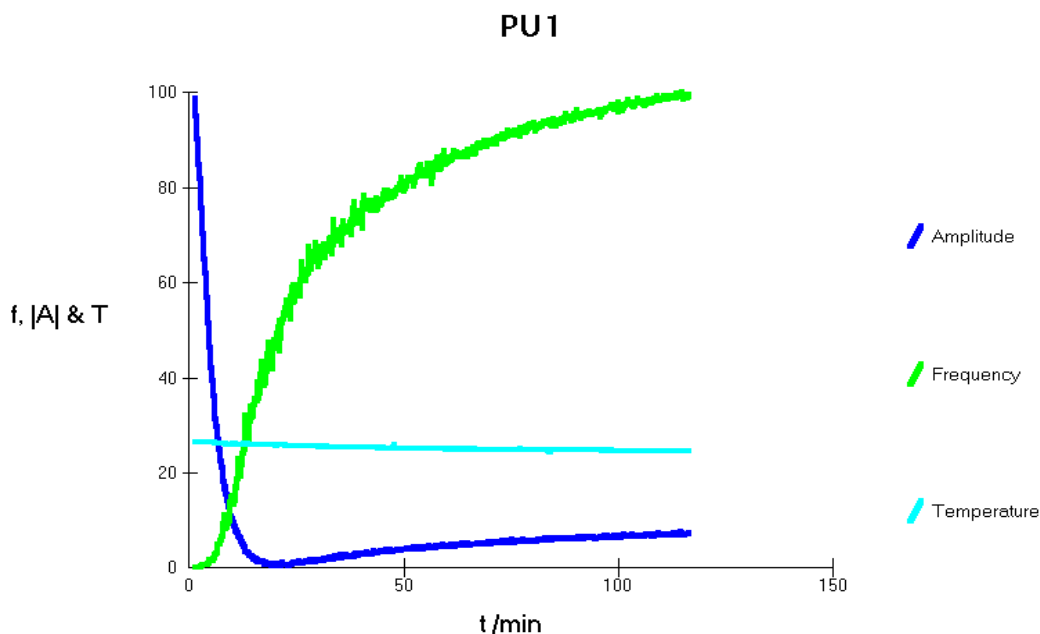
In the early stages of the cure of a liquid polymer, chain extension causes the viscosity of the liquid to increase. Either simultaneously or subsequently, crosslinking occurs causing an increase in modulus and, in many cases, resilience. These two processes are monitored separately by the Scanning VNC, thus two-dimensional cure monitoring is achieved.

This two-dimensional representation of cure is produced by causing the monitoring needle of the Scanning VNC to vibrate at different frequencies and indirectly measuring the amplitude of vibration. If the amplitude of vibration is plotted against frequency then a resonance peak can be constructed. The resonance amplitude and frequency of this peak is dependant on the physical properties of the fluid that the needle penetrates. If the fluid is a reactive system that cures then the nature of the resonance peak changes as the cure progresses. Figure 10 (Section 2.7.3) shows a typical series of resonance peaks recorded during the cure of a polyurethane elastomer.

The two-dimensions are taken as the amplitude and position (frequency) of the resonance peak. Thus traces of both the resonance amplitude and frequency against time can be built up.

The Scanning VNC records the resonance amplitude and frequency, every 5 seconds or so (depending on computer speed) by recording the amplitude at three different frequencies. These points are fitted to a quadratic equation from which the maximum

amplitude and the resonance frequency are calculated. Figure 12 shows the amplitude and frequency plots for a PU cure, the temperature of the sample holder is also shown.

Figure 12: Scanning VNC Amplitude and Frequency Plots for a PU Cure

So the Scanning VNC monitors processes by which liquid polymers are converted to elastomeric or glassy solids. This process is generally caused by the chemical reaction of the functional groups of the liquid polymer, as for example in the cure of polyurethanes, epoxies, unsaturated polyester resins, polysulphides and liquid silicone rubbers. These types of material are used in the manufacture of a multitude of products including automotive parts, paints and coatings, solid wheels (*i.e.* skate board wheels), golf balls, drive belts, wiper blades, prototype parts, electrical applications, conveyor belts, sealants, adhesives and foams. The instrument has also been used to monitor the gelation and fusion of PVC plastisols, providing information on the rate and temperature at which these processes occur.

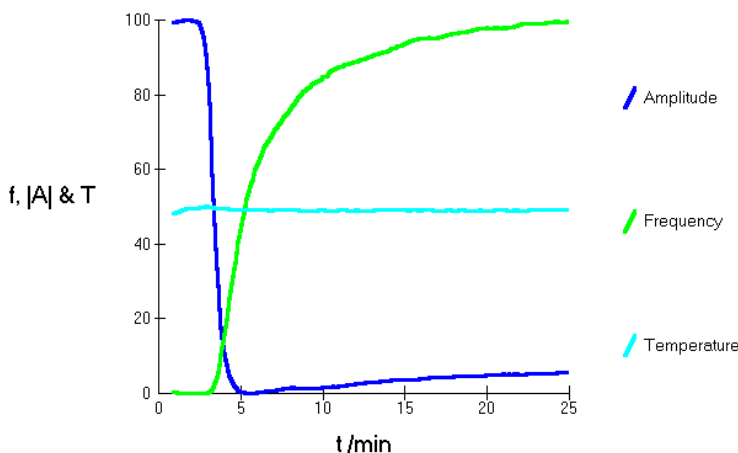
The instrument places a needle in the sample to be monitored, and follows the progress of cure in that sample by continuously measuring the amplitude of forced vibrations of the needle. When such forced vibrations are around the resonance frequency of the system as a whole then information on both storage modulus (G') and loss modulus (G'') or damping can be obtained¹. Initially, when the change is purely viscous, the damping of the needles vibration increases reducing the amplitude. When the liquid subsequently gels and develops elastic character, an increase in the resonance frequency of the needles vibration occurs. Monitoring the amplitude and frequency of the resonance peak provides a two-dimensional perspective on the process enabling differences in character to be readily distinguished.

The following examples show how the SVNC has been used to characterise the cure of various types of resin.

3.1 Polyurethanes

Figure 13 shows a typical SVNC trace for the cure of a polyurethane designated PU A. The cure in question was of a low molecular weight (1000) polypropylene oxide diol with a modified MDI (approximate functionality 2.1) in the presence of an organomercury catalyst. The NCO index used was 1.1.

