MTS Adhesives Project 1

Basic Mechanical Properties for Design

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Correlation of Modulus Measurements on Adhesives

Using Dynamic Mechanical and Constant Strain Rate Tests

G D Dean and B C Duncan
CORRELATION OF MODULUS MEASUREMENTS ON ADHESIVES
USING DYNAMIC MECHANICAL AND CONSTANT STRAIN
RATE TESTS

G D Dean and B C Duncan
Centre for Materials Measurement & Technology
National Physical Laboratory
Teddington, Middlesex TW11 0LW, UK

SUMMARY

Modulus data on polymeric materials are commonly obtained using dynamic mechanical tests. Commercial apparatus usually accommodates small test specimens and, thereby, enables measurements over a wide temperature range to be made rapidly. (Such measurements are commonly referred to as dynamic mechanical thermal analysis DMTA). These methods are readily applicable to adhesives, if bulk specimens are available, and therefore appear to offer a convenient and inexpensive route to the acquisition of certain data needed for design. There are however two features of dynamic testing that should be considered if high accuracy is required in the design application.

Modulus data for adhesives are conventionally obtained using a universal testing machine operating under constant speed of cross-head movement. A typical modulus measurement would involve a measurement time of about 20s. For most rigid, structural adhesives, the modulus value derived is only slightly dependent on the timescale of the measurement as determined by the cross-head speed (or strain rate) since these materials are generally not very viscoelastic. The more flexible adhesives are however more viscoelastic and the dependence of measurements on time and rate is far more evident. The timescale for a dynamic modulus measurement may be 100 or 1000 times less than that for a constant strain rate test and, depending on the adhesive, modulus values can be significantly higher from the dynamic test.

The other concern with the use of data from dynamic mechanical tests for design is the limited accuracy that is often obtained in the results from DMTA equipment. There are several sources of error associated with these measurements. Probably the largest stems from the small specimen size employed in most equipment. This leads to an error in strain measurement resulting from an uncertainty in the effective length of the specimen. The various sources of error are referred to in this report, and the application of various corrections to reduce the magnitude of the error is outlined.

Using models that relate the time and temperature dependent behaviour of polymers, it is possible to correlate dynamic modulus measurements with values obtained under constant strain rate. The application of models based on the WLF and Arrhenius functions are described in this report, and it is demonstrated that each function is applicable over separate temperature ranges defined with respect to the glass transition temperature of the polymer. Using results obtained on both a glassy and a more flexible adhesive, it is shown how the temperature dependence of the modulus appropriate to a constant strain rate test can be derived from dynamic mechanical data measured over ranges of temperature and frequency. The extra measurements needed to make this correlation offset the benefits of speed and simplicity of data acquisition using dynamic mechanical tests. Graphical methods for making the correlation are therefore also considered which, although possibly less accurate, are more rapid and easy to apply.
# CONTENTS

1. **INTRODUCTION** ................................................................. 1

2. **EXPERIMENTAL** ............................................................... 1
   2.1 Dynamic mechanical tests ................................................. 2
   2.2 Constant strain rate tests ............................................... 3
   2.3 Stress relaxation tests ................................................... 3

3. **MATERIALS** ............................................................................ 3

4. **CORRELATION OF MODULUS MEASUREMENTS FROM DIFFERENT TEST METHODS** ................................................. 4
   4.1 Correlation of constant strain rate and stress relaxation moduli .......................................................... 4
   4.2 Correlation of dynamic and stress relaxation moduli .......................................................... 5

5. **ANALYSIS OF DYNAMIC DATA USING TIME-TEMPERATURE SHIFT PROCEDURES** ................................................. 5
   5.1 Time/temperature correlation using the WLF function .......................................................... 6
   5.2 Conclusions regarding application of the WLF shift function .......................................................... 8
   5.3 Time/temperature correlation using the Arrhenius function .......................................................... 9
   5.4 Conclusions regarding application of the Arrhenius function .......................................................... 11

6. **GENERAL CONCLUSIONS** ..................................................... 11

7. **ACKNOWLEDGEMENTS** .......................................................... 11

8. **REFERENCES** .......................................................................... 12

**FIGURE CAPTIONS** .................................................................... 13
1 INTRODUCTION

In dynamic mechanical tests, a specimen is subjected to a sinusoidal vibration. Dynamic mechanical properties can be derived in a number of ways but the most straightforward is by measurement of the sinusoidal stress and strain in the specimen. Polymeric adhesives are viscoelastic and, for these materials, the stress and strain signals are out of phase. A dynamic modulus, which relates the dynamic stress to the dynamic strain, is then a complex number

\[ M^* = M' + iM'' \]  

where \( i = (-1)^{1/2} \).

\( M' \) is called the storage component and \( M'' \) is the loss component of the dynamic modulus, and both components can be derived from measurements of the amplitudes of the stress and strain signals and the phase angle between them. \( M' \) and \( M'' \) will both depend on the frequency of the applied vibration and the temperature.

