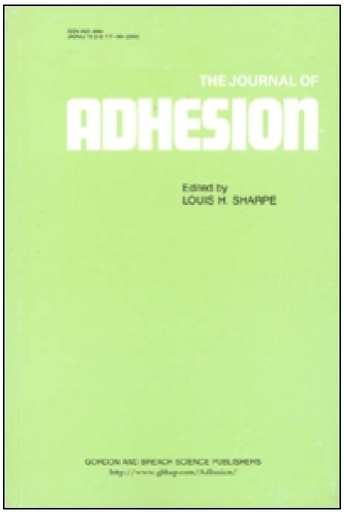

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Allen, K. W. and Shanahan, M. E. R.(1975) 'The Creep Behaviour of Structural Adhesive Joints-I', The Journal of Adhesion, 7: 3, 161 — 174
To link to this Article: DOI: 10.1080/00218467508075048
URL: http://dx.doi.org/10.1080/00218467508075048

J. Adhesion 1975, Vol. 7, pp. 161–174

Printed in Scotland

The Creep Behaviour of Structural Adhesive Joints—I

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(*Received February 21, 1975*)

The creep behaviour of two structural adhesives (a phenolic resin/polyvinyl formal composite and a modified epoxy novolac) has been studied in their glassy state when used to bond high tensile steel lap joints. Both characteristic delay times (periods after the application of load but before creep becomes discernible), and creep behaviour have been explained by zero order rate theory using an asymmetric potential energy barrier to account for endurance limits (loads below which creep does not occur). It has been shown that adherend separation should be associated with the maximum adhesive shear stresses found at the ends of the overlap.

INTRODUCTION

Structural adhesives have been in use in the aircraft industry for metal-to-metal bonding for over thirty years and a great deal of work has been done attempting to maximise bond strengths. However, most adhesives are polymeric and therefore viscoelastic so that simple static strengths alone may not give a satisfactory account of long term load bearing potential; and time dependent or creep data are necessary to complete the description.

Creep may be defined, at least for the purposes of this paper, as time dependent flow under constant load irrespective of whether any component is recoverable on removal of load. The present work was undertaken after it was realised that very little work on structural adhesive creep had been reported in the literature. Lap joints were chosen as the type of test piece so that results might be fairly representative of service conditions.

Hahn and Matting[1, 2, 3] have studied creep in lap joints, measuring deformation with a mirror-knife-edge device but most of their work was

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concerned with the effects of polymerisation occurring between joint construction and test. However, characteristic delay times (described later) were obtained with Redux 775. Delay times were also observed by Wake and Foulkes with this adhesive using a torsional shear test system.[4, 5, 6] More recently Eichhorn *et al.*[7] have studied creep and ageing in lap joints but mainly from the aspect of lifetime as a function of load. Other studies include that by Thomas on nitrile rubber-phenolic adhesives in lap joints[8] and the work of Shen and Rutherford on nylon-epoxide butt joints.[9]

The present work has studied the creep behaviour of single lap joints and how this varies with load and temperature, with a view to correlation with molecular mechanisms. Later work, to be reported elsewhere, investigated changes in creep behaviour with joint geometry thus enabling creep to be associated with the complex stress patterns found in loaded lap joints.