Figure 13: SVNC Traces for Cure PU A



(See "pu_a.csv" on program disk.)

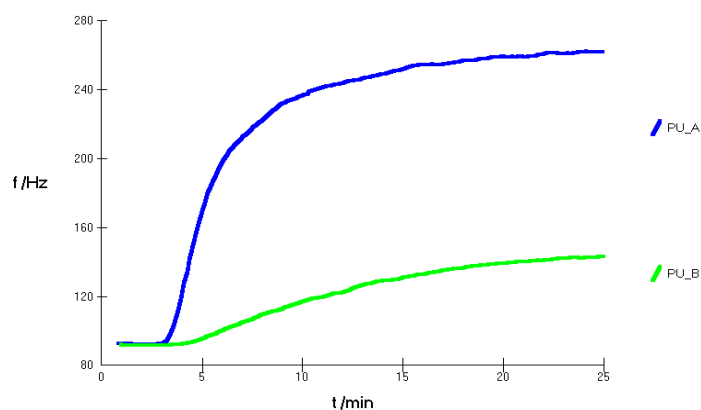
The figure shows the two SVNC traces, resonance amplitude and frequency, and the cure temperature which was 50 °C. Prior to the gel point, the amplitude trace indicates the change in the viscosity of the formulation, the resonance amplitude decreasing as the viscosity increases. Later in the cure, after the gel point, the amplitude starts to increase again. This indicates that the damping in the curing material is decreasing due to the development of resilience as the cure progresses and the polymer network becomes more complete: in this case the damping passes through a maximum at a characteristic point in the cure². This is the effect which is described in Section 2.5. This point generally occurs after the gel point which, in the case of the SVNC, is indicated by the initial shift in resonance frequency³. The continued increase in the resonance frequency indicates the increase in storage modulus as the cure progresses beyond the gel point.

The Scanning VNC can be used to study the effect of various formulation parameters, for example isocyanate index, crosslink density, effect of 1,4-butanediol and the catalyst content and type. For illustration the effect of catalyst type on the cure of a

simple PU formulation is shown in Figures 14 and 15. PU A is that shown in Figure 13 and contains Thorcat 535 (0.53%) - an organomercury catalyst. PU B is the same formulation except that the catalyst used is dibutyltin dilaurate (DBTL, 0.15%).

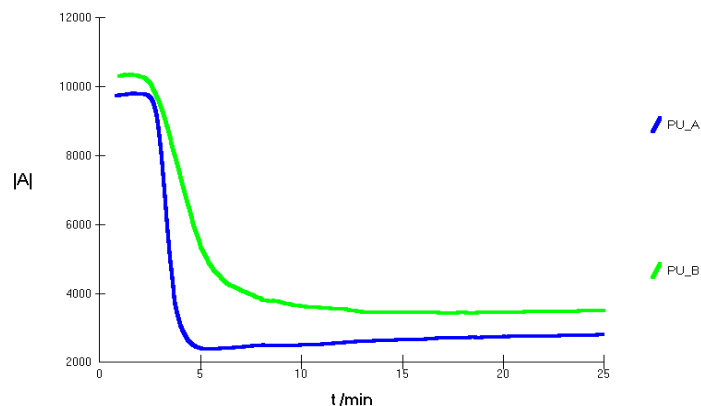
The traces clearly show significant differences between the two cure profiles. The most obvious difference is in the final resonance frequency achieved, the formulation containing Thorcat 535 (PU A) reaching the higher resonance frequency (260 Hz for PU A and 150 Hz for PU B). The two formulations contain an excess of isocyanate and the Thorcat 535 catalyses the reaction of isocyanate with urethane groups (allophanate formation) more effectively than DBTL. Thus after 25 minutes the DBTL cure contains a higher proportion of unreacted isocyanate groups, reducing the storage modulus of the material. In the Thorcat 535 cure these excess isocyanate groups become bound into the polymer network resulting in crosslinking and a higher storage modulus. This difference in storage modulus (G'), which is related to hardness, is reflected by the difference in the final resonance frequency.

Figure 14: SVNC Frequency traces for Cures Containing Different Catalysts



(See "pu_a.csv" and "pu_b.csv" on program disk.)

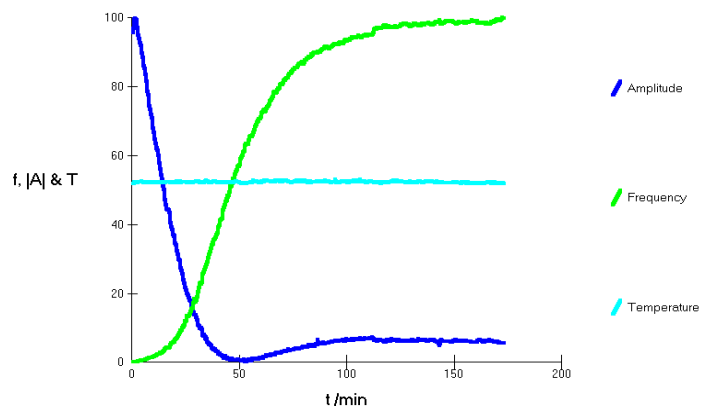
The resonance amplitude trace responds to changes in the viscosity before gelation and in the loss modulus (G'') or damping after gelation. Thus the initial decrease in the resonance amplitude results from the increase in the viscosity of the formulation as chain extension progresses. These traces also reflect the progress of crosslinking in these formulations (Figure 15). It has already been explained that the crosslink density of the Thorcat 535 formulation increases more rapidly and how the resonance frequency traces demonstrates this. The amplitude trace also shows this effect by the increase in the amplitude during the later stages of the Thorcat 535 cure. This is due to the reduction of the damping or loss modulus (G'') as the excess isocyanate groups react with the urethane groups.

Figure 15: SVNC Amplitude traces for Cures Containing Different Catalysts

(See "pu_a.csv" and "pu_b.csv" on program disk.)

3.2 Polysulphides

Liquid polysulphides are frequently used in sealants. Their proven ageing and weathering performance has found them wide use in the building industry whereas their resistance to fuels has made them useful sealants for the fuel tanks of aeroplanes.

