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Application of a stress-corrosion-cracking model to an analysis of the durability of glass/epoxy composites in wet environments

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Abstract

A stress-corrosion-cracking (S.C.C.) model has been applied to an analysis of the flexural fatigue behaviour of water-aged unidirectional glass/epoxy composites. The approach has been restricted to the initial stages of the fatigue life, i.e. when the damage consists mainly in the accumulation of broken glass fibres at the microscopic level. The fatigue behaviour of the aged material has been investigated at different strain levels, frequencies and strain ratios. The results demonstrate that the stiffness loss exhibits some of the main characteristic features which can be deduced from the delayed failure of a statistical population of glass fibres by a S.C.C. mechanism. This approach was supported by microscope observations which revealed that, within the investigated time range, the stiffness loss is proportional to the density of broken fibres in the vicinity of the loading point.

Keywords: A. Glass fibres; B. Fatigue; Glass/epoxy

1. Introduction

It is widely acknowledged that the prediction of the durability of composite systems under mechanical and environmental loading is greatly complicated by the occurrence of several interacting physico-chemical and mechanical degradation mechanisms. In the context of unidirectional glass-reinforced polymer composites, it has, however, been demonstrated that the fatigue life of the material in a wet environment is mainly dependent upon the activation of a major damage process, namely the delayed failure of the moisture sensitive fibres within the aged matrix [1–4]. The latter is generally attributed to the hydrolytic nucleation of flaws on the fibres surface and/or the enhancement of the sub-critical growth of the glass surface defects. At the macroscopic scale, these processes can result in a drastic reduction in the fatigue life of the aged composites [5,6].

Although the stress-corrosion behaviour of bulk and fibrous glasses has been extensively studied [7–11], the extension of the corresponding theories to the prediction of the fatigue behaviour of aged glass/epoxy composites has been the object of a limited number of investigations. The latter were essentially devoted to the effects of stress-corrosion-cracking (S.C.C.) upon macroscopic crack propagation within corrosive environments, i.e. in conditions where the glass fibres were directly exposed to the environment during a significant part of the composite lifetime.

The present investigation was focused on the analysis of the S.C.C. processes which occur during the initial stages of the fatigue life, i.e. when most of the damage consists in the accumulation of fibres failures at the microscopic scale. The importance of such processes on the subsequent development of a macroscopic damage and the associated fatigue failures has been largely demonstrated [1,12,13]. In a previous micro-mechanical investigation [14], we have shown that, during the initial stages of microscopic damage accumulation, the delayed failures of the glass fibres within the uncracked composite matrix obeyed a typical S.C.C. behaviour. The corresponding model was derived from a combination of the Weibull statistical distribution of the fibres strength with a classical power law expression for the

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sub-critical crack growth rate. In the context of this study, it was attempted to extend this theory to the prediction of the initial stiffness losses which occur within a composite under static and cyclic fatigue conditions, at various frequencies and stress ratio. The approach is based on the establishment of an empirical linear relationship between the delayed fibres failures processes and the macroscopic stiffness loss, which was derived from in situ microscope observation of the aged composite.

2. Experimental details

2.1. Materials

The composite material under investigation was an unidirectional glass/epoxy composite. The polymer matrix was based upon a Bisphenol-A epoxy prepolymer (DGEBA) crosslinked using an anhydride hardener. ECR glass fibres (Owens Corning Fibre Glass) have been used as a reinforcement. Curved composite beams corresponding to the industrial application have been elaborated using a filament winding process. The specimens had a 10×5 mm^2 rectangular cross-section and their radius of curvature was ca. 700 mm. The average fibres volume fraction was 55 vol.%.

In addition to the curved beams, parallelepipedic flat specimens have been used in order to perform specific in situ microscope observation of the damage development within the composite. For that purpose, 2-mm thick composite plates have been elaborated using an improved filament winding technique which ensured a low void fraction (less than 0.5 vol.%). The low thickness of the plates and the good quality of the impregnation process allowed to detect optically the failures of the glass fibres at the micrometer scale (see below), which was not possible with the thick curved beams. The composite plates have been manufactured using Advantex® E glass fibres (Owens Corning) and a DGEBA/anhydride matrix cured 2 h at 80 °C followed by an hour at 140 °C. The fibre fraction was 57 vol.%. 100 mm$\times$10 mm$\times$2 mm^3 specimens were cut from the plates for the flexural tests.

