Crack Growth of Structural Adhesive Joints in Humid Environments

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The adhesive fracture energy, G_c , of aluminium-alloy and steel joints, bonded with a rubber-toughened epoxy adhesive, has been measured using monotonically-loaded tests. Such tests have been conducted at different levels of relative humidity and two surface pretreatments have been employed for the substrates prior to bonding: a simple grit-blast and degrease ('GBD') pretreatment or a silane primer ('GBS') pretreatment. When G_c was plotted against the crack velocity, three regions of fracture behaviour could be distinguished. At low rates of displacement the crack grew in a stable manner, visually along the interface, and relatively low crack velocities could be readily measured. This was termed 'Region I' and here the value of the adhesive fracture energy was relatively low and decreased steadily as the relative humidity was increased. On the other hand, at relatively high rates of displacement the crack grew in a stick-slip manner mainly cohesively in the adhesive layer at approximately 20 km/minute. This was termed 'Region III', and here the value of G_c was relatively high and independent of the relative humidity. In this region the crack was considered to grow faster than the water molecules were able to reach the crack tip, which explains the independence of G_c upon the test environment. In between 'Region I' and 'Region III', a transition region was observed which was designated as 'Region II'. The major effect of the 'GBS' pretreatment, compared to the 'GBD' pretreatment, was to increase the value of G_c both in 'Regions I and III', although the presence of the silane primer had the greater effect in 'Region I'.

Keywords: Accelerated testing, Durability, Environmental attack, Fracture mechanics, Structural adhesives

INTRODUCTION

The use of structural adhesives offers many advantages when compared with other more traditional joining methods such as welding, riveting and mechanical fasteners [1]. However, as with any technology, there are some potential disadvantages associated with the use of adhesives. In particular, adhesive joints may suffer environmental attack when exposed to relatively hot and humid environments. The development of a sound accelerated-ageing test method to assess the susceptibility of an adhesive 'system' (i.e. the adhesive/primer (if any)/substrate and substrate surface pretreatment in combination) to such attack would represent a significant advance, especially if such tests could be completed in a relatively short time-scale [2].

The aim of a sound and meaningful accelerated ageing test must be to accelerate the mechanisms of attack seen during the service-life of the bonded joint, and not to induce misleading and irrelevant mechanisms. For example, it is well known that to accelerate the rate of environmental attack it is not possible simply to raise the temperature of the environment, since unrealistically high test temperatures will indeed change the mechanisms of attack. One method of accelerating the rate of attack which has recently been explored in detail by Kinloch and co-workers (e.g. [3]) has been the use of cyclic-fatigue tests, using a fracture-mechanics approach, conducted in aqueous and salt-water environments at relatively low temperatures, i.e. at temperatures less than about 30°C. This has yielded a test method which gives a quantitative 'ranking' order for the durability of adhesive systems and, furthermore, the results may be combined with a finite-element analysis of a bonded component or structure to give an estimate of its fatigue life in the environment of interest [4]. However, the cyclic-fatigue tests require expensive test equipment and are often time-consuming to undertake, typically involving continued use of the fatigue test equipment for several months.

The main aim of the present work is to study the use of monotonically-loaded tests as a method for assessing the joint durability. Fracture-mechanics tests have been conducted, using a tapered double-cantilever beam (TDCB) specimen and the essence of the test procedure is the examination of the failure behaviour over a wide range of rates of displacement. In order to assess joint durability, tests have been carried out at various levels of relative humidity. Further, two different substrates, an aluminium-alloy and a steel, have been employed, along with either (a) a grit-blast and degrease ('GBD') pretreatment or (b) a silane primer ('GBS') pretreatment prior to bonding. The adhesive employed was a commercially-available rubber-toughened epoxy. In addition, the loci of failure have been assessed using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) to help identify the mechanisms of failure.

