MTS Adhesives Project 5
Measurements For Optimising Adhesives Processing
Report 10

A Comparison of Techniques for Monitoring
the Cure of Adhesives

A OLUSANYA

The Performance of Adhesive Joints

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the Cure of Adhesives

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This report represents the part of the deliverable for Task 3c - Cure

Reports for Task 3c

Report 10; A Comparison of Techniques to Assess the Cure of Adhesives
Report 11; The Relationship Between Degree Of Adhesive Cure And The Mechanical Performance Of Simple Joints
Report 12; Tests to Assess the Cure Development of Structural Adhesives for Construction
Report 13; Measurements to Assess the Cure Development of Structural Adhesives for Construction

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A Comparison of Techniques for Monitoring the Cure of Adhesives

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ABSTRACT

In this report a number of techniques capable of monitoring the cure of adhesives, viz. DSC, ultrasound, mechanical testing, rheometry etc. are compared. A mathematical treatment of the data to compare the results on common axes is also appraised. The objective of this work is to provide a validation regime for the comparison of the measured cure parameter obtained by various methods, compensating for the varying sensitivity of the selected method.

Particular reference is given to the following:

The influence of the instrument compliance of a constant stress rheometer is assessed and a technique for the correction of data is presented.

A high frequency NDT method based on the reflection of RF frequencies has been shown to be capable of monitoring ambient temperature curing adhesives.

An ultrasound technique developed at NPL and capable of providing data in a ‘real-time’ environment has also been assessed and has been shown to be of value when monitoring the cure of relatively thick, 0.5 - 2mm, adhesive joints.
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APPENDIX

A.1. INTRODUCTION

A.2. COMPLIANCE CORRECTION

A.3. CONCLUSIONS
1. Introduction

The rate of cure of an adhesive is often the critical rate determining step in a manufacturing process. The physical behaviour of a curing adhesive during processing can also have considerable influence on the overall manufacturing route. Therefore there has been a considerable amount of work undertaken to develop techniques which can monitor and 'measure' the state of cure of adhesives. The term cure should be applied strictly to the hardening by chemical reaction which commonly occurs in the structural adhesives and not for example, to contact-type adhesives, whose solutions or lattices already consist of the polymerised adhesive. In this latter case the term which should be used is "open time".

Presently there are no reliable production line measurement systems available to determine the relevant physical parameters which are most affected during the curing process. This project has investigated a number of laboratory methods to monitor and quantify the 'cure' of adhesives and developed non destructive testing methods which are capable of monitoring and giving physical property data relating to an adhesive during the curing process. A comparison was made with data from the industrial collaborators, British Steel Welsh Laboratories and Taywood Engineering in an attempt to correlate laboratory measurements with industry specific tests.

2. Materials

Two one part and two two component epoxy adhesives were examined in this study. Three of these adhesives have been designed for semi-structural applications in the automotive sector, where they are used in the bonding of strengthening members for car bonnets and in conjunction with weld bonding for door panels. The third is used for the external bonding of structural plate reinforcement to concrete and cast iron substrates in the construction sector.
This technique is used to i) increase the load carrying capacity of structural members and ii) reduce deflection of structural members. Structural strengthening applications include:

- Increasing the load capacity of bridges to accommodate increased axle loads
- Increasing the load capacity of floor slabs in buildings to accommodate change of use
- Minimising deflection and hence crack movement and growth in car park decks, roof slabs etc.
- Restoring strength to repaired structures that have suffered from fire damage, reinforcement corrosion or impact damage.

Recommended cure schedules from the manufacturer’s data sheets are shown in Tables 1 and 2.

**Table 1: Basic cure properties of the test adhesives.**

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Type</th>
<th>Cure Temperature (°C)</th>
<th>Curing Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>3M DP190G</td>
<td>2 part toughened Epoxy</td>
<td>25</td>
<td>12 hours</td>
</tr>
<tr>
<td>PPG 3289Y5000</td>
<td>Polybutadiene/Epoxy</td>
<td>190</td>
<td>20 min</td>
</tr>
<tr>
<td>3M Scotchweld 7823G</td>
<td>Corrosion resistant epoxy</td>
<td>120/180</td>
<td>180/30 min</td>
</tr>
</tbody>
</table>
Table 2: Basic cure properties of Sikadur 31 LT PBA 2-part toughened epoxy adhesive.

<table>
<thead>
<tr>
<th>Cure Temp. (°C)</th>
<th>Time Days</th>
<th>Strength Gain %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>7</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>14</td>
<td>72</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>70</td>
</tr>
<tr>
<td>20</td>
<td>7</td>
<td>75</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
<td>78</td>
</tr>
</tbody>
</table>

3. Measurement Techniques for the monitoring and assessment of the cure state of an adhesive

The cure of the selected adhesives was measured and evaluated by three basic techniques:

- Differential Scanning Calorimetry - measurement of the heat evolved during the chemical curing process

- Mechanical testing; tensile testing of 'cured' bulk adhesive specimens, lap shear joint tests and measurement of the shear storage modulus by rheological testing

- Non-destructive testing including ultrasound and high frequency dielectric testing
3.1. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a method which has been widely used to determine the kinetics of cure by following the exotherm of the reaction. The instrument used in this study was a Perkin-Elmer DSC 7 using Version 3.2 isothermal software. The experimental programme consisted of a temperature ramp run from ambient to 220°C, dependent on the cure cycle of the adhesive, to determine the total energy for the curing reaction. A series of measurements of the energy evolved with time when the specimen was held at various temperatures was then made to determine the effective percentage completion at these specific temperatures. This series of measurements enabled a time-temperature conversion profile to be calculated. Conversion graphs based on energy output for the four test adhesives are shown in Figures 1 - 4.

