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**Strain Rate and
Temperature
Dependence of the
Properties of Adhesives.
Prediction of High-Rate
Data**

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March 1999

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SUMMARY

Stress-strain data in tension and shear have been obtained over wide ranges of strain rate and at different temperatures on bulk specimens of a toughened epoxy and a toughened acrylic adhesive. The results are intended for use with elastic-plastic models in finite element analyses of the impact behaviour of bonded joints. The tensile tests were carried out using electromechanical, servohydraulic and impact machines which provided stress-strain curves at strain rates between 10^{-4} and 100 s^{-1} and temperatures of -40 , 0 , 23 and 50 °C. The shear measurements were made at 0 , 23 and 50 °C and gave curves of effective stress ($\bar{\sigma}$) versus effective strain ($\bar{\epsilon}$) at effective strain rates between 10^{-4} and 10^{-1} s^{-1} that corresponded to the strain rates in the tensile tests.

Values of Young's modulus (E) and Poisson's ratio (ν_e) were determined from the tensile data in the strain range 0.0005 - 0.0025 . Significant increases in E and decreases in ν_e were observed for each adhesive with increasing strain rate and decreasing temperature. These effects are attributed to relaxation processes which are operative in the materials over the ranges of strain rate and temperature investigated.

The yield stresses increase with increasing strain rate and decreasing temperature for both materials. For the epoxy adhesive, the shapes of the stress-strain curves show little variation with strain rate and temperature. However, deviations are observed between the tensile curves and the $\bar{\sigma}$ versus $\bar{\epsilon}$ curves from the shear data at corresponding effective strain rates and temperatures. These deviations, the magnitudes of which are essentially independent of strain rate and temperature, are attributed to the effects of cavitation during yielding under tension. For the acrylic adhesive, the tensile stress-strain curves exhibit progressive shape changes with varying strain rate and temperature. Deviations between these curves and the corresponding $\bar{\sigma}$ versus $\bar{\epsilon}$ curves also increase with increasing rate and decreasing temperature.

The dependence of yield stresses on strain rate and temperature has been successfully modelled using a generalised form of Eyring's theory. The model accounts for contributions to the yield stress from the α and β relaxation processes and provides accurate predictions of the yield behaviour at impact rates by means of extrapolation or rate-temperature equivalence.

1 INTRODUCTION

Details have previously been reported¹ of elastic-plastic models for the non-linear stress-strain behaviour of adhesives. The models assume that non-linearity arises from shear yielding in the material and are currently employed in finite element analyses of stress and strain distributions in adhesive joints. Values of the parameters appearing in these models were derived using a combination of uniaxial tension and shear tests at corresponding strain rates for a toughened epoxy and a toughened acrylic adhesive at 23 °C. From these results, and from related data on compressive and butt-joint specimens, it was concluded that the von-Mises shear yield criterion (possibly with a small pressure dependence) was satisfactory only for stress states and stress levels unable to initiate cavitation of the dispersed rubber particles or crazing of the glassy matrix. When the hydrostatic component of stress is sufficient to cause cavitation or crazing, then a modified or alternative criterion is required. In tensile tests, cavitation was evident for each adhesive at strains above about 0.02 by stress whitening and a progressive decrease in Poisson's ratio or increase in volume.

Recognising the possible involvement of two yield mechanisms, we present and discuss in this report the strain rate and temperature dependence of tensile and shear data for the epoxy and acrylic adhesives respectively. Since the impact behaviour of adhesive joints is of particular importance, emphasis is given to methods for predicting data at the high strain rates associated with impact loading.

2 OUTLINE OF ELASTIC-PLASTIC MODELS

2.1 SHEAR YIELDING

With the elastic-plastic models, the linear region usually observed in a tensile stress-strain curve at low strains (≤ 0.01) is characterised by a value for Young's modulus E and Poisson's ratio ν_e . The onset of non-linearity in the curve is then attributed to plastic deformation and subsequent increases in stress (now regarded as the yield stress) are associated with strain hardening. It is usually assumed that the yielding involves a predominantly shear mechanism which, for multiaxial stress states, requires some critical combination of the principal stress components σ_1 , σ_2 and σ_3 .

2.1.1 Yield Criteria

According to the von Mises criterion, yielding occurs when the second invariant of the deviatoric (shear) stress tensor

$$J_{2D} = \frac{1}{6} [(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2] \quad (1)$$

reaches a critical value. For many types of adhesive it has been shown that this value further depends on the hydrostatic stress component

$$J_1 = \sigma_1 + \sigma_2 + \sigma_3 \quad (2)$$

and it has been proposed that yielding will occur at an effective stress $\bar{\sigma}$ given by

$$\bar{\sigma} = \sigma_T = \frac{\sqrt{3}(\lambda + 1)}{2\lambda} J_{2D}^{1/2} + \frac{(\lambda - 1)}{2\lambda} J_1 \quad (3)$$

Here σ_T is the yield stress under uniaxial tension. The parameter λ equals σ_C / σ_T where σ_C is the yield stress under uniaxial compression associated with the same effective plastic strain (see below) as σ_T . We note that the principal stresses, σ_T and σ_C are all true stresses, referred to the strained cross-sectional areas, and that the value of λ provides a measure of the sensitivity of the yield behaviour to the hydrostatic component of stress.

An alternative criterion, given by

$$\sigma_T^2 = \frac{3J_{2D}}{\lambda} + \frac{(\lambda - 1)}{\lambda} \sigma_T J_1 \quad (4)$$

has been used with some success in modelling the yield behaviour of plastics. If the yielding is insensitive to the hydrostatic stress component, then $\sigma_C = \sigma_T$, $\lambda = 1$ and equations (3) and (4) each reduce to the von Mises criterion

$$\sigma_T = \sqrt{3} J_{2D}^{1/2} \quad (5)$$

With the elastic plastic models, all normal strains ϵ are defined as true (natural) strains $\epsilon = \ln(1 + \epsilon')$ where ϵ' is the corresponding engineering strain. In the non-linear region of a tensile stress-strain curve, the strain ϵ_T is regarded as the sum of an elastic component $\epsilon_e = \ln(1 + (\sigma_T / E)) \approx \sigma_T / E$ and a plastic component ϵ_{pT} that is non-recoverable. For multiaxial loading, an effective plastic strain $\bar{\epsilon}_p$ may be equated to ϵ_{pT} and defined in the form of equations (3) or (4) in terms of principal components ϵ_{p1} , ϵ_{p2} and ϵ_{p3} of plastic strain. An effective strain $\bar{\epsilon}$ may then be defined by

$$\bar{\epsilon} = \epsilon_T = \epsilon_e + \bar{\epsilon}_p \quad (6)$$

with $\epsilon_e = \ln(1 + (\bar{\sigma} / E)) \approx \bar{\sigma} / E$.

2.1.2 Strain Hardening and Flow

The effects of strain hardening may now be specified by the dependence of $\bar{\sigma}$ on $\bar{\epsilon}_p$. From measurements of ν_p , the plastic component of Poisson's ratio¹, values can be determined for the flow parameter

$$\tan \psi = \frac{3(1 - 2\nu_p)}{2(1 + \nu_p)} \quad (7)$$

which provides a measure of the volume change during the predominantly shear yielding and is required for relating increments of plastic strain to the components of stress. For yielding at constant volume it follows that $v_p = 0.5$ and thus $\psi = 0$.

2.2 DILATATIONAL YIELDING

Yield processes in adhesives may involve the onset of cavitation and substantial volume increases if the hydrostatic component of stress is sufficiently large. Such processes are evident for both the toughened epoxy and acrylic adhesives by the stress whitening and marked fall in Poisson's ratio that occur for tensile strains above about 0.02. At these strains deviations are also observed between the tensile stress-strain curves and corresponding plots of effective stress $\bar{\sigma}$ versus effective strain $\bar{\epsilon}$ derived from the shear data assuming $\lambda=1$ (see Figures 8 and 10 of this report). These deviations are attributed to the cavitation that occurs under tension and are associated with the large apparent strain-dependencies of λ values determined from tensile and shear data¹.

To allow for the effects of cavitation, there is a need to modify or extend the yield criteria represented by equations (3) and (4). Criteria have been proposed for craze initiation in glassy polymers² and for the dilatational yielding in toughened polymers associated with shear of the matrix polymer connecting cavitated rubber particles^{1,3}. However, further studies are required to ascertain the applicability of such criteria to multiaxial stress-strain data on the toughened adhesives.

3 DETERMINATION OF PARAMETERS

This section summarises methods for obtaining the model parameters required in calculations for different stress states and different polymeric materials. Since values for most of the parameters will depend on strain rate and temperature, they should be determined over ranges of these variables appropriate to a given application.

3.1 MODULUS AND POISSON'S RATIO

Values of E and ν_e are derived from measurements of stress, strain and transverse strain in tensile tests at low strains where the stress-strain plot is essentially linear.

3.2 STRAIN HARDENING FUNCTION ($\bar{\sigma} = f(\bar{\epsilon}_p)$)

If yielding under uniaxial tension involves shear deformation with no cavitation then $\bar{\sigma}$ and $\bar{\epsilon}_p$ can be identified with σ_T and ϵ_{pT} , respectively, and thus determined from tensile tests¹. However, for the toughened epoxy and acrylic adhesives cavitation occurs under uniaxial tension and an alternative test method such as shear or uniaxial compression must be employed. These methods require a knowledge of the value of λ (see section 3.3 below) and are based on the relationships²

$$\bar{\sigma} = \frac{\sqrt{3}(\lambda + 1)}{2\lambda} \sigma_s = \frac{\sigma_c}{\lambda} \quad (8)$$

$$\bar{\epsilon}_p = \frac{\sqrt{3}(\lambda + 1)}{4\lambda(1 + \nu_p)} \gamma_p = \frac{\epsilon_{pC}}{\lambda} \quad (9)$$

where σ_s and γ_p are the shear yield stress and shear plastic strain, respectively, and ϵ_{pC} is the plastic strain under uniaxial compression.

3.3 SHEAR YIELD PARAMETER λ

The determination of a value for λ requires measurements under two different stress states each of which produce shear yielding with no cavitation. If cavitation does not occur under uniaxial tension then λ may be derived either from tensile and compressive data or from tensile and shear data using^{1,2}

$$\lambda = \frac{\sigma_c}{\sigma_T} = \frac{\sqrt{3}(\sigma_s / \sigma_T)}{2 - \sqrt{3}(\sigma_s / \sigma_T)} \quad (10)$$

Since cavitation occurs under tension for both the toughened epoxy and acrylic adhesive, then λ may be evaluated from shear and compressive data. This method is based on the relation²

$$\lambda = \frac{2 - \sqrt{3}(\sigma_s / \sigma_c)}{\sqrt{3}(\sigma_s / \sigma_c)} \quad (11)$$

which follows from equation (8). It should be emphasised that the stresses σ_T , σ_c and σ_s in (10) and (11) each refer to the same effective plastic strain and effective plastic strain rate. Methods for obtaining these stresses are given in a previous report².

4 A MODEL FOR THE STRAIN RATE AND TEMPERATURE DEPENDENCE OF YIELD STRESS

Variations in the yield stress with strain rate and temperature may be described for polymers on the basis of a model introduced by Eyring and coworkers⁴. The model considers that an increase in stress increases the net rate of molecular rearrangements in the material, and that a peak or plateau in the stress-strain curve is obtained when the strain rate produced by these rearrangements equals the applied strain rate. The molecular motions are represented by thermally activated transitions across a potential energy barrier separating two minima (Fig 1). It is then proposed that the levels of the minima are respectively raised and lowered by an amount σv where σ is the applied stress and v the volume of the moving molecular segments (the so-called activation volume). The barrier height, or activation energy, Q is thus effectively lowered and raised for

transitions in the forward and reverse directions respectively. The strain rate $\dot{\epsilon}$ is then assumed to be proportional to the net molecular flow rate in the forward direction.

$$\begin{aligned}\dot{\epsilon} &= kv_o \left[\exp\left(-\frac{(Q - \sigma v)}{RT}\right) - \exp\left(-\frac{(Q + \sigma v)}{RT}\right) \right] \\ &= \dot{\epsilon}_o \exp\left(-\frac{Q}{RT}\right) \sinh\left(\frac{\sigma v}{RT}\right)\end{aligned}\quad (12a)$$

$$= \frac{\dot{\epsilon}_o}{2} \exp\left(-\frac{(Q - \sigma v)}{RT}\right) \quad \text{for } \frac{\sigma v}{RT} \gg 1 \quad (12b)$$

where T is the absolute temperature, v_o involves the molecular vibration frequency and the entropy contribution to the free energy, k is a constant and $\dot{\epsilon}_o = 2kv_o$. For large stress it follows from (12b) that

$$\frac{\sigma_y}{T} = A \left[\ln 2C \dot{\epsilon}_y + (Q / RT) \right] \quad (13)$$

where $A = R/v$, $C = 1/\dot{\epsilon}_o$ and σ and $\dot{\epsilon}$ have been equated to the yield stress σ_y and applied strain rate $\dot{\epsilon}_y$, respectively, measured at the peak or plateau of the stress-strain curve. Hence plots of σ_y/T against $\log \dot{\epsilon}_y$ at different temperatures should be linear and parallel, having a slope characterised by A and intercepts determined by the values of C and Q .