Figure 16: SVNC Traces for the Cure of a Liquid Polysulphide

(See "sulphide.csv" on program disk.)

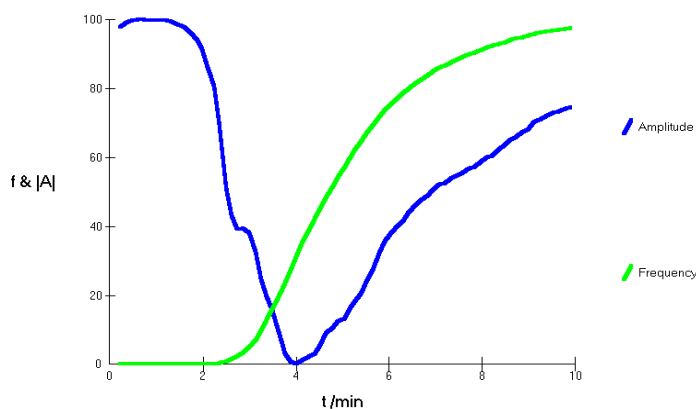
Figure 16 shows the Scanning VNC traces for the cure of a typical liquid polysulphide sealant. The curing agent used is manganese dioxide which oxidises the thiol end groups of the polysulphide to disulphide linkages effecting chain extension and crosslinking. As with the polyurethane example the increase in the viscosity in the early stages of the cure is indicated by the decrease in the resonance amplitude. The development of resilience, or reduction in damping, after the gel is indicated by the increase in the amplitude during the later stages of the cure. The resonance frequency

trace shows the increase in storage modulus or hardness as the cure progresses, reaching a final value of 170 Hz.

3.3 Silicones

Cured silicone polymers often have high resilience. The development of this resilience can be clearly observed using the SVNC as shown in Figure 17 which shows the cure of a silicone gum at 120 °C. Note the large increase in the resonance amplitude as the resonance frequency increases after the gel point.

Figure 17: SVNC Traces for the Cure of a Liquid Silicone

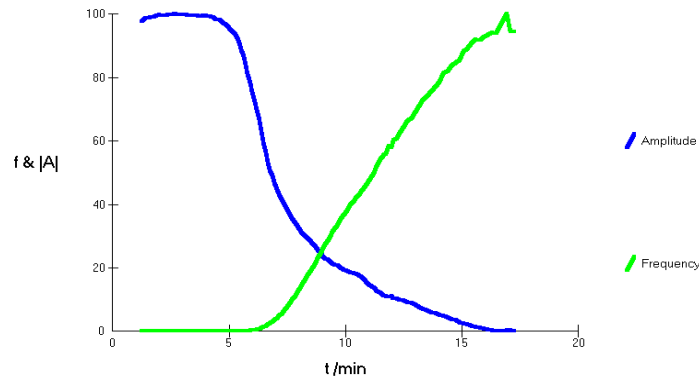


(See "silicone.csv" on program disk.)

3.4 Epoxy Cures

The examples described so far are for liquids that cure to rubbery solids. Generally epoxides cure to hard and glassy plastics. This means that the cured products have very high loss moduli which results in the resonance amplitude being very low. This limits the instrument's ability to monitor to the very latest stages of this type of cure as it becomes increasingly difficult to locate the maximum of the resonance peak as the epoxide hardens causing the resonance amplitude to become very small (see SVNC Operating Manual RTL/2843 Sections 5.2 and 9). Ultimately the resonance peak may disappear altogether.

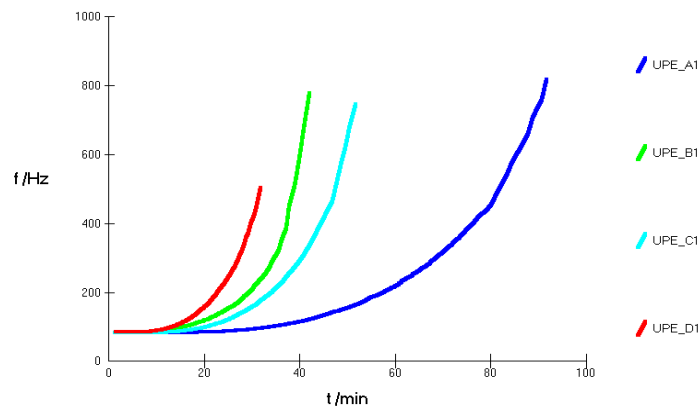
Although the instrument has this limitation for systems that cure to very hard products, it still provides useful information about these cures. Figure 18 shows the Scanning VNC trace for a typical epoxy resin. The resonance frequency reached 420 Hz before monitoring ceased.

Figure 18: SVNC Frequency Traces for Epoxy Resin Cures

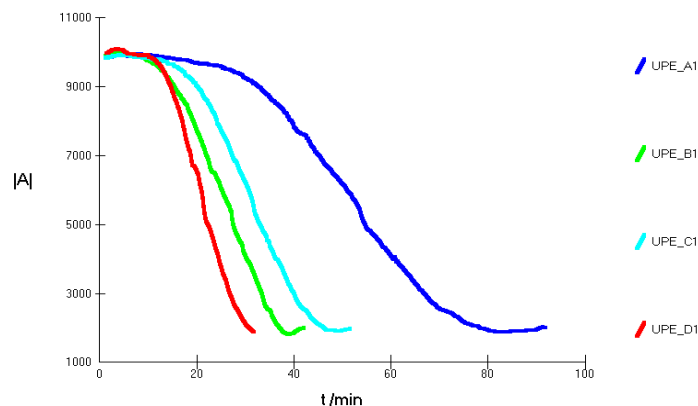
(See "epoxy.csv" on program disk.)

3.5 Unsaturated Polyester Resins

These resins also cure to hard products, making monitoring of the later stages of cure difficult. However useful information about the cure can again be gained using the SVNC with monitoring continuing well into the cure. Figures 19 and 20 show the SVNC cure traces of a typical unsaturated polyester resin at 50 °C and the recorded resonance frequencies have increases to around 800 Hz. The three cures shown are of formulations containing different amounts of a peroxide and a cobalt accelerator.