3.2. Mechanical Testing

Standard ISO tensile test specimens were prepared. Results of mechanical tests using SIKA 31PBA LT adhesive are shown in Figure 5 and lap shear strength values for PPGY5000 adhesive measured at three temperatures are shown in Figure 6.
3.3. Rheological Testing

A TA Instruments CSL 500 constant stress rheometer, (formerly Carri-Med), was used to produce shear modulus/cure time graphs for the test adhesives at constant temperatures, Figure 7. This instrument is capable of measuring the mechanical properties from the fluid/paste state to the solid phase. Typical data obtained for the four test adhesives, ($G'$ is instrument compliance corrected), at a range of temperatures is shown in Figures 8 to 11.

The mechanical test data were compared with the mechanical properties of cured samples of the respective bulk adhesive obtained by dynamic mechanical thermal analysis using a Polymer Laboratories DMTA instrument and Polymer Labs Plus 5 software. The shear modulus calculated from mechanical testing using an INSTRON 4505 test machine and video extensometer on a cured sample of 3M 7823G at 120°C, was $35.5 \pm 5\text{mpa.}$ at a test speed of 1mm/min, (approx. 1%/min strain rate). This measured value is an order of magnitude greater than that obtained using the rheometer. This was traced to the compliance of the rheometer. A large proportion of the strain occurs in the drive shaft or in the joint connecting the drive shaft to the geometry rather than in the test material. This results in the modulus values to being underestimated. Further analysis of the rheometer system indicated that for stiff materials the torque used to tighten the geometry to the air-bearing shaft was a major influence on the instrument compliance and thus on the measured value of shear modulus. This is shown in Figure 12. To facilitate the application of a constant tightening torque to the rheometer draw rod, item 8, Figure 7, using a torque wrench, the original knurled finish was replaced with a 13mm ‘hex’ head.

Values of the overall instrument compliance obtained by bonding the selected test geometry to the base geometry by cyanoacrylate adhesive, at different effective tightening torques of the geometry draw rod are shown in Table 3.
Table 3. Draw rod torque compared to machine compliance

<table>
<thead>
<tr>
<th>Draw-rod torque (cNm)</th>
<th>Machine compliance (rad/cNm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>410</td>
</tr>
<tr>
<td>30</td>
<td>390</td>
</tr>
<tr>
<td>40</td>
<td>390</td>
</tr>
<tr>
<td>50</td>
<td>392</td>
</tr>
<tr>
<td>70</td>
<td>257</td>
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</table>

As can be seen from Table 1 the machine compliance exhibits a 35% increase by increasing the torque from 20-50cNm to 70cNm. Tightening the draw-rod above 70cNm produced minimal change in the machine compliance and subsequent tests were carried out with a draw rod tightening torque of 70cNm.

This method of determining the instrument compliance test is valid due to the very thin layer of cyanoacrylate adhesive used. As the adhesive film is very thin it also then has a modulus greater than that of the instrument and therefore the compliance measurement determined is that for the rheometer. With a value of the instrument compliance established the physical property data are then recalculated using a spreadsheet. This procedure is explained in detail in Appendix 1.

Further modifications, such as using a splined spindle to attach different specimen geometries could offer advantages in maximising the output torque of the motor. The addition of splines on the air bearing shaft and the measurement geometries creates a positive fit between the two components thus increasing the torque transfer with minimal backlash. A modification of this nature increases the measurement range of the 'standard' instrument at a reasonable cost without major redesign.

The effect of correcting for the instrument compliance on the calculated physical property data for adhesives can be seen in Figures 11 and 13.

The data presented in Figures 8 and 10 for 3M 7823G epoxy and PPG Y5000 butadiene epoxy adhesive are corrected for instrument compliance.
A comparison of the effect of temperature between these two materials is interesting. The 3M material exhibits the typical behaviour of an epoxy material, i.e. modulus decreasing with increasing temperature, however it can be seen in Figure 10 that the modulus of the PPGY5000 adhesive increases with increasing temperature. This effect, increase of mstorage modulus with temperature is typical of the behaviour of rubber materials, however this effect is non reversible. It is proposed that this behaviour is a consequence of the two competing reactions which are occurring in this modified adhesive. The epoxy component in this adhesive behaves as expected, i.e. it softens as the temperature rises, the rubber component however begins to cross link, (vulcanise) as the temperature increases and thus the modulus of the material increases, non-reversibly, with increasing temperature.

3.4. Monitoring of cure using ultrasound

The greatest practical use of cure is in the production of components whether they be plastic, composite or adhesively bonded systems. The most technologically advanced major users of adhesives are in the aerospace sector where the high cost product and the high product safety factors have led to a large knowledge base of optimised adhesives and procedures. This sector routinely use non-destructive test methods particularly ultrasound to monitor the integrity and the state of cure of adhesively bonded components.