Using commercial dynamic mechanical equipment, \( M' \) and \( M'' \) can be measured in the typical frequency range from \( 10^{-2} \) to \( 10^2 \) Hz. In most apparatus, a dynamic tensile or flexural deformation is applied to the specimen in which case \( M^* \) is the complex Young's modulus \( E^* \) but in some equipment the complex shear modulus can be determined. Measurements are made rapidly since the timescale of a test is only a few cycles of the applied vibration. Small test specimens are usually accommodated so an appropriate temperature range can be scanned quite rapidly whilst measurements are made at selected temperature intervals.

Thus in comparison with conventional methods for measuring the variation of modulus with temperature using universal testing machines, dynamic moduli can be determined relatively rapidly, cheaply and using smaller test specimens. Dynamic methods therefore appear to be attractive for determining modulus data needed for design with adhesives.

There are however two reasons why such data may not be sufficiently accurate. The first is that adhesives are to some extent viscoelastic. This means that properties vary with time, rate and frequency, and the timescale of a measurement in a dynamic test will in general be much shorter than that pertaining to a conventional test carried out at constant cross-head speed (strain rate). The second is that measurements made using commercial dynamic mechanical apparatus can be susceptible to errors arising from various sources.

The main purpose of the work reported here was to explore the use of procedures for deriving the temperature dependence of the modulus appropriate to any required timescale from dynamic mechanical data obtained over a range of temperature. These procedures are based on the equivalence of the time and temperature dependence of the modulus of polymeric materials, and the applicability of both the WLF and the Arrhenius functions for describing this equivalence will be assessed in section 5 of this report. Before these models can be applied, it is necessary to show how modulus values obtained from different tests (dynamic, stress relaxation and constant strain rate) can be correlated. This is explained in section 4 through the use of an effective time which can be derived for each test. In section 2, some of the sources of error in the measurement of dynamic modulus will be introduced and methods for applying corrections will be explained.

2 EXPERIMENTAL

In this section, the apparatus and procedures used to measure modulus using dynamic mechanical and constant strain rate methods are described. Also included is a brief description of stress-relaxation tests since these measurements are used to clarify the
relationship between modulus values determined using dynamic and constant strain rate methods.

2.1 Dynamic mechanical tests

2.1.1 NPL apparatus

A schematic diagram of the NPL apparatus is illustrated in figure 1. A tensile loading arrangement is shown in which the specimen is clamped between two grips. The lower grip is connected to an electromagnetic vibrator that is driven by a power amplifier and signal generator. A sinusoidal signal is applied to the vibrator, and the amplitude and frequency are set manually. The upper grip is attached to a rigid frame through a force transducer. Tensile specimens are parallel sided strips whose length should be greater than 100 mm if high accuracy in modulus measurements are required. The specimen is enclosed in an environmental chamber through which air is circulated and thermostatically controlled in a remote conditioning unit. Separate experiments have revealed that, within the timescale of a typical series of measurements at a particular temperature, the temperature throughout the specimen is constant to ± 0.2 °C.

The dynamic tensile strain in the specimen can be determined either from a measurement of the displacement of the vibrator table or by means of extensometers attached to the specimen. When the displacement of the vibrator table is used, the grip separation is the gauge length of the specimen. A correction to this length [1,2] must be applied arising from non-uniformity of strain in the regions of the specimen near the grips and deformation of the specimen within the grips. A further correction [1,2] is needed to deduct the contribution to a displacement measurement from the finite compliance of the test arrangement. Both of these sources of error are avoided if extensometers are used for strain measurements. For the dynamic measurements reported here, extensometers were employed that were used for tensile studies on adhesives and are described in reference [3].

The frequency range spanned by the apparatus is typically 0.01 Hz to 100 Hz. Above this range, resonances in the specimen, force transducer or components of the loading assembly invalidate the force measurement [1,2]. When compliant materials (E<100 MPa) are tested, specimen resonance can limit the upper frequency to below 100 Hz.

The main disadvantage of this apparatus in comparison with commercial equipment is that it is relatively large and thermal equilibrium will take longer to achieve when the temperature is scanned. A sequence of measurements over a wide temperature range will therefore take longer to carry out. Precautions are taken to ensure that the recorded temperature is accurately representative of the temperature of the specimen.

2.1.2 Commercial dynamic mechanical equipment

For the research investigations reported here, high accuracy in dynamic modulus measurements is needed, and the NPL apparatus was used for the acquisition of all the data. This high accuracy was achieved through the use of large specimens. With commercial equipment, small specimens are generally used, and certain corrections are then necessary if moderate levels of accuracy are to be achieved. In this subsection, the application of corrections is illustrated using data from apparatus manufactured by Polymer Laboratories.

