The torsional creep of carbon fibre reinforced epoxide resins

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The torsional creep of composite specimens containing 60% by volume of unidirectional HT–S carbon fibre, and of unreinforced epoxide resin has been studied. Measurements were made at temperatures of 25, 50, 75 and 90° C, in two environments — air and water. Torsional preloads of up to 40% of the ultimate torsional strength were applied. All the specimens showed primary and secondary creep behaviour during the 170 h test period, and a few resin ones tertiary creep. The effects, on the secondary creep rate, of varying the proportion of hardener in the matrix and the cure schedule were marked. The lowest creep rate for a given set of test conditions was obtained when the stoichiometric amount of hardener was used and the maximum cure given. Using specimens of this optimum type, more detailed studies of creep were performed. In all cases the activation energy for secondary creep lies between 5 and 6.3 kcal $(\text{g mol})^{-1}$ indicating that the same basic mechanism occurs in each instance. The shear stress, τ, was found to be proportional to the logarithm of the secondary creep rate.

1. Introduction

To design a fibre composite structure which will sustain a constant load over a long period of time, possibly at temperatures of 100° C or more and in a hostile environment, requires in addition to a knowledge of the usual thermo-mechanical properties, information on fatigue and creep behaviour.

In this paper we examine some aspects of the creep of unidirectional carbon fibre reinforced epoxide resin composites and pure epoxide resin specimens exposed to air or water at temperatures between ambient and 90° C. Solid specimens were stressed in torsion at preloads of up to 40% of the ultimate torsional strength of the material for a period of 170 h. This mode of stressing was chosen because the stress field, though not constant over a cross-section of the specimen, is one principally involving shear stress and thus the response will be governed largely by the properties of the matrix and interface; in addition relatively large shear strains are produced for low preloads thus making strain recording simpler. When the shear strain is large, tensile stresses are produced

because of the displacement of material around the periphery of the specimen. However, calculations for carbon fibre composites indicate that for the present situation these stresses are negligible. It has been suggested that the varying stress field could lead to simultaneous primary, secondary and tertiary creep. Thin-walled tubular specimens would minimize this effect but were precluded because of cost. It appears however, that to observe a constant, secondary creep rate for any length of time implies that secondary creep must be occurring throughout the specimen, irrespective of the shear stress distribution. Inaccuracies will only occur where the slope of the creep curve changes indicating a transition from primary to secondary or secondary to tertiary creep. Since the majority of the observations here involved the secondary regime specimen geometry did not pose a problem. Apart from the generation of creep data, part of the programme was concerned with a study of the influence of the amount of hardener, and the cure schedule, on creep performance.

2. Previous work

Much of the previous work on the creep of composite materials has been concerned with the performance of systems composed of metal wires in a metal matrix, where both phases may deform plastically. Work on epoxide or polyester resin systems reinforced with fibres such as carbon, boron or glass, which are elastic to failure, has usually involved longitudinal tensile or flexural creep measurements on crossply or unidirectional materials. Holmes and Wright [1] working with HT–S carbon fibre epoxide laminates, stressed in tension at 121° C, noted very little creep even at preloads approaching 90% of the ultimate strength. Dobson [2] in a more detailed investigation of flexural and tensile creep at preloads of up to 10% of the ultimate strength, and at temperatures of 40 and 80° C, noted that for all specimens except those made from HM fibres which had had no surface treatment, creep strain saturated with time. He suggested that the initial non-recoverable creep was due to the removal of fibre kinks, while the continuous strain observed with HM fibre composites was due to poor bonding allowing the resin matrix to flow around the fibres. Further studies on carbon fibre epoxide resin laminates and unidirectional specimens have been made by Soliman [3], at 71° C and preloads of up to 95% of the ultimate strength. He observed all three stages of creep (primary, secondary and tertiary) and noted that irrecoverable deformation occurred. Koeneman and Kicher [4] worked at 22° C stressing in tension, and also studied the behaviour of the unreinforced epoxide resin. Sturgeon [5] stressed carbon composites in tension at ambient temperature and 80° C, at preloads of 40% and 80% of the mean ultimate strength, for periods of up to 1000 h. He found that while the actual creep strain was very small it continued to increase throughout. Greenwood [6] used composites made from HM–S carbon fibre and an epoxide resin stressed in four-point bending at temperatures of 180 and 200° C, at a preload of 67% of ultimate. He noted that creep occurred and that failure started under the influence of compressive stresses in the vicinity of the loading anvils.

Vaughn *et al.* [7] used HM–S carbon fibres in a polyimide matrix and worked with flexural stressing at preloads of 50% and 75% of ultimate, at temperatures of 285 and 316° C. They noted all three stages of creep and commented that for the same load and time flexural stressing produced much more creep strain than tensile loading.