Figure 19: SVNC Frequency Traces for Unsaturated Polyester Resin Cures

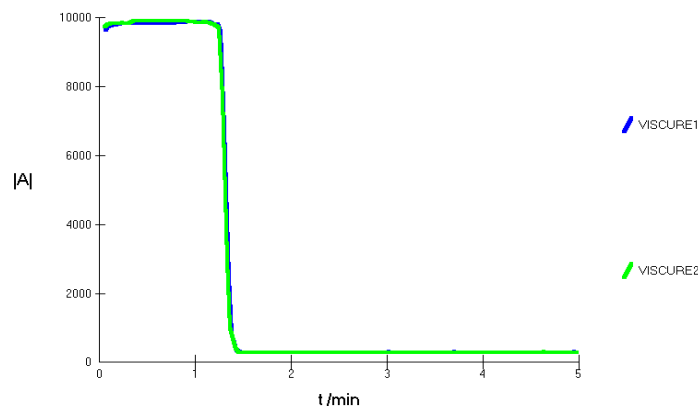
(See "upe_a1.csv", "upe_b1.csv", "upe_c1.csv" and "upe_d1.csv" on program disk.)

Figure 20: SVNC Amplitude Traces for Unsaturated Polyester Resin Cures

(See "upe_a1.csv", "upe_b1.csv", "upe_c1.csv" and "upe_d1.csv" on program disk.)

3.6 Visible Light Cure

With an appropriate initiator system vinyl or acrylic monomers can be cured by the action of either UV or visible light. Figure 21 shows traces for duplicate cures of triethyleneglycol dimethacrylate (TEGDMA) in the presence of a visible light initiator system. The sample was placed in a 4 mm deep sample holder and then the probe was lowered into it. Monitoring was started when a visible light (400 - 500 nm) was shone, *via* an optical guide, on the sample.

Figure 21: Fixed Frequency VNC Trace of Visible Light Initiated Cure of TMPTMA.

(See "viscure1.csv" and "viscure2.csv" on program disk.)

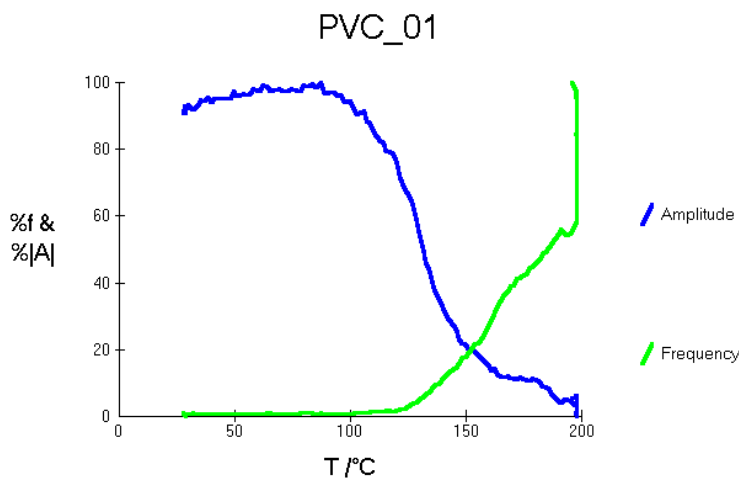
3.7 PVC Plastisols

For the cure of thermosetting resins the amplitude and frequency responses are plotted against time, however the fusion of a PVC plastisol is a temperature dependant process

and the two sets of resonance data can be plotted against temperature. The SVNC can be supplied with a temperature controller which allows the temperature of the heat stage to be increased in a controlled manner and by using a relatively thin film of plastisol (*e.g.* 1 mm) the temperature of the liquid can be assumed to be that of the heat stage.

Figure 22 shows the percentage changes in the resonance amplitude and frequency as the temperature is increased at 10 °C/minute. At temperatures up to about 80 °C there is no change in the resonance frequency, indicating that the plastisol is still liquid. During this period the resonance amplitude increases slightly, reflecting the decrease in viscosity as the temperature of the liquid increases. At temperatures above 80 °C the resonance amplitude decreases, indicating that the viscosity is increasing, as the temperature increases to 200 °C. The maximum rate of viscosity increase seems to be occurring at about 125 °C. This increase in viscosity is caused by the plasticiser diffusing into and swelling the particles of PVC.

Figure 22: Change in Resonance Amplitude and Frequency with Increasing Temperature (10 °C/minute)

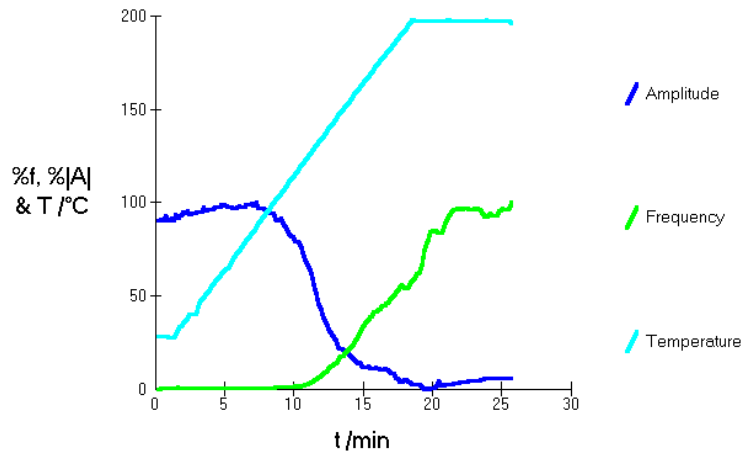


(See "pvc.csv" on program disk.)

The liquid does not become a solid (*i.e.* fusion) until the temperature reaches around 120 °C. This is indicated by the temperature at which the resonance frequency first starts to increase. After this point the plastisol cannot flow any longer. When the temperature reaches 200 °C, the resonance frequency continues to increase, indicating that diffusion of the plasticiser into the particles occurs more slowly than the temperature increase, thus when the temperature reaches 200 °C the diffusion process still has some "catching up" to do for this particular plastisol.

Figure 23, showing the changes with time, demonstrates that the resonance frequency does reach a final steady value after about 23 minutes indicating that the diffusion process has been completed. The final resonance frequency is 150 Hz.