2.2. Three-point bending tests

The fatigue properties of the curved composite beams have been determined under a three-point bending condition by means of an hydraulic fatigue machine which operated at frequencies between 0.5 and 5 Hz. A span to depth ratio of 26 ensured that the shear effects were minimised. The experiments were performed at imposed deflection using strain ratios, $R=\varepsilon_{\min}/\varepsilon_{\max}$, which ranged from 0.7 to 1. During the tests, the relative stiffness loss was continuously monitored from the measurement of the maximum load. A water bath allowed to perform the fatigue experiments in immersion at constant temperature, in order to avoid water desorption from the aged composite specimens during fatigue cycling.

In addition, flexural tests have been carried out using the flat composite coupons and a specific three point bending device which was equipped with an optical microscope. This device, which is fully described elsewhere [6,15], allowed to locate and to quantify the broken fibres within a restricted composite volume located on the tensile side of the specimen and beneath the loading nose. The experiments have been repeated under monotonic and relaxation conditions.

3. Description of the stress corrosion model

The delayed failure of glass fibres within an aged epoxy composite is assumed to involve the sub-critical growth of cracks from pre-existing fibres surface defects. A wide amount of experimental evidence has been accumulated to demonstrate that the mode I sub-critical crack growth rate, v, within glasses is related to the stress intensity factor, K_{I}, by means of the following power law expression:

$$v=\frac{\mathrm{d}a}{\mathrm{d}t}=AK_{\mathrm{I}}^{n}, \quad (1)$$

with

$$K_{\mathrm{I}}=Y\sigma\sqrt{a}, \quad (2)$$

where a is the crack length, σ is the applied stress and Y is a shape factor close to $\sqrt{\pi}$. A and n are to parameters which can be considered to be constant in a given physico-chemical environment.

According to Eq. (1), the time to failure, t_{f}, of a glass fibre under a given stress loading, $\sigma(t)$, can be expressed as follows:

$$\int_{0}^{t_{\mathrm{f}}}\sigma(t)^{n}\mathrm{d}t=\frac{2K_{\mathrm{IC}}^{2-n}}{AY^{2}(n-2)}\sigma_{i}^{n-2} \quad (3)$$

where σ_i is the strength of the fibre in an inert environment, i.e. without stress corrosion cracking. Under a sinusoidal stress loading, the integral term in Eq. (3) can be written explicitly:

$$\int_{0}^{t_{\mathrm{f}}}\left[\sigma_{\max}\left(\frac{1+R}{2}+\frac{1-R}{2}\sin(2\pi\nu t)\right)\right]^{n}\mathrm{d}t=\frac{2K_{\mathrm{IC}}^{2-n}}{AY^{2}(n-2)}\sigma_{i}^{n-2}, \quad (4)$$

where $\sigma_{\max}$ is the maximum applied stress, ν is the frequency and R is the stress ratio. The first term of this equation corresponds to the integral of a periodic function within a known interval. For sufficiently high values of t_f (i.e. $t_f \gg 1/\nu$), it can easily be shown that the integral term is proportional to t_f:

$$\lambda t_f = \frac{2K_{IC}^{2-n}}{AY^2(n-2)}\sigma_i^{n-2}\sigma_{max}^{-n}, \tag{5}$$

where λ is a numerical constant less than unity which depends upon R and n. Under a relaxation condition, i.e. for $R=1$, $\lambda=1$. For other stress ratios, λ can easily be numerically evaluated. Eq. (5) can be simplified as follows:

$$\lambda t_f = C\sigma_i^{n-2}\sigma_{max}^{-n}, \tag{6}$$

with

$$C = \frac{2K_{IC}^{2-n}}{AY^2(n-2)}.$$

These calculations demonstrate that, if the S.C.C. model is appropriate, the lifetime of a glass fibre should be a decreasing function of its initial strength. If a statistical population of fibre defects is now considered, it is therefore possible to associate the statistical distribution of the fibres strength, σ_i, with the lifetimes distribution [16]. Previous investigations [9,17] have firmly established that the strength distribution of E-glass fibres can adequately be described using a Weibull [18] expression:

$$P_s(\sigma_i) = e^{(-(\sigma_i/\sigma_0)^m)} \tag{7}$$

where m is the Weibull modulus and σ_0 is a scale factor including the gauge length of the fibre. Substituting Eq. (5) into Eq. (7), it comes:

$$P_s(t) = e^{\left(-\left(\frac{\lambda^{1/n-2}t^{1/n-2}\sigma_{max}^{n/n-2}}{c^{1/n-2}\sigma_0}\right)^m\right)} \tag{8}$$

