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Activation theory for creep of matrix resin and carbon fibre-reinforced polymer composite

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Activation theory used in metals and polymers has been used to model creep of unidirectional composite and resin matrix, using the concept of internal stress. The model fits the experimental creep curves very well for a range of materials. The results obtained for a brittle epoxy and its carbon fibre-reinforced composite with two fibre orientations are reported. The model parameters, such as internal stress, activation volume and activation energy, have been measured experimentally and compared with model-fit values, and their influence on creep is discussed. Finally, an approach to predict the creep rupture of unidirectional composites using internal stress is presented.

1. Introduction

The models available in the literature to simulate the visco-elastic behaviour of polymers are broadly based on mechanical analogs, integral equations and power laws [1]. All of them are empirical methods yielding little information on the creep process and have been used with different degrees of success in various materials. Another model which has been extensively used in metals in understanding the plastic deformation mechanisms is based on an activation theory approach. The strain rate as per this theory [2, 3] is given by

$$\dot{\varepsilon}[\sigma^*, \varepsilon(c)] = \dot{\varepsilon}_0 \exp(-H_0/kT) \times \sinh(V\{\sigma_a - \sigma_i[\varepsilon(c)]\}/kT) \qquad (1)$$

where $\dot{\varepsilon} = A\exp(S/k)$ is the pre-exponential term, H_0 is the activation energy in the absence of stress, S is the entropy of activation. V is the activation volume. σ^* is the effective stress given by

$$\sigma^* = \sigma_a - \sigma_i$$

where σ_a is the applied stress, and σ_i is the internal stress which can be a combination of residual and deformation-induced stresses. For analysis in this paper, residual stresses are considered to be small. So the internal stress is shown as a function of creep strain in Equation 1.

Earlier applications of the activation theory to polymers were used in conjunction with mechanical analogues in order to model the yield and subsequent plastic behaviour during a constant-rate tensile test [4]. Later, activation theory was used by Wilding and Ward [5–7] again in conjunction with mechanical analogues, to model the creep and relaxation of polymers but without considering the influence of internal stress. Wilding and Ward [8] used a high activation volume/high energy Eyring dash pot for low stresses, and a low activation volume/low energy dash pot for high stresses, in order to fit the creep curves. But the models (i.e. the combination of dash pots and springs) have to be frequently changed to suit different materials and different stress regimes, making this approach undesirable. Mindel and Brown [9] derived an equation similar to activation theory starting with a Sherby–Dorn type equation and suggested that internal stress could be related to recoverable strain and could be the reason for decreasing creep rate in primary creep region. But they never measured internal stress to examine such a concept. Bauwens-Crowet and Bauwens [10] used the three-element model and concept of internal stress to model the creep of polycarbonate, but again the internal stress was not measured.

Internal stress in polymers had been measured before by various techniques [11], such as stress dip test, strain dip test and stress relaxation test. Fotheringham and Cherry [12] measured internal stress in linear polyethylene, by the stress dip test, to study the deformation kinetics during constant-rate tensile tests. Kubat *et al.* [13] measured internal stress and activation volume from stress-relaxation experiments to model the relaxation behaviour of polyethylene, and more recently [14], they have predicted creep reasonably well from relaxation data. But they had to use a power law and activation theory separately in different regimes to model the entire creep and relaxation data. In previous studies using the activation theory to model the creep of polymers, the activation parameters were varied arbitrarily to obtain the best fit. In a few studies, where some of these parameters were measured and used in the simulation, a concrete definition of these parameters and their relation to microscopic/molecular mechanisms is lacking. In addition, there are very few references in the literature relating to the modelling of creep in continuous fibre-reinforced polymer composites using an activation theory approach, with the exception of the work by Pink and Campell [15, 16]. They have used the activation theory approach to study the deformation mechanisms in a glass-reinforced epoxide by constant-rate tests. However, a rigorous analysis of the parameters and the influence of fibre volume fraction and orientations on the activation parameters and their correlation to matrix properties, is lacking.

In view of the lack of a comprehensive model to fit and elucidate the creep behaviour of polymers and composites as reviewed above, it is shown in this paper that the activation theory can be exclusively used to model the creep behaviour of carbon fibre-reinforced polymer composites and the respective matrix resins. Internal stress, activation volume and activation energy measured experimentally are compared with the values obtained by fitting the experimental creep curves to the activation theory. Their significance in understanding the visco-elastic deformation of polymers and composites is discussed.