Figure 23: Change in Resonance Amplitude and Frequency and Temperature with Time (10 °C/minute experiment)

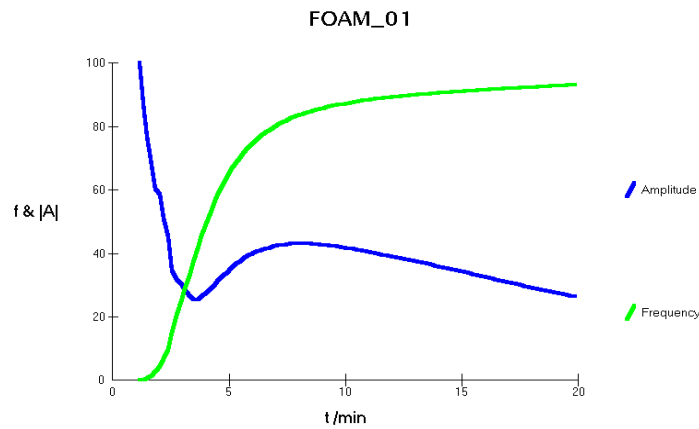


(See "pvc.csv" on program disk.)

3.8 Polyurethane Foams

The stand of the Scanning VNC has a sample holder/heat stage with a small capacity - approximately 0.5 ml. Obviously this is not suitable for a PU foam and so an alternative sample holder is provided. This second holder allows a disposable vending machine cup, with a volume of 200 ml, to be firmly held in position. The formulation can be mixed in this cup, the cup is then placed in position on the stand and the cure

Figure 24: Resonance Amplitude and Frequency Plots of a Flexible PU Foam.



(See foam_01.csv on program disk.)

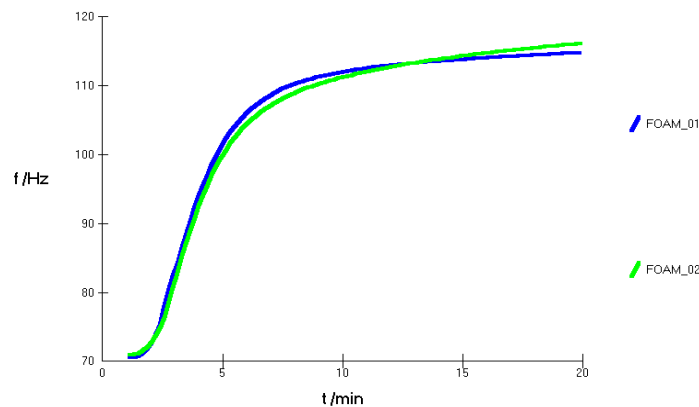
monitored (see SVNC Operating Manual RTL/2843 Section 7.2). In this test about 30 g of material was mixed in a suitable cup and the cure monitored.

Figure 24 shows a Scanning VNC trace for a flexible foam, comparing the resonance frequency, indicative of changes in the elasticity or modulus of the sample, and resonance amplitude, indicative of changes in the viscosity of the sample.

Figures 25 and 26 compare the resonance amplitude and resonance frequency traces respectively for two replicates of the same cure. These duplicate traces indicate that a good level of reproducibility can be attained.

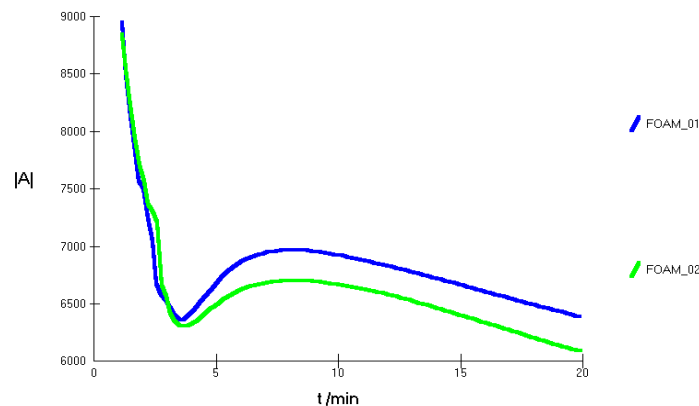
The resonance frequency remains unchanged until the curing liquid gels. At this point the resonance frequency start to increase and continues increasing as the storage modulus of the curing foam increases. The gel time of the formulation can be

Figure 25: Comparison of Resonance Frequency Traces for Duplicate Cures



(See foam_01.csv and foam_02.csv on program disk.)

Figure 26: Comparison of Resonance Amplitude Traces for Duplicate Cures



(See foam_01.csv and foam_02.csv on program disk.)

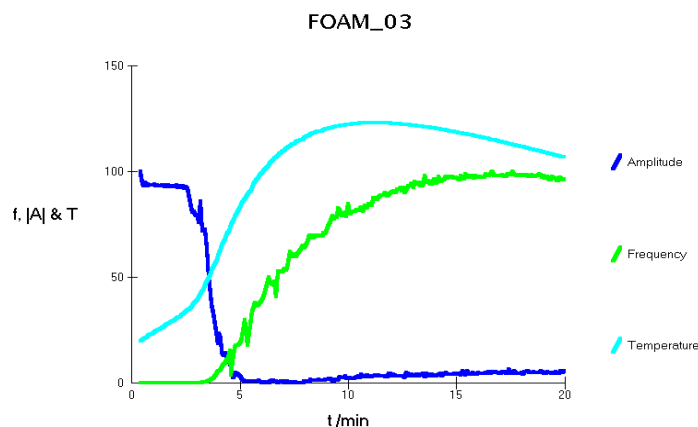
estimated by calculating the time at which the frequency trace has increases by 5% of its total change. In the case of the two traces of Figure 25 this occurs after 2.3 and 2.1 minutes. Formulation changes, for example isocyanate index, may be expected to affect the final modulus of the cured foam and this would be reflected in differing final resonance frequencies.

The amplitude traces (Figure 26) show the changes in the damping character of the curing formulation. The initial decrease in resonance amplitude is caused by the increase in viscosity that occurs before the gel point. In these traces a minimum occurs just after the gel point at 3.8 and 3.6 minutes. This minimum indicates the point of maximum damping and the subsequent increase in resonance amplitude is the result of an increase in the resilience of the foam as the crosslink density continues to increase. The decrease in amplitude that occurs after about 8 minutes is most probably due to the effect of the foam cooling as the exotherm subsides.