EXPERIMENTAL

Materials and Surface Pretreatments

To determine the adhesive fracture energy, G_c , an adhesively-bonded tapered double-cantilever beam (TDCB) specimen was employed, see Figure 1. The adhesive employed was a hot-cured rubber-toughened epoxy-paste adhesive that was based upon a diglycidyl ether of bisphenol-A epoxy cured with dicyandiamide. The substrates were manufactured from either steel (Grade BS 970 070M55) or aluminium alloy (Grade BS 7075 (unclad)). Their compositions are given in Tables 1 and 2 respectively.

For both types of substrate, two different surface pretreatments prior to bonding were employed. The first surface pretreatment consisted of degreasing the substrates in a liquid bath of boiling 1,1,1-trichloroethylene which was followed by grit-blasting using 60 μ m-78 μ m mesh alumina particles. The substrates were then vapour degreased above a bath of boiling trichloroethylene and allowed to cool to room temperature. This pretreatment is denoted as the 'GBD' pretreatment. In the second pretreatment employed, the previous grit-blasting and

degreasing procedures were first undertaken which was then followed by the application of a silane-based primer, to give the 'GBS' pretreatment. A 1%w/w solution of γ -glycidoxypropyltrimethoxy silane (GPS) solution, using a 90:10 by weight of ethanol:deionised water mixture, was prepared and its pH was adjusted to approximately five by the addition of acetic acid. This solution was stirred for 60 minutes to allow complete hydrolysis of the GPS to occur. The solution was then painted onto the surfaces of the substrates that were to be bonded, using a small brush. The substrates were drained onto a tissue and the GPS layer was cured at 93°C for 60 minutes. This procedure is very similar to that recommended by Digby and Shaw [5].

Joint Preparation

At the end of the substrates where the load was to be applied, a thin layer of silicon-based release agent was painted over a length of about 90 mm of the substrate surface to act as a precrack. Applying the release agent with a 'chevron-shaped' end was found to give a precrack that tended to promote stable failure, as opposed to unstable failure, as described below.

The adhesive was degassed under vacuum for a short time at 80°C and was then applied to the faces of the substrates to be bonded using a spatula. The thickness of the adhesive layer was 0.4 mm and was controlled via thin steel wires inserted into either end of the TDCB specimen. The adhesive layer was cured by heating the adhesive for two hours at 130°C, as monitored via an *in-situ* thermocouple, and the joints were then cooled in the oven overnight.

Fracture-Mechanics Tests

Tests were conducted at a constant rate of displacement, $\dot{y}$, of the crosshead of the tensile testing machine and the crack length was monitored as a function of time using a video camera. The rate of displacement used for these monotonically-loaded tests was varied between 0.005 to 10 mm/minute. The tests were conducted at $21 \pm 2^\circ\text{C}$ in an environmental chamber which permitted a

wide range of relative humidities to be employed. The relative humidity, RH, in the environmental chamber was controlled using various salt solutions [6] and was measured using a hair hygrometer. The experimentally measured RH values were in close agreement with the expected RH values, see Table 3.

The value of the adhesive fracture energy, G_c , was determined using the expression:

$$G_c = \frac{P_c^2}{2b} \cdot \frac{dC}{da} \quad (1)$$

where P_c is the critical load for crack growth as discussed below, a is the crack length, b is the width of the specimen and C is the compliance of the specimen ($C = y/P$; where y is the displacement and P is the load).

Examination of the Fracture Surfaces

In the present work, a 'JEOL JSM 5300' scanning electron microscope was used to examine the surfaces of the fractured joints. As it is not always possible to determine with certainty the locus of failure using a scanning electron microscope (for example, a very thin layer of adhesive or oxide would not be detectable), X-ray photoelectron spectroscopy was also employed. The apparatus used in the present study was a 'VG Scientific Sigma Probe' spectrometer. Survey spectra were acquired with a pass energy of 100 eV and the high resolution spectra with a pass energy of 50 eV. Quantitative surface chemical analyses and peak fitting were undertaken on the high resolution spectra using the software provided by the manufacturer.

