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Creep of a glass-flake-reinforced epoxy adhesive for space applications

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Hysol 9313 epoxy adhesive, a crosslinked bisphenol-A type epoxy filled with glass flakes, will be used in the optic mounting joints of a space X-ray telescope. During the extended period of earth storage of the telescope prior to its launch, these epoxy joints will be loaded and must be dimensionally stable to maintain the optical assembly alignment. To evaluate the long-term shear creep behaviour of Hysol 9313 epoxy, its momentary creep curve and ageing shift rate at 21°C, 27°C below its glass transition temperature, were measured in its linear viscoelastic region. The ageing effective-time theory was then applied to calculate creep strains of this epoxy under tensile and shear stresses after it was aged for various times. Results were verified by comparing the calculated results with experimental data. Using the anticipated loading profile for these adhesive joints during earth storage of the telescope, the shear strain of these epoxy joints was calculated to be greater than the required 0.1% shear strain even 2 months after unloading. Alternative storage methods to minimize the creep stresses acting on these joints are therefore recommended. Copyright © 1996 Elsevier Science Ltd.

(Keywords: epoxy adhesive; creep; viscoelasticity)

INTRODUCTION

The Advanced X-ray Astrophysics Facility (AXAF) programme will use the epoxy Hysol 9313 to bond many joints, including the optic mounting joints, in a space telescope. During the extended period of earth storage of this X-ray space telescope prior to its launch, these adhesive mounting joints will be loaded by gravitational pulls. The anticipated loading profile for these adhesive joints has been determined to be 69 kPa shear stress for a minimum of 2 months followed by a 207 kPa shear stress for 3 years after Hysol 9313 epoxy is cured and aged for a total of 5 days. After the launch of this telescope, loads on these epoxy joints will be removed. It is desired to limit the maximum shear creep of this epoxy to less than 0.1% after unloading so that the telescope alignment will remain within specification for the in-orbit performance. It is, therefore, essential to determine accurately the maximum residual shear creep strain of Hysol 9313 epoxy after 3-year loading to assure its usage as the joint adhesive.

During the 3-year storage of the space telescope prior to its launch, ageing of the Hysol 9313 epoxy is expected to occur and must be factored into the calculations. Ageing is a basic feature of the glassy state and is found in all glasses including polymeric, monomeric, organic and inorganic. Struik[1] has examined the physical origin of ageing and its effects on mechanical, dielectrical, fracture and transport properties of a material. He found that the temperature range in which the ageing occurs in a polymer is between the glass transition temperature T_g and its first secondary transition. For Hysol 9313, this range is from 50°C to −50°C. Therefore, for the prediction of the long-term creep behaviour of this epoxy from its short-term creep tests at 21°C, a knowledge of its ageing behaviour is indispensable.

The general views on ageing were deduced from the ideas about time–temperature superposition developed by Williams, Landel and Ferry[2] based on the free-volume concept. In the 1960s, the WLF treatment was extended to the temperature range below T_g[3–5] to generalize the ageing effects. It was concluded that ageing induces horizontal shifts of the mechanical and dielectric response curves along the log time scale and that the free-volume concept can indeed be applied in the temperature range below T_g, although the theoretical basis for the free-volume concept does not exist in that temperature range[6]. In terms of the ageing effect on creep, ageing does not change the shape of the creep curve; it only changes all relaxation times by exactly the same factor so as to horizontally shift the creep curve along the time scale. Actually, all polymers age in a similar way. The effect of ageing on small-strain creep, or other mechanical and dielectric properties, can be summarized by the following equation[1]:

$$-\mathrm{d}(\log a_{te})/\mathrm{d}(\log t_e) = \mu = \text{constant} \qquad (1)$$

where a_{te} is the horizontal shift factor after the material was aged for t_e seconds and μ is the 'double-logarithmic shift rate'.

In almost all the polymers studied by Struik[1], the shift rate μ was a constant over wide ranges of t_e. Above T_g, μ is zero. Just below T_g it increases rapidly to about unity

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and the value of unity remains over a wide temperature range below T_g. At low temperatures, close to the temperature of secondary relaxation or β relaxation, the ageing begins to cease and μ approaches zero. Since the shift rate is a constant for a polymer at a given temperature, it is possible to predict the long-term creep behaviour of the polymer from its short-term creep tests using the effective-time theory.