Recently Chwirut [8] has studied the tensile creep of boron fibre epoxide resin laminates in some detail. Preloads of up to 90% of the ultimate strength were used, measurements were made at 24 and 149° C and stressing was for a maximum of 100 h. He found that significant creep occurred in all cases.

3. Theory

Many empirical equations have been proposed to link creep properties with time, stress and temperature; see Gittus [9] for instance. Eyring [10] tried to account for the effects of applied shear stress and temperature on creep as follows. He considered creep to be due to the transition of a particle over an energy barrier and assumed that the applied shear stress aided the process by supplying energy mechanically. Assuming that the model can be extended to an activated volume of material and that the activation energy is independent of temperature, Dushman *et al.* [11], and Ishai [12], showed that the shear flow rate $\dot{\alpha}$, was given by

$$\dot{\alpha} = \text{constant } (kT/h) \exp\left(-Q/kT\right) \sinh\left(\frac{\tau V_0}{2kT}\right)$$

$$(1)$$

where k is Boltzmann's constant, h is Planck's constant, T the absolute temperature, Q the activation energy, τ the mean shear stress, and V_0 the activated volume.

If $\tau V_0 \gg 2kT$ the sinh term can be replaced by an exponential giving

$$\dot{\gamma} = \text{constant } (kT/h) \exp\left(-Q/kT\right) \exp\left(\frac{\tau V_0}{2kT}\right)$$

$$(2)$$

where the shear flow rate has been replaced by the secondary creep rate $\dot{\gamma}$. Therefore at constant temperature

$$\tau = \text{constant} + 2kT/V_0 \ln \dot{\gamma} \qquad (3)$$

An alternative, simpler, relationship between the secondary creep rate, activation energy, and temperature is

$$\dot{\gamma} = \text{constant} \exp\left(-Q/kT\right) \qquad (4)$$

4. Materials and specimen preparation

Unidirectional specimens 6.35 mm × 6.35 mm × 150 mm containing 60% by volume of HT–S

carbon fibre were prepared by a wet lay-up technique using a liquid bisphenol A type epoxide resin (Ciba Geigy MY 750) cured with the stoichiometric amount (80 p.p.h.*) of methyl nadic anhydride hardener and 2 p.p.h. of benzyl dimethyl amine accelerator. Other specimens were made with 70 p.p.h. and 90 p.p.h. of hardener respectively. The matrix in the former will not be fully cross-linked, while in the latter it will contain excess unreacted hardener and so be more susceptible to chemical reaction with, for instance, water. Similar series of specimens of unreinforced epoxide resin were also manufactured.

Cure, because of its influence on cross-linking, is very important in determining long term composite properties, and two recommended curing schedules were used. The short cure consisted of $2\frac{1}{2}$ h at $120°$ C followed by 3 h at $180°$ C. The long cure was similar to the above but with an extra 6 h at $200°$ C.

A few of all types of specimen had 100 mm of their centre section turned down to a diameter of approximately 6.1 mm, but most were employed in the as-made form.

5. The creep apparatus

To determine the torsional creep strain two rigs were built in which 6 specimens, stressed at various preloads, could be exposed to an air or water environment. The basic mechanism for stressing a specimen in torsion is shown in Fig. 1.

One end of the square cross-section sample is inserted in a square hole in the brass torsion wheel on the right hand side of Fig. 1, and the other end clamped in a similar hole in the split brass block on the left. This block is attached to a rigid steel frame-work and the torsion wheel is free to rotate and move axially about a stub axle attached to the same structure. Thus the specimens are free from end loading during testing. The wheel and block are accurately aligned with their inner surfaces 100 mm apart. A thin stainless steel strip, fixed to the torsion wheel and running in a groove around its rim, passes over two PTFE pulleys which are well clear of the rest of the apparatus. The load required to produce a given maximum static shear stress in the test piece is applied to the end of this strip. In the air rig the PTFE pulleys were replaced with metal roller bearings. In either case the pulley wheels and torsion wheel
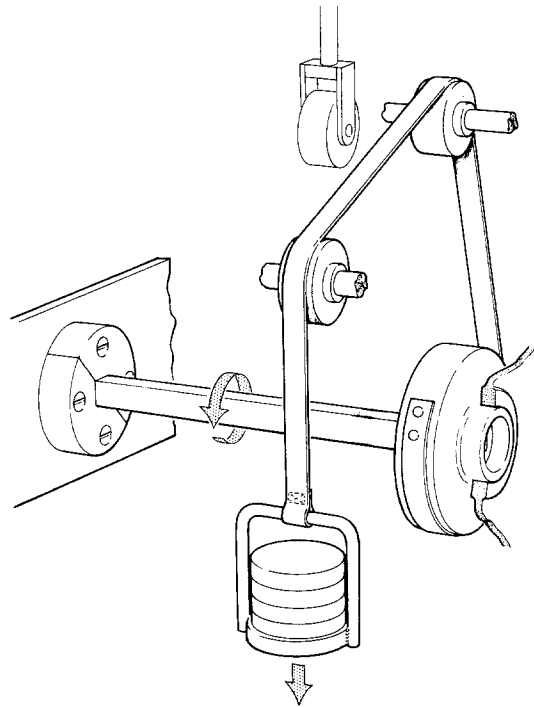