The internal stress measured experimentally can be used to predict creep rupture of unidirectional composites, which is the ultimate goal of this project. The present authors view creep rupture to be an extension of visco-elastic deformation. So an accurate model to predict visco-elastic deformation is a priori to predict creep rupture and this paper is the first step towards achieving this goal. In Section 5.3, an approach based on internal stress has been presented to predict creep rupture of unidirectional composites.

2. Experimental procedure

The epoxy resin and AS4/3501-6 prepregs were supplied by Hercules Corporation. Laminates were made in-house in an autoclave. Tensile coupons as per ASTM D638 were used for the resin and substandard specimens of size 165 mm x 12.7 mm with 38.1 mm tab were used in case of composites. The tab used was glass epoxy and structural adhesive AF-191 supplied by the 3M company was used to bond them to the test coupons. The coupons of epoxy and composite were cut from plates using a diamond saw and finally polished with 1 μm diamond paste. For successful prediction of creep behaviour of any composite laminate, whether unidirectional or cross-ply, the creep compliance data of the composite parallel to the fibre, S_{11}, perpendicular to the fibre, S_{22}, and in shear, S_{66}, are needed. S_{11} was found to be time-independent. S_{66} was measured using $[10]_8$ off-axis samples with fibres oriented at 10° to the loading axis. Samples with fibres oriented perpendicular to the loading axis (90°) were used for measuring S_{22}. The cross-linked brittle epoxy (3501-6) was chosen to study the effect of reinforcement (carbon fibres) on the creep behaviour of neat resin.

Resistance strain gauges were used for measuring strain in epoxy and composite. The data were logged using a data acquisition system built into a 386 SX computer. The internal stress measurements and differential strain rate testing were conducted in an MTS 808 with 458.2 microconsole. The creep test was conducted using ATS 2320 creep tester.

The constant-load creep tests were repeated at different stress levels at room temperature. A single specimen was used for measurement of internal stress at a creep stress level. At several stages of creep, the unloading was done in steps to determine the internal stress as shown in Fig. 1a. The unloading rate used was two orders of magnitude greater than the loading rate ($10^{-4}\,s^{-1}$). Depending on whether the new stress level is greater or smaller than the internal stress level, the observed creep rate will be positive or negative, as shown schematically in Fig. 1b. If the stress level is equal to the internal stress, the observed creep rate will be zero. Unloading steps were chosen such that creep rate could be measured as rapidly as possible. Then the internal stress was determined by finding the stress at which the creep rate became zero on the creep rate–stress plot as shown in Fig. 1c.

Activation volume was determined from a set of stress–strain curves obtained using different strain rates. The difference in stress between two curves at two different strain rates was used to calculate the activation volume according to Equation 2

$$V = [\mathrm{d}H/\mathrm{d}\sigma^*]_{T,\mathrm{structure}} = kT\left(\frac{\partial \ln\dot{\varepsilon}}{\partial\sigma^*}\right)_T \tag{2}$$

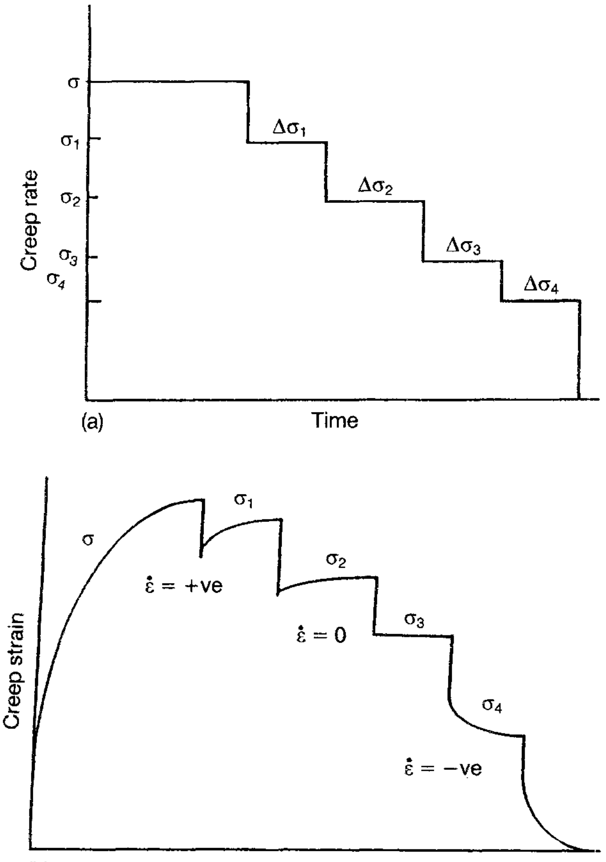

Figure 1 (a–c) Schematic illustrations of the step unloading method to measure internal stress. (d) Schematic illustration of the differential strain-rate testing for activation volume measurement.