During long-term creep of a polymer at temperatures where ageing is active, the creep is accompanied by ageing. Consequently, the properties of the material change with increasing creep time. The Boltzmann's superposition principle[7] is no longer valid even at infinitesimally small strains[1]. Because the ageing affects the long-term creep tests, the so-called 'short-term' creep tests are now defined as the tests in which the testing time remains small compared with the ageing time of the sample at the beginning of the test. Properties determined by the short-term tests are called 'momentary' properties. Since all mechanical relaxation times change in a systematic way during ageing as demonstrated in equation (1), the long-term creep properties are related to the short-term or momentary creep properties through the effective time as shown below:

$$J'_{t_e}(t) = J_{t_e}(\lambda) \tag{2}$$

where $J'_{t_e}(t)$ is the long-term shear creep compliance of a material at time t after it was aged by time t_e, and $J_{t_e}(\lambda)$ is the momentary shear creep compliance of the same material at time λ after it was aged by time t_e. The effective time, λ, is related to t through[1]

$$\begin{aligned} \lambda &= t_e \ln(1 + t/t_e) && \text{if } \mu = 1 \\ \lambda &= (t_e/\alpha)[(1 + t/t_e)^{\alpha} - 1] && \text{if } \mu < 1 \end{aligned} \tag{3}$$

where

$$\alpha = 1 - \mu \tag{4}$$

The above treatment of the long-term creep using the effective-time theory is valid only for temperatures in the ageing range with $0.7 < \mu < 1.0$[1].

Basically, procedures for determining the long-term creep behaviour of a material are first to acquire the shift rate μ, followed by the measurement of the momentary creep compliance, and finally the calculation of the effective time λ. The time–temperature superposition can be employed to expand the creep time for the momentary creep curve of a material provided that the creep time for each creep test at a given temperature is significantly less, preferably by 10 times, than the ageing time of that material at the same temperature.

Using the effective-time theory, the long-term creep behaviour of any material can be related to its momentary creep properties for which the time–temperature superposition and the Boltzmann's superposition principle are applicable. If the epoxy studied is linear viscoelastic under the 207 kPa creep stress, its momentary creep recovery after load removal can be expressed as[7]

$$\mathcal{L}(\gamma(\lambda)) = s\mathcal{L}(\sigma(\lambda))\mathcal{L}(J(\lambda)) \tag{5}$$

where $\mathcal{L}$ stands for Laplace transform, s is the Laplace dummy variable, γ is the creep strain and σ is the creep stress. If the loading and unloading on this epoxy can be approximated as step functions, shear strains at $\lambda > \lambda_1$, or after load removal, can be related to the creep compliance by

$$\gamma(\lambda) = (J(\lambda) - J(\lambda - \lambda_1))\sigma \tag{6}$$

In this study, a progressive reduction in creep stresses during the creep tests was applied first to establish the region of linear viscoelastic behaviour for Hysol 9313 epoxy. The advantage of identifying the linear region is twofold. First, if the creep behaviour of this epoxy under 207 kPa creep stress is linear viscoelastic, the Boltzmann superposition principle can then be applied to determine the creep recovery behaviour. Second, a higher creep stress, rather than the 207 kPa, can be employed for the creep measurements in the linear viscoelastic region in which the creep rate is independent of the creep stress. Once the value of creep stress was finalized for the creep measurements, the momentary master creep curve at 21°C after 6-h ageing was established using the time–temperature superposition principle. A sequence of the creep and recovery tests was then employed for the determination of the ageing shift rate.

Using the ageing theory with experimentally determined momentary creep curve and ageing shift rate, short- and long-term tensile creep strains of this epoxy aged for 1 day, 5 days and 6 days with or without refreshing were calculated and compared with experimental results. To stimulate the actual usage loading condition for this epoxy adhesive in the telescope, shear lap joints between Invar bars were loaded with a force of 1334 N and their creep displacements were monitored for 47 days and compared with predictions. Based on the anticipated loading profile for the optic mounting joints in the space X-ray telescope during the earth storage, shear creep strains of this epoxy adhesive were also calculated, and their impacts on the optical assembly alignment are evaluated.