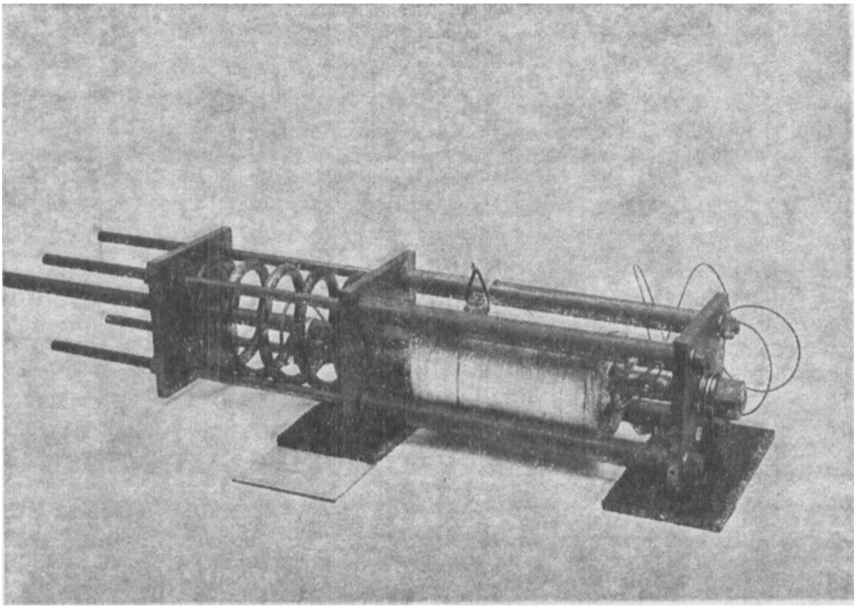

FIGURE 1 Creep Rig.

EXPERIMENTAL

Spring loaded test rigs were used to apply a load to lap joints. These rigs are a modification of a design originally used by Bonded Structures Ltd.[10] to investigate creep rupture and one is shown in Figure 1. A system of plates is used to apply a tensile load to a lap joint by means of load bars and selfaligning bearings. An essentially constant load is obtained from a medium sized car suspension spring under compression. The load applied is calculated from measurements of spring compression and a knowledge of the spring stiffness. Movement of the adherends is measured with an inductance transducer clamped to one adherend with its ferrite core attached to the second adherend, as shown in Figure 2. The electrical outputs from transducers on several rigs are fed into a scanner unit enabling simultaneous monitoring of up to four experiments on one chart recorder.

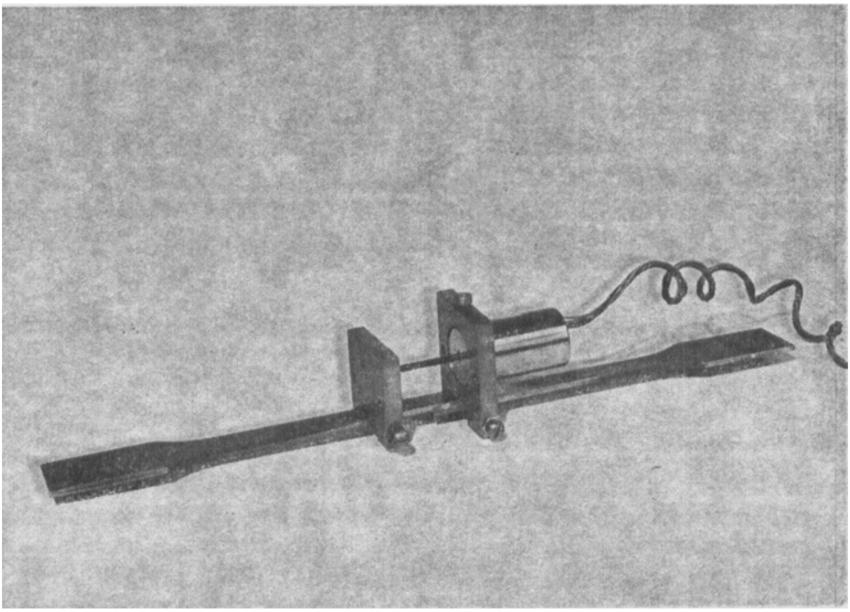

FIGURE 2 Lap joint and transducer assembly.

The joint and transducer are surrounded by a cylindrical, thermostatistically controlled oven shown in Figure 1. This enabled tests to be conducted at elevated temperatures, but the tolerance of the transducers imposed an upper limit of 75°C. A small d.c. motor with unbalanced load was clamped to one load bar of the rig to produce small amplitude vibrations in the system. This effectively overcomes any tendency for the core to stick within the barrel of the transducer as a result of the slight bending associated with the asymmetric loading of single lap joints.