Figure 1 Diagram of torsion creep rig unit.

were carefully aligned in a plane perpendicular to that of the specimen cross-section.

Originally the deflection of the load pan was measured with a dial gauge, but later to improve accuracy and ease of recording an electrical method was used. For the air rig 0 to 1000 Ω potentiometer windings were attached to the back of each torsion wheel and a fixed contact attached to the framework of the rig such that as the wheel rotated due to specimen movement the voltage between the fixed contact and one end of the winding varied. A stabilized d.c. voltage of 100 mV was applied across each potentiometer. A slightly different system was used for the water rig as here it was necessary to protect the potentiometer windings from the water. An additional PTFE pulley, free to rotate on a bearing and with the steel tape passing underneath it, was set between the other two pulleys as shown in Fig. 1. A 0 to 1000 Ω potentiometer with its centre spindle set in a fixed position was attached to this central pulley. As the specimen and hence steel tape moved, the potentiometer rotated and the voltage between the centre contact and one end changed.

In both cases the voltage changes were recorded

*p.p.h. = parts per hundred.

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on a multichannel chart recorder. Each potentiometer was calibrated; for the air rig where the working temperature varied the calibration was carried out at different temperatures. The complete structure of the air rig was contained in a large, well-insulated box. The temperature of the air was maintained at the appropriate value by a combination of hot air blowers and infra-red lamps. Thermocouples in the vicinity of each specimen monitored the temperature continuously.

Wherever possible the components of the water rig were coated to protect them against corrosion. The whole structure was placed in a bath of demineralized water heated to the appropriate temperature. The water was circulated through an ion exchange column and the conductivity periodically monitored. Typical conductivity values were in the range 1.0 to $1.3 \mu\Omega^{-1}$. The water temperature in the vicinity of each specimen was also recorded. To reduce the evaporation of the hot water a layer of expanded polystyrene pellets was spread over the surface.

All bearings were periodically checked and any sudden changes in creep strain investigated, often by repeating the run. The maximum load applied to give a 40% preload was approximately 7.3 kg, giving a stress of 53 MPa in the steel tape. As the maximum tape temperature was only about $0.07\,T_{\mathrm{m}}$, where T_{m} is the melting temperature of the steel, it was assumed that creep in the latter was negligible. The PTFE pulley wheels, operating at ambient temperature, were also checked for deformation under loading but no signs of damage or dimensional change were noted