EXPERIMENTAL

A mould was fabricated to produce 0.127 mm thick epoxy sheet samples. Hysol 9313 epoxy (a bisphenol-A type of epoxy) and glass flake fillers (Siltex 44 fused silica) were mixed according to the documented procedure and injected into the mould. The concentration of the glass filler is 80 wt%. These epoxy sheets were then cured at room temperature for 5 days. All epoxy films cut from the sheet were refreshed by being exposed in a 60°C oven for 5 min prior to all testing, to erase any previous ageing or thermal history.

A Sintech Automated Tester (Sintech Corp., MA) was used for determination of the tensile properties of the epoxy film. Refreshed epoxy films were conditioned and tested at 21°C and 50% relative humidity (r.h.) at a strain rate of 100% elongation per minute. The dynamic mechanical responses of the refreshed epoxy film samples in a tensile mode were evaluated using a Rheometrics Solid Analyzer RSAII (Rheometrics Inc., NJ). A temperature sweep from −80 to 120°C at 10°C min^{-1} with a 1 Hz frequency was employed to determine the β and glass transitions of this epoxy based on the loss modulus.

Tensile creep behaviour of all epoxy film samples of size 10 mm by 3 mm was measured with a Seiko TMA/SS100 thermo-mechanical analyser (Seiko Instruments Inc., Japan). All samples were loaded and unloaded with

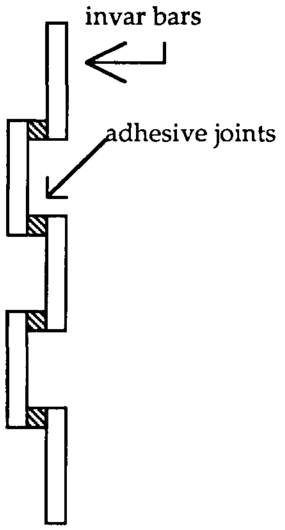

Figure 1 Test specimen for the shear creep measurements

Table 1 Mechanical and thermal properties of the Hysol 9313 epoxy film

E (GPa)	σ_b (MPa)	ϵ_b (%)	T_g (°C)	T_β (°C)
3.44 (0.022)	25.2 (3.17)	0.8 (0.1)	48	−50

Standard deviation given in parentheses

the maximum loading rate of 500 g min^{-1}. Epoxy film samples refreshed and quenched from 60°C were mounted within 1 min after they were removed from the oven in the Seiko analyser for the creep analyses. A progressive reduction in creep stresses during the creep tests was applied first to establish the region of linear viscoelastic behaviour for Hysol 9313 epoxy. Once the value of creep stress was finalized for the creep measurements, the momentary master creep curve at 21°C after 6-h ageing was established using the time–temperature superposition principle. A sequence of the creep and recovery tests was then employed for the determination of the ageing shift rate according to the procedures outlined by Struik[1].

The Seiko TMA measures tensile creep of a thin film which, in turn, can be converted into shear creep through

$$J(t) = 2(1 + \nu)D(t) \qquad (7)$$

provided that the film is isotropic and linear viscoelastic, and the Poisson's ratio is time-independent[8]. Here, $J(t)$ is the shear creep compliance, $D(t)$ is the tensile creep compliance and ν is the Poisson's ratio. In this study, we attempted to extract the Poisson's ratio from the measured bending stiffness of this epoxy film using the plate-bending equation[9] shown below:

$$P = (3bh^3/12L^3)[E/(1 - \nu^2)]W \qquad (8)$$

where P is the bending force, b is the sample width, h is the sample thickness, L is the bending length, E is the tensile modulus and W is the vertical displacement. An L&W Bending Resistance Tester (Lorentzen & Wettre, Sweden) was used to determine the bending force of Hysol 9313 epoxy film with a 20 mm bending length and a 15° bending angle. Five refreshed samples were conditioned and tested at 21°C and 50% r.h.