Cure monitoring using ultrasound techniques has been developed as a method for following the whole cure process. This technique can accommodate the rapid heating rates typically encountered in processing which are not easily obtainable in other cure characterisation techniques. Since the measurement involves non-moving parts, and the results obtained are directly related to the final mechanical properties of the required component, ultrasound testing has a considerable practical potential as a reliable method of measuring the degree of cure in commercial injection or compression moulding situations.
3.4.1. Ultrasound Theory

The longitudinal elastic component of modulus for the material is given by:

\[ L = \rho V_L^2 = K + \frac{4}{3} G \]

Equation 1

where

- \( L \) - longitudinal modulus
- \( K \) - bulk modulus
- \( G \) - shear modulus
- \( \rho \) - density
- \( V_L \) - longitudinal wave velocity.

Therefore modulus is proportional to \( V_L^2 \). By measuring \( V_L \), the changes in modulus can be calculated.

When a viscoelastic material is considered however the viscoelastic effects must be taken into account:

\[ L^* = L' + iL'' \]

Equation 2

where

- \( L^* \) - complex longitudinal modulus
- \( L' \) - storage longitudinal modulus
- \( L'' \) - loss longitudinal modulus
The internal damping due to viscous effects is given by the loss tangent

\[ \tan \delta_L = \frac{L''}{L'} \]  

Equation 3

The standard equation for sinusoidal wave motion in an elastic medium is described by:

\[ P = P_0 \exp \left( i \omega (t - \frac{x}{v}) \right) \]  

Equation 4

where

- \( P \) - acoustic pressure
- \( P_0 \) = amplitude of the wave at \( x = 0 \)
- \( \omega \) = frequency
- \( t \) = time and \( x \) = distance through material

Substituting in the complex quantity, \( V^* = V' + iV'' \) for velocity in a viscoelastic material for conditions where \( V''^2 \ll V'^2 \) gives:

\[ P = P_0 \exp \left( -\frac{\omega V''}{V'^2} x \right) \exp \left[ i \omega \left( t - \frac{x}{v} \right) \right] \]  

Equation 5

Thus a wave travels through a material with a velocity \( V \) which is dependent upon the longitudinal storage modulus and is attenuated with distance due to loss effects. Therefore by measuring the longitudinal compression wave velocity we can directly measure the change in longitudinal storage modulus of the curing material, and by measuring the attenuation of the waveform during cure we obtain data proportional to \( \tan \delta_L \), equation 6
\[
\tan \delta_L = \frac{-20 \log \frac{P_2}{P_1}}{\pi \omega} \times v
\]

Equation 6

where \( P_2 = \) amplitude through the sample
\( P_1 = \) amplitude through the blank
\( v = \) velocity

and \( \omega = \) frequency

Obtaining accurate absolute values of \( \tan \delta_L \) is difficult since the measured attenuation or absorption is not due solely to viscous dissipation within the curing sample. Losses also occur due to reflections between the ultrasonic transducer/moulding tool, moulding tool/curing material. Losses can be accounted for by measuring the attenuation of reverberations within the moulding cavity similar to a technique for thin adhesive joints by Challis\(^4\), however, for thick heavily filled/reinforced composite mouldings the reverberated signal is difficult to resolve.

A method using two samples of different thickness and measuring the difference in attenuation, thus removing coupling and reflection losses, has also been proposed\(^3\). However, the use of this method in an industrial environment is impractical since the curing properties of a defined material thickness are of interest. For all practical purposes the accuracy afforded by the current experimental set-up is sufficient.
3.4.2. NPL Ultrasound Method

The ultrasonic cure measuring equipment was adapted from a system developed by the NPL for measuring the elastic constants of materials, a block diagram of which is shown in Figure 14. Two PZT 2.5MHz contact probes were used to pass and receive a longitudinal wave through a curing sample of adhesive. The transmitting crystal was excited using short pulses of 0.75 ms duration with a repetition frequency of 5KHz to generate the longitudinal wave. The received pulse, after passing through the sample, is amplified by a wide band amplifier and displayed on the oscilloscope. The time base of the oscilloscope, which is synchronised with the repetition frequency, is delayed by a crystal controlled circuit which can be altered in steps of 1ns.

The time delay between transmitting and receiving the pulse is measured by setting the delay circuits to bring a predetermined cross-over of the pulse to coincide with the cross wires of the oscilloscope. The time of flight of the signal through the sample is determined from the time shift of the received signal on placing the sample between the probes and subtracting the reference time for 'no sample' from measurements with the probes in contact.

As the thickness of the sample section is known, the velocity of the pulse can be calculated since the time of flight is known. The velocity of the ultrasonic pulse is known to be proportional to the square root of the sample's longitudinal modulus. Therefore as the sample changes phase from liquid to solid, as a result of increased cross-linking density, the sample modulus increases and the velocity of the pulse through the sample increases thus giving a measure of the state of cure. During the test the attenuation of the signal is also measured using an attenuation box capable of resolving steps of 0.5 dB. The attenuation of the signal is proportional to the loss factor of the material due to viscous damping. Therefore, as the material cures, and the material changes from a viscous liquid to a solid, the attenuation of the ultrasonic pulse through the sample will rise at the glass transition temperature, Tg, and then fall due to the increased transmission of the wave in the solid.