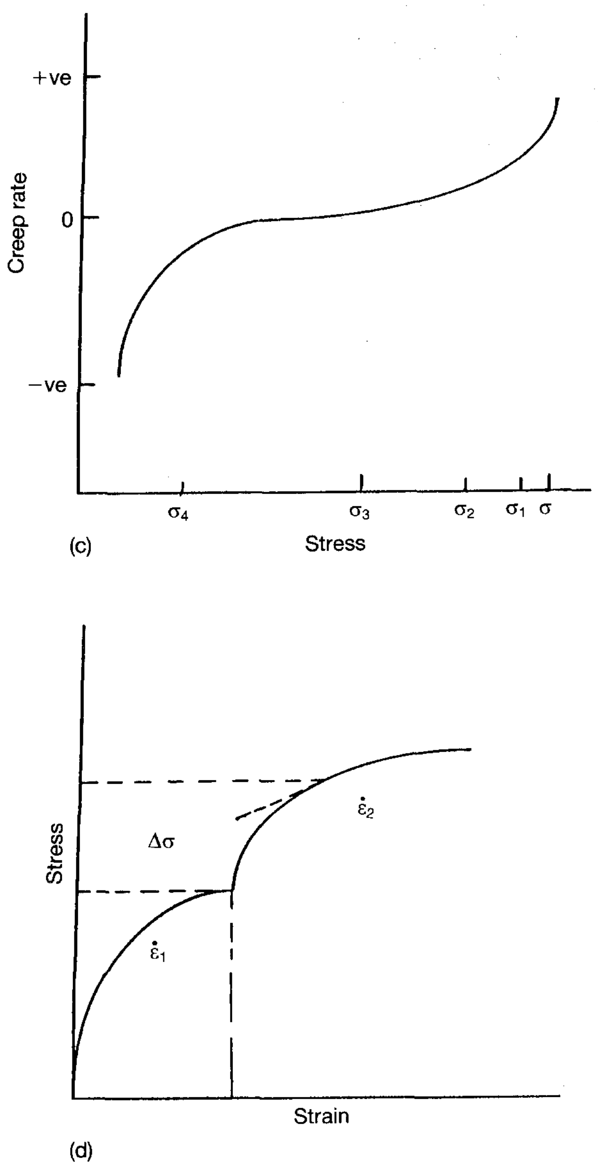

Figure 1 (continued).

The activation volume was also determined from a single specimen. A specimen was loaded at constant strain rate to a strain level. Then suddenly the strain rate was increased and the resulting change in the stress level was measured, as shown in Fig. 1d. This was repeated for different strain levels. The activation volumes measured by both methods were in good agreement. The measurement was done in the strain-rate range of 10^{-4}–$10^{-2}\,\mathrm{s}^{-1}$ with 1 to 2 orders of increase. The tests were repeated at higher temperatures in the range 295–373 K.

The activation enthalpy was determined using the following equation [2]

$$H(\sigma^*, T) = -kT^2\left(\frac{\partial \ln \dot{\varepsilon}}{\partial \sigma}\right)\left[\left(\frac{\partial \sigma}{\partial T}\right)_{\dot{\varepsilon}} - \left(\frac{\sigma_i}{E}\right)\left(\frac{\mathrm{d}E}{\mathrm{d}T}\right)\right] \tag{3}$$

The partials in the above equation were determined from constant strain-rate tests described above. By extrapolating the enthalpy curve to zero stress, activation energy was determined.

3. Numerical modelling

The experimental internal stress values were fit to a power-law function of creep strain as shown below in the present study

$$\sigma_i = \sigma_i^0 + A\varepsilon(c)^n \tag{4}$$

where σ_i^0 is the internal stress measured immediately upon loading (this is further discussed in Section 5.1) and A and n are empirical constants obtained by best fit. Here it should be borne in mind that the power law is a good approximation only in the experimental strain window, because the internal stress should not exceed the applied stress. The internal stress should either level off to a constant value [13] leading to steady state creep or can approach the level of applied stress [14] leading to zero creep rate. Experimental results indicate that activation volume is a function of effective stress and its functional form is found to be

$$V = C\exp(-B\sigma^*) \tag{5}$$

Using Equations 1, 4 (the best-fit power-law equation for experimentally measured internal stress) and 5, the experimental creep curves at various loads were fit by the least square method. With the constants C and B thus obtained, the activation volume was defined at various effective stresses. These values were compared with the experimentally measured values to examine consistency of the activation theory to model the creep of a composite and a resin.