Tensile creep behaviour of 1-day aged and 5-day aged epoxy film samples after refreshing was also measured by the Seiko TMA analyser for a 5-day creep and for a 1-day creep, respectively. One-day tensile creep strains of a 6-day old epoxy sample were also recorded without refreshing. To simulate the actual loading condition encountered by the adhesive joint on the telescope during earth storage, four adhesive lap joints using the Hysol 9313 epoxy were prepared between Invar bars as shown in *Figure 1*. Once the epoxy was injected into the joints, it was allowed to age and cure for 5 days prior to the application of a 1334 N load, or a shear stress of 1.7 MPa. The load was taken off at specified time for the displacement measurements. Thicknesses of all joints were measured after unloading. The displacements of Invar bars were obtained within 5 min after unloading and the load was put on 10 min after.

RESULTS AND DISCUSSION

Modulus, break stress, elongation at break, T_g and T_β of the Hysol 9313 epoxy are listed in *Table 1*. Since the storage temperature of this epoxy will be 21°C, or 27°C below T_g, it is clear that the ageing effects on creep will be significant. The Poisson's ratio is not listed in *Table 1* due to the experimental difficulties in obtaining a correct value. Within the 20 mm bending length used for the bending stiffness measurements, the thickness of the epoxy film samples tested varied from 0.145 to 0.16 mm. This thickness non-uniformity significantly affects the Poisson's ratio calculation since the bending force is proportional to the thickness to the cubic power [see equation (8)]. An erroneous value of 0.543 was obtained for the Poisson's ratio of the Hysol 9313 epoxy film based on the measured bending force, although ν is always smaller or equal to 0.5 for isotropic solid polymers. Therefore, to convert the tensile creep compliances to shear creep compliances, a Poisson's ratio of 0.5 will be used since it will provide a conservative estimation [see equation (7)].

By comparison of creep compliance curves of Hysol 9313 epoxy film under various creep stresses, from 1.2 to 9.6 MPa, it was found that the creep curve shape is independent of the creep stress at and below the stress of 4.8 MPa. In other words, Hysol 9313 epoxy film can be considered as linear viscoelastic at creep stresses at and below 4.8 MPa. In all the following creep studies, 2.4 MPa was selected as the creep stress. It should be pointed out that the creep data of all the creep tests we did at times less than 5 min of the elapsed time should be treated with reserve. Due to the viscoelastic nature of the polymer, an inherent uncertainty is present in creep data for elapsed times less than about 10 times the loading period[10].

The creep curves of the Hysol 9313 epoxy films under 2.4 MPa creep stress after ageing for 6 h at various temperatures are plotted in *Figure 2*. Using the time–temperature superposition principle, the master curve for the 6-h aged momentary creep was constructed and is also shown in *Figure 2*. The time–temperature shifting method worked extremely well on these data. As shown in *Figure 2*, the 6-h aged epoxy would reach the glass transition region after 10^6 s (less than 12 days) if there were no ageing.

It was found that the following equation can always describe the momentary creep behaviour of any material[1]. There is no molecular theory to explain this general

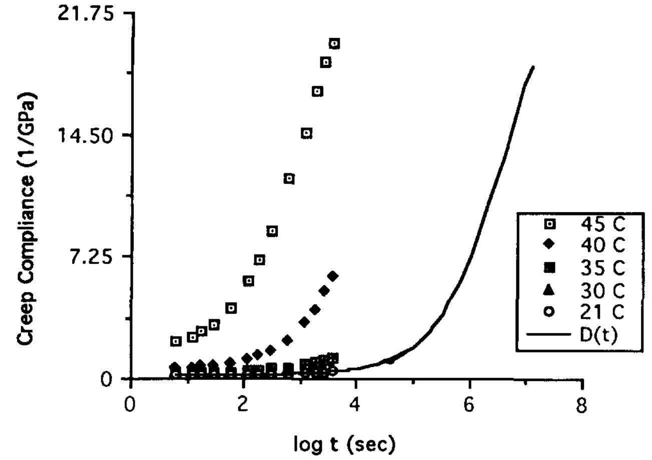

Figure 2 Six-hour aged momentary creep curve for the Hysol 9313 epoxy adhesive at 45, 40, 35, 30 and 21°C; the solid curve is the master curve after time–temperature shifting