Typical results for adhesives 3M DP190 and PPGY5000 are shown in Figures 15 and 16.
The advantage in using this ultrasound method devised by the NPL is that as shown by the data represented in Figures 15 and 16 that practical real time on-line measurement is possible over a wide range of temperatures and the method is applicable to sections up to 5mm thick.

3.5. Microwave Dielectric Monitoring of Cure

The use of adhesives in the construction sector is increasing especially for subsequent repair and reinforcement. Methods to monitor cure on site are required. With the increase in traffic levels and legislation allowing increased lorry axle loads, current maximum design loads on road bridges are being approached. Current practice involves the closing of the road network whilst specialists undertake the in-situ reinforcement through the bonding of steel reinforcement panels to the underside of the bridge deck. In applications such as these, the adhesive can be the width of a carriageway and have a thickness of up to 25mm. Having reinforced the structure in this way the engineer is now left with limited means to test the development of modulus/cure in the adhesive which is critical for effective transfer of load to the reinforcing system. Some basic mechanical tests for on-site analysis are available but more extensive tests require adhesive samples being transferred to an off-site testing facility. As the adhesive curing cycle is reliant on the site environmental conditions data collected in this manner have to be closely scrutinised. Data on the curing behaviour in-situ will aid the site engineer’s assessment in the analysis of structure loading, safety and the timetabling of road opening schedules. Within this programme initial investigations have been made into a robust method to monitor cure that could be used on-site. A reflectometric coaxial sensor measuring dielectric properties at microwave frequencies has been used to monitor the cure of a typical adhesive used in bridge deck reinforcement, Figure 17. This method is particularly suited for this application as access to the component to be monitored is only required from one face.
3.5.1. Theory of microwave monitoring of cure

The advantage of microwave dielectric measurement over traditional capacitance cells is the removal of the large conduction term which dominates and masks measurements at low frequencies.

The ionic conduction contribution is given by:

\[ Ionic\_contribution = \frac{\sigma}{\omega \varepsilon_0} \]

**Equation 7**

where \( \sigma \) = ionic conduction
\( \omega \) = frequency

and

\( \varepsilon_0 \) = permittivity of free space

Using typical values for a polymer at a frequency of 10kHz, typical of capacitance cell measurements:

\[ \sigma = \mu [C] q \]

**Equation 8**

where \( \mu \) = ion mobility = \( 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \)

\([C] = \text{ion concentration} = 1 \times 10^{17} \text{ cm}^{-3}\)

and \( q = \text{charge on an electron} = 1.6 \times 10^{-19} \text{ C} \)

The ionic conduction contribution falls from 20 at 10kHz to \( 2 \times 10^4 \) at 1 GHz.
3.5.2. Reflectometric coaxial sensors

If a coaxial line is connected to an electromagnetic signal source at one end but is open-circuited into air at the other, fringing electromagnetic fields emerge from the open end of the line. At low frequencies, these are largely evanescent, which (in this context) is to say that no power is transferred from these fields to the free space around the end of the line. The electromagnetic power is therefore all reflected back again down the coaxial line to the source. In these circumstances microwave engineers say that the admittance presented to the line by the fringing fields is purely reactive. This has the consequence that, if $T$ is the complex reflection coefficient of the signals from the end of the line, we have $|T| = 1.0$. As the frequency increases through the microwave band, however, a significant proportion of the signal comes to be radiated into free-space, and so we have $|T| < 1.0$. Furthermore, if the end of the line is surrounded by a dielectric of complex permittivity $\varepsilon^*$, the phase of $T$, $\theta$, is significantly affected by the value of $\varepsilon^*$. Even at low RF frequencies, where no significant radiation occurs, a lossy dielectric ($\varepsilon'' > 0.0$) will absorb power, thus giving $|T| < 1.0$. Since the reflection coefficient from any termination of a coaxial line is intimately related to the admittance it presents, the admittance presented by the fringing fields to the line depends critically upon the dielectric properties of the materials through which the fields pass. This principle provides the basis of a convenient technique for measuring dielectric properties $^5$-$^8$ - the open-ended coaxial dielectric sensor. Non-invasive dielectric sensors based upon this principle are used at RF and microwave frequencies in conjunction with reflectometers, such as Automatic Network Analysers (ANAs), to determine complex permittivities of a wide range of dielectric materials.
The reflection coefficient, $\Gamma$ is given by,

$$\Gamma = \frac{Z_l - Z_o}{Z_l + Z_o}$$

Equation 9

where $Z_l =$ the impedance of the line

and

$Z_o =$ the impedance of the sample

The mathematical relationship correlating complex permittivity, $\varepsilon^*$ to the reflection coefficient, $\Gamma$ is obtained by electromagnetic field modelling (9).

where

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

The various modes of use of the NPL coaxial sensor is shown in Figure 18 and the geometry in Figure 19. The sensor was constructed with the following properties:

- a, inner conductor radius, 1.994 mm
- b, outer conductor radius, 7.545 mm
- Lucentine - $\varepsilon'_b$, bead permittivity, = 2.538

This sensor is referred to as a 14-mm sensor because it was constructed from General Radio stock precision 14-mm airline. This diameter was originally chosen because it produces a fringing capacitance of about 0.1 pF into air, found to be the optimum for measuring biological tissues at a frequency of 1 Ghz. The circular flange at the end of the line was added to aid the solution of the complex equations. The dielectric bead was required both to support the inner-conductor and to present a well-defined interface plane into liquid and air dielectrics. The design of the bead preserves a characteristic impedance of 50 $\Omega$ in the line.