4. Results

4.1. AS4/3501-6 $[10]_8$ composite

Because specimens with the fibre oriented at 10° to the loading axis were used for measuring the shear modulus, the plots of data for this composite are in terms of shear stress and strain. The internal stress and creep curves at different stress levels up to 72% UTS (presented here as plots of creep rate versus creep strain) are given in Figs 2 and 3, respectively, for

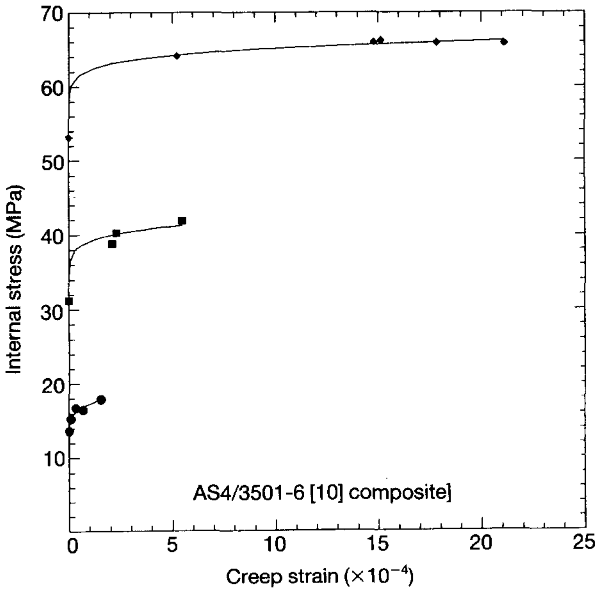

Figure 2 Internal stress as a function of creep strain at 295 K: (●) 18.55 MPa, (■) 41.96 MPa, (◆) 66.26 MPa, (——) best fit.

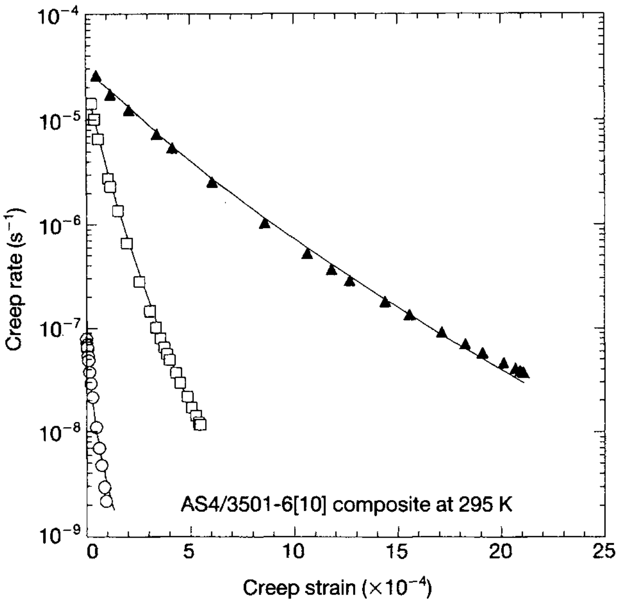

Figure 3 Comparison of (——) simulated and experimental creep curves at 295 K: (▲) 66.26 MPa, (□) 41.96 MPa, (○) 18.8 MPa.

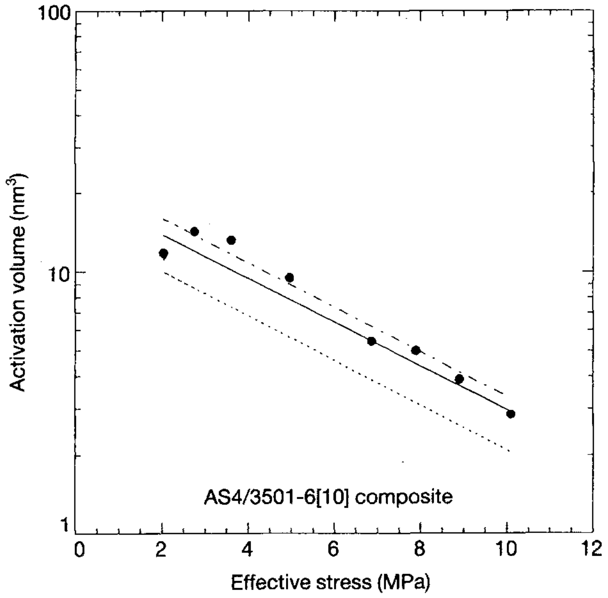

Figure 4 Comparison of (●) experimental and model-fit activation volume values at 295 K: (——) 18.8 MPa, (– – –) 42 MPa, (···) 66 MPa.