Both rigs were situated in a temperature controlled laboratory. When working conditions had been established the temperature variation in the water rig was not more than $\pm 2^\circ$ C. The variation at a specific point in the air rig was also $\pm 2^\circ$ C, though the spatial temperature variation could be as much as $\pm 4^\circ$ C. Bearing surfaces in either rig were designed to minimize frictional effects. The size of these was estimated by noting the load to initiate movement in the absence of a specimen. Usually 50 to 100 g was required, which is not significant compared with the preload of 1.8 to 7.3 kg.
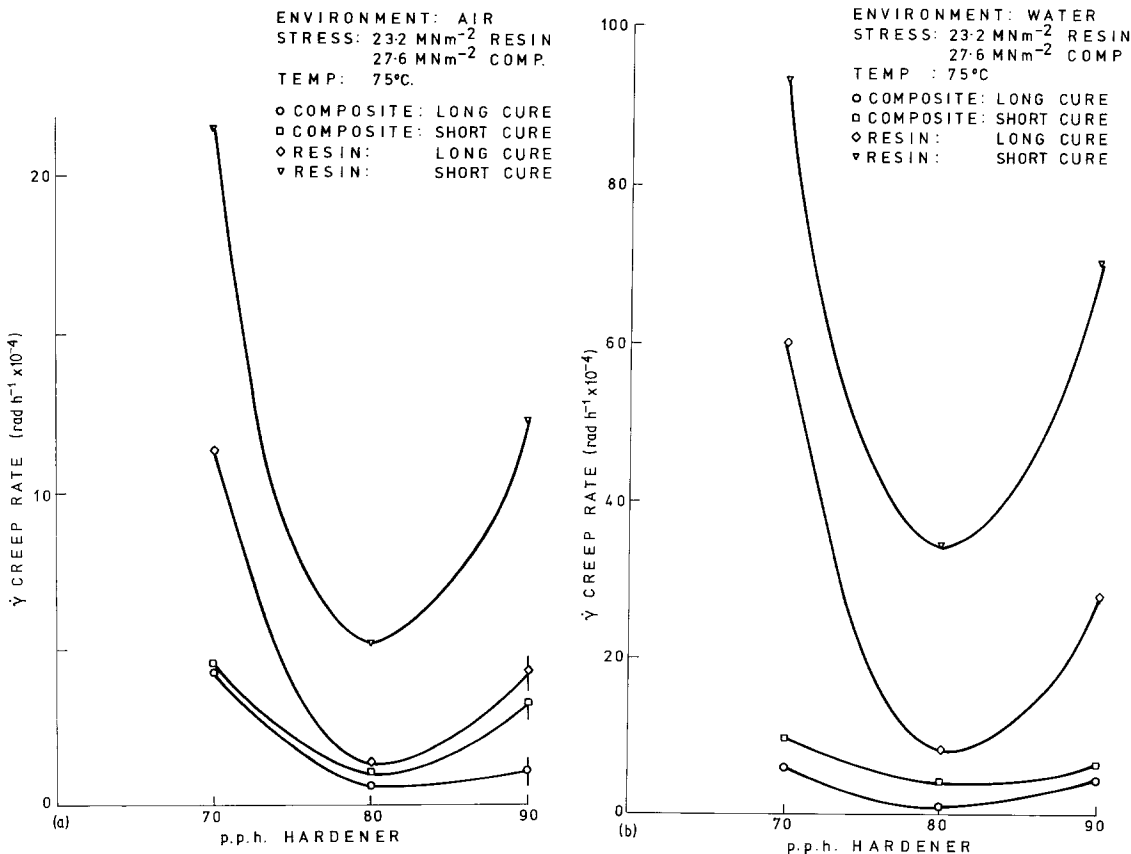

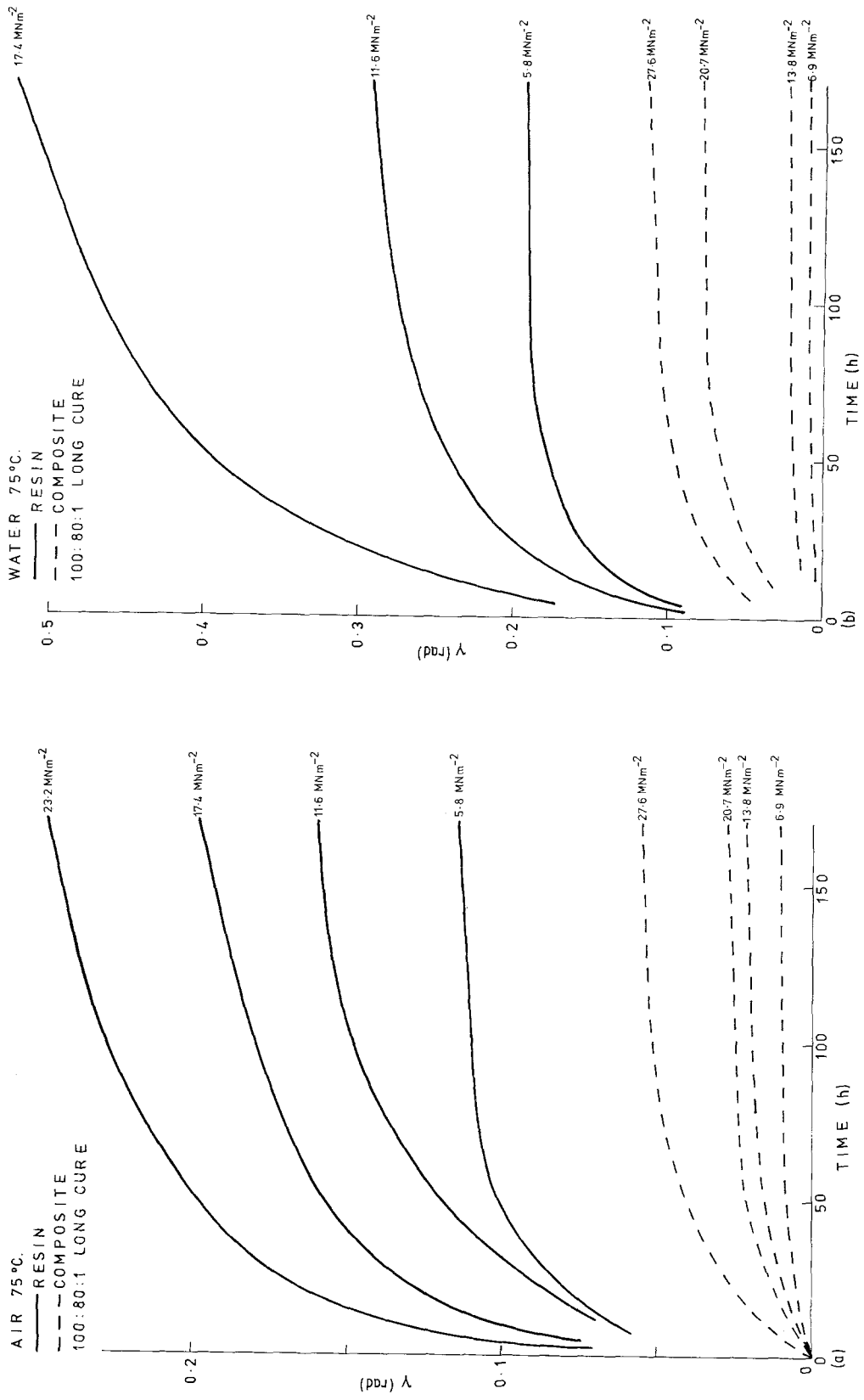*Figure 2* Creep rate versus p.p.h. hardener and cure schedule, (a) for air, (b) for water.