With this instrument, the specimen is deformed in parallel with a compliant suspension element, and the force is determined from the current in an electromagnetic vibrator used to maintain a constant displacement amplitude applied to the specimen. The specimen can be deformed under flexure or tension, but glassy plastics of thickness above 1 mm are generally
loaded in flexure because of the greater sensitivity in strain measurement and a smaller compliance correction.

Corrections must be applied for apparatus compliance, shear deformation (in flexure tests) and clamping error. The clamping error arises because the strain field in the specimen in the vicinity of, and within, the grips is more complex than that assumed by simple formulae for specimen deformation. The measured separation between the grips is then not an accurate representation of the gauge length of the specimen and a length correction must be applied.

The derivation of a length correction in flexure is described in references [1] and [2] and involves measurements at a series of grip separations \( L \). Results are first corrected for apparatus compliance and shear deformation and then values for the apparent modulus \( E_a \) are calculated for each grip separation. The ratio of \( L/E_a \) is plotted against \( L \) at each grip separation, and the length correction is derived from the intercept of the best linear fit on the \( L \) axis. This is illustrated in figure 2 where results are shown for a specimen of the 2-part epoxy having a thickness of 2 mm. The length correction is 0.6 mm so, if the maximum span of 19 mm is used, there is an error of about 5% in the measured length if no correction is applied. This will give an error in \( E \) of 15% since in a flexure test \( E \propto L^3 \). The magnitude of the length correction depends upon the modulus and thickness of the specimen and on the clamping pressure. In general, therefore, the correction needs to be evaluated for each specimen that is tested and will vary with temperature.

The short specimen lengths employed in many commercial instruments for dynamic testing permit relatively high heating rates to be employed for the acquisition of modulus data over a range of temperature. Precautions should however be taken to ensure that recorded temperatures accurately represent the temperature of the specimen, and therefore that the thermal lag in heating the specimen at these rates is negligible.

2.2 Constant strain rate tests

These tests were carried out using standard tensile specimens loaded in an Instron 4505 universal testing machine. Details of the apparatus, extensometry, test procedures and data analysis are given in reference [4].

2.3 Stress relaxation tests

Stress relaxation measurements were made using the same apparatus and test specimens that were employed for constant strain rate tests. A tensile strain in the range 0.25% to 0.4% was applied rapidly to the specimen using a cross-head speed of 100 mm/min. The set strain level was thus reached in less than 0.5s and was held at a fixed level for the remainder of the test (typically 100s). The load sustained by the specimen was recorded with time and the stress relaxation function \( E(t) \) was derived by dividing the stress at each time by the constant applied strain (see section 4).

3 MATERIALS

Two types of adhesive have been studied for the work reported here. The first is a polyurethane adhesive supplied by 3M and identified as Scotchwell 3532. This is a 2-part cold curing adhesive. Sheets of the bulk adhesive were cast with a thickness of 3 mm using the procedure described in reference [5]. The sheets were left to cure for 7 days at 23 °C. Subsequent dynamic mechanical analysis indicated that the glass-to-rubber transition temperature \( T_g \) was about 20 °C and did not change further with time even after exposure to elevated temperatures.
Test specimens of width 10 mm and length 120 mm were cut from the sheets for dynamic mechanical measurements and were stored in sealed vessels maintained at 50% relative humidity to establish a constant level of absorbed water.

The second type of adhesive was a cold-curing, 2-part epoxy supplied by Evode under the identifier TE251. Sheets of the bulk adhesive were cast as described in reference [5] and allowed to cure for 7 days at 23 °C. These were subsequently postcured at 80 °C for 30 minutes to prevent any further curing with time or temperature. The glass transition temperature was about 80 °C. Test specimens for dynamic measurements were cut from sheets of 2 mm thickness and were stored in sealed vessels with silica gel to maintain a low water content.

4 CORRELATION OF MODULUS MEASUREMENTS FROM DIFFERENT TEST METHODS

4.1 Correlation of constant strain rate and stress relaxation moduli

In the Introduction, two methods for measuring modulus were referred to, one under a sinusoidal load and displacement of constant frequency and the other under constant cross-head speed and strain rate. In order to correlate the timescale of the modulus measurement in these two types of test, it is instructive to consider the concept of an effective time for each test. The relevance of this effective time as a common variable to both tests is best explained by reference to a third type of test for determining modulus and this is the stress-relaxation test.

In a stress relaxation test, a strain \( \varepsilon_0 \), which, for convenience, will be considered here as a tensile strain, is applied rapidly to the specimen and is held constant for all subsequent time. The resulting tensile stress \( \sigma(t) \) decreases with time for a viscoelastic material, and a stress-relaxation modulus \( E(t) \) is defined by the equation

\[
E(t) = \frac{\sigma(t)}{\varepsilon_0} \tag{2}
\]

It was shown in a previous report [4] how the shape of a stress/strain curve obtained at an arbitrary constant strain rate can be related to the stress-relaxation function \( E(t) \). To do this, it is convenient to express \( E(t) \) as an explicit function of time. A suitable function for describing the stress relaxation of a polymer over a restricted region of time at temperatures within and below the glass transition temperature is

\[
E(t) = E_o + Dt^n \tag{3}
\]

where \( E_o \), \( D \) and \( n \) are parameters for the polymer material. An illustration of stress relaxation data modelled by equation (3) is given in figure 3 for the polyurethane adhesive.