Various studies⁵⁻⁷ of the yield behaviour of amorphous glassy polymers have shown that the yield stress increases more rapidly with increasing strain rate and decreasing temperature at low temperatures and high strain rates than at high temperatures and low strain rates. An extension to equation (13) has therefore been proposed based on the assumption that the yield stress comprises additive contributions from the glass-rubber α relaxation process and the secondary β process. The extended equation is then

$$\frac{\sigma_y}{T} = A_\alpha \left[\ln 2C_\alpha \dot{\epsilon}_y + (Q_\alpha / RT) \right] + A_\beta \sinh^{-1} \left[C_\beta \dot{\epsilon}_y \exp(Q_\beta / RT) \right] \quad (14)$$

As illustrated in Figure 2, the β contribution to σ_y/T is represented by an inverse sinh function. This follows from (12a) recognising that at certain rates and temperatures $\sigma v/RT$ for the β process will be small or zero. At a given temperature (Fig 2), the plot of σ_y/T versus $\log \dot{\epsilon}_y$ exhibits limiting slopes at low and high strain rates determined by the values of A_α and $A_\alpha + A_\beta$ respectively.

5 EXPERIMENTAL

5.1 MATERIALS

The adhesive materials used in this investigation are listed in Table 1 and are identical to those for which data have previously been reported¹.

Table 1. Materials Investigated

Adhesive type	Supplier / code
1-part toughened epoxy	Ciba / LMD 1142
2-part, ambient - temperature curing acrylic	ITW Plexus / MA310

Standardised procedures⁸ were used to prepare sheets of the bulk adhesives of thickness between 2 and 3 mm. Sheets of the epoxy adhesive were cured at 150 °C for 2 hours. The acrylic adhesive was cured at room temperature and then post cured at 40 °C for 2 hours to minimise any subsequent changes in properties.

Both tensile and shear tests were carried out on specimens machined from the sheets. Standard dumbbell-shaped specimens (ISO 3167) and Arcan V-notched square plates were used in the tensile and shear tests, respectively, at low strain rates¹ (Section 5.2). The tensile tests at high strain rates (Section 5.3) employed dumbbell-shaped specimens of overall length 75 mm and width of 5 mm in the narrow section.

5.2 MEASUREMENTS AT LOW STRAIN RATES (10^{-5} - 10^{-1} s⁻¹)

Both tensile and shear tests at low strain rates were carried out using an Instron universal testing machine type 4505. The measurements were made at 50, 23 and 0 °C for each material.

5.2.1 Tensile Measurements

For the determination of Young's modulus E and Poisson's ratio ν_e , extensometers^{1,9} were employed to measure longitudinal strains over a 50 mm gauge length and transverse strains (in the width direction) were measured using an Instron clip-on extensometer. Values of E and ν_e were usually derived from data over the strain range $0.0005 \rightarrow 0.0025$ and were reproducible to within about $\pm 1\%$ and $\pm 3\%$ respectively.

For determining stress-strain curves and Poisson's ratios over wide ranges of strain up to failure, both longitudinal and transverse strains were measured using a Messphysic ME64 videoextensometer. Details of these measurements are included in reference 1.

5.2.2 Shear Measurements

Shear stress-strain data were obtained from measurements on Arcan notched-plate specimens with the aid of extensometers developed at the NPL^{1,10}. The results were corrected for non-uniformities in stress and strain within the specimens on the basis of finite-element calculations¹.

5.3 TENSILE MEASUREMENTS AT HIGH STRAIN RATES (10^{-2} - 100 s^{-1})

5.3.1 Measurements with a Servohydraulic Machine

An Instron 1143 servohydraulic test machine was used to generate tensile data at crosshead speeds between about 0.1 mm s^{-1} and 2 ms^{-1} , corresponding to strain rates in the range 2×10^{-3} - 40 s^{-1} .

Loads were measured using a lightweight Kistler piezo-electric load cell with a 50 kN force capacity. Crosshead displacements were determined using a LVDT transducer built into the test machine. At strain rates up to about 1 s^{-1} , strains were measured using Instron clip-on extensometers having a 25 mm gauge length and 2.5 mm travel. The outputs from the load cell, displacement transducer and extensometers were recorded on a Gould Data Systems 840 digital storage oscilloscope with 16 bit resolution. The data were transferred to a PC for analysis using Gould Transfer Acquisition (v2.10.12) software.

At the lower strain rates, plots of strain versus crosshead displacement were modelled using a quadratic function¹¹. For each material, the model parameters had little sensitivity to strain rate and were thus employed to calculate strains from the displacement measurements in high-rate tests. For some high-rate tests, these calculated strains were compared with strains determined using a high-rate extensometer based on a linescan camera¹². Provided that the specimen does not form a neck during extension, these checks indicated that the strains estimated from the crosshead displacement are reliable.

5.3.2 Measurements with Impact Apparatus

A Rosand IFW5 falling weight impact machine with a tensile test frame¹³ was used to generate data at impact velocities between 1 ms⁻¹ and 4 ms⁻¹ (strain rates 25-100 s⁻¹). With this apparatus, a falling weight strikes the free-hanging lower grip of the specimen clamped at its upper end to the frame. The force transmitted through the specimen was measured by a 50 kN Kistler piezo-electric force transducer attached to the top of the specimen frame and the fixed upper grip. The force signal was recorded on a computer that controls the impact apparatus, and was analysed using Rosand IFW5 (v1.08) software. The displacement of the grips was calculated from integration of the force-time signal. Strains were determined from these displacements using the model functions derived from the tests on the servohydraulic machine (see Section 5.3.1).

5.3.3 Identification of Data Sets and Corrections to Strain Values

The peak or plateau yield stresses obtained from repeated high-rate tests at a given strain rate were typically scattered by $\pm 2\%$ about the mean value. To aid in the analysis and presentation of data, those stress-strain data sets were thus identified for which the peak or plateau stress was close to the mean value within each scatter band.

Some of the high-rate data sets exhibited errors apparently associated with the inaccurate synchronisation of the force-time and displacement-time recordings at the start of the test. This effect was corrected for by adding or subtracting a small constant increment to each strain value to ensure that the initial linear region of the stress-strain curve passed accurately through the origin. Stress-strain curves obtained with the impact apparatus often showed an initial region of low slope and positive curvature, possibly resulting from the finite time for a stress wave pulse to travel along the specimen or from the take-up of slack within the loading train. To correct for this effect a constant increment was subtracted from each strain value so that the linear part of the stress-strain curve again passed through the origin.

5.3.4 Estimation of Transverse Strains and True Stresses

Values of the transverse engineering strain ϵ_t' were required for the calculation of true tensile stresses, $\sigma_T = \sigma' / (1 + \epsilon_t')^2$, from the measured engineering stresses σ' . Since transverse strains were not determined in the high-rate tests, values were estimated from the longitudinal engineering strains ϵ' using relationships between ϵ_t' and ϵ' derived from the low-rate data.

For the epoxy adhesive, plots of ϵ_t' versus ϵ' at low strain rates exhibited curvatures corresponding to the broad maxima observed in the variation of Poisson's ratio with strain¹. However, each plot could be fitted approximately by a straight line of slope v_a , representing an average Poisson's ratio value over the strain range studied. Approximate values of ϵ_t' at high rates were then obtained using

$$\epsilon_t' = -v_a \epsilon' \quad (15)$$

For the acrylic adhesive, the plots of ϵ_t' versus ϵ' exhibited rather abrupt changes in slope at a strain level ϵ^* corresponding to the sharp peak in Poisson's ratio¹ and the associated onset of marked cavitation. These plots could be fitted approximately by two linear functions intersecting at $\epsilon = \epsilon^*$ and given by

$$\epsilon_t' = -\nu_1 \epsilon' \quad \text{for } \epsilon' \leq \epsilon^* \quad (16a)$$

and

$$\epsilon_t' = \epsilon_{t0}' - \nu_2 \epsilon' \quad \text{for } \epsilon' > \epsilon^* \quad (16b)$$

Table 2 lists the values obtained for ν_a , ν_1 , ϵ^* , ϵ_{t0}' and ν_2 at each temperature investigated. It should be noted that these values are averages over the range of strain rates employed in the low-rate tests and that the variations in ν_a and ν_2 with temperature probably reflect dependencies of these parameters on strain rate. However, the experimental scatter was too large to permit these dependencies to be modelled, so that the average low-rate values of the parameters were employed in estimating the high-rate values of ϵ_t' .

Table 2. Values of Parameters Characterising the Variation of ϵ_t' with ϵ'

Temperature (°C)	Adhesive Material				
	Epoxy	Acrylic			
	ν_a	ν_1	ϵ^*	ϵ_{t0}'	ν_2
50	0.35	0.38	0.03	-0.0041	0.26
23	0.29	0.38	0.02	-0.0054	0.118
0	0.25	0.35	0.02	-0.0051	0.066
-40	0.25	0.38			

6 RESULTS AND DISCUSSION

6.1 ELASTIC MODULI AND POISSON'S RATIOS

Accurate values of E and ν_e were obtained only in the low strain rate region at temperatures of 0, 23 and 50 °C (see Section 5.2.1). From the results for the epoxy adhesive in Figure 3, it is found that E increases on average by about 6% per decade increase in strain rate and by about 1% per °C decrease in temperature. At each temperature the E versus $\log \dot{\epsilon}$ plot shows a slightly negative curvature. This reflects the approach to the glassy plateau with increasing strain rate following the rubber-glass (α) relaxation region.

Larger modulus variations are observed for the acrylic adhesive (Fig 4), averaging about 10%/decade and -2%/°C over the temperature range studied. At each temperature, the plots in Figure 4 exhibit a slight positive curvature. This effect is most evident at 50 °C, and marks the onset of the broad secondary β -relaxation process¹⁴ in the glassy polymethyl methacrylate (PMMA) matrix polymer.

Despite the rather large experimental scatter in the measured v_e values (Section 5.2.1) they were observed to decrease significantly with increasing strain rate and decreasing temperature for each adhesive. The v_e values varied from about 0.41 to 0.37 for the epoxy and from about 0.44 to 0.36 for the acrylic adhesive over the range of strain rate and temperature studied. These variations again reflect the significant relaxation effects for both materials.

The dependence of E and v_e on strain rate and temperature could in principle be modelled in terms of parameters obtained from stress relaxation data. Such analyses would be somewhat complicated by the overlap of different relaxation regions and have not been undertaken in this project.

6.2 TENSILE STRESS-STRAIN CURVES

For both the epoxy and acrylic adhesive, families of tensile (true) stress-strain curves have been generated for strain rates in the range 10^{-4} - 100 s^{-1} at temperatures of 50, 23, 0 and -40 °C respectively. Results for the epoxy material are presented in Figures 5a-d. At each strain rate and temperature, substantial yielding occurs at strains in the range 0.04-0.06 as evidenced by a marked decrease in slope of the stress-strain curve. A gradual strain hardening is subsequently observed by a small increase in (yield) stress with increasing strain up to failure. With increasing rate and decreasing temperature, there is a small apparent increase in the strain level at which the substantial yielding sets in and the yield stress at any given strain exhibits a progressive increase.

The tensile results for the acrylic adhesive are shown in Figures 6a-d. At the lower strain rates and higher temperatures (50 °C and 23 °C), strain softening gives rise to a peak on the curve at a strain level between 0.02 and 0.04 that decreases with increasing rate and decreasing temperature. The magnitude of the strain softening also decreases with increasing rate and decreasing temperature, and the peak is replaced by a plateau region or a region of very slowly increasing stress. The height of the peak or plateau increases progressively with increasing rate and decreasing temperature and at -40 °C failure is observed at strains below that (~ 0.02) corresponding to the onset of the plateau.

6.3 EFFECTIVE STRESS-STRAIN CURVES FROM SHEAR DATA. COMPARISON WITH TENSILE CURVES

Plots of the effective stress $\bar{\sigma}$ versus effective strain, $\bar{\epsilon} = \bar{\epsilon}_p + (\bar{\sigma} / E)$, were calculated from shear σ_s and γ_p values using equations (8) and (9). In these calculations a value of $\lambda=1$ was employed for both adhesives at all strain rates and temperatures, assuming that in the absence of cavitation the yield behaviour can be described by the von Mises criterion. For

the epoxy adhesive this is consistent with the results of compression and shear data at room temperature and low strain rates from which a λ value close to unity was obtained using equation (11).