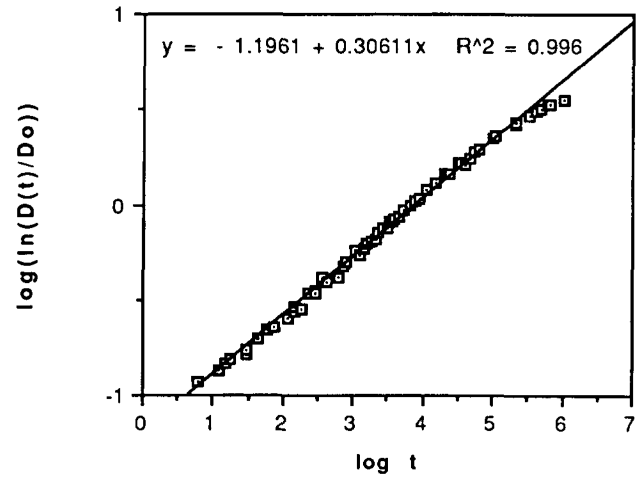

Figure 3 Determination of the constants in equation (1)

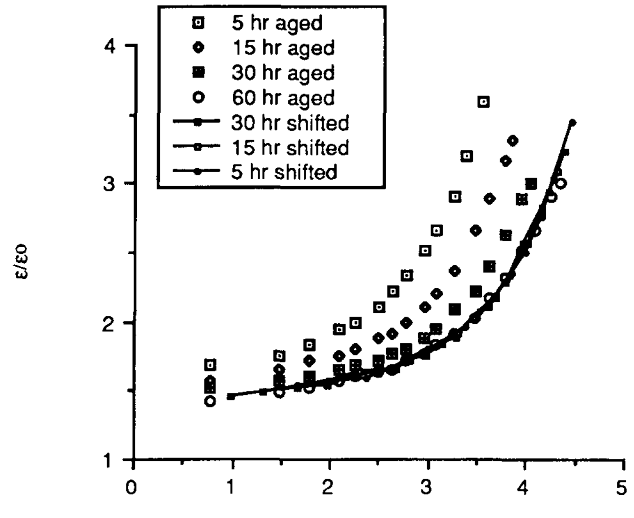

Figure 4 Isothermal tensile creep curves of the Hysol 9313 epoxy at 21°C for different ageing times

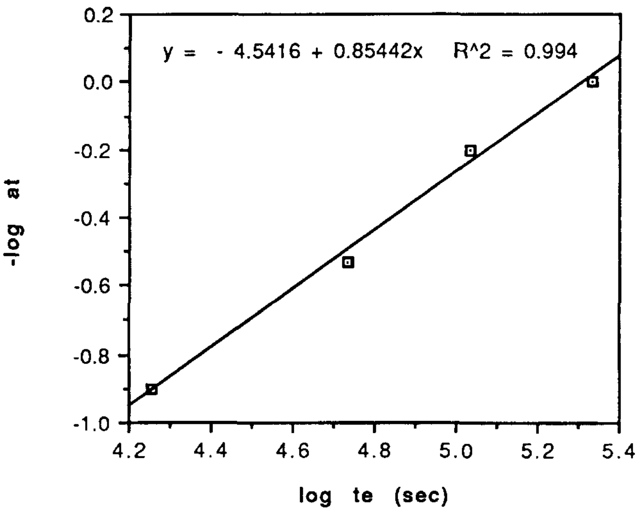

Figure 5 Logarithm of the ageing shift factors plotted against the logarithm of the ageing times for the Hysol 9313 epoxy. The slope of the drawn line is the ageing shift rate and equal to 0.85442

representation of creep[6] although the following equation is also applicable to other relaxation processes, such as stress relaxation, volume relaxation and dielectric relaxation. The equation is

$$D(t) = D_0 \exp\,(t/t_0)^m$$

or

$$\log \ln\,(D(t)/D_0) = m \log t - m \log t_0 \qquad (9)$$

where D_0 is the limited tensile creep compliance at $t = 0$ and t_0 is a time parameter related to the relaxation time. D_0 and t_0 depend on temperature, ageing time and the type of material. However, for a wide class of materials, m turned out to be remarkably constant and is about 1/3. It should be pointed out that equation (10) becomes the famous Andrade creep equation for $t \ll t_0$ (ref. 11). Fitting data of the momentary master creep to equation (9), D_0 was found to be 0.2 GPa^{-1}, t_0 is 8080.14 s and m is 0.30611. The goodness of the fit is demonstrated in *Figure 3*. These fitting values are similar to the values reported in the literature[12] for the bisphenol-A type of epoxy adhesive.