Lap joints were constructed from high tensile steel (BSS 514) of 0.2 cm thickness and 1 cm width at the overlap area widening at the ends. Their length was sufficiently great for stress patterns introduced by the loading points to be negligible at the overlap. Surface treatment of bonding areas was simply wet polishing with 600 emery paper followed by distilled water and acetone rinses. For the work discussed here, overlap length was restricted to 1 cm and two types of adhesive were used—a phenolic resin/polyvinyl formal (Redux 775) and a modified epoxy novolac (Redux BSL 906) both manufactured by Ciba-Geigy (U.K.) Ltd. After initial trials, with Redux 775 in which problems of joint alignment, glueline thickness and the appearance of bubbles of by-product within the adhesive were solved,[11] standardised joints containing two wire glueline spacers parallel to the axis of load were adopted for all the work. Cure was carried out in a spring loaded jig at 150°C for 100 minutes total oven time for Redux 775 and at 120°C for 90 minutes for BSL 906. Average glueline thicknesses, measured by removing side fillets and using an optical micrometer, were 0.010 cm and 0.0087 cm respectively for Redux 775 and BSL 906. Badly aligned joints and those with a glueline thickness significantly different from the mean were rejected. Lap joints were left for at least 24 hours after cure before testing in order to allow equilibrium to be attained. Thermal equilibrium before a test was ensured by enclosing the lap joint assembly within the oven for between one and two hours before applying the load.

RESULTS AND ANALYSIS

Creep curves were obtained for Redux 775 joints at five temperatures: 30, 40.5, 50.5, 58.5 and 75°C and only the upper two for BSL 906. Typical results for each of the adhesives are shown in Figures 3 and 4, where percentage shear creep strain within the adhesive layer, γ, is plotted against the logarithm of time t. The initial elastic strain on application of load is not recorded. Numbers above each curve refer to applied load in kN. It can be seen that there is usually a characteristic delay time, t_d, after the application of load but before any creep strain is discernible. Once creep has been