The stress/strain curve at constant strain rate \( k \) can then be derived from equation 3, as explained in reference [4], and takes the form

\[
\sigma(\varepsilon) = E_o\varepsilon + \frac{Dk^n\varepsilon^{1-n}}{1-n} \tag{4}
\]

It is evident that this curve has no linear portion, even at small strains, and at first sight would seem to imply that the behaviour was non-linear. In fact the behaviour is linear viscoelastic. For materials that are only weakly viscoelastic, such as the 2-part epoxy at
ambient temperatures, the curvature is only just discernible but for strongly viscoelastic materials, such as the polyurethane adhesive at ambient temperatures, the curvature is pronounced as shown in figure 4.

Taking the modulus \( E(\varepsilon) \), derived from a test under constant strain rate, as the gradient of the line between the origin and the strain \( \varepsilon \), the modulus at the strain \( \varepsilon \) given by the curve represented by equation (4) is

\[
E(\varepsilon) = \frac{\sigma}{\varepsilon} = E_0 + \frac{D_k n \varepsilon^{-n}}{1-n}
\]

Comparing equation (5) with equation (3), it is apparent that the constant strain rate modulus at \( \varepsilon \) and the stress relaxation modulus are comparable if the constant strain rate modulus is derived at an equivalent time \( t_{er} \) given by

\[
t_{er} = (1-n)^{1/n} \frac{\varepsilon}{k}
\]

This equivalence between moduli derived from these two tests is demonstrated in figure 5. Here constant strain rate moduli derived from tests on the polyurethane and 2-part epoxy adhesives at different strain rates are plotted with stress relaxation data on an equivalent time axis. The equivalent time for the stress relaxation points is simply the time under the constant applied strain.

4.2 Correlation of dynamic and stress relaxation moduli

The concept of an equivalent time can also be applied to data from dynamic tests. Here dynamic modulus values \( E(f) \) at a frequency \( f \) can be correlated with an equivalent time \( t_{ed} \) in a stress relaxation test given by [6]

\[
t_{ed} = \frac{0.1}{f}
\]

This means that dynamic moduli obtained at frequencies of 0.1 Hz and above should be the same as stress relaxation data measured at times less than 1s. Data from these two types of test will not generally therefore overlap, but visual correlations can be made as shown in figure 5. Together these tests extend the time range over which data can be presented.

In conclusion, the various tests that can be used to generate modulus data each operate over specific time ranges. The equivalent time for each test can be deduced from a knowledge of relevant test conditions, and data from each test can then be compared on plots of modulus against equivalent time.

5 ANALYSIS OF DYNAMIC DATA USING TIME-TEMPERATURE SHIFT PROCEDURES

The relationship between the time and the temperature dependent behaviour of polymers can be illustrated by reference to equation (3). This equation describes the dependence of modulus upon measurement time. It is applicable over restricted ranges of time at temperatures comparable with and below the glass-to-rubber transition temperature \( T_g \) of the polymer. Other, more complicated functions are more appropriate at these lower temperatures but, for purposes of illustration, equation (3) is satisfactory. Equation 3 can be written
\[ E(t) = E_0 + A \left( \frac{t}{\tau} \right)^n \]  

(8)

where \( \tau \) is a parameter that defines the position of the curve on the time axis and effectively represents a mean relaxation time for the mechanism giving rise to the time-dependence of modulus. When this mechanism is the glass-to-rubber transition, then for measurement times \( t << \tau \), the polymer behaves like a glass whereas when \( t >> \tau \), the polymer exhibits rubber-like behaviour. The parameter \( \tau \) increases with decreasing temperature so, at sufficiently low temperatures, \( t < \tau \) and the measured modulus is typical of that of a glassy polymer. As the temperature is raised, \( \tau \) decreases progressively until, at sufficiently high temperatures such that \( t > \tau \), the modulus becomes that for the rubber phase. The glass transition temperature \( T_g \) lies in the region of temperature for which \( t \sim \tau \).

Another way of illustrating the correlation between time- and temperature-dependent behaviour is through plots of \( E \) as a function of time at different temperatures such as those shown in figure 5. In figure 6, the time range has been extended, and schematic curves of modulus against log measurement time are shown at two temperatures \( T_1 > T_2 \). This figure illustrates that the change in \( \tau \) with temperature gives rise to a shift in the curve along the time axis. The shift is to the right if the temperature is lowered and to the left if it is raised.

It will now be shown how, from a knowledge of the dependence of \( \tau \) upon \( T \), dynamic moduli measurements over ranges of temperature can be used to derive the variation of \( E \) with time and temperature outside the time range of these measurements. Choice of a suitable function for relating \( \tau \) to \( T \) depends on the temperature range of interest as discussed next.