CRACK PROPAGATION STUDIES AT 55%RH

Introduction

Before considering the effects of the relative humidity of the test environment on the bonded joints in detail, it is useful to consider the general form of the relationships which were obtained between the adhesive fracture energy, G_c , and the corresponding crack velocity, $\dot{a}$. These are shown in Figures 2 and 3 for the aluminium-alloy and the steel joints that were tested at 55% relative humidity, RH, (which was the ambient RH in the air-conditioned laboratory) where the data are plotted in the form of $\log_{10} G_c$ versus $\log_{10} \dot{a}$. In these figures, results for the two pretreatments (i.e. the 'GBD' and 'GBS') are given for both types of joints. Three different regions of crack growth behaviour may be identified and these have been labelled 'Region I', 'Region II' and 'Region III', following the classic studies of Wiederhorn [7] on crack growth in glass. 'Region I' occurred at relatively low rates of displacement and the fracture was stable in nature and was visually interfacial, whereas 'Region III' was observed at relatively high rates of displacement and the fracture was unstable and essentially cohesive in the adhesive layer. 'Region II' was the transition region between 'Region I' and 'Region III'.

'Region I' Behaviour

This region was observed at relatively low rates of displacement, $\dot{y}$, and the crack propagated in a stable manner visually along the substrate/adhesive interface. During crack growth in 'Region I', the load was essentially constant at a value of P_c , and a typical load, P , versus displacement, y , curve associated with stable crack growth is shown in Figure 4. The average value of the load, P_c , for crack growth was employed to determine the value of the adhesive fracture energy, G_c , as indicated above (see Equation (1)).

For a test at a given rate of displacement, $\dot{y}$, the relationship between crack length, a , and time, t , was linear as shown in Figure 5 which leads, of course, to a constant value of the crack velocity, $\dot{a}$, throughout the test, as the crack propagates down the length of the TDCB specimen. The higher the rate of displacement employed within ‘Region I’, then the higher the resulting crack velocity, as illustrated in Figure 6. Thus, for a given joint system, the crack velocity, $\dot{a}$, is controlled by the rate of displacement, $\dot{y}$, of the crosshead. A theoretical relationship between $\dot{a}$ and $\dot{y}$ may be derived using simple beam theory [8], assuming that the load, P_c , at fracture remains constant for a given TDCB test. Thus, the derivative of the compliance is given by:

$$\dot{C} = \frac{1}{P_c} \cdot \dot{y} \quad (2)$$

Rearranging Equation (1) using Equation (2) yields:

$$\dot{a} = \frac{P_c}{2bG_c} \cdot \dot{y} \quad (3)$$

The values of the crack velocity, $\dot{a}$, versus the applied rate of displacement, $\dot{y}$, of the crosshead from both the experiments and Equation (3) are shown in Figures 6a and b for the aluminium-alloy and the steel joints, respectively. The agreement between the experimental and the theoretical values is relatively good.

As may be seen from Figures 2 and 3, for the aluminium-alloy and steel joints respectively, in ‘Region I’ the value of G_c is not greatly dependent upon the value of the corresponding crack velocity, $\dot{a}$. The locus of joint failure associated with this type of stable

crack growth in 'Region I' was always visually interfacial between the adhesive and the substrate. In Figures 2 and 3, the final point shown for the G_c versus $\dot{a}$ relationships (i.e. at the highest value of $\dot{a}$) for 'Region I' behaviour represents the fastest crack velocity that could be recorded. Indeed, increasing the rate of displacement of the test above this value by a small increment led to the observation of 'Region II' or 'Region III' behaviour.

'Region III' Behaviour

'Region III' behaviour was observed at relatively high rates of displacement, $\dot{y}$. Here the crack grew in an unstable, stick-slip manner with the crack growing in an uncontrolled way, at a relatively fast velocity, and then arresting. These observations are clearly in direct contrast to the results from 'Region I'. Furthermore, unlike that found in 'Region I', the locus of joint failure in 'Region III' was always essentially cohesive through the adhesive layer.