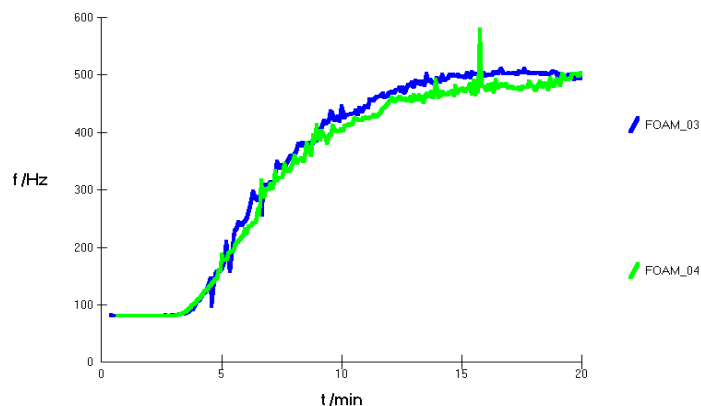
The SVNC is also capable of monitoring temperature, for example *via* a thermocouple placed in the curing sample.

The Scanning VNC can also be used to monitor the cure of rigid foams. Figures 28 to 30 show traces for such cures.

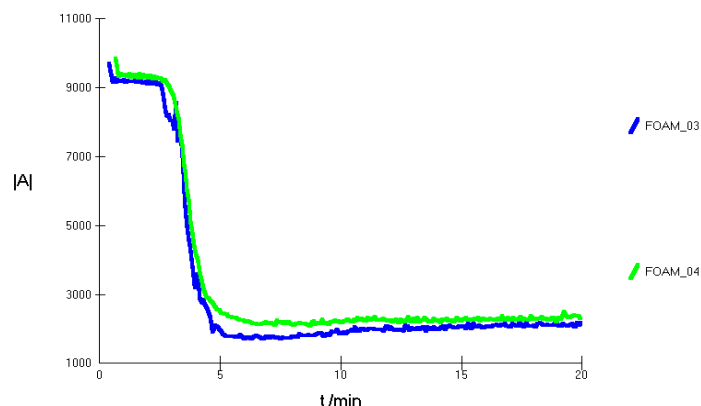
Figure 28: Resonance Amplitude and Frequency Plots of a Rigid PU Foam.



(See foam_03.csv on program disk.)

Figure 29: Comparison of Resonance Frequency Traces for Duplicate Cures

(See foam_03.csv and foam_04.csv on program disk.)

Figure 30: Comparison of Resonance Amplitude Traces for Duplicate Cures

(See foam_03.csv and foam_04.csv on program disk.)

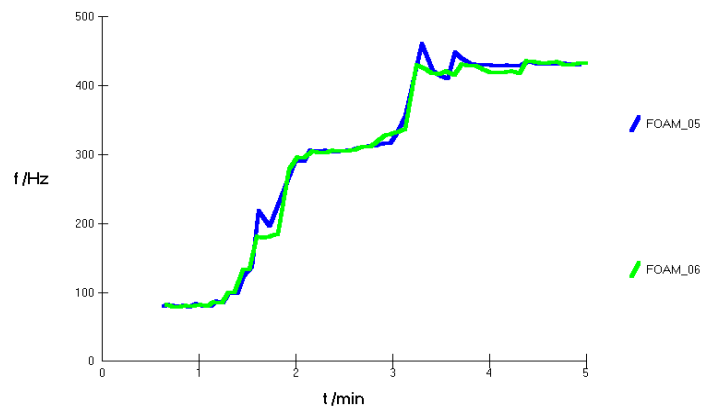
These traces are similar to those shown in Figures 24 to 26 indicating how the viscosity and modulus of the formulation changes during cure. The main difference between the traces for the flexible and rigid foams is seen in the frequency traces. The resonance frequency for the rigid foams reaches a much higher value (~500 Hz) than that for the flexible foams (~115 Hz). This is due to the higher storage modulus of the rigid foams.

Figure 28 suggests that the resonance frequency starts to decrease after around 15 minutes. It is thought that this effect is due to cooling effects as the exotherm subsides, rather than any reduction in the crosslink density of the foam. Because of these cooling effects, the later parts of the cure traces for foams should be interpreted with caution.

In general foaming formulations have to be designed so that the rise occurs before the gel time. Thus as the formulation is foaming it is still a viscous liquid and so is able to rise around the instrument's probe/needle. Obviously there are many processes occurring during the cure of a foam, changes in viscosity, temperature, density and depth of needle/probe penetration. The traces obtained are the result of a combination of these effects, albeit the traces can be used as a useful measure of the process of cure during the formation of a PU foam. The instrument does not give any indication of the foam's rise, however the data obtained can be used in conjunction with such data to provide a comprehensive characterisation of the foaming process.

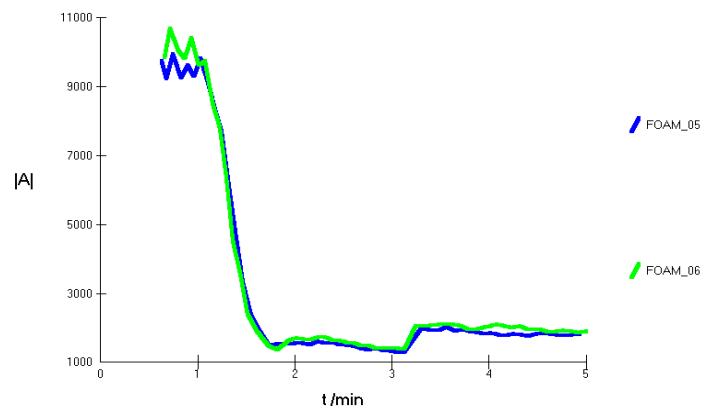
The cure of the rigid foam shown in Figures 29 and 30 is fairly slow. Figures 31 and 32 show the SVNC traces for a typical refrigerator insulation PU foam which has a significantly faster cure. These cures were monitored using the Fast Cure option of the SVNC menu rather than the Monitor option.

Figure 31: Resonance Frequency Traces for a Typical Insulation PU Foam



(See foam_05.csv and foam_06.csv on program disk.)