The $\bar{\sigma}$ versus $\bar{\epsilon}$ plots for the epoxy adhesive (Figs 7a-c) are similar in shape to the tensile (effective) stress-strain curves in Figures 5a-c. However, at corresponding strain rates and temperatures, deviations are observed (Fig 8) between the tensile curves and the effective stress-strain curves from the shear data. As illustrated in Figure 8, the tensile yield stress σ_T at high strains is less than the effective stress $\bar{\sigma}$ from the shear results. These deviations are attributed to the cavitation that occurs during tensile yielding. The magnitude of this effect, as characterised by the high-strain value of $\sigma_T / \bar{\sigma} \approx 0.85$, is essentially independent of strain rate and temperature over the range of these variables investigated.

Figures 9a-c show the $\bar{\sigma}$ versus $\bar{\epsilon}$ plots obtained from the shear data for the acrylic adhesive. The effective stress generally increases with effective strain to a maximum value that is attained for $\bar{\epsilon} \sim 0.04-0.05$ and then either remains essentially constant or, at the higher temperatures and lower rates, decreases slightly (strain softens) with further increases in strain. These effects are similar to those exhibited by the tensile curves (Figs 6a-c). However, deviations are again observed between the effective stress-strain curves in tension and shear at corresponding effective strain rates and temperatures. Fig 10 illustrates that the maximum effective stress in tension σ_T is lower than the maximum $\bar{\sigma}$ value from the shear data and is attained at lower values of effective strain. The differences between the effective stress-strain curves in tension and shear now increase with increasing rate and decreasing temperature (Fig 10) a result that we attribute to the increasing effects of cavitation or crazing during tensile yielding.

6.4 DEPENDENCE OF YIELD STRESSES ON STRAIN RATE AND TEMPERATURE

Figure 11 shows plots of σ_y/T versus $\log \dot{\epsilon}_y$ obtained from the tensile data for the epoxy adhesive at -40, 0, 23 and 50 °C respectively. In the absence of well-defined peaks or plateaus on the stress-strain curves, the yield stresses σ_y and strain rates $\dot{\epsilon}_y$ were each selected at an arbitrary strain of 0.06. It will be observed that the plots are quite well-fitted by equation (14) with the values of parameters in Table 3. We note that the value for A_β is larger than that for A_α , a result consistent with a relatively small volume of the motional unit for the β -process. Furthermore the activation energy Q_β for the β -process is correspondingly lower than Q_α for the α -process.

Table 3. Values of Parameters Characterising the Dependence of Yield Stresses on Strain Rate and Temperature

	Epoxy LMD 1142		Acrylic MA 310		
	Tension	Shear (effective stress)		Tension	Shear (effective stress)
$A_\alpha \times 10^3$ (MPa K ⁻¹)	6.63	6.79	$A \times 10^3$ (MPa K ⁻¹)	7.0	11.9
$Q_\alpha \times 10^{-5}$ (J/ mole)	2.05	2.56	$Q \times 10^{-5}$ (J/ mole)	2.08	2.19
C_α (s)	6.00×10^{-26}	8.28×10^{-34}	C (s)	7.5×10^{-28}	8.0×10^{-31}
$A_\beta \times 10^3$ (MPa K ⁻¹)	13.0				
$Q_\beta \times 10^{-5}$ (J/ mole)	1.22				
C_β (s)	1.61×10^{-24}				

The shift direction required to superpose the plots in Figure 11 at different temperatures may be resolved into horizontal and vertical components determined by the values of Q_β and $Q_\alpha - Q_\beta$ respectively. The magnitude of the vertical component represents an effective scaling of stress values required to obtain superposition of stress-strain curves by a corresponding strain rate-temperature equivalence.

Figure 12 presents plots of $\bar{\sigma}_y/T$ versus $\log \dot{\epsilon}_y$ obtained from the shear data for the epoxy adhesive (Figs 7a-c) at an effective strain level of 0.06. A good fit to the data is obtained using a single Eyring function (equation (13)) for the α -process. This is consistent with the fact that the β -process sets in at higher strain rates and lower temperatures than were studied in the shear tests (see Fig 11). The values of A_α and Q_α given in Table 3 are similar to those obtained from the tensile data, indicating a close connection between the yielding mechanisms in shear and tension.

Plots of σ_y/T versus $\log \dot{\epsilon}_y$ derived from the tensile data for the acrylic adhesive are presented in Figure 13. At low strain rates and high temperatures (50 °C and 23 °C) the yield stresses σ_y and strain rates $\dot{\epsilon}_y$ were taken to correspond to the peaks in the stress-strain curves in Figures 6a and b. Since the strain-softening effect and resulting peaks were not observed at the higher rates and at 0 °C, the σ_y and $\dot{\epsilon}_y$ values were then determined for a strain level of 0.022, corresponding to the onset of the plateau on the stress-strain curves or marked reduction in the rate of strain hardening. No results are included in Figure 13 at -40 °C since, at this temperature, failure occurred prior to the attainment of plateaus in the stress-strain curves (Fig 6d).

The plots in Figure 13 are reasonably well fitted by a single Eyring function (equation (13)) with the values of A , Q and C given in Table 3. However, for the strain rates and temperatures studied in this project, the σ_y/T values for the acrylic adhesive are probably

determined by substantial contributions from both the α and β relaxation processes. This suggestion is consistent with the shape of the E versus $\log \dot{\epsilon}$ plots in Figure 4 and with published yield studies^{5,6} of the matrix polymer (PMMA) at temperatures between 22 °C and 100 °C. Assuming that $(\sigma v / RT) \gg 1$ for both processes, equation (12b) gives, in place of (14)

$$\frac{\sigma_y}{T} = A_\alpha \left[\ln 2C_\alpha \dot{\epsilon}_y + (Q_\alpha / RT) \right] + A_\beta \left[\ln 2C_\beta \dot{\epsilon}_y + (Q_\beta / RT) \right] \quad (17)$$

This equation may be identified with (13), giving relationships between the derived A , Q and C and the different parameters for the respective α and β processes.

Figure 14 shows plots of $\bar{\sigma}_y / T$ versus $\log \dot{\epsilon}_y$ obtained from the shear data for the acrylic adhesive. The effective stresses $\bar{\sigma}_y$ and effective strain rates $\dot{\epsilon}_y$ here correspond to the peaks of the curves in Figures 9a-c. However, for the three highest rates at 0 °C, failure occurred (in local regions of stress concentration) before the shear stress had reached a plateau or maximum, and values of $\bar{\sigma}_y$ and $\dot{\epsilon}_y$ were obtained by extrapolation to a strain level of 0.05. The plots in Figure 14 can again be fitted by a single Eyring function with values of A , Q and C given in Table 3. It will be seen that the Q value is similar to that obtained from the tensile data and should be noted that the value of each parameter is probably determined by contributions from the respective α and β processes.

From the successful application of the generalised Eyring model to the tensile and shear results, it follows that accurate predictions could be made of the yield stresses at impact rates (100 s^{-1}). This could involve either an extrapolation of results at a given temperature or a rate-temperature shift procedure using data obtained at different rates and temperatures.

7 CONCLUSIONS

- For both the epoxy and acrylic adhesives, the Young's modulus E and Poisson's ratio ν_e exhibit a significant dependence on strain rate and temperature. The variations in E could be modelled in terms of parameters obtained from stress relaxation data, but this may be complicated by the overlap of α and β relaxation regions.
- For each adhesive, deviations are observed between the tensile stress-strain curves and the effective stress ($\bar{\sigma}$) versus effective strain ($\bar{\epsilon}$) curves calculated from the shear data at corresponding effective strain rates and temperatures. These deviations are attributed to the effects of cavitation on the tensile yield process. They are essentially independent of strain rate and temperature for the epoxy adhesive but increase with increasing rate and decreasing temperature for the acrylic.
- The dependence of yield stresses on strain rate and temperature can be described successfully in terms of a generalisation of Eyring's model. This accounts for contributions to the yield stress from α and β relaxation processes. Accurate predictions of the yield behaviour at impact rates can then be made by extrapolation or by the use of strain rate-temperature superposition.

8 ACKNOWLEDGEMENTS

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9 REFERENCES

1. G.D. Dean, B.E. Read and B.C. Duncan, An evaluation of yield criteria for adhesives for finite element analysis. NPL report CMMT(A)117 (1999).
2. B.E. Read, G.D. Dean and B.C. Duncan, Characterisation of the non-linear behaviour of plastics for finite element analysis. NPL report CMMT(A)114 (1998).
3. A. Lazzeri and C.B. Bucknall, Polymer 36 (1995) p 2895.
4. H. Eyring, J. Chem. Phys. 4 (1936), p 283.
5. C. Bauwens-Crowet and G. Homès, C.R. Acad. Sci. (Paris) 259 (1964), p 3434.
6. J.A. Roetling, Polymer 6 (1965), p 311.
7. C. Bauwens-Crowet, J-C. Bauwens and G. Homès, J. Polym. Sci. A2, 7 (1969), p 735.
8. ISO 15166:1998 Adhesives - Methods for preparing bulk specimens. Part 1: Two-part systems. Part 2: Elevated-temperature curing, one-part systems.
9. B.E. Read and G.D. Dean, Polymer 25 (1984), p 1679.
10. B.C. Duncan and G.D. Dean, Test methods for determining shear property data for adhesives suitable for design. NPL report CMMT(B)56 (1996).
11. B.C. Duncan, Development of a high rate extensometer, NPL report CMMT(A)109, (1998).
12. B.C. Duncan, Methods for measuring strains at high rates. NPL report CMMT(A)133, (1998).
13. B.C. Duncan and A. Pearce, Comparison of impact and high rate tests for determining properties of adhesives and polymers needed for design under impact. NPL report CMMT(A)134, (1999).
14. N.G. McCrum, B.E. Read and G. Williams, Anelastic and dielectric effects in polymeric solids. Wiley, London (1967). Republished by Dover Publications Inc, New York (1991).

FIGURE CAPTIONS

- Fig 1 The Eyring model.
- Fig 2 Contributions to σ_y/T from the respective α and β relaxation processes according to the generalised Eyring model.
- Fig 3 Dependence of Young's modulus E on strain rate $\dot{\epsilon}$ for the epoxy adhesive at the temperatures indicated.
- Fig 4 Dependence of Young's modulus on strain rate for the acrylic adhesive at the temperatures indicated.
- Figs 5a-d Tensile stress-strain data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to a strain of 0.06. Fig 5a, 50 °C; Fig 5b, 23 °C; Fig 5c, 0 °C; Fig 5d, -40 °C.
- Figs 6a-d Tensile stress-strain data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the peaks in stress. Fig 6a, 50 °C; Fig 6b, 23 °C; Fig 6c, 0 °C; Fig 6d, -40 °C.
- Figs 7a-c Effective stress versus effective strain plots derived from shear data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to an effective strain of 0.06. Fig 7a, 50 °C; Fig 7b, 23 °C; Fig 7c, 0 °C.
- Fig 8 Comparison of effective stress-effective strain curves determined from tensile data (filled points) and shear data (open points), respectively, for the epoxy adhesive. The temperatures and effective strain rates $[\dot{\epsilon}(s^{-1})]$ for the corresponding pairs of curves are indicated.
- Figs 9a-c Effective stress versus effective strain plots derived from shear data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the stress maxima. Fig 9a, 50 °C; Fig 9b, 23 °C; Fig 9c, 0 °C.
- Fig 10 Comparison of effective stress-effective strain curves determined for the acrylic adhesive from tensile data (filled points) and shear data (open points) respectively. The temperatures and effective strain rates $[\dot{\epsilon}(s^{-1})]$ for the corresponding pairs of curves are indicated.
- Fig 11 Dependence of σ_y/T on $\log \dot{\epsilon}_y$ for the epoxy adhesive at the temperatures indicated, where σ_y and $\dot{\epsilon}_y$ are the tensile yield stress and corresponding strain rate at a strain level of 0.06. The continuous lines were obtained by fitting equation (14) to the data, with the values of parameters in Table 3. The dashed line indicates the shift direction required to superpose the curves obtained at different temperatures.

- Fig 12 Dependence of $\bar{\sigma}_y/T$ on $\log \dot{\bar{\epsilon}}_y$ for the epoxy adhesive at the temperatures indicated, where $\bar{\sigma}_y$ and $\dot{\bar{\epsilon}}_y$ are the effective stress and corresponding effective strain rate obtained from the shear data (Figs 7a-c) at a strain of 0.06. The continuous lines were obtained by fitting equation (13) to the data giving the values of parameters in Table 3.
- Fig 13 Dependence of σ_y/T on $\log \dot{\epsilon}_y$ for the acrylic adhesive at the temperatures indicated. Here σ_y and $\dot{\epsilon}_y$ are the tensile yield stress and strain rate, respectively, at the peaks of the stress-strain curves in Figs 6a-d or (at high rates and low temperatures) at a strain level of 0.022. The continuous lines were obtained by fitting equation (13) to the data giving the values of parameters in Table 3.
- Fig 14 Dependence of $\bar{\sigma}_y/T$ on $\log \dot{\bar{\epsilon}}_y$ for the acrylic adhesive at the temperatures indicated. Here $\bar{\sigma}_y$ and $\dot{\bar{\epsilon}}_y$ are the effective stress and effective strain rate, respectively, at the peaks of shear curves in Figures 9a-c. For the three highest rates at 0 °C, the $\bar{\sigma}_y$ and $\dot{\bar{\epsilon}}_y$ values were obtained by extrapolation to an effective strain of 0.05. The continuous lines were obtained by fitting equation (13) to the data giving the values of parameters in Table 3.