The above expression can be linearised as follows:

$$\mathrm{Log}(\ln(1/P_s(t))) = \frac{m}{n-2}\mathrm{Log}t + \frac{mn}{n-2}\mathrm{Log}\sigma_{max} + \frac{m}{n-2}\mathrm{Log}\lambda + \text{constant} \tag{9}$$

Accordingly, a log–log plot of $\ln(1/P_s)$ against time should be linear. In a previous micro-mechanical investigation [15], we have demonstrated that such an approach can satisfactorily be used to describe the delayed failure of E-glass fibres within an elementary volume of aged composite under a relaxation condition. During the initial stages of damage accumulation, i.e. before the nucleation of cracks or delamination, it was observed that the effects of stress transfer upon the delayed fibres failures can be neglected. Accordingly, the observed fibres failure behaviour within the elementary volume was very close to the theoretical prediction for an equivalent fibres bundle under S.C.C. conditions.

Provided that a relationship can be established between the microscopic damage and the resulting macroscopic behaviour, a similar S.C.C. approach could be extended to the prediction of the composite stiffness loss during the first stages of fatigue life. In the following section, the occurrence of such a micro/macro relationship will be established empirically from microscopic observations. On this basis, the macroscopic stiffness loss will be assimilated to the fibres probability of survival and the above S.C.C. formalism will be subsequently applied to static and cyclic fatigue data.

4. Experimental results and discussion

4.1. Micro/macro empirical relationship

The relationship between the microscopic damage and the stiffness loss was investigated on the basis of a micro-mechanical analysis of the composite material under monotonic and relaxation conditions. From microscope observations of three-point bending specimens, the number of broken fibres within a restricted area (1.5 mm×7 mm^2) located on the tensile side of the specimen and beneath the loading nose was quantified. Due to the heterogeneous nature of the flexural loading, a significant part of the initial damage was concentrated within this critical area. These observations have been repeated during the initial stages of damage development, i.e. before the appearance of transverse matrix cracks within the area under investigation. In addition to the measurements of the density of broken fibres, the stiffness loss was also monitored.

These experiments demonstrated (Fig. 1) that the stiffness loss was linearly related to the measured number of broken fibres, irrespective to the nature of the loading (monotonic or relaxation). Although a theoretical analysis of this experimental relationship is beyond the scope of this paper, it demonstrates that the macroscopic stiffness loss is linearly related to the microscopic damage occurring within the elementary composite volume under investigation. This property was subsequently used to express the stiffness loss as a function of the probability of survival, P_s, of the glass fibres. P_s can be written as the ratio of the number of the broken fibres, N_f, to the total number of fibres, N_t, within the elementary composite volume:

$$P_s = 1 - \frac{N_f}{N_t} \tag{10}$$

According to the microscope observations, the relative stiffness loss, S/S_0 can be written as follows:

$$\frac{S}{S_0} = 1 - \alpha(1 - P_s)N_t = (1 - \alpha N_t) + \alpha P_s N_t \tag{11}$$

where S_0 is the initial stiffness and α is the slope of the S/S_0 vs N_f empirical relationship. By substituting Eq. (8) into Eq. (11), the following expression can be derived:

$$\frac{S}{S_0}(t) = (1 - \alpha N_t) + \alpha \exp\left[-Kt^{m/n-2}\sigma_{\max}^{mn/n-2}\lambda^{m/n-2}\right]N_t \tag{12}$$

where K is a scaling constant. An approximate expression for Eq. (12) can be written as follows:

$$\frac{S}{S_0}(t) \approx \exp\left[-K^* t^{m/n-2}\sigma_{\max}^{mn/n-2}\lambda^{m/n-2}\right] \tag{13}$$

where K^* is a constant depending upon K and α. On the basis of the empirical micro/macro relationship, it comes therefore that the dependence of the relative stiffness upon the applied maximum stress, the λ factor and time should theoretically follow the same kind of theoretical expressions than P_s in a fibres bundle subjected to S.C.C. [cf. Eq. (9)]. The only difference will be in the various scaling factors introduced in the analysis, the exponents associated to the variables t, $\sigma_{\max}$ and λ being unchanged in the theoretical expressions.