Figure 32: Resonance Amplitude Traces for a Typical Insulation PU Foam

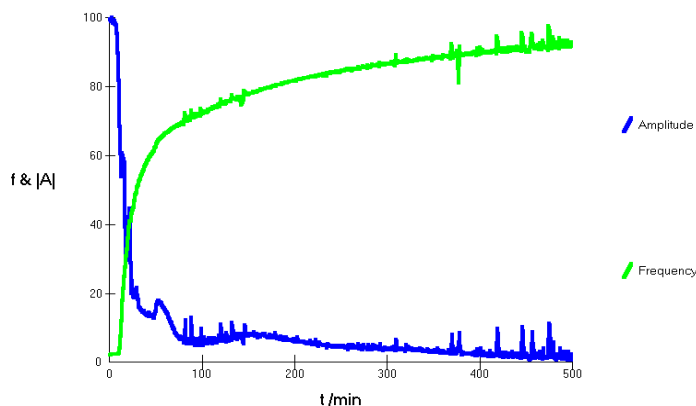


(See foam_05.csv and foam_06.csv on program disk.)

3.9 Cure Monitoring of Thin Films

The new stand arrangement of the Scanning VNC allows accurate positioning of the instruments probe. In this way the cure of relatively thin films can be monitored. Figure 33 shows the cure traces for a film of a silicone polymer which was only 200 μm thick. To do this the amplitude of the needles vibration had to be reduced by adjusting the power setting used during the "In-air resonance" characterisation to 2000 (see SVNC Operating Manual RTL/2843 Section 6.1.2.3). The probe was positioned so that it was 100 μm (0.1 mm) from the surface of the heat stage.

Figure 33: ScanningVNC Traces for the Cure of a Thin Film



(See thinsil.csv on program disk.)

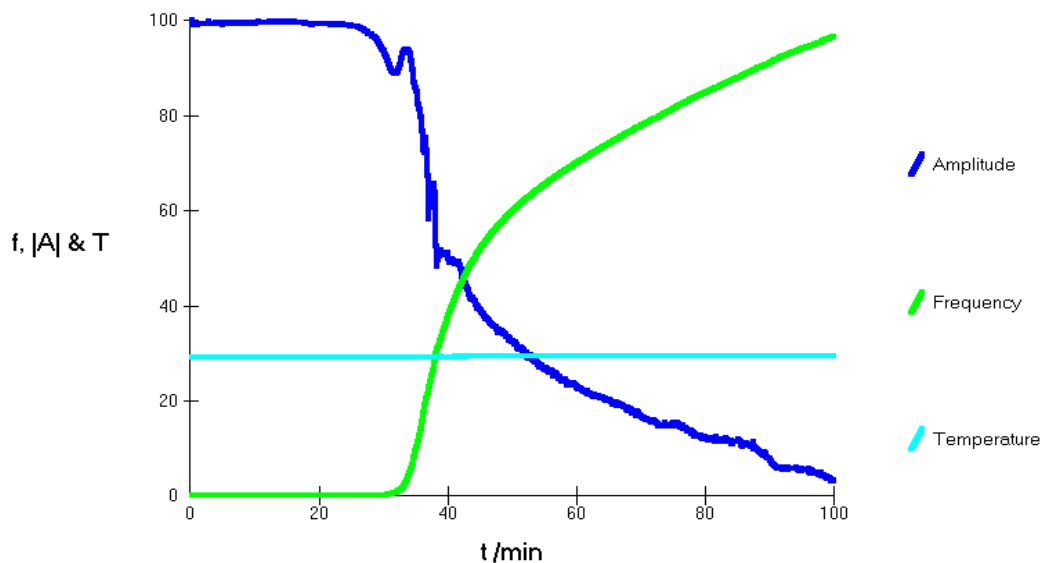
3.10 Comparison of Fixed Frequency Monitoring and Scanning Frequency Monitoring

In Scanning mode the Scanning VNC generally records data every 6 seconds or so, this can be reduced by monitoring the cure at fixed frequency. Thus data points can be collected at a faster rate at fixed frequency, however only one trace is generated and so less information about the cure is provided (see SVNC Operating Manual RTL/2843 Section 6.1.2.6).

Figure 34 shows a typical Scanning VNC traces for the cure of a liquid silicone polymer. The amplitude trace shows how the viscosity of the liquid decreases at the start of the cure and how damping increases after the gel point. The Frequency trace remains unchanged until the gel point. Upon gelation the resonance frequency starts to increase and this increase continues as the modulus of the curing solid increases.

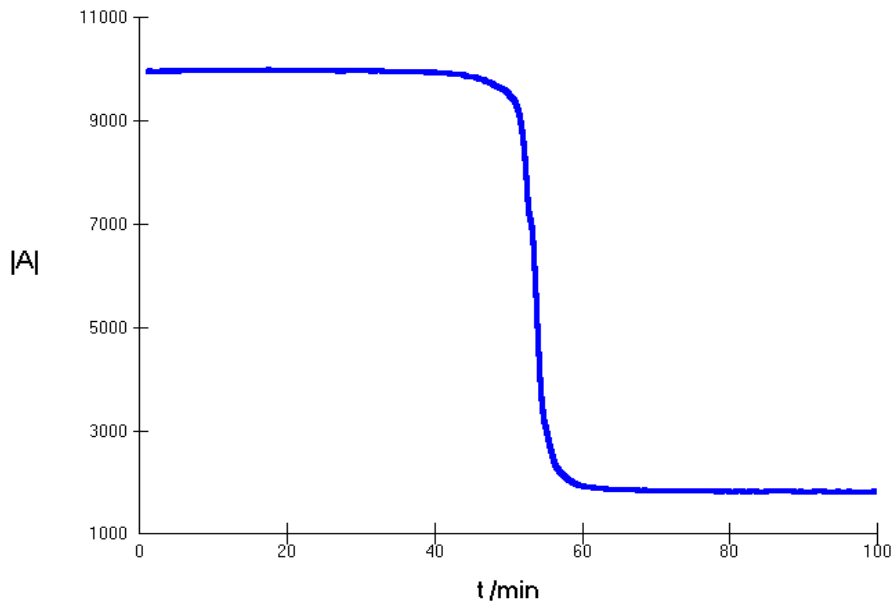
It can be seen that both the resonance frequency and resonance amplitude are still changing after 100 minutes of cure, indicating that the cure process is incomplete at this stage.

Figure 34: Scanning VNC Trace for a Liquid Silicone Polymer



(See sil_scan.csv on program disk.)