This type of unstable crack growth has a significant effect on the associated load, P , versus displacement, y , curve which now had a characteristic saw-tooth appearance, as may be seen from Figure 7. The peak values of the load, P_c , represent the value of the load for the onset of crack growth and the average of these values was used to determine the value of the adhesive fracture energy, G_c , as indicated above. The values of G_c obtained are of the order expected for this type of adhesive [4]. When unstable crack growth was observed the crack propagated at a relatively high velocity, which was too high to be measured using the video camera. However, an approximate value of the crack velocity was estimated from previously published data by Gledhill and Kinloch [9]. They applied a grid of conductive paint to the side of the TDCB specimen and, via the change in electrical resistance of the grid as the crack propagated and ruptured the paint grid, obtained the relationship between G_c and $\dot{a}$ for a similar adhesive system which exhibited unstable crack growth. Using the data of Gledhill and Kinloch, the crack velocity corresponding to the G_c value in 'Region III' for the present tests was about 20 km/minute for both the 'GBD'-

and ‘GBS’-pretreated joints. This value was therefore taken to represent the resulting crack velocity for unstable crack growth in the present studies. This is obviously an approximation, but the absolute value of the crack velocity associated with the unstable crack growth ‘Region III’ has no significant effect on the interpretation of the results obtained in the present study.

Finally, it is noteworthy that Arnott and Kindermann [10] have also studied the effect of a constant rate of displacement on the value of G_c of structural joints. Although they did observe in their experiments what we have termed ‘Region III’ behaviour, such cohesive in the adhesive failure was still associated with stable crack growth

‘Region II’ Behaviour

‘Region II’ is a transition region between ‘Region I’ and ‘Region III’. Two sub-types of ‘Region II’ were identified as explained below, denoted as ‘Region IIa’ and ‘Region IIb’ respectively.

In the transition region ‘Region IIa’ data could be obtained for joints where the values of G_c were intermediate between those recorded in ‘Region I’ and those in ‘Region III’. This behaviour may be seen clearly in Figures 2 and 3 for the ‘GBD’-pretreated aluminium-alloy and steel joints, respectively. In ‘Region IIa’, the locus of joint failure associated with this type of stable crack growth was always visually interfacial between the adhesive and the substrate, as was observed in ‘Region I’.

In ‘Region IIb’ it was not possible to obtain experimental data in the transition region between ‘Region I’ and ‘Region III’, as it was for ‘Region IIa’. Furthermore, in some instances the increase in the value of G_c on going from ‘Region I’ to ‘Region III’ behaviour was relatively low. The regions denoted ‘Regions IIb’ in Figures 2 and 3 for the ‘GBS’-pretreated aluminium-alloy and steel joints, respectively, illustrate both of these aspects for the ‘Region IIb’ behaviour.

Thus, the term ‘Region IIb’ is simply used to represent a change in the type of crack growth, i.e. from stable to stick-slip crack growth, which is always accompanied by a change from visually interfacial to cohesive in the adhesive failure, as the rate of displacement, $\dot{y}$, is steadily increased.

Effect of Substrate

As noted above, the results for the values of G_c as a function of corresponding crack velocity, $\dot{a}$, are shown for the aluminium-alloy and steel joints in Figures 2 and 3, respectively. For the data associated with both ‘Region I’ and ‘Region III’, there is no statistical difference in the values of G_c associated with the aluminium-alloy and steel joints for a given type of surface pretreatment.

Effect of Surface Pretreatment

The effect of the type of surface pretreatment employed is evident in all three regions of the fracture behaviour of these joints, as may be seen from Figures 2 and 3.