AS4/3501-6 $[10]_8$ composite. In Fig. 2 the solid line indicates the best-fit power law, at respective creep stresses. In Fig. 3 the theoretical creep curves as predicted by activation theory are plotted with experimental results. The model simulates the experimental creep curves very well.

The applicability of activation theory is again verified by the same magnitude of calculated and experimental activation volume values plotted in Fig. 4. Here the lines correspond to calculated values by numerical fitting of creep curves at different creep stresses and the legend represents experimental values measured by the method explained in the previous section. Constant strain-rate tests at temperatures 295 and 373 K were conducted to determine the activation energy. The activation volume as shown in Fig. 5, is dependent more on effective stress than temperature. The activation enthalpy calculated from these values is plotted in Fig. 6 as a non-linear function of effective stress.

4.2. AS4/3501-6 $[90]_{16}$ composite and 3501-6 epoxy

The internal stress, creep curve and activation volume plots for $[90]_{16}$ and 3501-6 composite are given in Figs 7–12, respectively. Solid lines in Figs 7 and 10 represent the best-fit power laws for internal stress, whereas in Figs 8, 9, 11 and 12 they represent theoretical values for creep rates and activation volume determined by the model. In all the figures the legends correspond to experimental values. From Figs 8 and

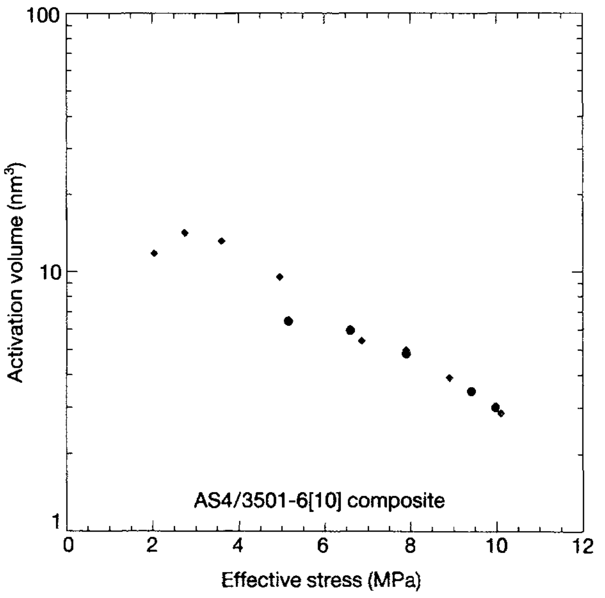

Figure 5 Activation volume as a function of effective stress at (◆) 295 K, and (●) 373 K.

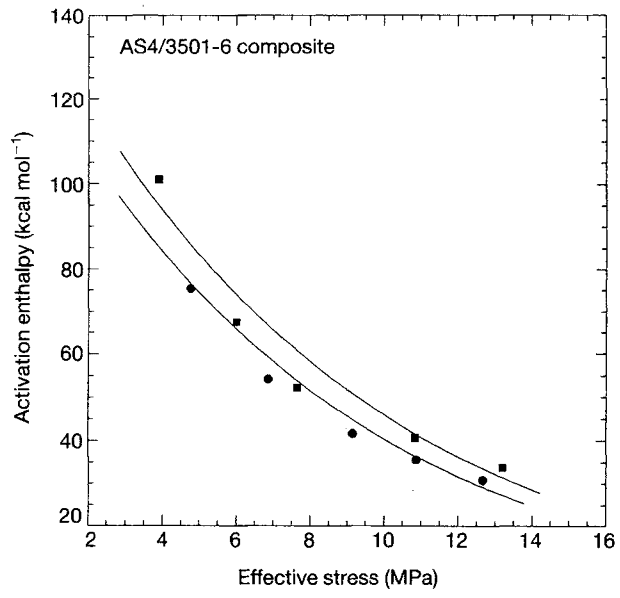

Figure 6 Activation enthalpy as a function of effective stress for AS4/3501-6 composite with two fibre orientations: (●) 90°, (■) 10°.