Figure 35 shows the single trace monitored at fixed frequency for the cure of the same formulation. This trace is affected by both changes in viscosity and modulus. In the early part the trace is predominantly representative of changes in the viscosity of the sample. The later part of the trace is mainly affected by the modulus of the curing solid. Thus a single trace is produced which is representative of the cure, however it is more difficult to interpret this simple trace in terms of viscosity and modulus changes than the dual trace of the Scanning VNC. However there is the potential for recording data more quickly with the fixed frequency option. Figure 35 shows that the trace stops changing after about 70 minutes, however the trace of Figure 34 shows that changes are still occurring after 100 minutes. Thus in the fixed frequency mode the instrument cannot detect the changes occurring during the later stages of the cure.

Figure 35: VNC Trace Recorded at Fixed Frequency

(See sil_fix.csv on program disk.)

3.11 Assessment of Cured Rubbers

A simple characterisation of the properties of cured rubbers has been carried out using the Scanning VNC. In this characterisation the probe of the Scanning VNC was allowed to rest on the surface of the sample and then the resonance frequency and amplitude of the needles vibration was determined. Increases in resonance frequency would indicate an increase in the storage modulus or hardness of the sample.

This type of characterisation has been carried out on three rubber samples of different Shore A hardnesses. Table 2 shows that the resonance frequency increases as the hardness increases and the resonance amplitude decreases.

Table 2: Effect of Shore A Hardness on Resonance Frequency and Amplitude

Shore A Hardness	Resonance Amplitude	Resonance Frequency
40	8380	114 Hz
50	8330	121 Hz
60	6553	156 Hz

3.12 Summary

The SVNC is a simple, robust instrument which is capable of recording the progress of the cure of liquids and pastes setting to rubbers or glasses. This relatively low cost curemeter is designed for use by non-rheologists, however it is capable of distinguishing the effect of various formulations changes. This is achieved by separately characterising cure in terms of the viscous and elastic changes providing information on key cure parameters: onset of viscosity increase; gel time; build up of modulus and resilience. This Section has illustrated this ability with respect to PU, polysulphide, silicone, epoxy and unsaturated polyester cures as well as the fusion of a PVC plastisol. The SVNC is ideal for both development of new formulations and quality control during production.

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INDEX

- A**
Application Time, 3
- B**
Branching Theory, 3
- C**
Chain Extension, 3, 31
Complex Viscosity, 8
Computer, 16
Crosslink Density, 11, 15
Crosslinking, 3, 31
Cure, 1, 3, 15, 31
 Application Time, 1, 3
 Branching Theory, 3
 Chain Extension, 3, 31
 Changes During, 15
 Complete, 4
 Crosslinking, 3, 15, 31
 Damping, 32
 Demould, 1
 Elasticity, 3, 15
 Entanglements, 15
 Epoxy, 36
 Exotherm, 16
 Gel Point, 1, 3, 5, 11, 15
 Gel Time, 14, 26
 Glassy, 1
 Glassy Products, 36, 37
 Hard Products, 36, 37
 Liquid Polymer, 3
 Model System, 11
 Modulus, 3
 Molecular Weight, 4
 Monitoring, 19
 Network, 3
 Network Flaws, 15
 Onset of, 4
 Polysulphide, 35
 Polyurethane, 32
 Foam, 40
 Flexible, 41
 Rigid, 42
 Profile, 1
 Resilience, 31, 36
 Sealant, 35
 Silicone, 36
 State of, 4
 Thin Films, 45
 Unsaturated Polyester Resin, 37
 Viscosity, 15
 Viscous, 32
 Visible Light, 38
 Vitrification, 1
 Work Life, 1, 3, 15
- D**
Damping, 1, 8, 11
 Maximum, 11
- E**
Elasticity, 1, 3, 15
Entanglements, 15
Epoxy, 36
Exotherm, 16
- F**
Fixed Frequency, 45
Fluid Flow, 4
Frequency, 26
- G**
G', 15
G'', 15
Gaussian condition, 3
Gel Point, 3, 5, 11, 15, 30, 32
Gel Time, 14, 26
- L**
Liquid Polymer; Cure, 3
Loss Modulus, 8, 11
- M**
Maximum Damping, 11
Modulus, 3
 G', 9, 15, 32
 G'', 9, 15, 32
 In-phase, 7
 Loss, 8, 11
 Out-of-phase, 7
 Stiffness, 3
Molecular Weight, 4
Monitoring, 3, 31
 Amplitude, 32

- Fixed Frequency, 45
- Frequency, 32
 - Elasticity, 30
- Monsanto Rheometer, 7
- Oscillatory Measurements, 5
- PVC Plastics, 38
- Resilience, 31
- Resonance, 19
 - Amplitude, 19
 - Frequency, 19
- Resonance Peak, 31
- Rheometers, 15
- Thin Films, 45
- Two-dimensional, 31, 32
- Visible Light Cure, 38
- Monsanto Rheometer, 7
- N**
- Network, 11
 - Formation, 14
- Network Flaws, 15
- O**
- Oscillatory Measurements, 5
- P**
- Phase Angle, 7, 8
- Polysulphide, 35
- Polyurethane, 33
 - Foam, 40
 - Flexible, 41
 - Rigid, 42
 - Gel Point, 33
 - Resilience, 33
 - Storage Modulus, 33
 - Trace, 34, 35
- Process Control, 3
- Product Control, 3
- PVC Plastics, 38
- R**
- Resilience, 31
- Resonance
 - Amplitude, 19
 - Frequency, 19
- Resonance Frequency, 26
- Rheometers, 15
- S**
- Scanning VNC, 15, 16
- Sealant, 35
 - Polysulphide, 35
- Shear Modulus, 4
- Silicone, 36
- State of Cure, 4
- Stiffness, 3
- Storage Modulus, 8
- T**
- Thin Films, 45
- Trace
 - Damping, 1
 - Elastic, 1
- Transducer, 16, 19, 23
 - Model, 19, 23
 - Elastic, 27
- U**
- Unsaturated Polyester Resin, 37
- V**
- Vibrator, 16, 19, 23
 - Elastic Model, 27
 - Model, 19, 23
- Visco-elastic, 7
- Viscosity, 4, 15, 24
 - Amplitude Attenuation, 24
 - Complex, 8
- Viscous Properties, 3
- W**
- Work Life, 3, 15