Results have been encouraging. Typical reflection results are shown in Figure 20 with the derived permittivities and loss factors in Figure 21. These results indicate that the potential exists for the development of a prototype test instrument. Further evaluation of the technique is recommended.
4. **Comparison of data**

With such a large amount of information available for qualitatively and quantitatively determining the cure of adhesive systems, there is a requirement to present the information from all these disparate tests on common axes. Figure 22 highlights the difficulties in comparing cure data collected by different measurement techniques. A logical arrangement would be to compare the measured curing data as a dimensionless property. By adopting the concept of conversion calculated from the physical properties measured, data can be represented on a single set of axes. For example the conversion, cure, of a material can be represented thus:-

\[
\alpha = \frac{G''_n - G''_0}{G''_\infty - G''_0}
\]

Equation 10

where \( \alpha \) = conversion

\( G''_n \) = storage modulus at time \( n \)

\( G''_0 \) = initial storage modulus

\( G''_\infty \) = storage modulus at infinite time ie. fully cured

\[
\alpha = \frac{H_n}{H_T}
\]

Equation 11

where \( H_n \) = heat evolved at time \( n \), (isothermal experiments)

and \( H_T \) = total heat evolved for curing reaction, (fully cured material from temperature ramp experiment)
The development of the mechanical properties as described by $G'$, $G''$ etc. during the curing process (with respect to time and temperature) was also measured by constant stress rheometry as shown in Figures 2 and 3.

The Kamal equation (Equation 12) is a sigmoidal mathematical model which has been used to model the curing behaviour of polyester dough moulding compounds.

It was felt that the similarity in the materials used may aid the analysis of cure data obtained by the various techniques, ultrasound, high frequency dielectric and differential scanning calorimetry obtained in this study. Using constant stress rheometry and DSC data for PPGY5000 adhesive as an example.

\[
\alpha = \frac{\left( \frac{n-1}{k_t} \right)^{1}}{1 + \left( \frac{n-1}{k_t} \right)^{1}}
\]

Equation 12

where $\alpha =$ conversion

$n =$ order of reaction

and $k_t =$ rate constant

Use of the Kamal equation to redefine the data presented in Figure 22 can be seen in Figure 23. Within experimental error, the use of this technique to model the cure kinetics proved satisfactory. Figures 24 and 25 show DSC data and mechanical property data obtained by constant stress rheometry converted to conversion/time graphs. It can be seen that the “time constant” of the two techniques is radically different. The comparison of data in this manner indicates the sensitivity in the inter-relation of cure techniques. For the case of DSC the bulk of the thermal output of the curing reaction occurs below 90% conversion and the equipment is not as sensitive over the final cure period to reliably measure thermal energy changes over the final period of curing.
Rheological measurement, monitoring the physical property changes during cure seem to be relatively slower processes in which the curing process gradually tends towards a diffusion controlled process as the system solidifies. In terms of manufacturing processes this information on the state of the mechanical properties is much more useful than the state of the chemical reaction.

There are difficulties in using the concept of a conversion factor primarily with the determination of the final cured state. Cure may continue slowly after the point where further curing is not obvious from the measurements, i.e. low measurement technique sensitivity. It was found especially in the case of ambient temperature cured adhesives measured by constant stress rheometry, that the shear storage modulus increased by 100% after three days from the value of 24 hours, (23.3MPa. to 54.7MPa. at 20°C). The final cured state may be more rigorously defined at the stage where there are no changes in a materials glass transition temperature as measured by a method such as DMTA..

Another problem in determining the final cured state is the differing thermal behaviour of the various types of adhesive. For example if we compare the behaviour of an epoxy 3M7823G and the butadiene-epoxy, PPGY5000, Figures 8 and 10. It can be seen that 3M7823G exhibits the expected trend of softening at temperatures above 140°C. The modulus of the PPGY5000 material tends to increase at higher temperatures and extended cure times. A possible explanation of this behaviour is due to the composition of the PPG material. This material is more strictly defined as a butadiene adhesive with epoxy chains incorporated into the butadiene matrix. Therefore at relatively low temperatures the epoxy material is polymerising and at elevated temperatures and extended cure times, greater than 60 minutes, a non-reversible cross-linking reaction, (vulcanisation) of the butadiene material occurs which results in the material becoming stiffer up to approximately 220°C after which the material scorches and degrades.

Figure 26 compares the conversion factors derived from lap shear strength in Figure 6(10), with the conversion factors derived from shear storage modulus data in Figure 10.

The conversion data for PPGY5000 is calculated assuming that the epoxy curing mechanism is complete after 60 minutes at 190°C, i.e. $G'_{\infty} = 20.2$MPa. not 33.0MPa. after 180minutes. This additional increase of 12.8MPa. is due to the additional cross-linking reaction.
It can be seen from Figure 26 that there is a reasonable correlation between the rate of cure between the two measurement methods. This has been confirmed in other studies (10).

Using the ‘average’ rate of reaction, (from multiple temperature experiments), and the equilibrium constants from the Kamal equation, the temperature dependence of the curing reaction can be modelled. Information of this nature is of importance when using automated process control equipment for manufacturing. Even with these complications the Kamal equation proved a useful tool in modelling the curing behaviour as defined by various physical properties.