Figure 3 Creep strain versus time as a function of torsional preload (a) in air, (b) in water. The test temperature is 75° C.
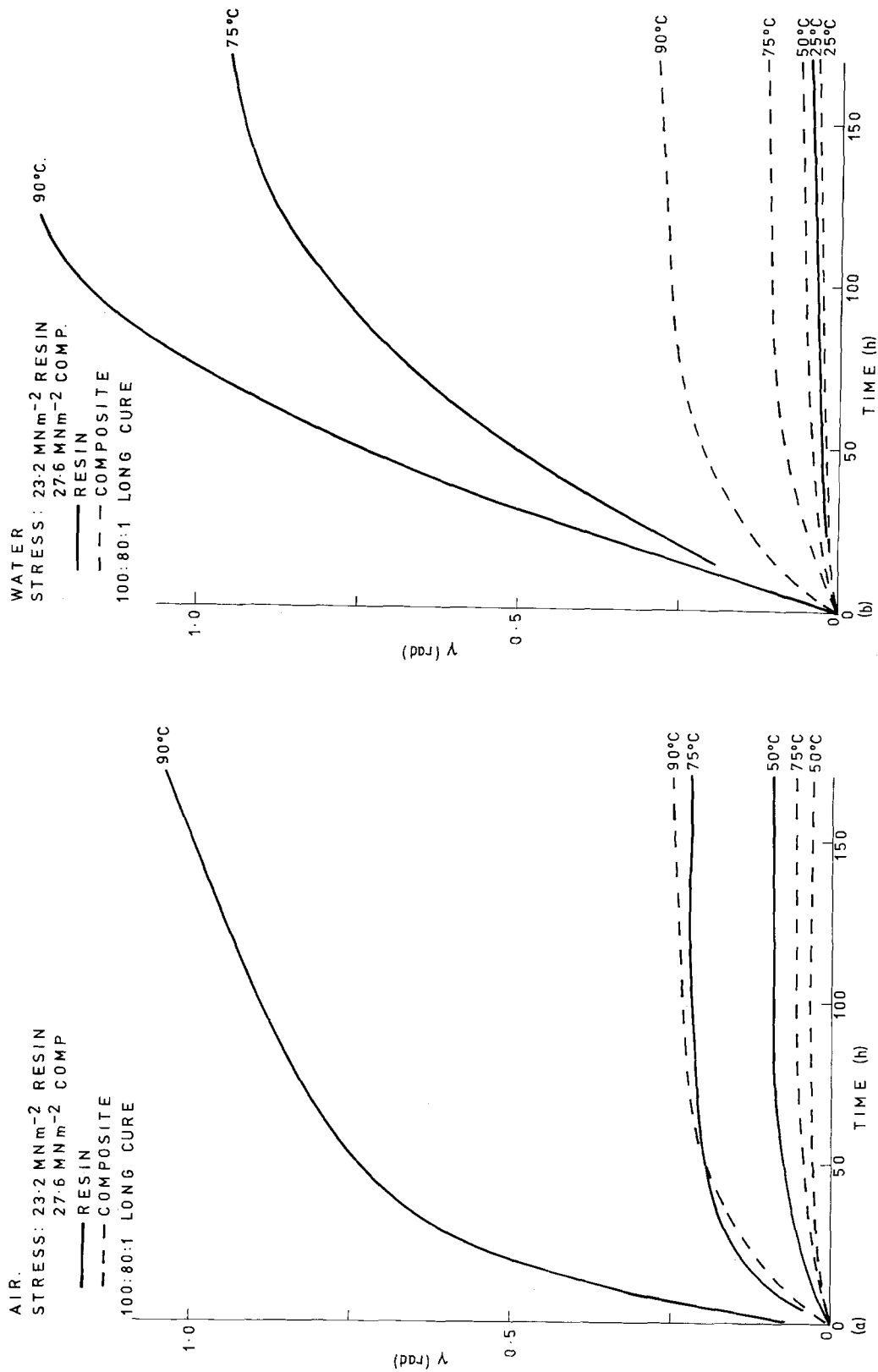
Figure 4 Creep strain versus time as a function of temperature for specimens stressed at 40% of the ultimate torsional strength (a) in air, (b) in water.