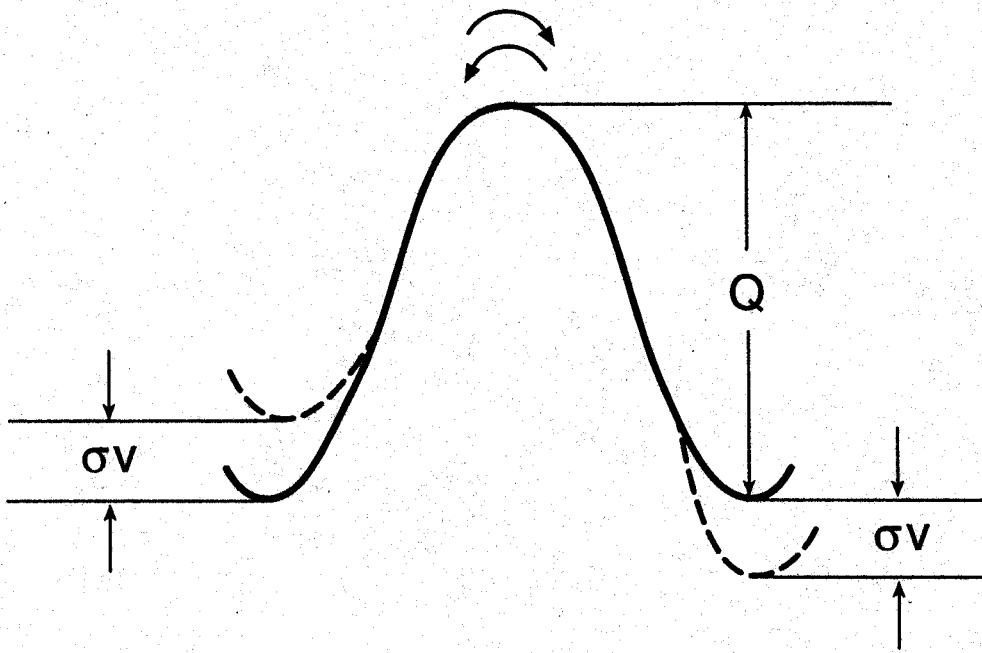


Fig 1 The Eyring model.

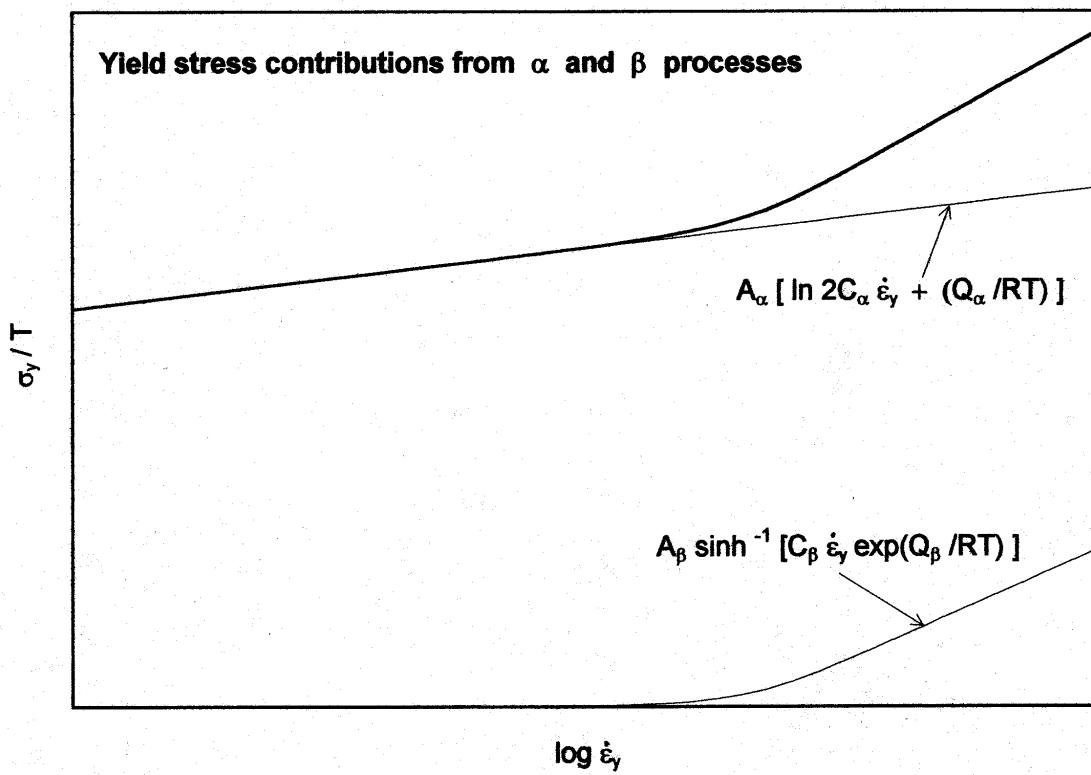


Fig 2 Contributions to σ_y/T from the respective α and β relaxation processes according to the generalised Eyring model.

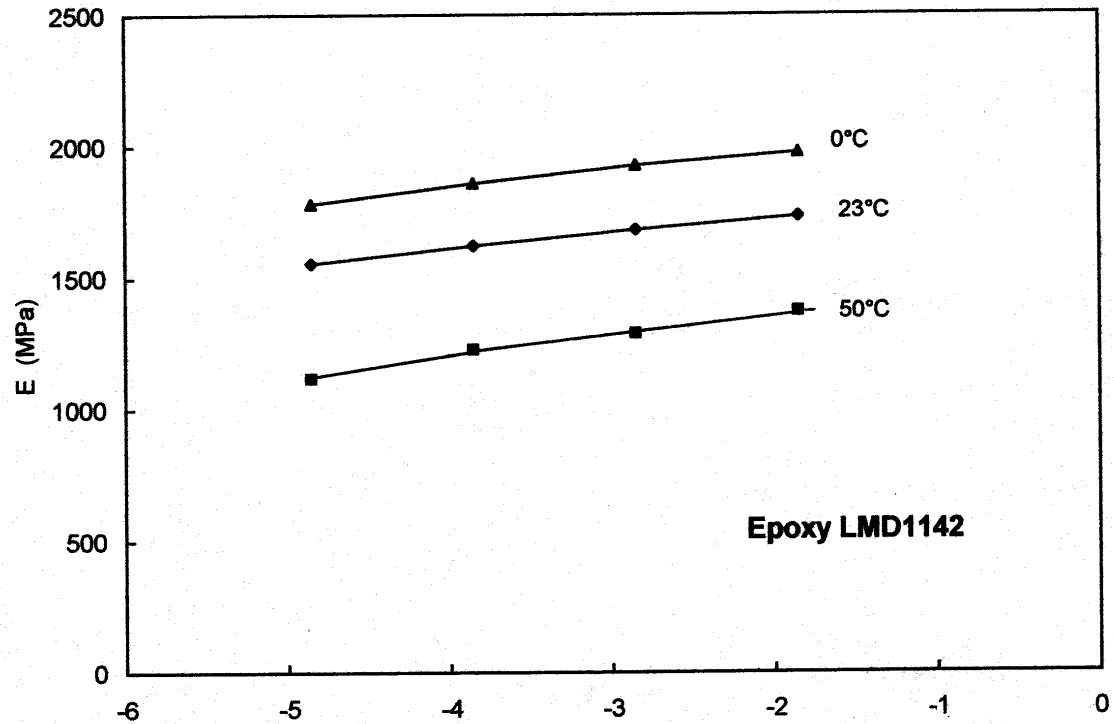


Fig 3 Dependence of Young's modulus E on strain rate $\dot{\epsilon}$ for the epoxy adhesive at the temperatures indicated.

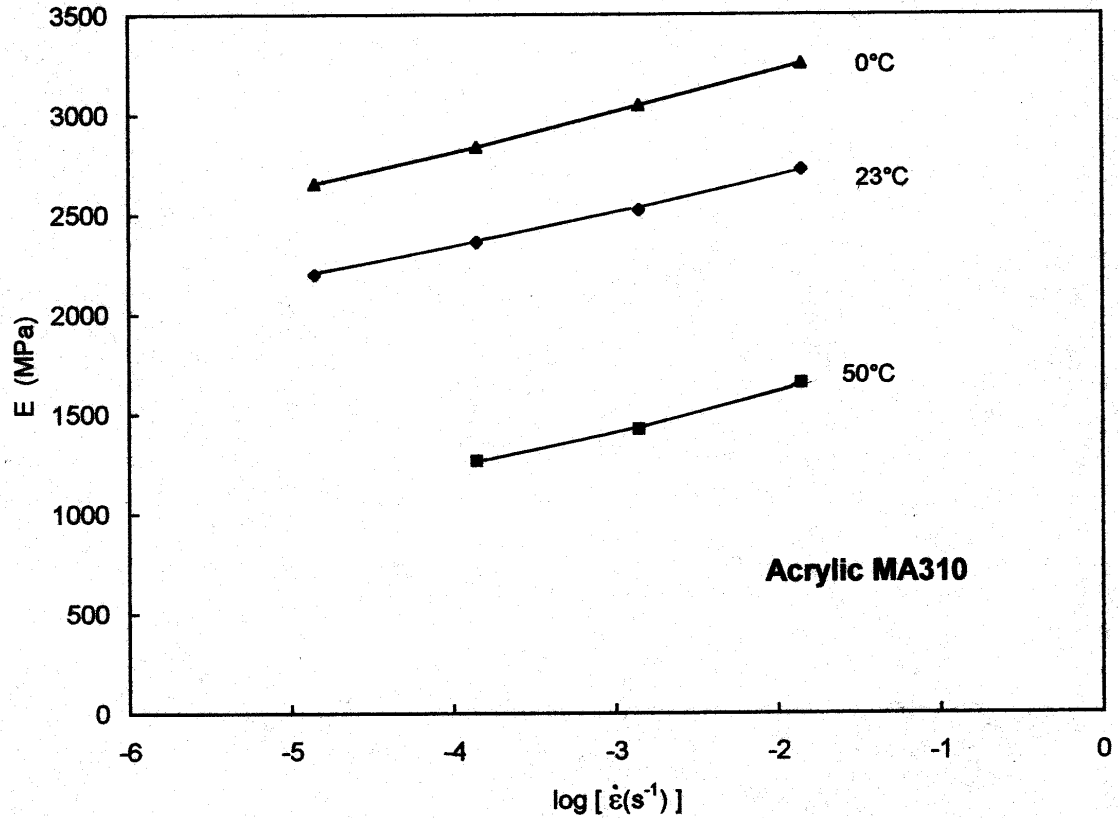


Fig 4 Dependence of Young's modulus on strain rate for the acrylic adhesive at the temperatures indicated.