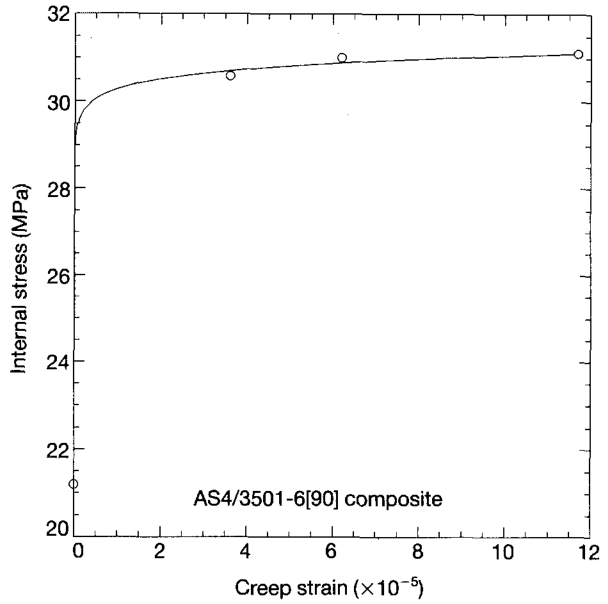

Figure 7 Internal stress as a function of creep strain at 295 K: (○) 31.02 MPa, (——) best fit.

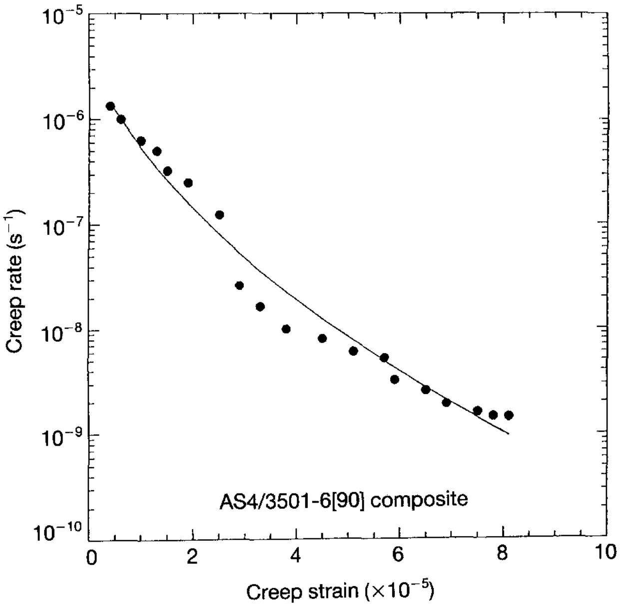

Figure 8 Comparison of (——) simulated and experimental creep curves at 295 K: (●) 31.02 MPa.

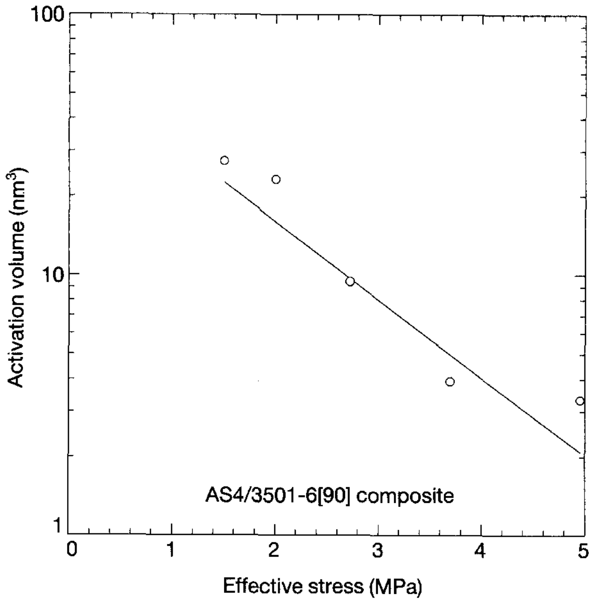

Figure 9 Comparison of (○) experimental and (——) model-fit activation volume values at 295 K, for 31.02 MPa.

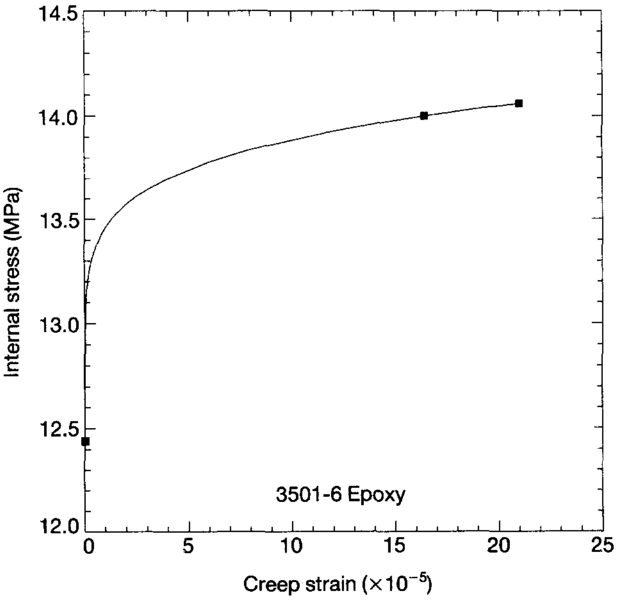

Figure 10 Internal stress as a function of creep strain at 295 K for epoxy [3501-6]: (■) 14.13 MPa, (——) best fit.