In ‘Region I’, the values of G_c for the ‘GBS’-pretreated joints are clearly higher than for the ‘GBD’-pretreated joints for both the aluminium-alloy and the steel substrates, although the locus of failure was visually at, or very close to, the adhesive/substrate interface for all these types of joint. Nevertheless, it is noteworthy that the slope of the G_c versus $\dot{a}$ relationship is not affected by the surface pretreatment employed.

In ‘Region III’, the values of G_c for the ‘GBS’-pretreated joints were again somewhat higher than for the ‘GBD’-pretreated joints, and this was observed for both the aluminium-alloy and the steel joints, even though the locus of failure was essentially cohesive in the adhesive layer in all cases. The values of G_c , considering both types of substrate, were $1010 \text{ J/m}^2 (\pm 100 \text{ J/m}^2)$ and $780 \text{ J/m}^2 (\pm 100 \text{ J/m}^2)$ for the ‘GBS’- and ‘GBD’-pretreated joints, respectively. This

intriguing observation is discussed in more detail below, when the mechanisms of failure are examined.

Finally, considering the onset of ‘Region II’ behaviour, the maximum velocity that could be sustained in ‘Region I’, before the transition to ‘Region III’ behaviour was observed, was far greater for the ‘GBD’-pretreated joints than for the ‘GBS’-pretreated joints. For instance, the maximum velocity measured in ‘Region I’ for the ‘GBD’-pretreated aluminium-alloy joints was 5 mm/minute, whereas for the ‘GBS’-pretreated aluminium-alloy joints it was 1 mm/minute. Thus, the transition ‘Region II’ occurred in the ‘GBD’-pretreated joints at a significantly higher rate of displacement than in the ‘GBS’-pretreated joints.

EFFECT OF RELATIVE HUMIDITY

Introduction

To explore the interactions between the relative humidity and the rate of displacement, firstly the relationships shown above between the adhesive fracture energy, G_c , and the corresponding crack velocity, $\dot{a}$, at 55%RH were studied for the ‘GBD’-pretreated aluminium-alloy joints as a function of the relative humidity. These results are shown in Figure 8.

In ‘Region I’, the slopes of the G_c versus $\dot{a}$ relationships obtained at the different values of RH are essentially the same, although the height of the G_c versus $\dot{a}$ relationship, with respect to the G_c axis, is very dependent upon the value of the relative humidity employed. For example, $G_c \approx 700 \text{ J/m}^2$ at 0%RH but $G_c \approx 300 \text{ J/m}^2$ at 100%RH. It is very noteworthy that there is ‘Region I’ behaviour observed at 0%RH, and it is considered that the use of P_2O_5 would indeed give a 0%RH test environment, see Table 3. This demonstrates that ‘Region I’ behaviour is not solely the result of the presence of water molecules at the crack tip. This observation from the present work is discussed further below.

Considering ‘Region III’, it may be seen that there is no significant effect of the relative humidity on the value of G_c in this region where unstable, stick-slip crack growth is observed. Indeed, since the locus of failure is cohesive in the adhesive and the timescale of the experiment gives relatively little scope for water diffusion and plasticisation of the adhesive, this observation would indeed be expected.

Effect of Relative Humidity and Surface Pretreatment in ‘Region I’

Introduction

From the above results, it is evident that the most pronounced effects of varying the relative humidity are seen in ‘Region I’, when the crack velocity is relatively low and the joints exhibit a visual locus of failure at the adhesive/substrate interface. The effect of relative humidity was therefore explored in detail by selecting a rate of displacement which should essentially lead to ‘Region I’ behaviour, although as will be seen below some ‘Region III’ behaviour was still recorded at the lowest relative humidities. The ‘GBD’-pretreated aluminium-alloy joints were therefore tested at a rate of displacement of 0.02 mm/minute whilst the ‘GBS’-pretreated aluminium-alloy joints were tested at a rate of displacement of 0.005 mm/minute. The resulting average crack velocities were 1.15 ± 0.20 mm/minute and 0.25 ± 0.10 mm/minute for the ‘GBD’- and ‘GBS’-pretreated joints, respectively.