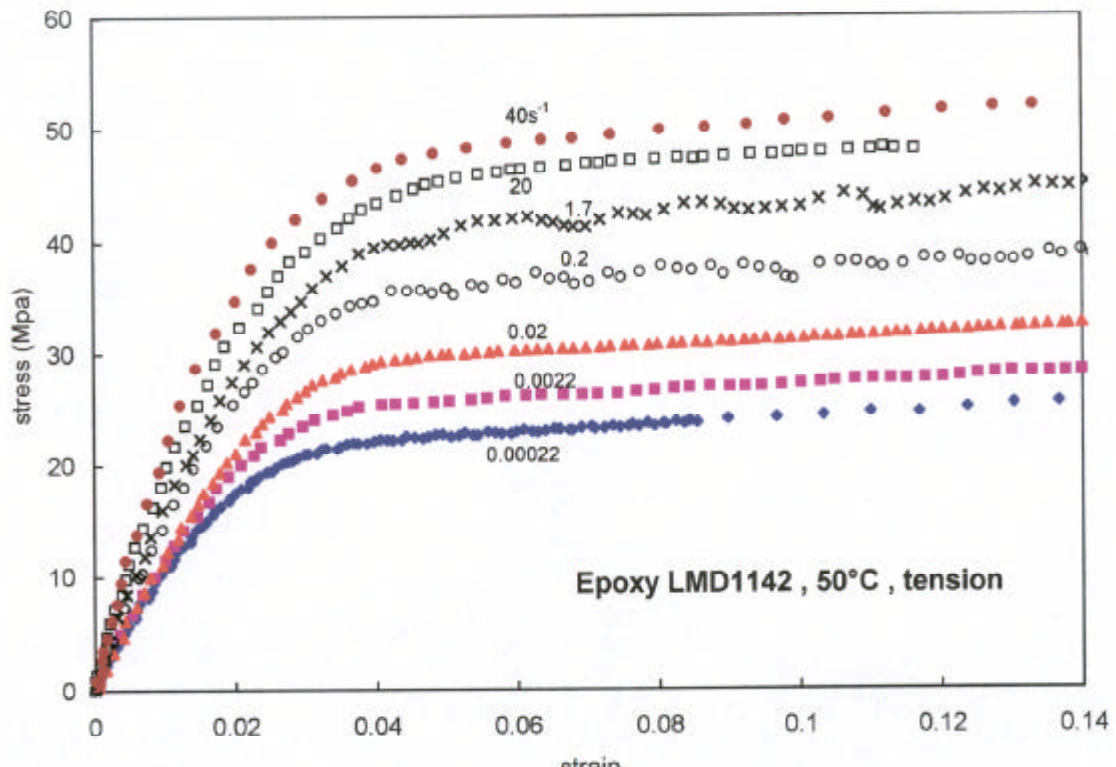


Fig 5a: Tensile stress-strain data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to a strain of 0.06 at 50 °C

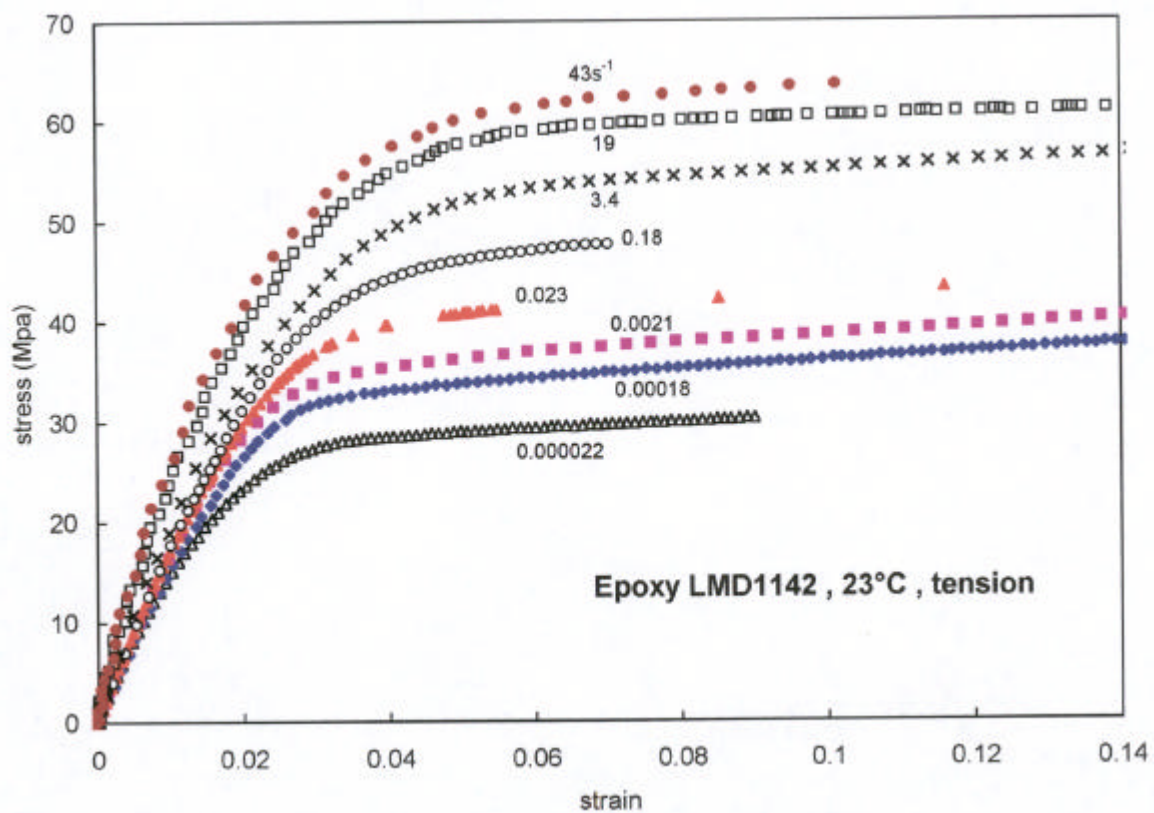


Fig 5b: Tensile stress-strain data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to a strain of 0.06 at 23 °C.

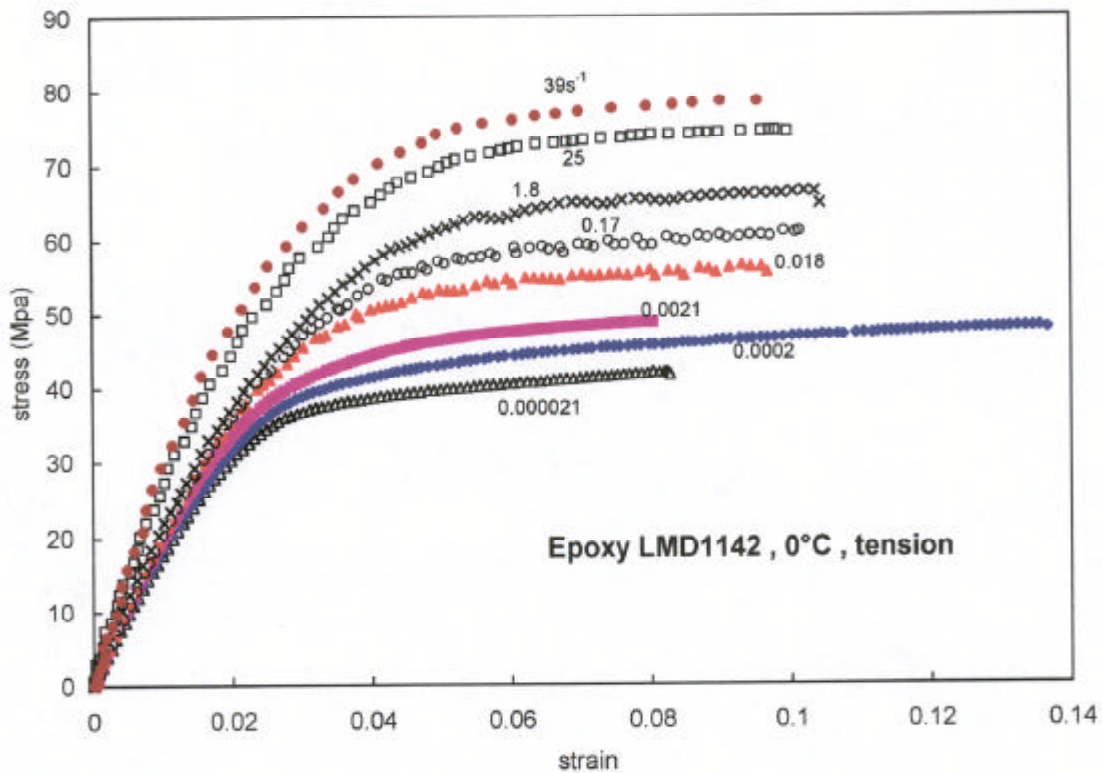


Fig 5c Tensile stress-strain data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to a strain of 0.06 at 0 °C.

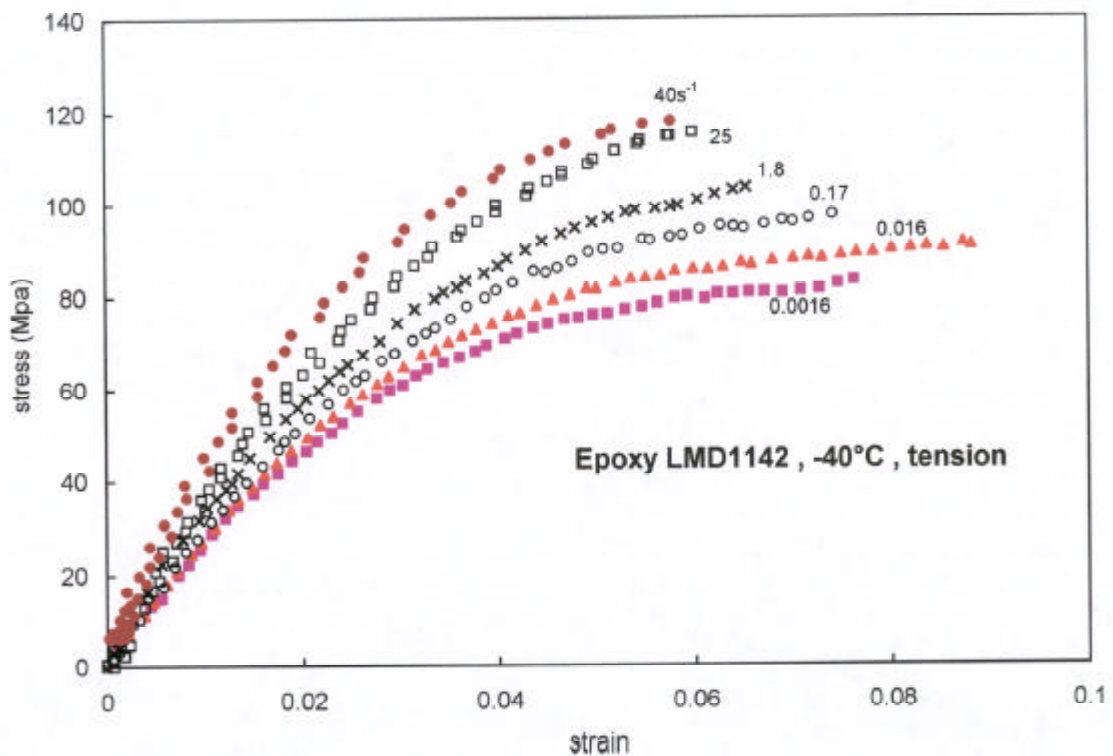


Fig 5d Tensile stress-strain data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to a strain of 0.06 at -40 °C.

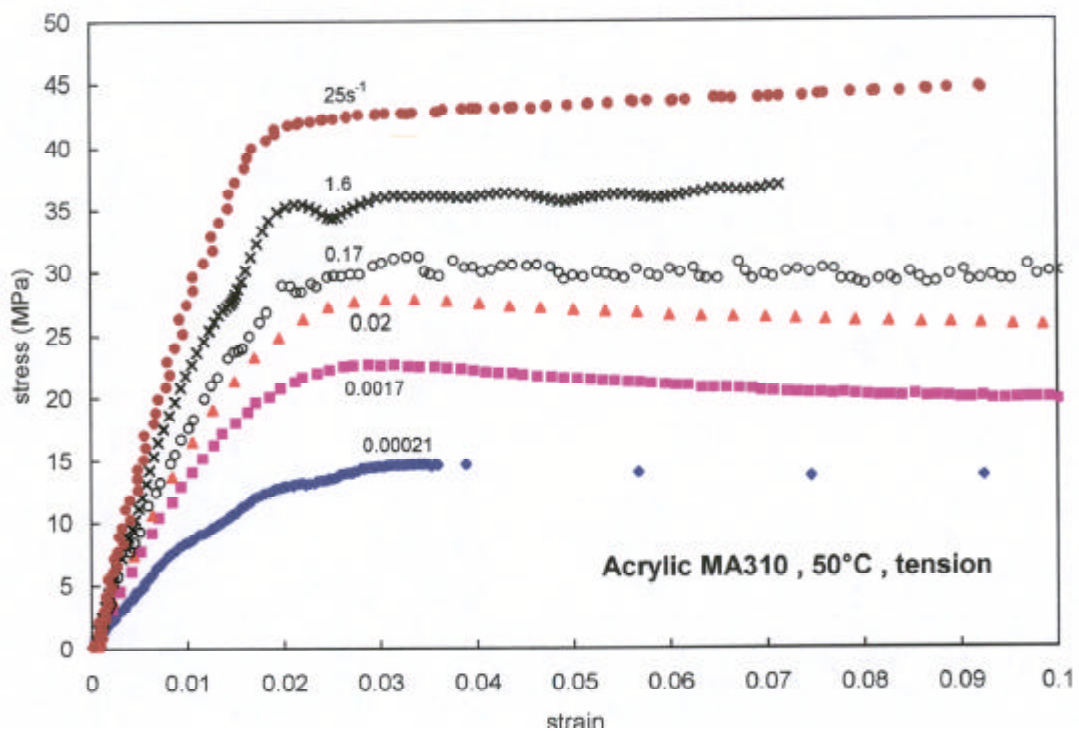


Fig 6a Tensile stress-strain data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the peaks in stress at 50 °C.