6. Experimental results

Resin and unidirectional fibre composite specimens tested under all conditions initially showed primary creep. After 15 to 100 h, and for the remainder of the time for which the test was continued, most samples also showed constant rate secondary creep. A few resin specimens, made with 70 p.p.h. of hardener, given a short cure, and stressed in water at 90° C with a high preload, exhibited tertiary creep and failure after about 100 h exposure. After testing most specimens showed some degree of permanent set.

To limit the number of tests conducted and ensure that the most detailed study was undertaken on a practically useful system it was decided, having established the general pattern of creep behaviour, to study all types of specimen under one set of conditions – namely a preload of 40% of the ultimate torsional stress and a temperature of 75° C in air and water environments. This enabled the proportions of hardener and the cure schedule which gave specimens with the lowest creep rate to be identified.

The results are shown in Figs. 2a and b for air and water respectively. The secondary creep rate (in $rad\,h^{-1}$ for specimens 100 mm long and 6.35 mm square in cross-section) is plotted as a function of the amount of anhydride hardener in the epoxide resin matrix. Results are given for the unreinforced resin and composite specimens both of which have received short and long cures. Several expected trends are clear; the secondary creep rate is greater in water than in air, for resin or compostie specimens in which non-stoichiometric amounts of hardener were used, for specimens which had received a short cure, and for specimens not containing fibres. Less expected was the observation that an excess of hardener caused a marked increase in the creep rate in air as well as in water, where a reaction was expected with the excess anhydride. The greatest stability against creep is shown by specimens made with the stoichiometric amount of hardener and cured for a longer time at a higher temperature. The remainder of this work was carried out with this type of specimen.