The ‘GBD’-Pretreated Aluminium-Alloy Joints

The results for the ‘GBD’-pretreated aluminium-alloy joints tested at a rate of 0.02 mm/minute are shown in Figure 9 where the value of G_c is given as a function of the measured RH. The straight line plotted through these data represents the best statistical fit via a linear regression analysis to the results which exhibited stable crack growth, i.e. ‘Region I’ behaviour. As may be seen, the vast majority of the joints tested exhibit ‘Region I’ behaviour and there is a clear

dependence of the value of G_c upon the RH, with the value of G_c decreasing steadily as the RH is increased. However, at the lowest values of RH, a few joints exhibited ‘Region III’ behaviour and thus failed cohesively through the adhesive layer with a relatively high value of G_c being recorded.

The ‘GBS’-Pretreated Aluminium-Alloy Joints

The results for the ‘GBS’-pretreated aluminium-alloy joints tested at a rate of 0.005 mm/minute are shown in Figure 10 where the value of G_c is given as a function of the measured RH. Again, the straight line plotted through these data represents the best statistical fit via a linear regression analysis to the results which exhibited ‘Region I’ behaviour. As observed for the ‘GBD’-pretreated joints, the vast majority of the joints tested exhibited ‘Region I’ behaviour and the value of G_c decreases steadily as the RH is increased. However, at the lowest values of RH, the joints consistently exhibited ‘Region III’ behaviour and thus failed cohesively through the adhesive layer with a relatively high value of G_c being recorded.

There are some noticeable differences arising from the effects of the two different surface pretreatments. Firstly, at relatively low values of RH, the transition from ‘Region III’ to ‘Region I’ behaviour is far more marked for the ‘GBS’-pretreated joints than for the ‘GBD’-pretreated joints. Indeed, for the ‘GBS’-pretreated joints one could infer that a critical RH of about 20%RH exists, below which interfacial attack and weakening of the joints does not occur. The concept that a minimum, or critical, concentration of water needs to be present in order for the mechanism of environmental attack to proceed has been previously suggested (e.g. [11, 12]) and obviously is in agreement with the transition currently observed between the ‘Region I’ and the ‘Region III’ behaviour, as discussed in detail below. Secondly, for the ‘GBS’-pretreated joints the levels of G_c are significantly higher for both ‘Region I’ and ‘Region III’ behaviour. This may be readily seen from Figure 11, where the data from Figures 9 and 10 are directly compared. The underlying

mechanisms for this observation are discussed below. (Note: in Figure 11 the slope for the results of G_c versus RH for the ‘GBD’-pretreated joints (see Figure 9) is re-plotted to have the same slope as for the ‘GBS’-pretreated joints (see Figure 10), since this is within the experimental scatter band.)

MECHANISMS OF FAILURE IN ‘REGION I’

Introduction

The above results have led to several interesting observations and highlight the interaction between the rate of displacement, the relative humidity of the test environment and the type of surface pretreatment employed. The mechanisms of failure responsible for these observations will now be considered.

The Relationship Between G_c and $\dot{a}$

From the results shown in Figures 2, 3 and 8 the relationship between G_c versus $\dot{a}$ may be described by a power-law equation of the form:

$$G_c \propto \dot{a}^n \quad (4)$$

where the slope of the relationship is given by the power, n . Furthermore, the value of n clearly is relatively low in value and is independent of the RH, the type of substrate and the surface pretreatment employed.