The sensitivity and the profile of the various measurement techniques during the cure cycle must be taken into account when deciding upon a monitoring method for each specific application. This is highlighted by the data presented in Figure 25, where the DSC data from Figure 1, the UTS data from Figure 5, and ultrasound data are placed on common axes.

It can be seen that there is no agreement between any of the different measurements. The closest agreement is between the respective 40°C ultrasound and DSC measurements. However when this is balanced by the corresponding data at 20°C the correlation is poorer.

Further work should be undertaken to try to understand the temperature dependence of the correlation between ultrasound and DSC measurements. The 40°C ultimate tensile strength measurements lie between the respective 20°C and 40°C ultrasound and DSC measurements. For the ultrasound measurement system this could be attributed to the frequency at which the measurements are carried out as the higher the measurement frequency the effective lower temperature response of the adhesive material. The results as shown in Figure 25 seem to indicate that for the 20°C ultrasonic measurement, at frequency of 5kHz, the material has a similar response to an ultimate tensile strength measurement at 40°C. This hypothesis needs to be tested using a range of ultrasound frequencies based upon a central frequency of 5kHz and correlating these with ultimate tensile strength tests, of which there is data available in the literature.
The sensitivity of the ultrasound measurements also change with temperature. This is probably due to the fact that the material is curing quicker at the elevated temperature. This is seen in Figure 25 as the 20°C ultrasound signal is not detected until 100 minutes have elapsed, compared to 25 minutes at 40°C.

5. Conclusions

Comparison of measurement techniques has highlighted the variations in sensitivity between experimental methods. Methods which simulate industrial practice are of great importance. It has been shown in this study that there is a reasonable correlation between the rate of cure measured by the increase in lap shear strength and shear modulus obtained by constant stress rheometry. This trend has been confirmed by other studies (10).

The ultrasonic measurement system developed by NPL has uses in 'on-line' monitoring and process control. Further development is being undertaken to increase the working temperature of the ultrasound sensors to operate at temperatures of 300°C. The results correlating ultrasound velocity and ultimate tensile strength as shown in Figure 25 indicate the possibility of a correlation between an ultrasonic measurement performed at 20°C at a frequency of 5kHz and ultimate tensile strength measurement at 40°C. This could be due to a measurement frequency effect. This hypothesis needs to be tested using a range of ultrasound frequencies, correlating the results with ultimate tensile strength tests, of which there is data available in the literature.

The high frequency reflectometric coaxial sensor has given some promising results. The single sided nature of the sensor lends itself well to industrial applications were there is limited access to the joint or section to be monitored.

In order to further develop this technique, funding is being sought under a collaborative framework i) to increase the working temperature range of the sensor which is currently limited to 40°C and ii) to simplify the electronics such that a low cost testing unit can be manufactured.
The use of the 'Kamal' equation has proved useful in modelling the data and provides a basis for a comparison of techniques, and for potential use in on-line process control.

The modification of rheometry testing equipment and the establishment of a method to account for instrument compliance in the measurement of the physical properties of relatively stiff materials are results to be consolidated in international standards and instrument improvements.

To reduce the influence of the draw-rod tightening torque on the experimental data a follow-on adhesives project will make further modifications to the air bearing shaft, incorporating splines to improve the torque transfer between the rheometers motor and the selected measurement geometry.
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Figure A1: Compliance correction for Carri-Med CSL\textsuperscript{2} 500
7. REFERENCES


8. ACKNOWLEDGEMENTS

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APPENDIX
by M. Rides and A Olusanya, CMMT

A.1. INTRODUCTION

In testing of highly viscous fluids using an oscillatory rheometer, errors in the measured values of the dynamic moduli (shear storage modulus \( G' \) and shear loss modulus \( G'' \)) for the sample can result due to the compliance of the machine. The errors can be particularly large in testing adhesives during cure. The consequence of the errors is that the measured values are less than the true values with the error increasing with increasing stiffness of the sample. A method is presented for correcting the measured data for the effect of the instrument compliance. The correction procedure can be applied to the experimental data by, for example, the use of a spreadsheet.
A.2. COMPLIANCE CORRECTION

The testing of a sample using an oscillatory rheometer can be represented by Figure A1, where the stiffnesses of the machine and sample are given by $K_1$ and $K_2$ respectively. An applied torque $T_m$ results in the angular shear displacements $\theta_1$ and $\theta_2 \cdot \theta_1$ across the sample and the machine respectively.

The torsional stiffness and angular displacements are taken to be complex. The torsional stiffness $K_m$ and angular displacement $\theta_m$ are those for the machine and sample combined.