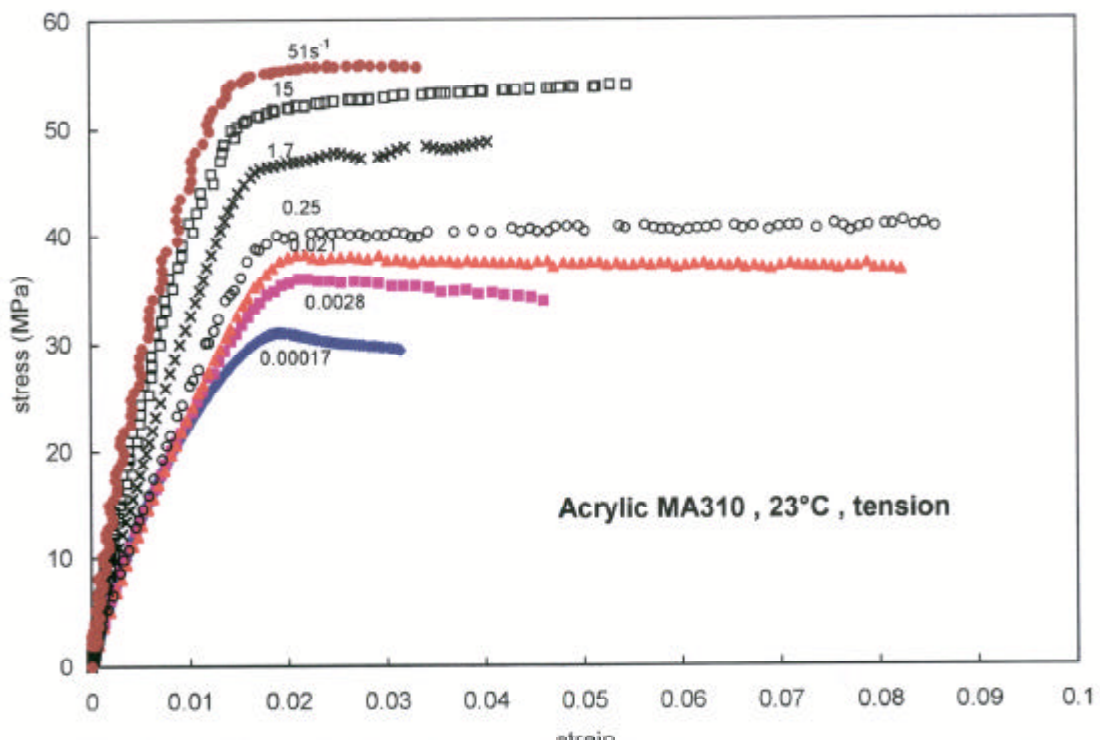


Fig 6b Tensile stress-strain data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the peaks in stress at 23 °C.

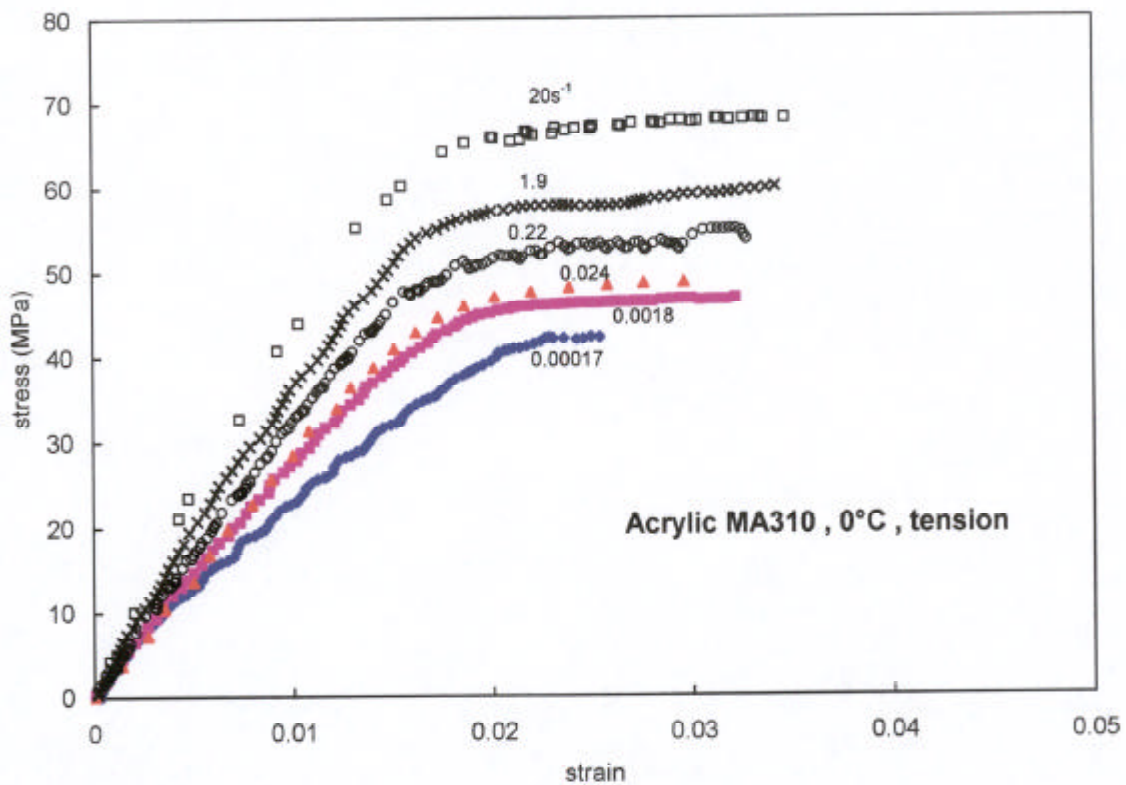


Fig 6c Tensile stress-strain data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the peaks in stress at 0 °C.

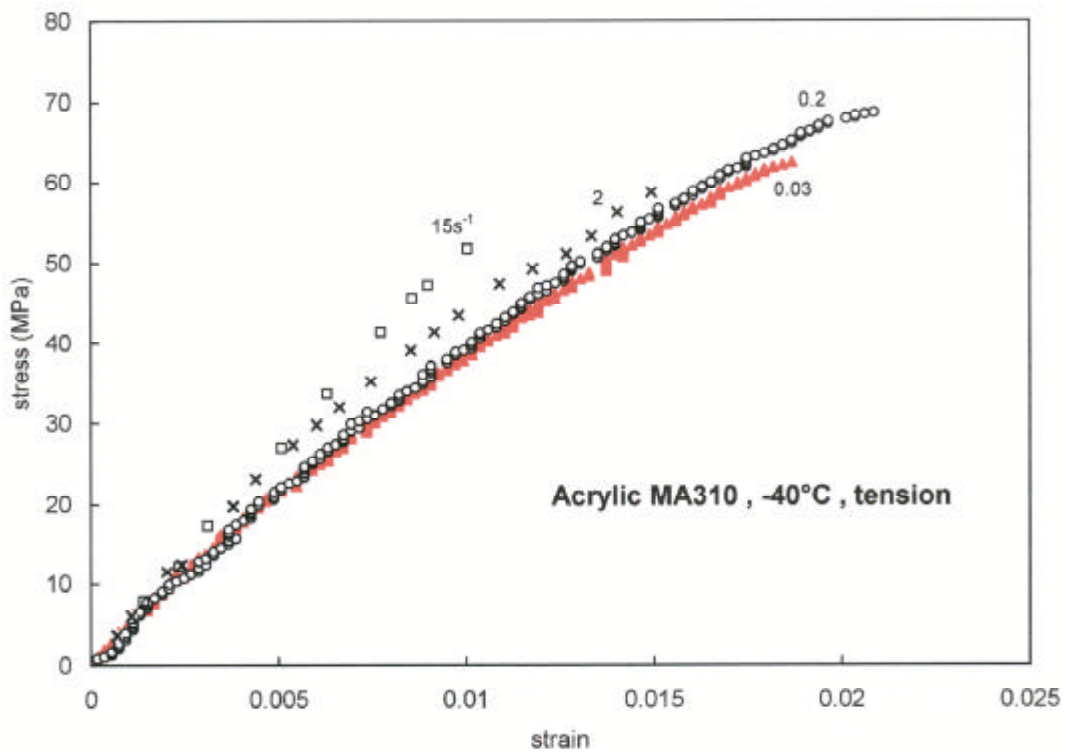


Fig 6d Tensile stress-strain data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the peaks in stress at -40 °C.

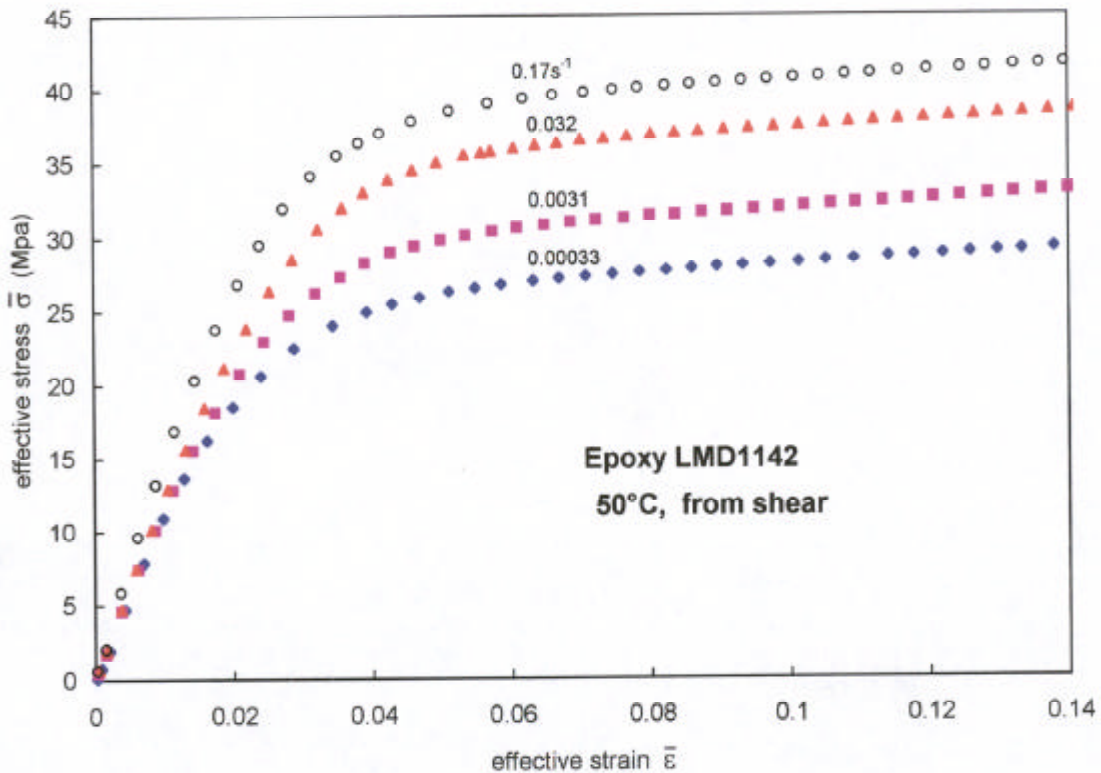


Fig 7a Effective stress versus effective strain plots derived from shear data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to an effective strain of 0.06 at 50 °C.

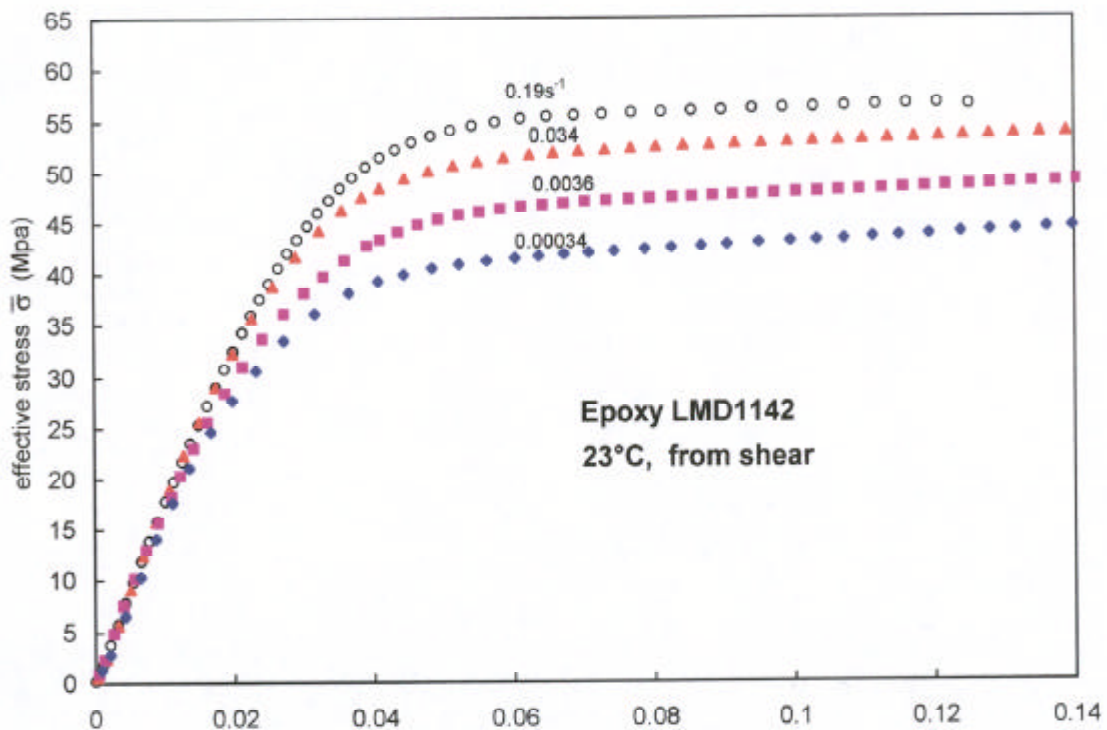


Fig 7b Effective stress versus effective strain plots derived from shear data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to an effective strain of 0.06 at 23 °C.