Tensile creep curves of the Hysol 9313 epoxy film sample with various ageing times are shown in *Figure 4*. These curves were then shifted along the logarithm time axis to obtain a single curve and, thus, to determine the ageing shift factors. By plotting the logarithm of the shift factors against the logarithm of the ageing times as demonstrated in *Figure 5*, the ageing shift rate was found to be 0.85442. This value agrees with the values reported by Vleeshouwers *et al.*[12].

LONG-TERM CREEP CALCULATION AND VERIFICATION

Using the effective-time approach as outlined by equations (3)–(5), tensile creep curves of Hysol 9313 epoxy aged for 1 day and for 5 days after refreshing were calculated and compared with experimental results, see *Figures 6* and *7*. It is clear from these plots that the ageing theory has captured the creep behaviour of this epoxy. It is also demonstrated that the ageing theory provides conservative

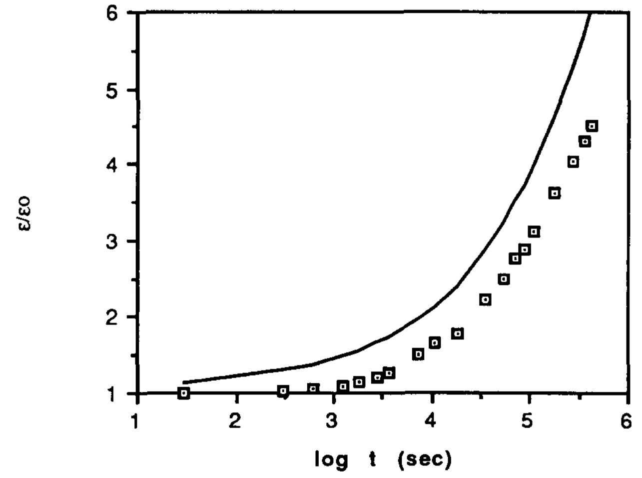

Figure 6 Tensile creep strains of the Hysol 9313 epoxy adhesive aged for 1 day after refreshing; open squares, data; solid curve, prediction

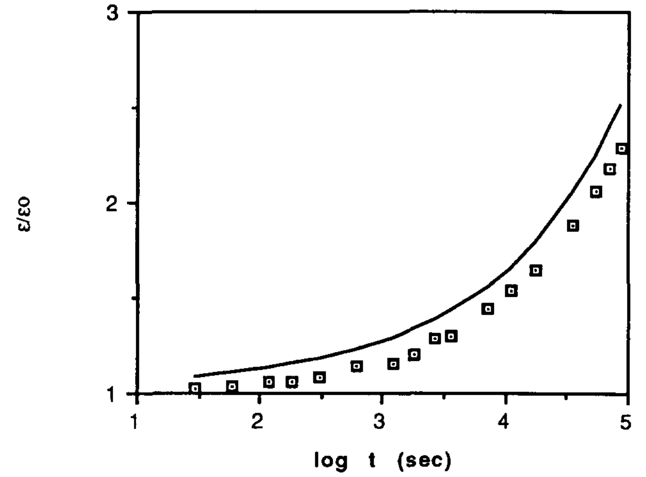

Figure 7 Tensile creep strains of the Hysol 9313 epoxy adhesive aged for 5 days after refreshing: open squares, data; solid curve, prediction