5.1 Time/temperature correlation using the WLF function

The variation of \( \tau \) with temperature in the region of the glass transition of amorphous materials has been considered by several workers (for example [7,8]) and is shown schematically in figure 7. As the temperature is lowered from above \( T_g \), \( \tau \) increases and starts to rise rapidly in the region of \( T_g \). At temperatures below \( T_g \), \( \tau \) appears to approach an infinite value at a temperature \( T_\infty \) some way below \( T_g \). This trend is described by the 

\[ \tau = \tau_0 \exp\left(\frac{\Delta H}{R(T-T_\infty)}\right) \]  

(9)

where \( \Delta H \) is the activation energy/mole for the glass-rubber relaxation mechanism and \( R \) is the universal gas constant/mole.

If equation (9) is substituted into equation (8), an expression for the variation of modulus with time and temperature is obtained. If the parameters \( E_0, A, n \) and \( \Delta H \) are independent of temperature, then the horizontal separation on a log (time) axis between curves at temperatures \( T_1 \) and \( T_2 \) is

\[ \log_{e} t_{e1} - \log_{e} t_{e2} = \frac{\Delta H}{R} \left( \frac{1}{T_1 - T_\infty} - \frac{1}{T_2 - T_\infty} \right) \]  

(10)

where \( t_{e1} \) and \( t_{e2} \) are arbitrary effective times at which the modulus is the same at temperatures \( T_1 \) and \( T_2 \) respectively. It is apparent from equation (10) that the horizontal
separation between curves is the same at all points on each curve and is dependent on \( T_1 \) and \( T_2 \) only.

Using equation (10), it is possible to define a shift factor \( a_T \) which represents the shift on a \( \log_e \) (time) axis between the curve at a temperature \( T \) and the curve at a reference temperature \( T_R \). Then

\[
a_{T} = \log_e t_e - \log_e t_r = \frac{\Delta H}{R} \left( \frac{1}{T_R - T_\infty} - \frac{1}{T - T_\infty} \right)
\]

Equation (11) can be expressed as

\[
a_{T} = \frac{C_1(T-T_R)}{C_2 + T - T_R}
\]

where

\[
C_2 = T_R - T_\infty
\]

and

\[
C_1 = \frac{\Delta H}{R(T_R - T_\infty)}
\]

Equation (12) is the WLF shift function [11]. It should be noted that \( C_1 \) and \( C_2 \) depend upon the choice of reference temperature and are only referred to as universal constants when \( T_R = T_g \). Equation (12) can be used to extend the frequency (or effective time) range of dynamic data but, as implied by figure 7, is only valid for temperatures around and above \( T_g \). This criterion is satisfied by the polyurethane adhesive in the temperature range close to ambient and above. The use of the WLF function for predicting modulus values against temperature at measurement times outside the range of dynamic measurements will now be illustrated using results obtained on this adhesive.

Measurements of the dynamic modulus of bulk specimens of the polyurethane adhesive were made using the NPL apparatus at frequencies of 0.01, 0.1, 1 and 10 Hz and at temperatures in the range from -5 to 35°C. The results are shown in figure 8 plotted on a log (effective time) axis. The solid lines are polynomial fits to the data at each temperature and enable the shift factor \( a_T \) to be determined between curves. Using a reference temperature of 20.2°C, values for \( a_T \) are listed in table 1 for each temperature.

**Table 1**

<table>
<thead>
<tr>
<th>( a_T )</th>
<th>4.88</th>
<th>3.96</th>
<th>3.14</th>
<th>2.18</th>
<th>1.0</th>
<th>0</th>
<th>-2.66</th>
<th>-4.31</th>
<th>-5.92</th>
<th>-7.66</th>
<th>-9.6</th>
<th>-13.5</th>
<th>-18.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T(K) )</td>
<td>305.5</td>
<td>303</td>
<td>300.5</td>
<td>298</td>
<td>295.5</td>
<td>293.2</td>
<td>288</td>
<td>285.5</td>
<td>283</td>
<td>280.5</td>
<td>278</td>
<td>273</td>
<td>268</td>
</tr>
</tbody>
</table>
Equation (12) can be rewritten.

\[ a_T = \frac{C_1(T-T_R)}{T-T_\infty} \quad \text{(13)} \]

The data in table 1 have been plotted in figure 9 on axes of \( a_T \) vs. \( \frac{T-T_R}{T-T_\infty} \), and values for \( C_1 \) and \( T_\infty \) were selected by an optimisation routine to give the best linear fit to the data. Whilst a satisfactory fit is shown, it is apparent that the correlation is beginning to depart from the WLF function at the lower two temperatures.

Once values for \( C_1 \) and \( T_\infty \) have been determined (see figure 9), the dynamic data in figure 8 over a range of temperature but at a single frequency can be used to derive the temperature dependence of modulus at any time outside the range covered by the dynamic measurements.