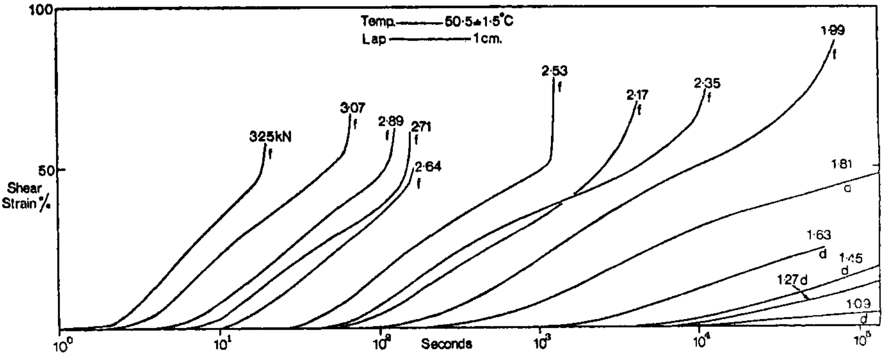

FIGURE 3 Creep: Redux 775 (50.5°C). f–failure d–discontinued

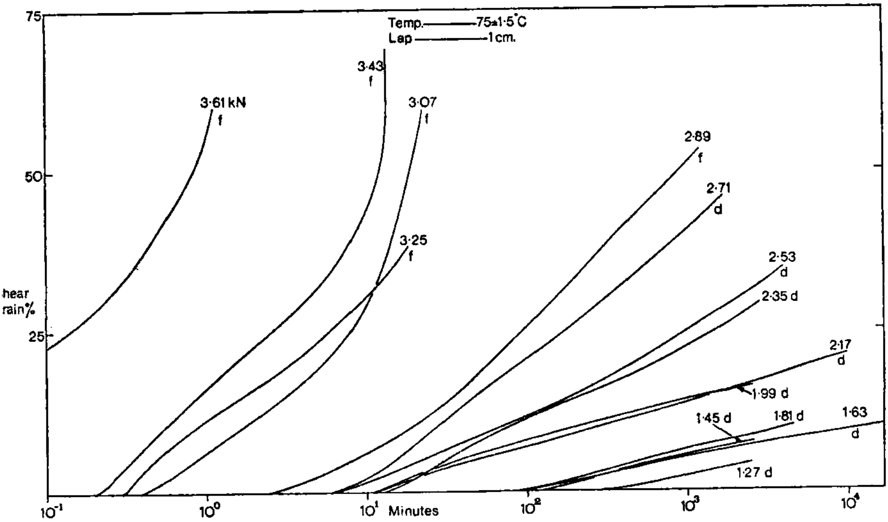

FIGURE 4 Creep: Redux BSL 906 (75°C). f–failure d–discontinued

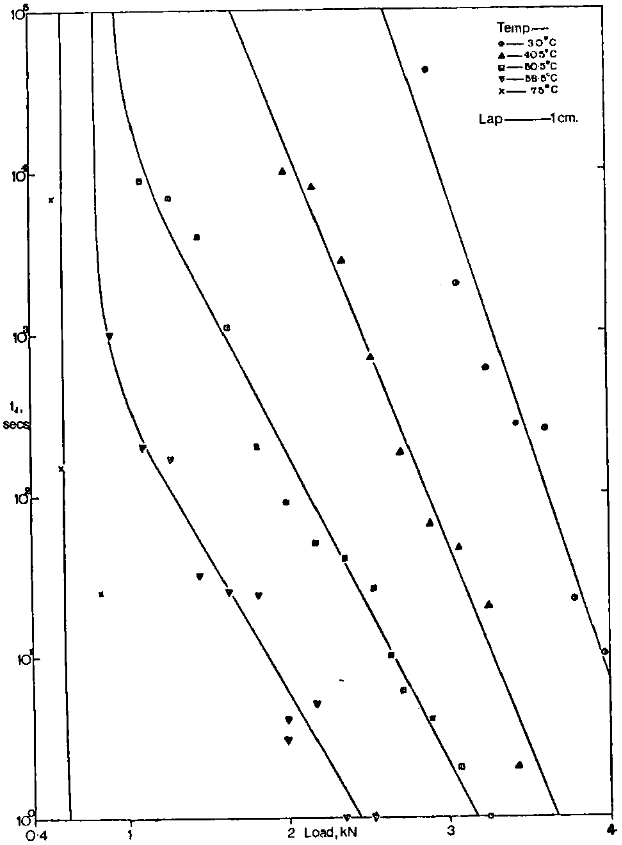

FIGURE 5 ln t_d vs. L: Redux 775.

established, it is essentially logarithmic and can be described by drawing the estimated best straight line through the creep section with an extrapolated intercept, t_0, at zero strain and gradient, k ($= \gamma/\ln(t/t_0)$). The two parameters t_d, and extrapolated creep rate at zero strain, $\dot{\gamma}(t_0)$ have been used here for analysis. It is readily shown that $\dot{\gamma}(t_0) = k/t_0$.

Figures 5 and 6 show ln t_d *vs.* applied load, L, for the two adhesives at the various test temperatures. Clearly the trend of this relationship was linear (except for Redux 775 at 75°C to be discussed later), and this suggested to us analogies with chemical reaction kinetics and led on to the use of chemical reaction rate theory. A modification of Eyring's theory, originally used to describe viscosity and plasticity,[12] has been developed but the phenomenon involved here is believed to be primary bond fracture. Also, in the case of Redux 775, there is apparently an endurance limit, i.e. an applied load below which creep does not occur (0.90 kN at 50.5°C and 0.80 kN at 58.5°C). This may be introduced into rate theory by assuming an asymmetric potential energy barrier as shown in Figure 7. The barrier represents that opposed to the fracture of some type of primary bond; the left hand side representing the bonded state and the right hand side the unbonded state. In the unstressed state, the barrier is biased against bond fracture by $2\alpha s_0$ where α is the

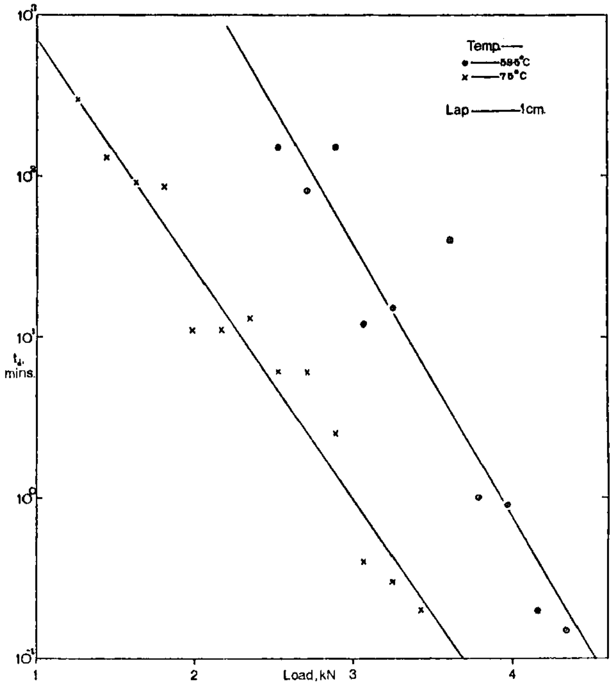

FIGURE 6 ln t_d *vs.* L: Redux BSL 906.