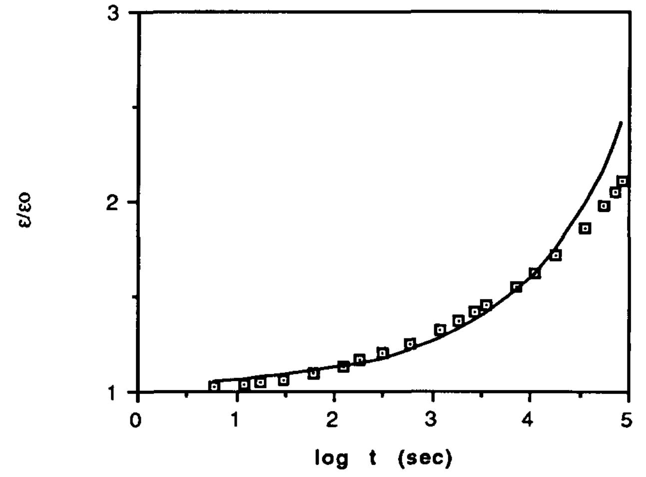

Figure 8 Tensile creep strains of the Hysol 9313 epoxy adhesive aged and cured for 6 days without refreshing: open squares, data; solid curve, prediction based on an age of 6 days

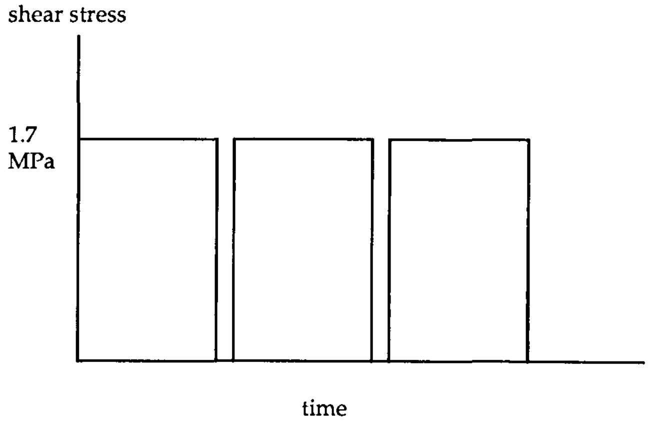

Figure 9 Loading and unloading profile for the shear creep measurements

estimates of the creep strains. However, it appears that the predicted and actual results are parallel but displaced. The reason for this discrepancy is not clear. Hysol 9313 epoxy adhesive is mixed with its hardener and injected into the optic mounting joints during its actual application. The curing reaction occurs initially and then the ageing process starts. Without accurate knowledge of the cure time required for this epoxy and without refreshing to establish its time zero, it is difficult to specify the ageing time for this epoxy in its application. Since some amount of time would be needed to cure this epoxy, predictions based on the ageing theory would provide a conservative estimate if the ageing process is assumed to start immediately after the epoxy is made. In *Figure 8*, the calculated tensile creep curve and experimentally determined creep strains for a 6-day old Hysol 9313 epoxy film without refreshing are compared. Calculations were done by assuming a 6-day age for the sample. Again, ageing predictions are conservative but illustrate the creep behaviour of this epoxy.

The loading and unloading profile for the shear creep experiment of the adhesive lap joints is shown in *Figure 9*. The shear stress used in this experiment was 1.7 MPa, and was assumed to be in the linear viscoelastic region (remember that the upper limit for linear viscoelastic behaviour of Hysol 9313 epoxy in tension is 4.8 MPa). To calculate the instantaneous creep strains after load removal at specified time, the Boltzmann superposition principle[7] is employed which states that resultant strains from independent stress increments are additive and can be expressed as

$$\gamma(t) = \sum_i \tau_i J(t - u_i) \qquad (10)$$

where γ is the shear strain, τ_i is the increment of the applied stress which is a derivative of $\tau(t)$ for a continuous stress application, and u_i is the time when discrete stress increment i is applied. Since the unloading time interval, less than 10 min, during the shear creep experiment is much smaller than the loading time, minimum of 7 days, the shear strains measured after unloading can be obtained simply by

$$\gamma(t) = \tau_0(J(t) - J(0)) \qquad (11)$$

where τ_0 is the shear stress used in the experiment.