11, it can be inferred that the model prediction and experimental creep rate values are in good agreement. The observed deviation in the strain rate is thought to be due to temperature excursion. A deviation in temperature by < 1°C can account for the increase and decrease in strain rate of the observed magnitude.

The activation volume values for both $[90]_{16}$ composite and resin are of the same order (2–20 nm^3). This is to be expected because the matrix dominates the behaviour of the $[90]_{16}$ composite specimen. The calculated activation volume agrees well with the experimental values in $[90]_{16}$ composite and resin.

5. Discussion

The preceding section clearly demonstrates that the activation theory model based on Equation 1 simulates the experimental creep curves very well at different stress levels for brittle epoxy and composite laminate with different fibre orientations.

5.1. Internal stress

Because the internal stress is defined to be due to elastic strain, a finite internal stress value will be measured immediately after loading as seen in Figs 2, 7 and 10. This is the reason for adopting a power law with a constant as in Equation 5 which is consistent with the present experimental results. The internal stress value at the start of creep depends on the rate of loading to a creep stress. The internal stress decreased with increasing loading rate [13, 14]. The internal stress was 70%–80% of applied stress immediately

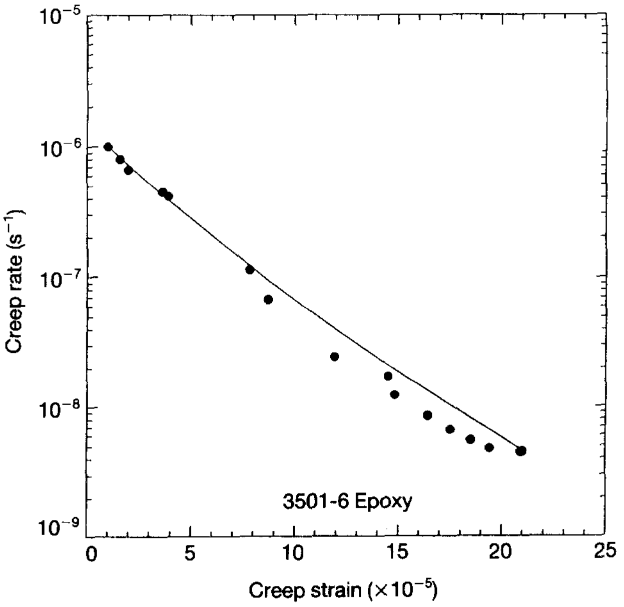

Figure 11 Comparison of (——) simulated (14.13 MPa) and (●) experimental creep curves at 295 K for epoxy [3501-6].

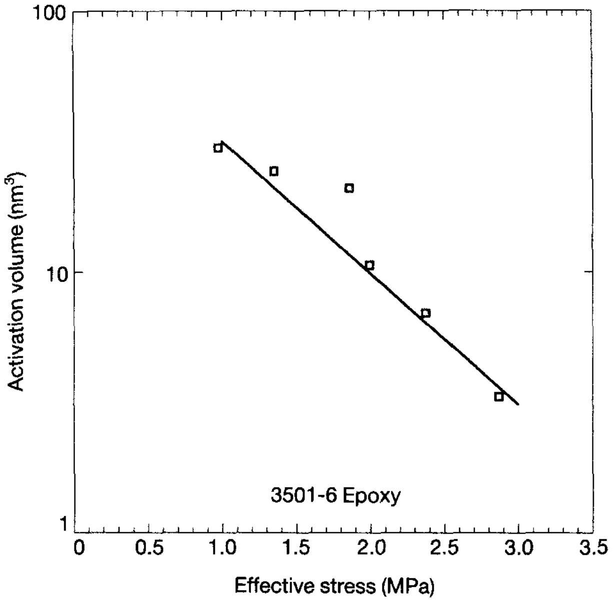

Figure 12 Comparison of (□) experimental and (——) model-fit activation volume values (14.13 MPa) at 295 K for epoxy [3501-6].

after applying the load (at a strain rate of 10^{-4} s^{-1}). The rate of increase was high in the beginning but decreased with creep strain and time, as illustrated in Figs 7 and 10.

The internal stress value for $[90]_{16}$ composite is approximately 89% of the applied stress, whereas it is 74% for neat resin. Because activation volume is of the same order of magnitude for both materials at a given effective stress, it is interpreted that the effect of reinforcing fibres is to increase the internal stress of the material. Their effect on creep of resin is indirect by altering the effective stress in the resin matrix.