activation volume and s_0 is the stress corresponding to the endurance limit load. Application of stress, s, lowers the free energy of activation for bond fracture, $\Delta F^{\ddagger}$, by αs and it is assumed that the free energy of activation for bond formation is increased by the same amount. If the usual Maxwell

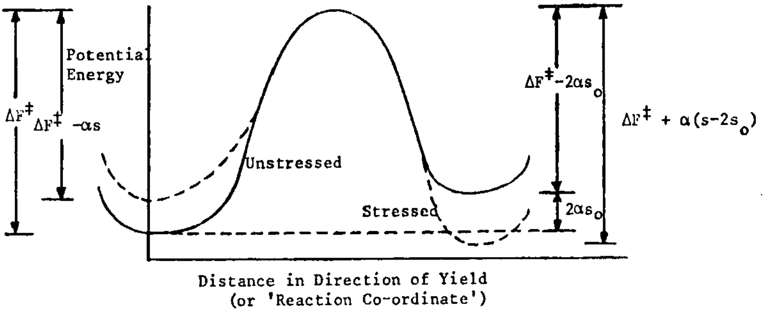

FIGURE 7 Asymmetric potential energy barrier assumed to describe delay time and creep behaviour

distribution of thermal energy is assumed and if zero order rate theory is applicable, then the rate of bond scission is given by

$$\left[\frac{dn}{dt}\right]_1 = AT \exp\left[\frac{-\Delta F^{\ddagger} + \alpha s}{RT}\right] \tag{1}$$

where n is the number of bonds at time t, A is a constant and R and T are respectively the universal gas constant and temperature (K). Similarly, the bond formation rate is given by:

$$-\left[\frac{dn}{dt}\right]_2 = -AT \exp\left[\frac{-\Delta F^{\ddagger} + \alpha(2s_0 - s)}{RT}\right] \tag{2}$$

The net bond scission rate is the addition of these two and after integration and rearrangement, it is readily shown that:

$$t_d = \frac{n_0}{AT} \exp\left[\frac{\Delta F^{\ddagger}}{RT}\right]\left\{\exp\left[\frac{\alpha s}{RT}\right] - \exp\left[\frac{\alpha(2s_0 - s)}{RT}\right]\right\}^{-1} \tag{3}$$

where t_d corresponds to the breakdown of n_0 bonds (either an entire population or a certain critical number). For large stresses Eq. (3) can be written:

$$t_d \simeq \frac{B}{T} \exp\left[\frac{\Delta F^{\ddagger} - \alpha s}{RT}\right] \tag{4}$$

where B is a constant, but at stresses approaching s_0, the second exponential term becomes important until at s_0, t_d becomes infinite.

Equation (4) represents a straight line on a logarithmic time scale and data in Figures 5 and 6 removed from endurance limits were therefore analysed by the method of least squares (regression of ln t_d on L). Endurance limits, where applicable, were determined from experiments not showing creep after more than 10^5 seconds. Although no endurance limits were obtained for BSL 906, it is believed that they would be found at lower loads at greater times. It has been assumed above that the stress, s, responsible for delay time behaviour is proportional to applied load L.

By extrapolation to t_d', the value of t_d given by Eq. (4) at zero stress, and using the thermodynamic relationship, $\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ represent respectively activation energy and entropy of activation, it is readily shown that:

$$\ln t_d' = \frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R} + ln\left[\frac{B}{T}\right] \tag{5}$$

Activation energies for the delay time process can thus be evaluated and are given in Table I with calculated standard errors. Results for Redux 775 at 75°C were not included for these calculations.