Figs. 3a and b illustrate the relation between creep strain and time as a function of the torsional preload. The results are for air and water environments and the test temperature was 75° C. The stresses quoted correspond to preloads of approximately 10%, 20%, 30%, and 40% of the ultimate torsional strength determined in a static torsion test. Each characteristic was plotted from results obtained on at least two specimens. For clarity some details have been omitted in the initial region. For any set of conditions composites show a much reduced creep strain compared with the unreinforced resin. The presence of water enhances creep.
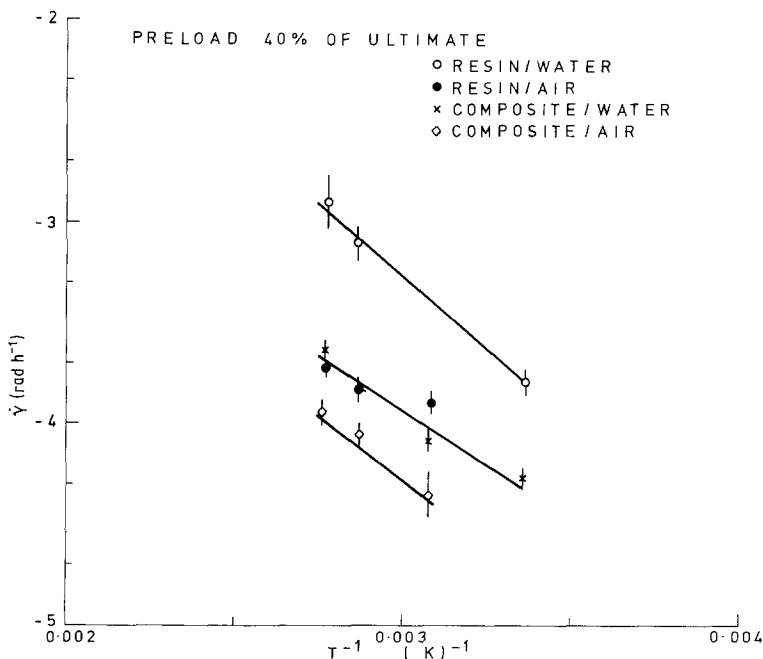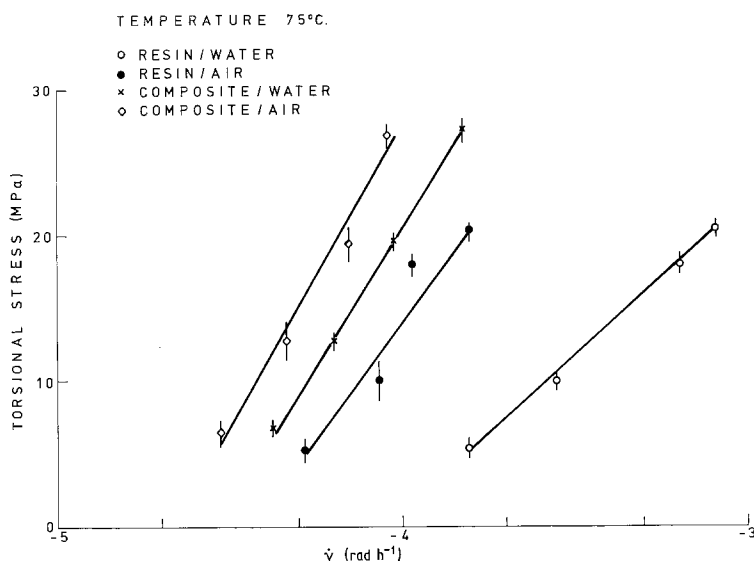

PRELOAD 40% OF ULTIMATE

○ RESIN/WATER
● RESIN/AIR
× COMPOSITE/WATER
◇ COMPOSITE/AIR

Figure 5 Creep rate versus reciprocal of absolute temperature.

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TEMPERATURE 75°C.

○ RESIN / WATER
● RESIN / AIR
× COMPOSITE / WATER
◇ COMPOSITE / AIR

Figure 6 Torsional stress versus creep rate.

Figs. 4a and b show the variation of creep strain with time as a function of temperature for specimens stressed at 40% of the ultimate torsional strength. Again, under similar conditions, composites creep less than resin specimens and creep is more pronounced in water than in air.

It was mentioned earlier that the secondary creep rate, $\dot{\gamma}$, might be expected to depend on the absolute temperature T, according to an equation of the form

$$\dot{\gamma} = \text{constant} \exp\left(-Q/kT\right) \qquad (5)$$

In addition it was shown that at constant temperature the applied creep stress in the secondary region should, on the basis of the Eyring model, be related to the creep rate, $\dot{\gamma}$, by an equation of the form

$$\tau = \text{constant} \ln \dot{\gamma} \qquad (6)$$

To establish if these types of relationship held for the resin matrix and composite materials the steady, secondary, creep strain rate was determined and the logarithm of $\dot{\gamma}$ plotted against the reciprocal of the absolute temperature, see Fig. 5, and the preload stress against the logarithm of the creep rate, see Fig. 6. In Fig. 5 the torsional stress is constant at 40% of the ultimate value, and in Fig. 6 the temperature is constant at 75° C. Values of Q, the activation energy, determined from the slopes of the lines in Fig. 5 are listed in Table I. Allowing for the errors involved Q is approximately constant for either environment and for specimens with or without fibres. In Fig. 6 the shear stress is in all cases, allowing for errors,

TABLE I Activation energies, with a preload of 40%.

Material	Environment	Activation energy $(\text{kcal} (g \, \text{mol})^{-1})$
Resin	Water	6.3 ± 0.9
Resin	Air	5.0 ± 0.8
Composite	Water	5.0 ± 0.8
Composite	Air	5.9 ± 0.7

proportional to the logarithm of the secondary creep rate.

7. Discussion
7.1. The effect of temperature and stress
The dependence of creep rate on temperature, at a preload of 40% of the ultimate torsional strength, can be accounted for adequately by a simple Arrenhius relation of the form exponential $(-Q/kT)$, rather than a more complex equation such as Equation 2. The activation energy, Q, is approximately constant for all types of specimen indicating that the same process is occurring irrespective of the presence or otherwise of fibres. As most specimens showed permanent set after testing the creep process presumably involves the breaking of bonds within the resin. The mean value of the activation energy is a half or less of the values reported for various relaxation processes in epoxides by Arridge and Speake [13] and Kreahling and Kline [14], and it has not been possible to relate the energy to a specific process occurring in the resin.