This can be achieved graphically by reference again to equation (9). This equation implies that a plot of dynamic modulus data at a particular frequency against \( \frac{1}{T-T_\infty} \) has the same shape for all frequencies, and a curve at one time or frequency can be simply shifted along the axis to generate the curve for another time or frequency. The shift factor \( a_t \) between the curve for data corresponding to an effective measurement time \( t_e \) and a reference curve at an effective measurement time \( t_{eR} \) is, from equations (9) and (12),

\[ a_t = \frac{1}{T-T_\infty} - \frac{1}{T_T-T_\infty} = \frac{1}{C_1C_2} \log_e \frac{t_e}{t_{eR}} \quad \text{(14)} \]

Figure 10 shows a plot of the dynamic data for the polyurethane adhesive at 1 Hz (\( t_{eR} = 0.1 \text{s} \)) taken from figure 8 and plotted against \( \frac{1}{T-T_\infty} \). Data corresponding to constant strain rate tests at 3%/min (\( t_e = 5.7\text{s} \) from equation (6)) have been derived by shifting the 1 Hz curve by \( 1.55 \times 10^{-3} \text{ K}^{-1} \) to the right (from equation (14)). Experimental constant strain rate moduli are also shown for comparison.

5.2 Conclusions regarding application of the WLF shift function

At temperatures above 0 °C, the WLF function (equation (11)) is able to accurately correlate the time (or frequency) and temperature variations of the modulus of the polyurethane adhesive. The temperature dependence of modulus, in time ranges appropriate to constant strain rate tests, can be accurately derived from dynamic mechanical measurements with temperature once the WLF constants \( C_1 \) and \( C_2 \) have been determined from other dynamic tests.

The effort needed to determine these constants offsets the benefits, in terms of speed, in acquiring modulus data by dynamic mechanical tests.

A short cut is possible, if some loss of accuracy is acceptable, by estimating a value for \( T_\infty \) using the relationship
\[ T_{\infty} = T_g - 50 ^\circ C \]  

\( T_g \) can be estimated as the temperature at which a plot of \( E'' \) vs \( T \) shows a peak. A dynamic test at a frequency between 0.1 Hz and 10 Hz is appropriate for this purpose. From this estimate of \( T_{\infty} \), a plot equivalent to figure 10 can be generated. The shift needed to construct the curve appropriate to a constant strain rate test can then be evaluated experimentally from a modulus measurement at that strain rate and at a single temperature.

5.3 Time/temperature correlation using the Arrhenius function

The analysis described in the previous section based on the WLF function has been concerned with a correlation of time and temperature-dependent behaviour at temperatures in the region of, and above, \( T_g \). At these temperatures, the molecular mobility is relatively high, corresponding to a short mean relaxation time \( \tau \), and the molecular structure is always at or close to equilibrium. When temperatures are lowered below \( T_g \), the associated reduction in molecular mobility means that non-equilibrium structures are generated unless exceptionally slow cooling rates are employed. For moderate or fast cooling through and below \( T_g \), the mean relaxation time decreases more slowly than predicted by an extrapolation of the Vogel-Fulcher function (equation (9)). Furthermore, the relaxation time at any temperature will depend upon the cooling rate or, more generally, the thermal history of the specimen. In consequence, because of the dependence of dynamic properties on the relaxation time for molecular motions (see equation (8)), measurements of dynamic modulus will depend on the thermal history of the specimen. This is illustrated in figure 11 where results for the 2-part epoxy adhesive are compared for specimens that have been either quenched or slow cooled in steps of 5 °C/day. Both specimens, even the one that has been slow cooled, will have molecular structures that are remote from their equilibrium states at temperatures well below \( T_g \) but, because of the finite relaxation times, slow rearrangements of the molecular structure will take place during storage. This is termed physical ageing and will give a progressive increase in \( \tau \) and, consequently, further slow changes to dynamic property measurements.

In exploring suitable functions for correlating time and temperature-dependent behaviour, it is necessary to recognise that it is difficult to acquire measurements on specimens having the same physical age state at all measurement temperatures. In order to test specimens whose properties are not changing significantly throughout any sequence of measurements, the results shown for the 2-part epoxy in figure 12 were obtained as the specimen was slow cooled from 85 °C. Specimens were dried before testing to avoid contributions from changes in water content. Measurements at each temperature were made at 24h intervals following cooling in steps of 5 °C, the cooling rate between steps being about 1 °C/min.

Shift factors have been derived from the data in figure 12 and are listed in table 2 using a reference temperature of 55 °C.