TABLE I

Calculated values of activation energies, $\Delta H^{\ddagger}$, for the delay time process and creep in Redux 775 and BSL 906

	Redux 775	Redux BSL 906
$\Delta H^{\ddagger}$ (delay time) (kJ mole^{-1})	588±22	318±117
$\Delta H^{\ddagger}$ (creep) (kJ mole^{-1})	612±27	529±124

Extrapolated creep at zero strain, $\dot{\gamma}(t_0)$ can be analysed in a similar manner. In Eqs. (1) and (2), $[dn/dt]$ is replaced by $\dot{\gamma}(t_0)$ and the overall creep rate is given by:

$$\dot{\gamma}(t_0) = AT\exp\left[-\frac{\Delta F^{\ddagger}}{RT}\right]\left\{\exp\left[\frac{\alpha s}{RT}\right] - \exp\left[\frac{\alpha(2s_0 - s)}{RT}\right]\right\} \tag{6}$$

and for stresses much greater than s_0:

$$\dot{\gamma}(t_0) \simeq AT\exp\left[-\frac{\Delta F^{\ddagger} + \alpha s}{RT}\right] \tag{7}$$

Figures 8 and 9 show values of $\dot{\gamma}(t_0)$ for the two adhesives with lines calculated for the regression of $\ln \dot{\gamma}(t_0)$ on L (ignoring points for Redux 775 for 0.54 kN at 75°C and 0.90 kN at 58.5°C since the approach of endurance limits is suggested). By analogy with Eq. (5), activation energies for creep may be calculated and are given in Table I. Results for 75°C with Redux 775 have been excluded since the trend of the behaviour is clearly different. Again it has been assumed above that the stress, s, causing creep behaviour is proportional to load, L. This is justified by the fact that creep strains are small or non-existent in the regions studied and behaviour is likely to be linear.

Stress distributions within these lap joints should be similar to those found under elastic conditions during the delay time (but not during creep) since no appreciable strain has been added to the initial elastic contribution. Since relatively rigid adherends have been used, Volkersen's analysis[13] of elastic strains (and stresses) within a lap joint should be reasonably accurate.

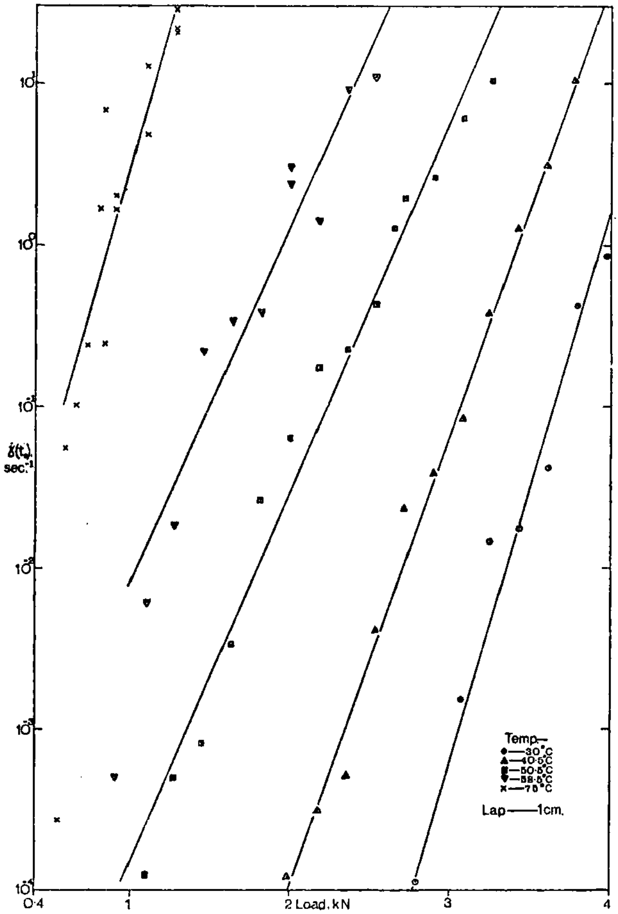

FIGURE 8 $\dot{\gamma}(t_0)$ *vs.* L: Redux 775.

It is readily shown from this theory that the total elongation of an adherend within the overlap is independent of the adhesive shear modulus, G, and is equal to Lc/Eh in the case of identical adherends where c is half the overlap length, E is the adherend Young's modulus and h is the adherend thickness (width being unity). It follows that overall adherend strain within the overlap remains constant during creep and consideration of Figure 2 shows that measured creep corresponds to displacement at the ends of the overlap.