In other methods such as mechanical analogues, a master curve at a reference temperature has to be formed from creep curves at different temperatures. This is often accomplished by horizontal shifting (along the time axis) of the creep curve (in the case of linear creep) and vertical shifting (along the strain axis) in the case of non-linear creep. Using this activation theory, with a knowledge of internal stress values (i.e. effective stress) at different temperatures, prediction of creep curves at another temperature is possible without resorting to vertical and horizontal shifting.

5.2. Activation volume and activation enthalpy

The relation of activation volume with effective stress is shown in Figs 5, 9 and 12. They show clearly that activation volume decreases with increasing effective stress. Earlier studies [12, 17] have examined the rate effect in polymers assuming constant activation volume. However, an exponential dependence on effective stress was observed in this study, for the entire creep strain range studied in both composite and matrix resin. Kubat and Rigdahl [18] also found an inverse linear relationship between effective stress and activation volume by analysing published results for various materials. However, they divided the relaxation curves into two regions, namely exponential and power-law regions, and attributed linear relationship with different proportionality constants.

The continuous variation of activation volume with effective stress indicates that the activation enthalpy is a non-linear function of effective stress, as shown in Fig. 6. It has been demonstrated in this paper that with such a non-linear functional formulation, a single theory can be used to model the entire creep curve.

Kubat and Rigdhal [18] have proposed that

$$V\sigma^* = \alpha kT$$

which gives a direct dependence for activation volume on temperature. But the results, as shown in Fig. 7, indicate otherwise. In the temperature range (295–373 K) studied, the activation volume is dependent more on the effective stress. This highlights the importance of effective stress rather than applied stress while interpreting the creep of composites. The activation volume data reported in this paper are of the same order of magnitude as reported in the literature for different polymers [4]. The activation enthalpy varied non-linearly with effective stress. The effect of the latter seems to be higher than the influence of temperature *per se*. The activation energy for $[90]_{16}$ composite is approximately 137 kcal mol^{-1} and for $[10]_8$ composite is approximately 151 kcal mol^{-1}. The high activation energy value suggests that the creep of this composite is due to a high-temperature process, such as the α relaxation process. For 3501-6 resin, the α relaxation process is around 239 °C and the β relaxation process is around − 65 °C. Hence, creep of this composite is believed to be due to the α relaxation process. More about this, as well as a detailed interpretation of internal stress and the influence of reinforcing fibres on the activation parameters of the pure resin, will be discussed in our next paper.

As demonstrated above, the present model predicts experimental creep curves very well. The parameters used in the model to predict creep curves, such as internal stress, activation volume and activation energy were determined directly from separate experiments. Although the experimental validity of the model was examined exclusively in epoxy and its composites of different fibre orientations in the present manuscript, the model appears to apply equally well to nylon (J2, manufactured by E.I. Du Pont de Nemours & Co., Inc.) and its composites. These results will be reported in the near future.

5.3. Creep rupture

From the above creep model, the functional relation of internal stress and creep rate with creep strain/time is known. This information can be used to predict creep rupture using an energy criterion. According to this, rupture will occur when the stored deformational energy reaches a critical value as represented by

$$1 = W_c/[W_0 + W_S] \qquad (6)$$

where W_c is the critical energy for fracture, W_0 is the elastic energy stored in the material instantaneously upon loading, and W_S is the energy stored with time due to the time-dependent deformation. This can be written in terms of internal stress and creep rate as

$$W_S = \int_0^t \sigma_i \dot{\varepsilon}_c \mathrm{d}t \qquad (7)$$

Given W_C and σ_{failure} (which is the applied stress), time to failure can be calculated [19].

6. Conclusions

In contrast to the previous efforts, activation theory was exclusively used to model the visco-elastic behaviour of unidirectional composite laminates by measuring the internal stress during creep in composites and polymers. The model based on activation theory represents very well the experimental creep curves of unidirectional laminate with different fibre orientation as well as the matrix resin. The internal stress increased with creep strain, thus causing a decrease in effective stress and creep rate. The activation volume decreased with effective stress and was approximated with an exponential function. Any creep curve can be closely simulated by a single activation model using the above functional approximations for internal stress and activation volume. It is interpreted that the effect of reinforcing fibres is to increase the internal stress in the resin thus influencing the creep of resin matrix indirectly by altering the effective stress. From the functional form of internal stress and creep rate, stored deformational energy in the material can be determined and this can be used in predicting creep rupture.

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