<table>
<thead>
<tr>
<th>( a_T )</th>
<th>17.9</th>
<th>15.1</th>
<th>12.1</th>
<th>9.4</th>
<th>6.6</th>
<th>3.1</th>
<th>0</th>
<th>-2.2</th>
<th>-4.8</th>
<th>-7.05</th>
<th>-9.8</th>
<th>-11.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T(K) )</td>
<td>358</td>
<td>353</td>
<td>348</td>
<td>343</td>
<td>338</td>
<td>333</td>
<td>328</td>
<td>323</td>
<td>318</td>
<td>313</td>
<td>308</td>
<td>303</td>
</tr>
</tbody>
</table>
Reference to figure 7 indicates that the WLF function is unsuitable at temperatures below $T_g$, and the applicability of the Arrhenius function has been explored. Accordingly to equation (9) is replaced by

$$\tau = \tau_0 \exp \frac{\Delta H}{RT}$$  \hspace{1cm} (16)

and the shift factor becomes

$$a_T = \frac{C(T - T_R)}{T}$$  \hspace{1cm} (17)

where

$$C = \frac{\Delta H}{RT_R}$$

With reference to equation (17), the results in table 2 have been plotted in figure 13 on axes of $a_T$ against $1/T \ K^{-1}$. It is apparent that the Arrhenius relationship is not valid over the whole temperature range. The broken line shown is a best linear fit to the data below 60°C which is an appropriate operating temperature range for this adhesive and being well below $T_g$ is also where the Arrhenius function is expected to be more applicable.

Modulus data as a function of temperature corresponding to tests at other timescales can be generated by the graphical method described in section 5.1. Based on the Arrhenius relationship and assuming no dependence of $E_o$, $D$ and $n$ (in equation (3)) and $\Delta H$ (in equation (16)) upon temperature, a plot of dynamic modulus against $1/T$ should have a constant shape which shifts along the $1/T$ axis with changing frequency or effective time for the modulus measurement. The shift factor, by analogy with equation (14), is

$$a_t = \frac{1}{CT_R} \log_e \frac{t_e}{t_{eR}}$$  \hspace{1cm} (18)

where $t_{eR}$ is the (reference) effective time at which measurements were made and $t_e$ is the effective time at which data are required.

In figure 14, dynamic moduli for the 2-part epoxy at a reference frequency of 1 Hz ($t_{eR} = 0.1s$) have been plotted against $1/T \ K^{-1}$. For this material $n = 0.05$ so, from equation (6), the effective time for a constant strain rate test at 1%/min is $t_e = 7s$. Using the value for $CT_R = 49.10^3 \ K$ given in figure 13, equation (18) predicts that the shift to the 1 Hz data in figure 14 needed to generate the data corresponding to a strain rate of 1%/min is $8.7 \ 10^5 \ K^{-1}$. This predicted curve is compared with measured values in figure 14. The measured and predicted curves have a similar shape and predicted moduli generally depart from measured values by less than 15% especially at the lower temperatures. It is worth noting that closer agreement between predicted and measured curves could have been obtained by deriving the shift from a measurement of modulus under constant strain rate at a single temperature rather than by calculation. This is considered to be associated with experimental uncertainty in the measurement of modulus (linked possibly with non-comparable states of physical ageing or water content of the specimens) rather than errors in the application of the Arrhenius function to the dynamic data.

By way of illustration, the shift in figure 14 derived from a single constant strain rate test performed at 55°C is $1.3 \ 10^4 \ K^{-1}$. In figure 15 this shift has been applied to the dynamic data and better agreement is observed between predicted and measured values.
5.4 Conclusions regarding application of the Arrhenius function

At temperatures where an adhesive exhibits glassy behaviour, the WLF function is not suitable for time-temperature correlations. Correlations based on the Arrhenius function are potentially more appropriate.

In contrast to a WLF analysis, correlations between time and temperature-dependent behaviour using the Arrhenius function require one experimental parameter $C$ since $T_m = 0$.

Using dynamic modulus measurements $E$ over a range of temperature at an arbitrary frequency, values for the variation of modulus with temperature corresponding to a different measurement time can be calculated from a plot of $E$ against $1/T$. Assuming the Arrhenius function is valid and the parameters that define the shape of the modulus relaxation do not change with temperature, then the above plot will shift along the $1/T$ axis without change of shape for different times of the modulus measurement.

The shift between these curves can be calculated using equation (18) and a knowledge of the parameter $C$. Alternatively, the shift can be derived experimentally from a modulus measurement at a minimum of one temperature at the effective time for which data are to be derived.

6 GENERAL CONCLUSIONS

This report has concentrated on the specific problem of transforming the results of modulus measurements obtained using dynamic mechanical methods to values appropriate to tests carried out under constant strain rate. The differences between modulus values obtained from these tests will depend upon the frequency and strain rate used for the measurements and on the viscoelastic state of the adhesive. For adhesives in their glassy state, such as the two-part epoxy TE251 at ambient temperatures, differences will be small, but at temperatures corresponding to the glass-to-rubber relaxation region (the polyurethane adhesive 3M3532 at ambient temperatures), differences will be large (up to a factor of 3).