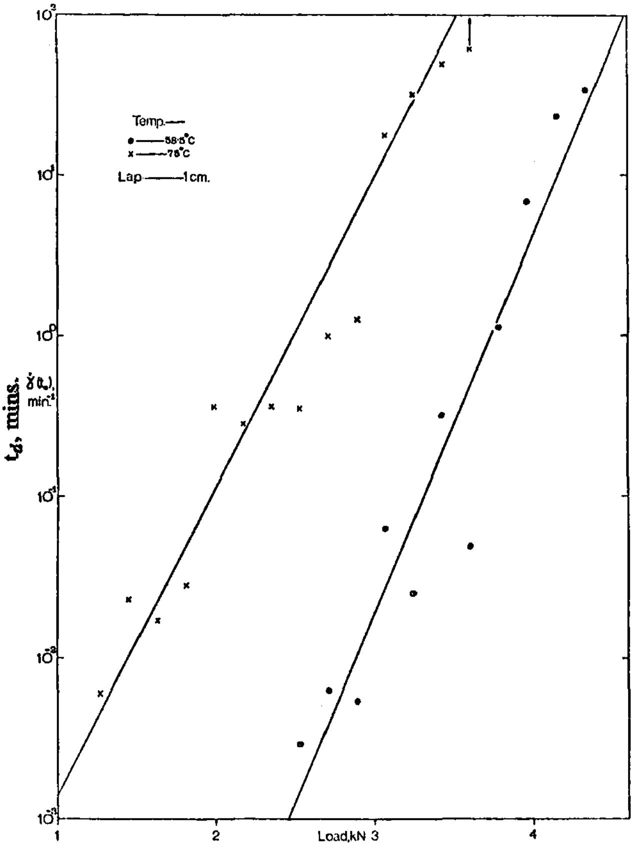

FIGURE 9 $\dot{\gamma}(t_0)$ *vs.* L: Redux BSL 906.

Delay time and creep behaviour should therefore be related to the maximum adhesive shear stresses at the ends of the overlap. Volkersen's analysis gives these maximum stresses, $\tau_{\max}$ (for identical adherends) as:

$$\tau_{\max} = \frac{L}{2}\left[\frac{2G}{Egh}\right]^{\frac{1}{2}} \coth\left[c\left(\frac{2G}{Egh}\right)^{\frac{1}{2}}\right] \tag{8}$$

where g is glueline thickness and other symbols have their previous meanings. Values of the adhesive shear moduli, G, at various temperatures were obtained from torsional pendulum experiments[14] and E was known to be 193 GN m^{-2} for the steel. From Eqs. (3), (4) and (8) and data from the best straight lines for ln t_d *vs.* L, values of the activation volume α were calculated. These are listed with relevant data including m ($= \tau_{\max}/L$), the stress factor, for both adhesives in Table II. It is not possible to estimate activation volumes for creep since Eq. (8) will no longer apply.

TABLE II

Activation volumes and related data for the delay time process in Redux 775 and BSL 906

	Temp (°C)	G (GN m^{-2})	Stress factor m ($= \tau_{max}/L$) $\times 10^{-4}$ (m^{-2})	Activation volume, α (m^3 mole^{-1})
Redux 775	30	1.31	1.51	1.16×10^{-3}
	40.5	1.28	1.50	1.01×10^{-3}
	50.5	1.18	1.47	8.11×10^{-4}
	58.5	1.17	1.46	7.50×10^{-4}
	75	1.01	1.40	—
BSL 906	58.5	1.05	1.47	7.34×10^{-4}
	75	0.69	1.32	7.24×10^{-4}

DISCUSSION

The proposed asymmetric potential energy barrier appears to explain both delay time and creep behaviour. At 75°C, tests using Redux 775 produced only 3 delay times from 14 experiments. Two alternative suggestions are advanced to explain this. If it is assumed that $\Delta H^{\neq}$ has the same value as that obtained from experiments at lower temperatures, then the extrapolated intercept (t_d) corresponds to about 0.35 seconds which is less than the minimum which the apparatus is capable of detecting. The entire part of the curve corresponding to Eq. (4) would then be inaccessible and the three observed values of t_d correspond presumably to an endurance limit region. Large amounts of scatter are inevitable since the predicted curve is virtually parallel to the ordinate. The solid line shown in Figure 5 corresponds to an estimated endurance limit of 0.60 kN.