Equation 3 describes the dependence of the secondary shear creep rate on shear stress at 75° C successfully. Values of the activated volume V_0,

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TABLE II Activated volumes at 75° C.

Material	Environment	Activated volume (m³)
Resin	Water	$0.9 \pm 0.04 \times 10^{-27}$
Resin	Air	$0.6 \pm 0.06 \times 10^{-27}$
Composite	Water	$0.5 \pm 0.03 \times 10^{-27}$
Composite	Air	$0.44 \pm 0.08 \times 10^{-27}$

obtained from the slopes of the lines in Fig. 6 are listed in Table II. The greatest, $0.9 \times 10^{-27} \, m^3$, is for resin in water and the least, $0.44 \times 10^{-27} \, m^3$, for a composite in air. Allowing for errors there is virtually no difference between the results for fibre reinforced materials in either environment and for resin in air. The large value of V_0 for resin stressed in water indicates the possibility of some plasticizing effect, which is suppressed in the presence of fibres, though this is not supported by the evidence of the activation energies. All the readings are approximately an order of magnitude less than those quoted by Ishai [12] for an epoxide resin, but the materials, temperature, and modes of stressing in the two cases are different. Assuming the activated volume to be spherical the diameter of the sphere is approximately 100 times less than the mean distance between fibres in a 60% by volume composite.

To obtain Equation 2 from Equation 1 it is necessary that $\tau V_0 \gg 2kT$. Using experimental values of V_0 and a temperature of 75° C, it is found that this inequality is only true for resin samples in water above 20% preload, and other materials/environments above 30% preload, and this must cast some doubt on the validity of the activated volumes obtained.

No attempt has been made to use spring and dashpot models to describe the behaviour of the materials, nor to fit equations to the overall creep results. It was not felt that the former approach would be useful in the present study, while the problem alluded to in the introduction, namely the effect of the varying stress field in causing initially both primary and secondary creep, precluded the latter approach over part of the time range.

7.2. The effects of the amount of hardener, cure schedule, and presence of fibres on the secondary creep rate.

The reduction in the secondary creep rate for specimens made with the stoichiometric amount of hardener, or for those given a long cure, is marked. It appears, Ferry [15], that the excess of resin, for specimens with less than the stoichiometric amount of hardener, or excess of hardener, for those with more than the stoichiometric amount, plasticizes the resin reducing the T_g and shear modulus. Similarly, for a given initial proportion of resin to hardener, a long cure schedule will use more of the hardener and give a stiffer specimen. This approach explains why a similar pattern of behaviour is obtained for specimens with an excess of hardener whether tested in air or water; though clearly the experimental work shows that irrespective of the amount of hardener or cure schedule, exposure to water increases the secondary creep rate, presumably because of additional plasticization. To develop the argument quantitatively is difficult since the shear modulus is a function of time, a non-linear function of shear stress, and the relationship between the deficit or excess of hardener and shear modulus is unknown.

With reinforced specimens two extra components, the fibre and the interface are introduced, It is unlikely that the fibres will deform permanently in shear though the interface may. However it is assumed that the fibre resin bond is sufficiently good that the latter possibility may be ignored. It is well known, both theoretically and experimentally, see for instance Hashin and Rosen [16] and Hancox [17], that the presence of fibres results in a material with a shear modulus considerably greater than that of the unreinforced matrix. Thus the secondary creep rate for fibre reinforced materials would be expected to be less than for the pure matrix, as is found experimentally.

8. Conclusion

The secondary, constant, creep rate for resin or fibre composite specimens stressed in torsion depends markedly on the amount of hardener in the epoxide resin and the cure schedule. The lowest creep rate was noted for specimens that had received the maximum cure and had been made with the stoichiometric amount of hardener. As far as long term properties are concerned it appears to be as detrimental to have too much hardener as to have too little.

Specimens containing carbon fibres had a significantly lower secondary creep rate than the unreinforced resin ones, irrespective of the manufacturing or testing conditions. This is

probably related to the higher shear moduli of composites.

An activation energy between 5 and 6.3 kcal $(g\,mol)^{-1}$ was found for all types of specimen stressed in either environment at a preload of 40% of ultimate. This indicates that the same basic creep mechanism is occurring in all cases. In addition it was noted that the shear stress was proportional to the logarithm of the secondary creep rate.

Acknowledgements

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