4.2. Static fatigue behaviour ($R = 1$)

Relaxation experiments have been carried out using the curved composite specimens after water conditioning for 20 days at 20 °C. From a preliminary study of the water sorption kinetics It was verified that these ageing conditions ensured the saturation of the superficial composite layers (about 350 μm) which were affected by the macroscopic damage up to a 10% stiffness loss. It was also found that the hydrolysis of the anhydride cured epoxy matrix was greatly reduced for the considered ageing time and temperature. This precaution allowed to avoid the heterogeneous ageing state which could result from the combination of a chemical degradation with the transient water diffusion steps. In terms of ageing, the superficial composite layers where most of the initial damage is concentrated can therefore be assumed to be homogeneous. This consideration simplifies considerably the application of the S.C.C. model as the stress corrosion parameters, A and n, may be regarded as constants through the damaged thickness.

The analysis of the stiffness loss curves was restricted to the initial stages of fatigue life (up to about 5% stiffness loss), i.e. before the development of a significant macroscopic damage. Under such conditions, the 'bundle' approximation may be assumed to remain valid and the corresponding S.C.C. expressions were applied to the analysis of stiffness loss. In Fig. 2, it can be seen that $\ln(S_0/S)$ is linearly related to the loading time in a log–log plot, which is consistent with the prediction of Eq. (13). Whatever the applied strain level, the slope of regression lines is roughly constant and yield a value of $m/n-2 = 0.4 \pm 0.05$. According to Eq. (13), the shift of the different curves along the stiffness loss axis should be linearly related to the logarithm of the applied strain. This can be verified in Fig. 3, where the slope of the regression line yield a value close to 5 for the ratio $mn/n-2$. Combining these two later numerical results, the following values can be extracted for the Weibull modulus and the static fatigue parameter: $m = 4.1 \pm 0.1$ and $n = 12.6 \pm 1.5$.

4.3. Cyclic fatigue behaviour ($R = 1$)

In the context of a S.C.C. model, the delayed failure of the fibres should be independent on the loading frequency. In other terms, this means that the fibres life-

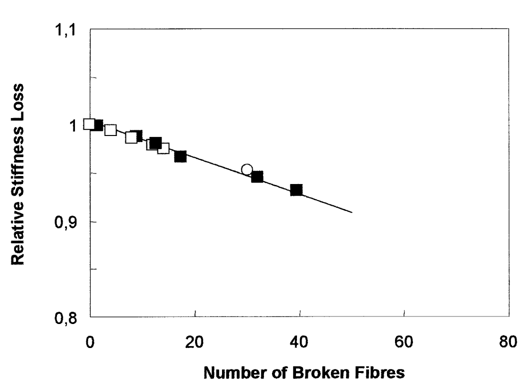

Fig. 1. Relative stiffness loss, S/S_0, against the number of broken fibres within the composite elementary volume under investigation (flat composite specimens). (□) $R=1$, $\varepsilon_{\max}=1.55\%$; (○) $R=1$, $\varepsilon_{\max}=2.0\%$; (■) monotonic loading.