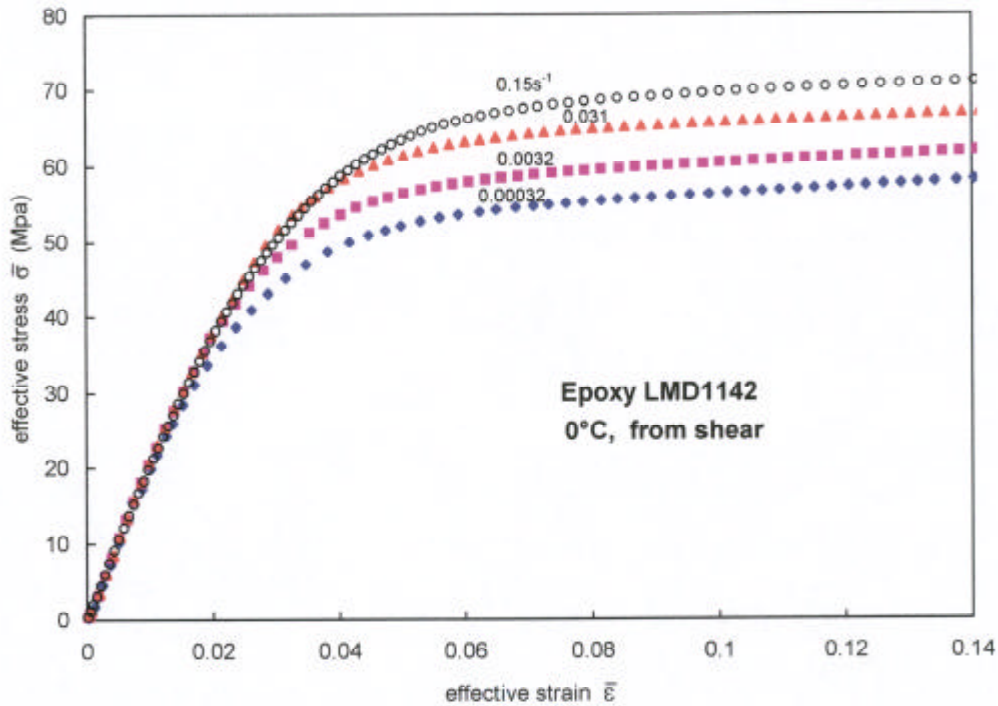


Fig 7c Effective stress versus effective strain plots derived from shear data for the epoxy adhesive at the specified strain rates (s^{-1}) corresponding to an effective strain of 0.06 at 0 °C.

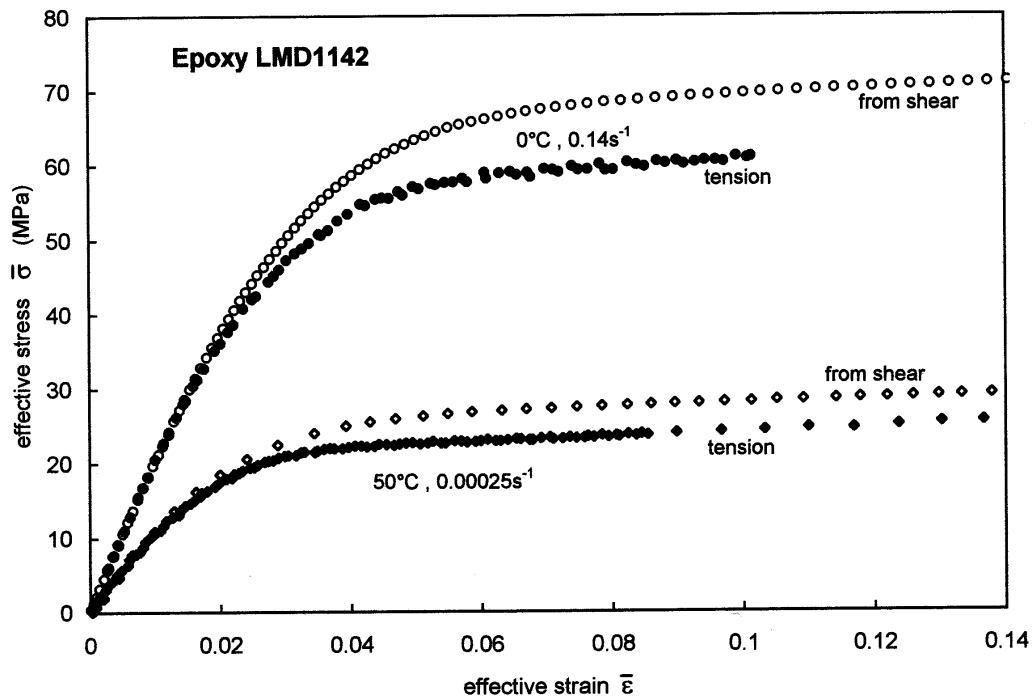


Fig 8 Comparison of effective stress-effective strain curves determined from tensile data (filled points) and shear data (open points), respectively, for the epoxy adhesive. The temperatures and effective strain rates $[\dot{\epsilon}(s^{-1})]$ for the corresponding pairs of curves are indicated.

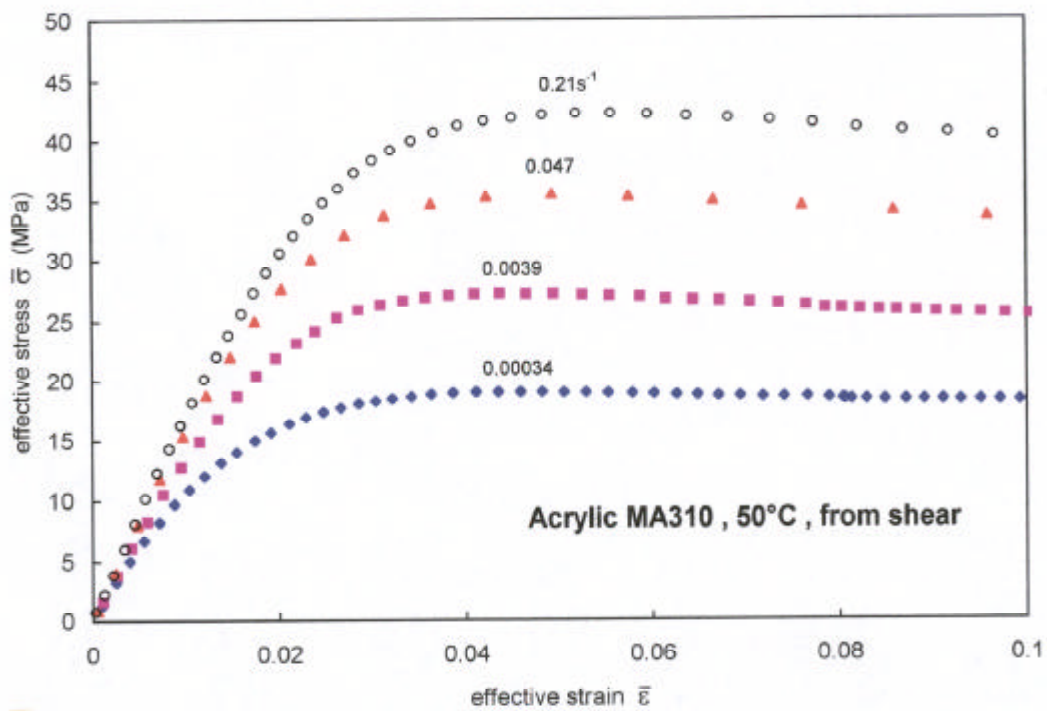


Fig 9a Effective stress versus effective strain plots derived from shear data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the stress maxima at 50 °C.

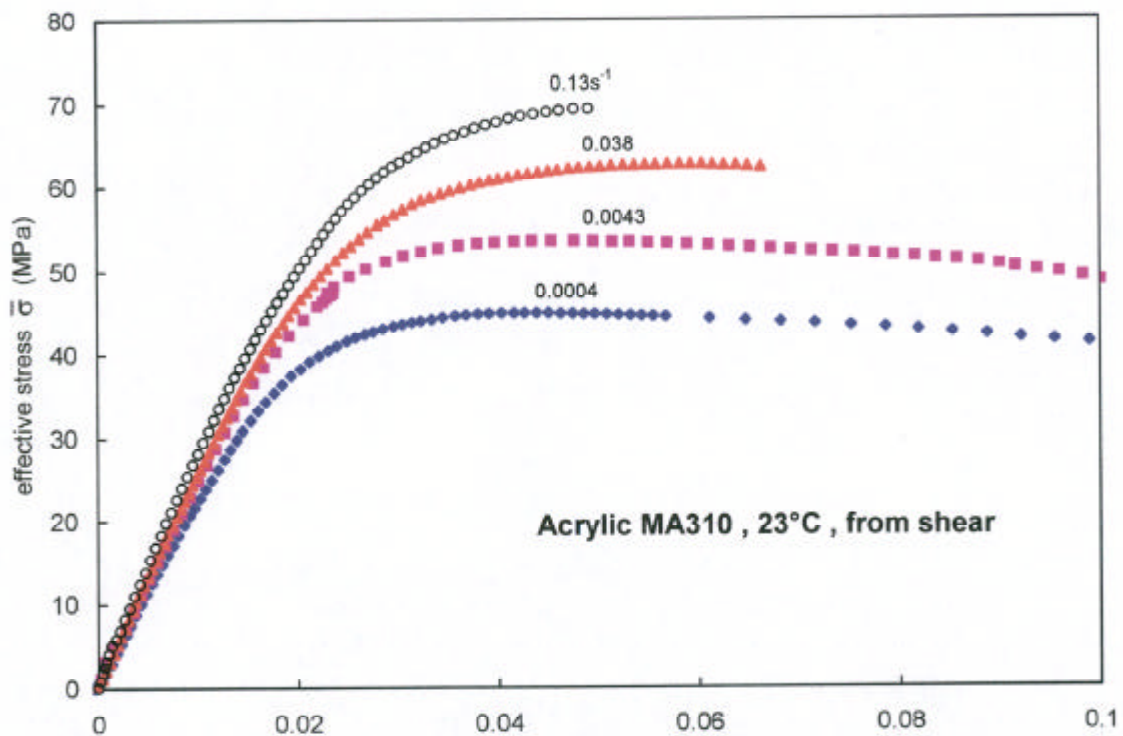


Fig 9b Effective stress versus effective strain plots derived from shear data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the stress maxima at 23 °C.

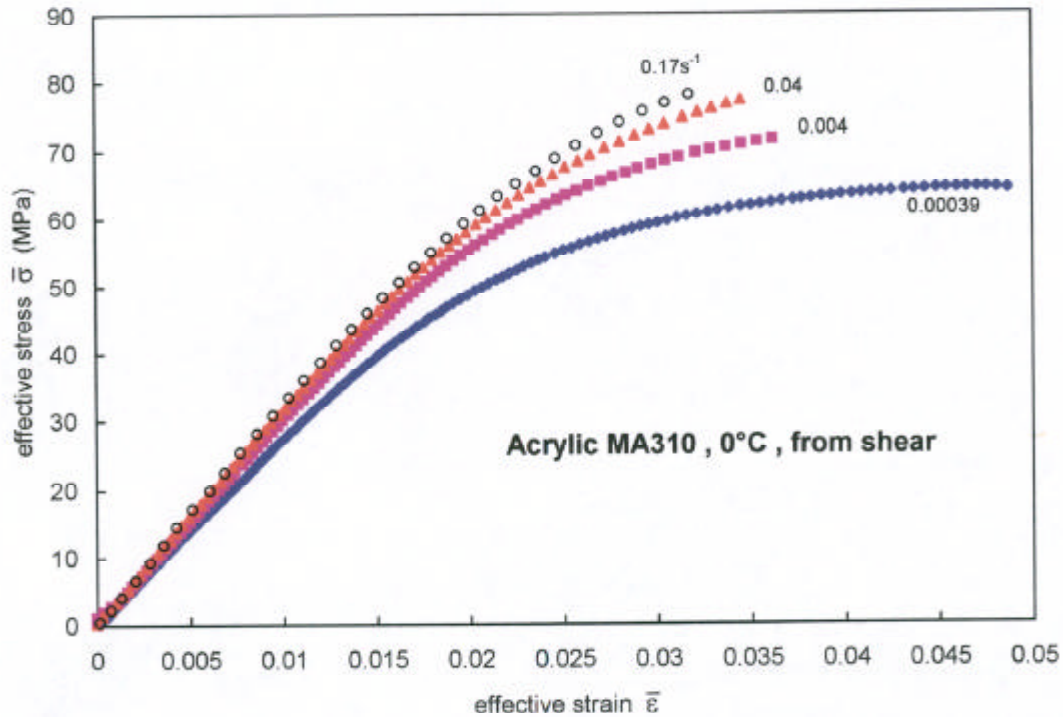


Fig 9c Effective stress versus effective strain plots derived from shear data for the acrylic adhesive at the specified strain rates (s^{-1}) corresponding to the stress maxima at 0 °C.