Long-term shear creep strains of Hysol 9313 epoxy in the lap joints after it was cured and aged for 5 days were measured and compared with calculations based on a 6-h and on a 5-day ageing time in *Figure 10*. Since the actual

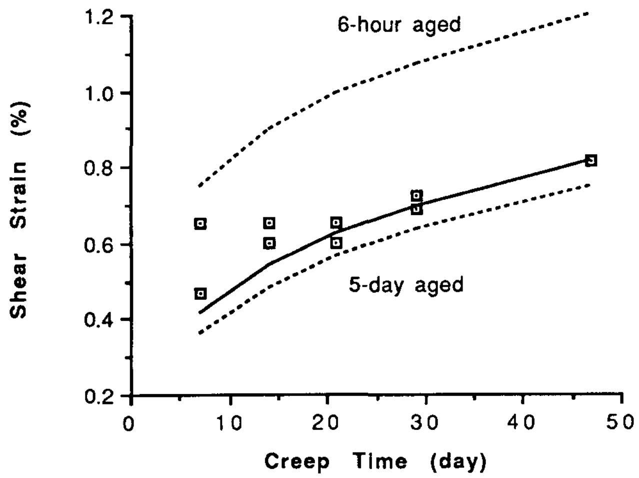

Figure 10 Shear creep strains of the Hysol 9313 epoxy adhesive aged and cured for 5 days without refreshing: open squares, data; solid curve, prediction based on an age of 80 h; dotted curves, upper and lower bounds calculated based on ageing times of 6 h and 5 days, respectively

cure time is not known, a 5-day ageing time was assumed if the epoxy joints were cured instantaneously after the mixing and injection, whereas a 6-h ageing time was used when 5 days are needed to cure this epoxy. A 6-h ageing time, rather than the 0-h ageing time, was applied for establishing the upper bound for the long-term creep behaviour since it is this ageing time that the only available momentary curve is based on. As shown in *Figure 10*, experimental data of the shear creep strains of these joints are clearly bracketed by the calculations based on a 6-h and on a 5-day ageing time. By assuming that the ageing process of the Hysol 9313 epoxy commences only after it is fully cured, one can also try to fit the experimental data to determine the approximate ageing time for these joints. As indicated in *Figure 10*, calculations of the creep strains for a 80-h aged epoxy sample reproduce the experimental results quite well. This suggests a 40-h cure time for this epoxy at room temperature which is in agreement with a previous finding[13].

LONG-TERM SHEAR CREEP PREDICTION

The anticipated loading profile for these adhesive joints using Hysol 9313 epoxy in the X-ray space telescope during its earth storage has been determined to be a 69 kPa shear stress for 2 months followed by a 207 kPa shear stress for 3 years after these joints have been aged and cured for 5 days. Again, by combining the ageing theory with the Boltzmann superposition principle, the resultant shear strains of these joints after unloading can be determined. It was found that the residual shear strain of these joints would be 0.2366% immediately after unloading (or launch of the telescope into space) and be further reduced to 0.1516% 1 month after the launch and to 0.1318% 2 months after the telescope was launched into orbit. The age of these adhesive joints was assumed to be 80 h. Based on the requirement for the optical assembly alignment, the shear strains of these joints cannot exceed 0.1%. Therefore, alternative earth storage methods for the telescope to reduce the creep stresses exerting on these joints must be explored.

CONCLUSION

The ageing effective-time theory was found to be adequate to predict the long-term tensile and shear creep behaviour of Hysol 9313 epoxy adhesive aged for various times. By fitting the experimental creep data of Hysol 9313 epoxy aged and cured for a fixed time without refreshing, it was also found that about 40 h would be needed to fully cure this epoxy at room temperature. However, the determination of the cure time assumed that the ageing process only commences after the cure is completed.

Hysol 9313 epoxy adhesive will be used in optic mounting joints of a space telescope. During the extended period of its earth storage, these joints will be loaded and must be dimensionally stable. Based on the anticipated loading profile for these joints, it was found the residual shear strains of these joints 2 months after unloading, or after the launch of the telescope into space, would be 0.1318%, and greater than the 0.1% strain allowed. Therefore, alternative methods for earth storage of the telescope to reduce the creep stresses exerted on these joints are recommended.

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