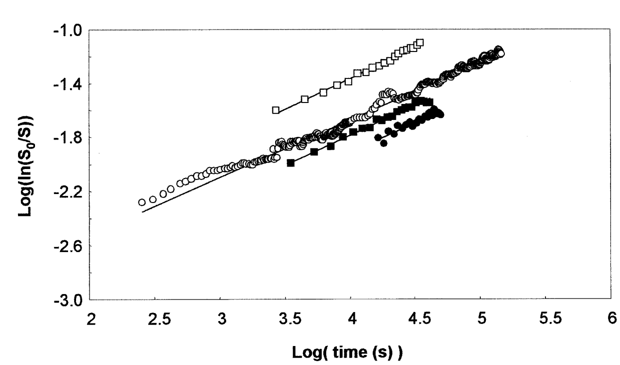

Fig. 2. Log–log plot of the logarithm of the reverse of the relative stiffness loss against time under relaxation conditions (curved composite beams; $R=1$). (●) $\varepsilon_{\max}=1.2\%$; (■) $\varepsilon_{\max}=1.4\%$; (○) $\varepsilon_{\max}=1.6\%$; (□) $\varepsilon_{\max}=1.9\%$.

times can be deduced from the integration of the subcritical crack growth rate over the loading period, irrespective of the loading rate. In order to verify the validity of this point, the stiffness loss curves obtained for aged curved composite specimens have been reported as a function of time and the number of cycles in Fig. 4. As the frequency is increased, a shift of the stiffness loss curve to increasing numbers of cycles can clearly be observed (Fig. 4a). For a given number of cycles, more time is spent at a given strain stress level at low frequency than at high frequency. As a result, the fibres surface defects have more time to grow during each loading cycle and the total number of cycles to failure is reduced.

Accordingly, the different stiffness loss curves can be reduced, within the experimental scatter, to a single curve if a time scale is considered (Fig. 4b). This result demonstrates that the relevant parameter regarding the frequency effect is the time spent at a given stress level, in accordance with the hypothesis of a fatigue response dominated by S.C.C. mechanisms. Within the frequency range under investigation, it can therefore be deduced that the dissipative processes associated to matrix and interface viscoelastic losses do not induce any significant changes in the delayed fibres fracture processes observed during the microscopic damage stages. This conclusion do not obviously hold for the macroscopic damage steps, i.e. when energy dissipation within the cracked areas can induce a substantial heating which can in turn affect the temperature dependent S.C.C. processes.

In Fig. 5, the logarithm of the reverse of the relative stiffness loss has been reported against time in a log–log plot for two different R values (0.7 and 1). In both cases, a linear relationship is observed, the value of the slope being independent on the strain ratio. This observation is consistent with the S.C.C. model which predicts that a change in the strain ratio must only induce a shift of the Log(ln(S_0/S) vs log(t) regression lines by a factor $m/(n-2)\log\lambda$ along the stiffness axis. The value of λ can be numerically computed from the first term of Eq. (4), but it should be emphasised that it is extremely sensitive to the estimate of n. A least-square fit procedure provided a value of $n = 14$ using the experimental value of $m/(n-2)\log\lambda$ and the above determined Weibull modulus. It can be noted that this result is consistent with the previous estimate derived from the static fatigue tests ($n = 12.6$), which further supports the validity of the S.C.C. approach.

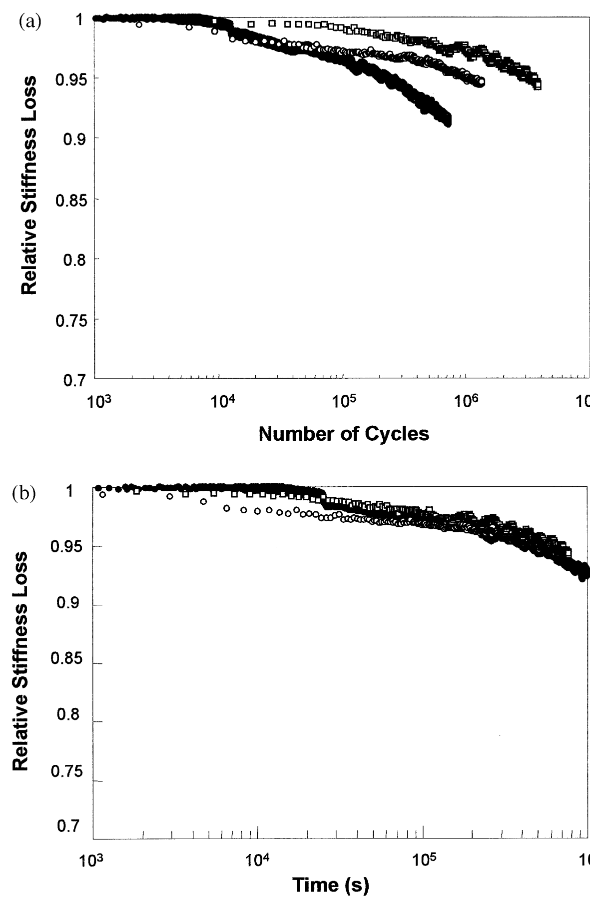

Fig. 4. Relative stiffness loss of the aged curved composite beams against (a) the number of cycles and (b) time. $R = 0.7$; (●) 0.5 Hz; (○) 2 Hz; (□) 5 Hz.