Torsional stiffness $K$ is defined as

$$K = \frac{\text{Torque, } T}{\text{Angular displacement, } \theta} \quad [1A]$$

$$T_m = K_1 (\theta_m - \theta_1) = K_2 \theta_1 = K_m \theta_m \quad [2A]$$
Thus

\[ \theta_m = \frac{(K_2 + K_1)}{K_1} \theta_1 \]  

[3A]

and

\[ K_m = \frac{K_2 \theta_i}{\theta_m} \]  

[4A]

Substituting for \( \theta_m \) using equation 2A gives

\[ K_m = \frac{K_2 K_1}{K_2 + K_1} \]  

[5A]

which can be rewritten in the form

\[ \frac{1}{K_m} = \frac{1}{K_1} + \frac{1}{K_2} \]  

[6A]

Thus from equation 6A it is clear that the stiffness (which is proportional to the reciprocal of the compliance) of the machine \( K_1 \) must be much larger than \( K_2 \) if its effect on results is to be negligible. Where this is not the case the following procedure will correct for the effect of the compliance of the machine.
If the sample stiffness $K_2$ is replaced by element of infinite stiffness ($K_2 = \infty$) then equation 6 can be rewritten

$$\frac{1}{K_{\infty}} = \frac{1}{K_1} + \frac{1}{\infty}$$  \[7\]

or

$$K_{\infty} = K_1$$  \[8A\]

where $K_{\infty}$ indicates the measured stiffness of the machine and an infinitely stiff sample.

Using equation 6 the stiffness of the sample can be expressed as a function of the measured stiffness $K_m$ and the machine stiffness $K_1$ thus

$$K_2 = \frac{K_m K_{\infty}}{K_{\infty} - K_m}$$  \[9A\]

Using this equation the true stiffness of the sample $K_2$ can be determined from the measured stiffness of the sample and machine $K_m$ and that of the machine and infinitely stiff sample $K_{\infty}$.

It is taken that these stiffnesses are complex such that

$$K_2' = K_2' + iK_2''$$  \[10A\]

$$K_m' = K_m' + iK_m''$$  \[11A\]
However it is assumed that there is no 'imaginary' or viscous part to $K_{\infty}$. Thus

$$K_{\infty} = K'_{\infty}$$  \[12A\]

Then equation 9A can be rewritten in complex form as

$$K'_{2} + iK''_{2} = \frac{(K'_m + iK''_m)K'_{\infty}}{K'_{\infty} - K'_m - iK''_m}$$  \[13A\]

$$= \frac{(K'_m + iK''_m)K'_{\infty}[(K'_{\infty} - K'_m) + iK''_m]}{[(K'_{\infty} - K'_m) - iK''_m][(K'_{\infty} - K'_m) + iK''_m]}$$  \[14A\]

$$K'_{2} + iK''_{2} = \frac{K'_{\infty}[\{K'_m(K'_{\infty} - K'_m) - K''_m K''_m\} + i\{K''_m(K'_{\infty} - K'_m) + K'_m K''_m\}]}{(K'_{\infty} - K'_m)^2 + (K''_m)^2}$$  \[15A\]

Splitting equation 15A into its the real and imaginary parts yields

$$K'_{2} = \frac{K'_{\infty}}{(K'_{\infty} - K'_m)^2 + (K''_m)^2} \left\{K'_m(K'_{\infty} - K'_m) - (K''_m)^2\right\}$$  \[16A\]

$$K''_{2} = \frac{K'_{\infty}}{(K'_{\infty} - K'_m)^2 + (K''_m)^2} \left\{K''_m(K'_{\infty} - K'_m) + K'_m K''_m\right\}$$  \[17A\]
and the sample loss angle $\delta_2$ is given by

$$\tan \delta_2 = \frac{K''_2}{K'_{2}} = \frac{K''_m(K'\_\infty - K'_m) + K'_mK''_m}{K'_m(K'\_\infty - K'_m) - (K''_m)^2} \quad [18A]$$

$$= \frac{K''_mK'_\infty}{K'_m(K'\_\infty - K'_m) - (K''_m)^2} \quad [19A]$$

The stiffness parameters $K'_m$, $K''_m$ and $K'\_\infty$ in equations 16A-19A are defined as

$$K'_m = \frac{T_m}{\theta_m} \cos \delta_m \quad [20A]$$

$$K''_m = \frac{T_m}{\theta_m} \sin \delta_m \quad [21A]$$

and

$$K\_\infty = \frac{T_-}{\theta_-} \cos \delta\_\infty = \frac{T_-}{\theta_-} \quad [22A]$$

In order to carry out this correction, when carrying out testing on samples it is necessary to obtain the following data:

- torque amplitude, $T_m$
- displacement amplitude, $\theta_m$
- phase shift, $\delta_m$
To obtain the value for $K'_\infty$ it is necessary to "lock" the machine. This can be done either by physically clamping the plates together or by sticking the plates together using a very thin film of adhesive. In the latter case even if the modulus of the adhesive is low compared with that of the rheometer material, because the thickness of the adhesive layer is small its stiffness is high.

In testing an 'infinitely stiff' sample with the plates effectively locked the parameters obtained are:

i) torque amplitude, $T'_\infty$

ii) displacement amplitude, $\theta'_\infty$

In this case it is assumed that the phase shift $\delta'_\infty = 0$ equating to a purely elastic response. The stiffness parameters defined in equations 20A - 22A can then be determined.

Thus values of true sample stiffness $K'_2$ and $K''_2$ corrected for the machine's compliance can be determined by substitution of the measured stiffness values (equations 20A - 22A) into equations 16A and 17A.