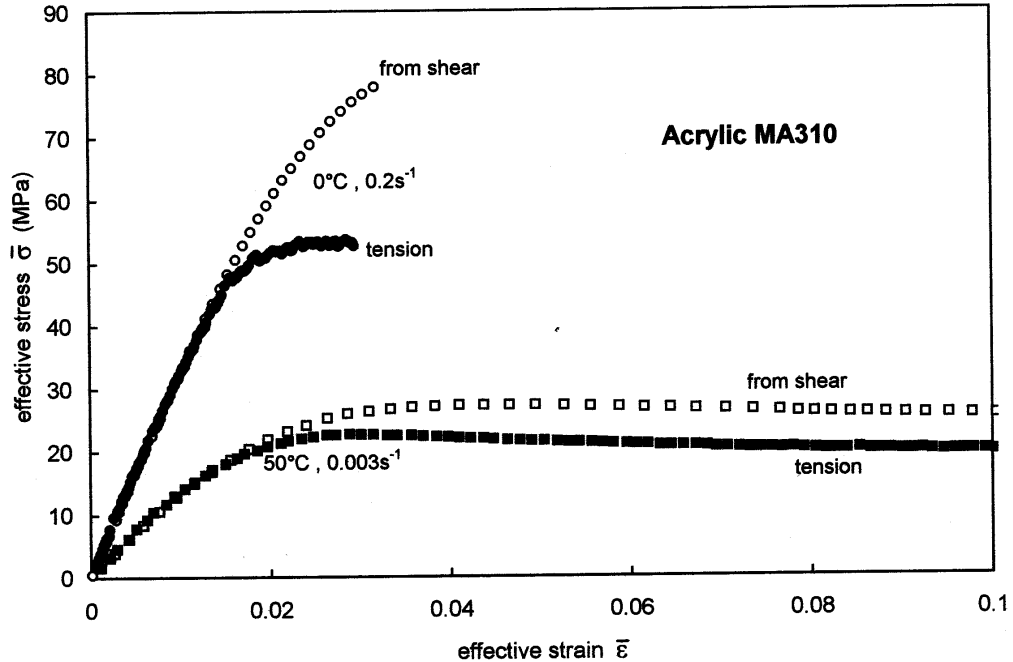


Fig 10 Comparison of effective stress-effective strain curves determined for the acrylic adhesive from tensile data (filled points) and shear data (open points) respectively. The temperatures and effective strain rates $[\dot{\epsilon}(\text{s}^{-1})]$ for the corresponding pairs of curves are indicated.

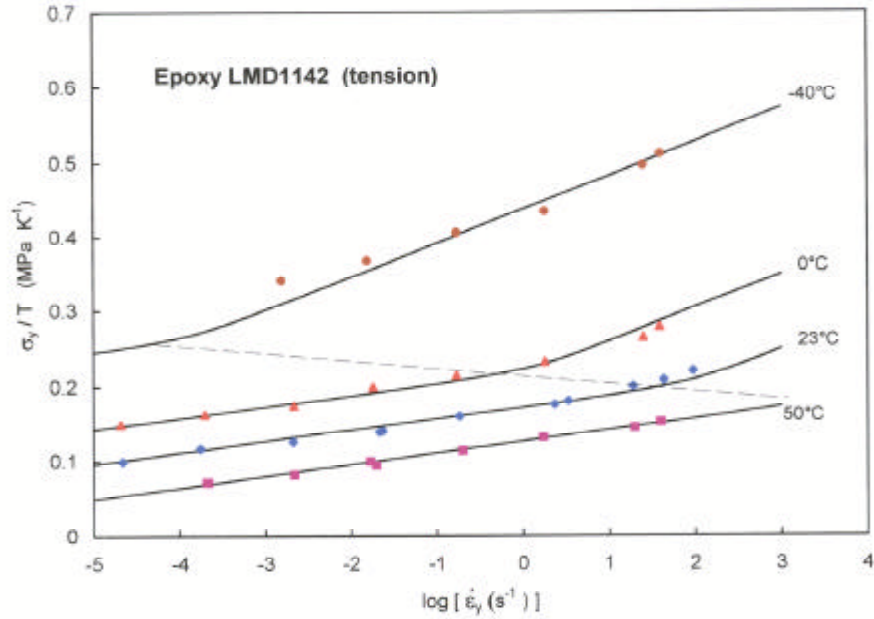


Fig 11 Dependence of σ_y/T on $\log \dot{\epsilon}_y$ for the epoxy adhesive at the temperatures indicated, where σ_y and $\dot{\epsilon}_y$ are the tensile yield stress and corresponding strain rate at a strain level of 0.06. The continuous lines were obtained by fitting equation (14) to the data, with the values of parameters in Table 3. The dashed line indicates the shift direction required to superpose the curves obtained at different temperatures.

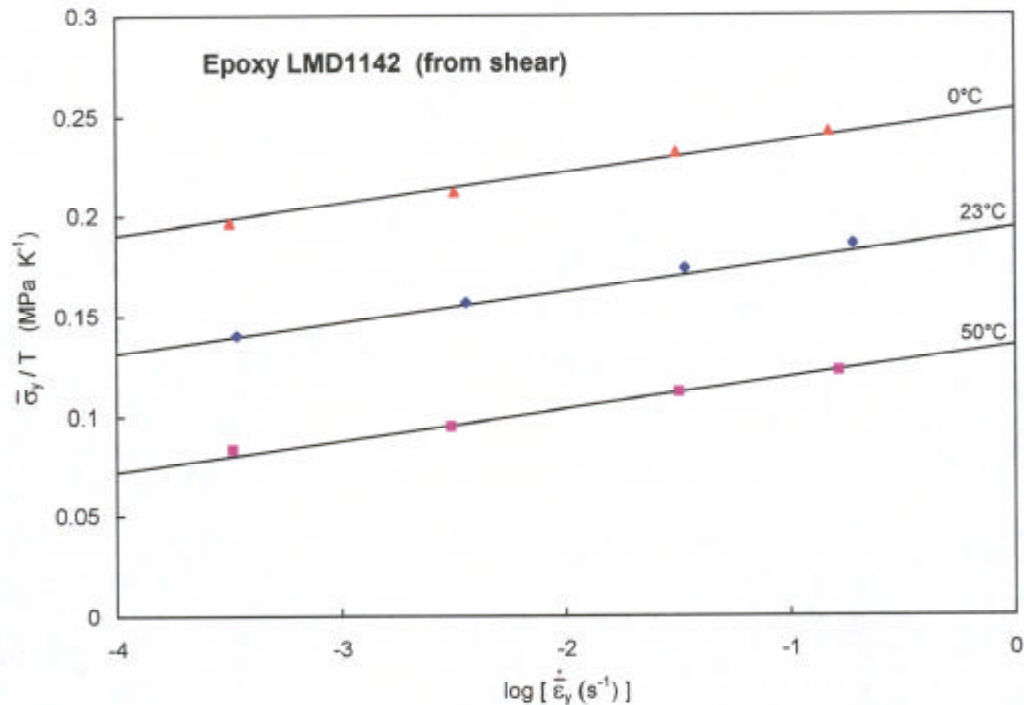


Fig 12 Dependence of $\bar{\sigma}_y/T$ on $\log \dot{\bar{\epsilon}}_y$ for the epoxy adhesive at the temperatures indicated, where $\bar{\sigma}_y$ and $\dot{\bar{\epsilon}}_y$ are the effective stress and corresponding effective strain rate obtained from the shear data (Figs 7a-c) at a strain of 0.06. The continuous lines were obtained by fitting equation (13) to the data giving the values of parameters in Table 3.

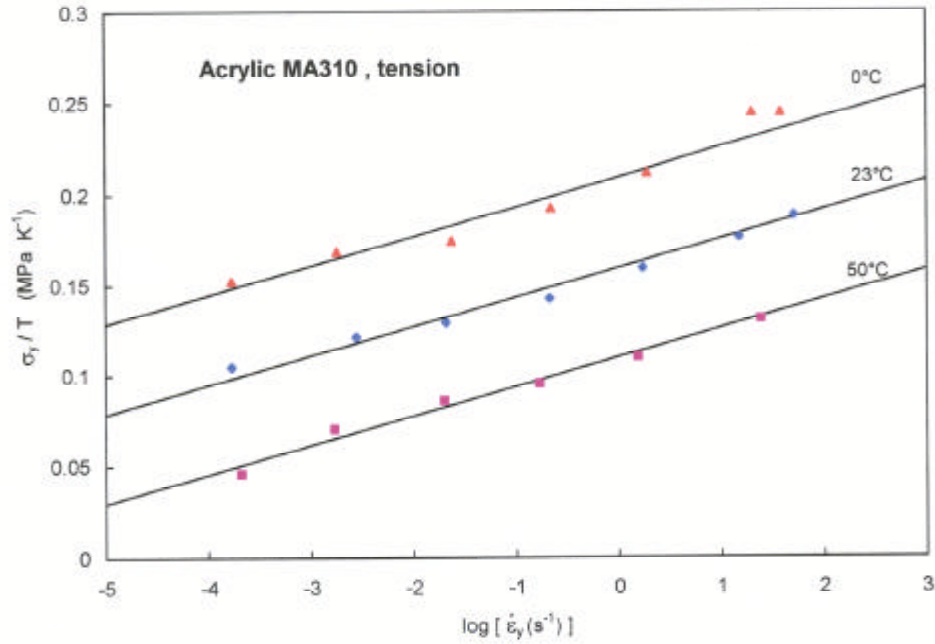


Fig 13

Dependence of σ_y/T on $\log \dot{\epsilon}_y$ for the acrylic adhesive at the temperatures indicated. Here σ_y and $\dot{\epsilon}_y$ are the tensile yield stress and strain rate, respectively, at the peaks of the stress-strain curves in Figs 6a-d or (at high rates and low temperatures) at a strain level of 0.022. The continuous lines were obtained by fitting equation (13) to the data giving the values of parameters in Table 3.

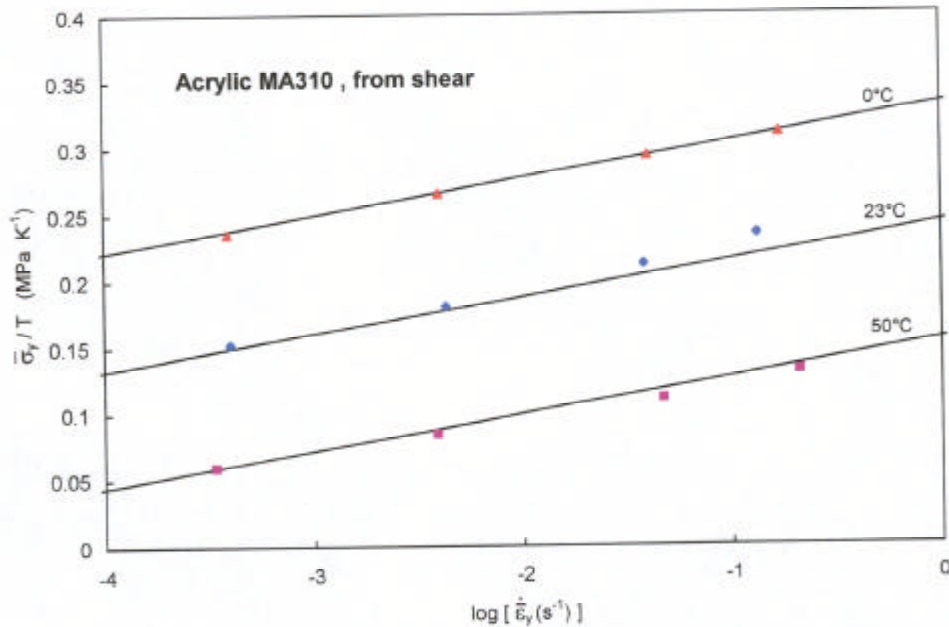


Fig 14

Dependence of $\bar{\sigma}_y/T$ on $\log \dot{\bar{\epsilon}}_y$ for the acrylic adhesive at the temperatures indicated. Here $\bar{\sigma}_y$ and $\dot{\bar{\epsilon}}_y$ are the effective stress and effective strain rate, respectively, at the peaks of shear curves in Figures 9a-c. For the three highest rates at 0 °C, the $\bar{\sigma}_y$ and $\dot{\bar{\epsilon}}_y$ values were obtained by extrapolation to an effective strain of 0.05. The continuous lines were obtained by fitting equation (13) to the data giving the values of parameters in Table 3.