Alternatively, it may be that 75°C is sufficiently near the glass transition region of Redux 775 to cause modification of behaviour. The glass transition temperature, T_g, was found to be about 80°C from torsional pendulum experiments.[14] It is known that the application of stress (or its associated strain) can lower T_g by increasing molecular segmental mobility.[15] Were this to occur with Redux 775, experiments at 75°C could be in the early stages of the rubbery state where behaviour might be expected to be unlike that in the glassy state. The first proposition is preferred however, since primary bonds are thought to cause delay times and their fracture would presumably not be affected by a glass transition.

Creep data at 75°C are however clearly unlike those at lower temperatures and it is considered that the second proposition above concerning the lowering of T_g is responsible in this case because creep will be affected by molecular segmental mobility. It is therefore believed that separate processes are responsible for delay time and creep processes. This is supported by the very different values of $\Delta H^{\ddagger}$ produced for BSL 906. The similarity in values for Redux 775 is thought to be coincidental. The large standard error for BSL 906 is attributable to the fact that experiments were conducted at only two temperatures. Since the degree of cross-linking and number of bonds per molecule concerned in creep phenomena are unknown, it is not possible to ascribe modes of behaviour to the dissociation of bonds of a given type. Delay time behaviour is however believed to be associated with primary bond fracture. The fact that strain does not apparently increase during the delay time is presumably due to lack of sensitivity in the measuring apparatus. Absolute displacements associated with shear strains in a glueline of only about 0.01 cm thickness are inevitably very small.

The significance of values of activation volume, α, is not understood and it appears that these decrease with increasing temperature. The order of magnitude obtained in the present work by indirect methods is however the same as that found by Ishai[11] by direct methods with an epoxy resin which is presumably a comparable cross-linking material. Present work gave values of about 10^{-3} m^3 mole^{-1} whereas Ishai obtained values of 2.5 and 2.3×10^{-3} m^3 mole^{-1} for delayed yielding in tension and compression respectively.

Matz *et al.*[17] suggested an asymmetric potential energy barrier to explain endurance limits found with various thermoplastics in which first order rate theory was applied, i.e. it was assumed that bond scission and formation processes were proportional to concentration. The present work assumes these to be independent of concentration. It is believed that although bond scission may well be proportional to concentration at a given stress, as the number of intact elements decreases, the stress level on a molecular scale will increase since the macroscopic stress remains constant. This will tend to counteract the otherwise decreasing scission rate. This would probably be equivalent to something between zero and first order theory, but the complication of the extra mathematics involved would not be justified by any improved representation. It is believed that zero order theory provides a reasonable and useful approximation to the true behaviour.

CONCLUSION

It has been found that zero order rate theory assuming an asymmetric potential energy barrier satisfactorily explains delay time and creep behaviour for two structural adhesives in the glassy state when used to bond lap joints. The existence of endurance limits is a consequence of the theory and although these were found experimentally only in a few cases, it is likely that they exist under all conditions applying to the adhesives when in their glassy state. Delay times are attributed to primary bond fracture and although insufficient evidence has been obtained to suggest mechanisms for creep, this may also be due to behaviour concerning primary bonds but of a different kind. The approach of the glass transition region changes creep behaviour; and above T_g it is probable that behaviour will be more akin to rubber viscoelasticity. From theoretical considerations (and work to be published elsewhere) it has been shown that the separation of adherends due to adhesive shear creep should be associated with the maximum adhesive shear stresses found at the ends of the overlap.

Acknowledgements

The authors wish to thank Professor W. C. Wake of The City University for all his help and encouragement.

The work has been carried out with the support of Procurement Executive, Ministry of Defence.

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Nomenclature

γ	percentage shear creep strain
k	gradient of logarithmic creep curve
t	time
t_0	intercept of creep curve with time axis
$\dot{\gamma}$	creep rate
$\Delta F^{\ddagger}$	free energy of activation
$\Delta H^{\ddagger}$	activation energy
$\Delta S^{\ddagger}$	activation entropy
R	universal gas constant
T	absolute temperature
n, n_0	number of bonds
s	stress
α	activation volume
L	load
t_d	delay time
s_0	endurance limit
t_d'	extrapolated delay time at zero stress
A, B	constants
$\tau_{\max}$	maximum adhesive shear stress
G	adhesive shear modulus
E	adherend Young's modulus
g	glueline thickness
h	adherend thickness
$2c$	overlap length
T_g	glass transition temperature