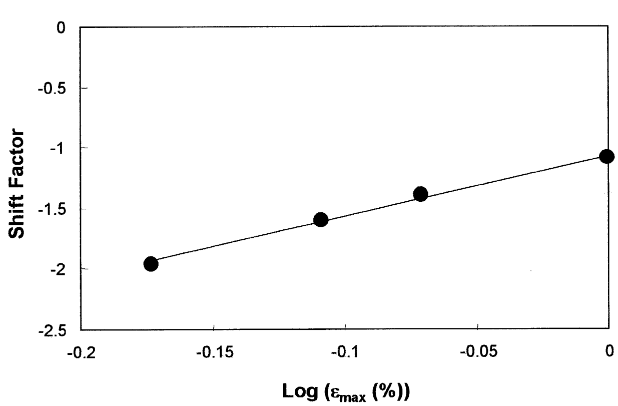

Fig. 3. Shift factor of the Log(ln(S_0/S) vs log(t) regression lines as a function of the applied strain level [$R = 1$; Log(t) = 4.2].

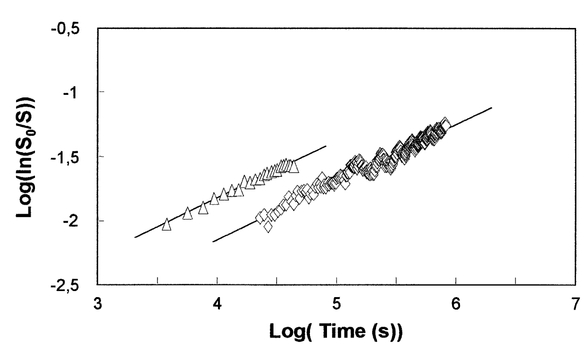

Fig. 5. Log–log plot of the logarithm of the reverse of the relative stiffness loss, S/S_0, against time under fatigue conditions (curved composite beams; $\varepsilon_{max} = 1.4\%$). (△) $R = 1$; (◇) $R = 0.7$.

5. Conclusion

The static and cyclic fatigue data of an aged unidirectional glass/epoxy composite have been analysed within the frame of a S.C.C. model. The analysis was restricted to the microscopic stages of damage development, i.e. when most of the stiffness loss can be attributed to the delayed fracture of the glass fibres. Under these conditions, it was demonstrated that the stiffness loss time dependence exhibits some of the main characteristics features which can be expected from a damage behaviour dominated by S.C.C. processes. The analytical expressions for the S.C.C. model have been derived by considering that the macroscopic stiffness loss is linearly related to the accumulation of broken fibres within an elementary volume of the composite. This assumption has been validated from microscopic observation of the fibre failure processes within the aged composite under both monotonic and relaxation conditions. If the broken fibres are supposed to act as non interactive defects, the damage behaviour of the unidirectional composite can be assimilated to the statistical response of a fibre bundle under a tensile loading. The corresponding expression for the stiffness loss have been derived from a combination of the statistical distribution of fibres strength and a power law expression for the sub-critical crack growth rates. This model has been satisfactorily applied to fatigue tests carried out at different frequencies and strain ratio. For a given strain level, it has been demonstrated that the time dependence of the stiffness loss can be described using a single parameter equal to $m/(n-2)$, where m and n characterise, respectively, the statistical distribution of the fibres surface defects and the sub-critical crack growth rates of these defects within a given physico-chemical environment. The S.C.C. model developed also integrates explicitly the effects of frequency and strain ratio. From these first results, it may therefore be envisaged to incorporate into the approach the effects of the ageing temperature and the water concentration within the loaded composite areas.

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