To determine the sample's shear storage modulus $G'$ and shear loss modulus $G''$ from the stiffness values the following geometry conversion factor must be applied. For a cylindrical element (or sample) of radius $R$ and length $L$ corresponding to a parallel plate geometry

\[
K' + K'' = (G' + iG'') \frac{\pi R^4}{2L} \tag{23A}
\]
Thus

\[ G'_2 = \frac{2L}{\pi R^4} K'_2 \]  \[24A\]

\[ G''_2 = \frac{2L}{\pi R^4} K''_2 \]  \[25A\]

and

\[ \tan \delta_2 = \frac{K''_2}{K'_2} = \frac{G''_2}{G'_2} \]  \[26A\]

A.3. CONCLUSIONS

A method has been presented for the correction of oscillatory rheometry measurements for results that are affected by the compliance of the machine. This error can be particularly large when testing stiff samples such as adhesives during cure.
Figure 1: Conversion of Sika 31PBA LT by differential scanning calorimetry

Conversion of Sika PBA 31 LT (by DSC)

Conversion (%)

Time (minutes)

- 40°C
- 20°C
- 10°C
Figure 2: Conversion of PPGY5000 by differential scanning calorimetry

Cure of PPG 3289Y5000 at Various Temperatures

Conversion vs. Time (s)

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

195 C 190 C 185 C 180 C 175 C 170 C 165 C
Figure 3: Conversion of 3M7823G by differential scanning calorimetry

3M 7823G Conversion (DSC)

Conversion vs Time (min)
Figure 4: Conversion of 3M DP190G by differential scanning calorimetry
Figure 5: Ultimate tensile strength measurements on SIKA 31PBA LT cured at 40°C.

ISO UTS measurements

Time after initiation of cure (minutes)
Figure 6: Ultimate tensile strength measurements on PPGY5000

Strength vs time for PPGY5000 rubber toughened epoxy adhesive

- 190°C
- 160°C
- 140°C

Time (min)

Strength (N/mm²)
Figure 7: Schematic of Carri-Med CSL\textsuperscript{2} 500 constant stress rheometer
Figure 8: Development of $G'$ by Constant Stress Rheometry for 3M 7823G structural adhesive
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Figure 10: Development of shear modulus $G'$ measured using constant stress rheometry for PPGY5000.
Figure 11: Development of shear storage modulus, $G'$, measured using constant stress rheometry for Sika 31PBA LT

SIKA 31PBA LT cured at 40°C by rheometry

![Chart showing the development of shear storage modulus over time.](chart.png)
Figure 12: Constant stress rheometer instrument displacement vs geometry tightening torque
Figure 13: Development of shear storage modulus, \( G' \), measured using constant stress rheometry for 3M 7823G, corrected values

Curing curve for 3M7823G at 120°C

- Measured Data
- Corrected Data (292.6 Nm/rad)
- Corrected Data (300.4 Nm/rad)
- Corrected Data (306.5 Nm/rad)
Figure 14: Schematic of NPL Ultrasonic Analyser

- NPL Ultrasonic Analyser
- Clock
  - 02:07
- Delay Circuit to 1ns
- DVM
  - 06:53
- Amplifier
- Pulsed Transmitter
  - 0.8 - 1.2 ms
- Sample
- Bandpass filter
- Transducers
Figure 15: Cure of 3M DP190G monitored by ultrasound

Ultrasonic Cure Conversion of 3M DP 190 2-part structural adhesive

Conversion vs. Time (min)
Figure 16: Cure of PPGY5000 monitored by ultrasound at 3.5MHz.
Figure 17: NPL reflectometric sensor

Reflectometric sensor
Figure 18: Modes of use of the 14mm open ended reflectometric sensor

(a) Sensor geometry for measuring an 'infinite half-space'

(b) Sensor geometry for measuring a single layer lamina

(c) Sensor geometry for measuring a multilayer lamina

Modes of use of the 14-mm open ended coaxial sensor.
Figure 19: Reflectometric coaxial sensor geometry
Figure 20: Reflection coefficient for Sika 31PBA at 20°C measured between 0.1GHz - 2.0GHz.

SIKA PBA31 LT 20°C cure at five frequencies

<table>
<thead>
<tr>
<th>Frequency (GHz)</th>
<th>Reflection Coeff. (real)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.00</td>
</tr>
<tr>
<td>0.2</td>
<td>0.99</td>
</tr>
<tr>
<td>0.5</td>
<td>0.98</td>
</tr>
<tr>
<td>1.0</td>
<td>0.98</td>
</tr>
<tr>
<td>2.0</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Time (minutes)
Figure 21: Permittivity, $E'$ and loss factor, $E''$ of Sika 31PBA at 20°C and 40°C at 0.2GHz.

SIKA PBA 31 LT cured at 20°C and 40°C
Measurement frequency = 0.2GHz

Permittivity, $E'$

Loss, $E''$

Time (minutes)
Figure 22: Comparison of the cure of PPGY5000 measured by DSC and constant stress rheometry.
Figure 23: Comparison of the cure of PPGY5000 measured by DSC and constant stress rheometry. Mathematical fit using Kamal equation.
Figure 24: Conversion of structural adhesive, 3M7823G at 150Deg C
Figure 25: Comparison of ultrasound, UTS and DSC data for SIKA 31PBA LT
Figure 26: Comparison of lap shear strength and shear modulus data for PPGY5000
Figure A1: Compliance correction for Carri-Med CSL 500 Constant Stress Rheometer

- Torque $T_m$
- Angular displacement $\theta_2$
- Machine stiffness $= K_1$
- Angular displacement $\theta_1$
- Sample stiffness $= K_2$

$K_m, \theta_m$