Although modulus data are conveniently obtained using constant deformation rate tests at a speed of typically 1 mm/min, there is nothing absolute regarding these conditions and the relevance of the data to design. Adhesives are viscoelastic and for design under a range of loading conditions, a knowledge of the modulus over wide ranges of time and rate is needed. Creep and stress relaxation tests are then relevant for data acquisition.

Transformation relationships based on the WLF and Arrhenius functions can be used to relate temperature dependent modulus values for one test to values appropriate to the other. Summaries of the use of these functions are given in sections 5.2 and 5.4. With regard to the use of these functions for data analysis, the graphical methods explained for data correlation are both simple and rapid. They should enable modulus values appropriate to constant strain rate tests to be derived of sufficient accuracy for most applications as long as suitable precautions and corrections have been used to achieve high accuracy in the measurement of the dynamic moduli data.

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Figure 1 Schematic of NPL Dynamic Mechanical Apparatus
Fig 2 Determination of the length correction for a specimen of the 2-part epoxy tested in flexure. $E_a$ is the apparent value for the tensile modulus and $L$ is the grip separation.
Fig 3  Tensile stress relaxation data $E(t)$ for the polyurethane adhesive under an applied strain of 0.6%. The continuous line represents the best fit using the empirical function $E(t) = E_0 +Dt^{-n}$. The experimental data points are also shown.

Polyurethane, $T = 22^\circ C$

- model $E(t) = E_0 + Dt^{-n}$

$n = 0.45$

$E_0 = 27$ MPa

$D = 112$ MPas$^{-n}$
Comparison of measured stress/strain curves for the polyurethane adhesive with curves predicted from stress relaxation data.

\[ \sigma = E_0 \epsilon + D k^n \epsilon^{1-n}/(1-n) \]

- experimental data
- model \( \sigma = E_0 \epsilon + D k^n \epsilon^{1-n}/(1-n) \)

\[ n = 0.45 \]
\[ E_0 = 27 \text{ MPa} \]
\[ D = 112 \text{ MPa s}^n \]

strain rate

\[ k = 7.0 \times 10^{-4} \text{s}^{-1} \]
\[ k = 2.8 \times 10^{-4} \text{s}^{-1} \]
\[ k = 1.4 \times 10^{-4} \text{s}^{-1} \]
\[ k = 0.7 \times 10^{-4} \text{s}^{-1} \]
\[ k = 0.35 \times 10^{-4} \text{s}^{-1} \]

Polyurethane, \( T = 22^\circ\text{C} \)
Fig 5 Correlation of moduli for the polyurethane adhesive derived from constant strain rate, dynamic mechanical and stress relaxation tests.

Polyurethane

- dynamic data
- stress relaxation data
- constant strain-rate data

E (MPa)

T = 10°C
T = 22°C
T = 30°C

10000
1000
100
10
1

effective time (s)
Fig 6  Schematic curves showing the variation of modulus $E$ with effective measurement time $t_e$ spanning the range between glassy and rubberlike behaviour. Decreasing the measurement temperature shifts data to the right.
Fig 7 Schematic diagram showing the variation of the mean relaxation time $\tau$ with temperature.
Fig 8  Variation of dynamic modulus of the polyurethane adhesive with effective time at different temperatures $t_e = 0.1/f$. 
Fig 9  Plot of $a_T$ vs $(T-T_R)/(T-T_w)$ based on the WLF function $a_T = C_1 (T-T_R)/(T-T_w)$ (see equation (12)). From the plot, $C_1 = 35.6$ and $T_w = 220K$. 

Polyurethane

$C_1 = 35.6$

$T_w = 220K$
Fig 10 Dynamic modulus data for the polyurethane adhesive at 1 Hz plotted against $1/(T-T_\infty)$ showing how, using equation (14), constant strain rate moduli at a strain rate of 3%/min can be predicted. Experimental data at 3%/min are shown for comparison.
Fig 11 Dynamic modulus against temperature measured on specimens of the 2-part epoxy adhesive corresponding to rapid and slow rates of cooling of the specimen.
Fig 12 Variation of dynamic modulus of the 2-part epoxy adhesive with effective time at different temperatures $t_e = 0.1/f$. 
Fig 13 Plot of $a_T$ vs $1/T$ for the 2-part epoxy based on the Arrhenius function for which

$$a_T = C \left(1 - \frac{T_R}{T}\right)$$

The reference temperature $T_R = 328K$. From the plot, $CT_R = 49.10^3K$. 
Fig 14 Dynamic moduli for the 2-part epoxy at a reference frequency of 1 Hz plotted against $1/T$ showing how values corresponding to constant strain rate measurements at 1%/min can be derived using equation (18). The shift predicted by equation (18) is $9.0 \times 10^{-5}$ corresponding to a value for n of 0.05 for the 2-part epoxy.
Fig 15 Experimental data from figure 14 compared with predicted data for which the shift is determined from the constant strain rate measurement at 55°C.