Previous workers [13-15] have found a similar relationship for crack growth in thermoplastic and thermosetting polymers, which is also associated with a relatively low value of n . Williams [14] has postulated that viscoelastic processes occurring at the crack tip control the

dependence of G_c upon the crack velocity, $\dot{a}$, and that the value of n is related to the polymer's viscoelastic properties by:

$$\tan \frac{\pi n}{2} = \tan \delta_r \quad (5)$$

where $\tan \delta_r$ is the viscoelastic loss factor. For the epoxy adhesive, from dynamic mechanical thermal analysis (DMTA) studies, the value of $\tan \delta_r$ at room temperature and a relatively low test frequency of 1 rad/s is 0.014 [16]. From Equation (5), this value of $\tan \delta_r$ yields a value of $n \approx 0.01$. This value of $n \approx 0.01$ would obviously give an excellent fit to the slopes of the G_c versus $\dot{a}$ relationships shown in Figures 2, 3 and 8, i.e. very little rate dependence of the value of G_c is observed in 'Region I'. Also, this value of n is in very good agreement with values from previous work where the 'bulk' fracture of epoxy polymers was studied [9].

Thus, from (a) the current values of n being very similar as deduced from the fracture tests and the DMTA studies and (b) by analogy to previous work [13-15], it appears that the viscoelastic processes which operate in the vicinity of the crack tip control the rate dependence of the toughness, G_c , of the present adhesive joints. This explains why no effect of the RH, substrate type or surface pretreatment used is observed with respect to the rate dependence; i.e. with respect to the slope, n , of the G_c versus $\dot{a}$ logarithmic relationship.

Constant Crack Opening Displacement Criterion

When the rate dependence of the G_c versus $\dot{a}$ relationship is governed by viscoelastic processes which occur in the viscoelastic-plastic zone ahead of the crack tip, then it is invariably found that the fracture process can be considered to be controlled by a critical value of the crack opening displacement, δ_t , where the value of δ_t is given by:

$$\delta_t = \frac{G_c}{\sigma_y} \quad (6)$$

and where σ_y is the uniaxial yield stress of the polymer or polymeric adhesive layer.

The yield stress of the adhesive used in the present studies was measured via plane-strain compression tests and was found to increase somewhat as the strain rate, $\dot{\epsilon}$, was increased, as would be expected: the uniaxial yield stress, σ_y , so deduced increased from 71 MPa to 75 MPa as the strain rate was increased over two decades.

From Equation (7), the value of the critical crack opening displacement, δ_c , may be deduced and since, there is very little rate dependence of the terms G_c or σ_y , then a constant value of δ_c , independent of crack velocity, is obtained. For the ‘GBD’- and the ‘GBS’-pretreated joints, the values of the critical crack opening displacement were calculated to be about 5 μm and 12 μm respectively. These values are not significantly dependent upon the type of substrate, but the far higher value of δ_c ascertained for the ‘GBS’-pretreated joints again reflects the superior durability offered by this form of surface pretreatment.

Environmental Attack

Introduction

First, it must be underlined that interfacial fracture in ‘Region I’ is not intrinsically the result of environmental attack, since joints tested at 0%RH were observed to exhibit ‘Region I’ behaviour and hence to fail visually along the interface between the adhesive and the substrate. However, there is a clear effect of the relative humidity of the test environment in ‘Region I’: the higher the relative humidity, the lower the adhesive fracture energy, see Figures 8 to 11. As commented above, the type of substrate (i.e. whether aluminium-alloy or steel) appears to play no significant role in the degree of environmental attack, but the choice of surface pretreatment (i.e. ‘GBD’ versus ‘GBS’) and the concentration of water (i.e. the RH) are critical factors, as may be seen

from Figures 9 to 11. Nonetheless, it should again be emphasised that, whilst the absolute value of G_c is a function of these parameters, the dependence of G_c upon the crack velocity, $\dot{a}$, is controlled by the viscoelastic nature of the epoxy adhesive, as discussed above.

These observations firstly imply that in ‘Region I’, at values of RH greater than 0%RH, as the RH increases then higher concentrations of water reach the vicinity of the crack tip and increasingly attack and weaken the interphase regions of the joints. Hence, the value of G_c decreases, although a critical concentration of water molecules may have to be attained in the case of the ‘GBS’-pretreated joints before any environmental attack mechanism may be initiated. Secondly, the water molecules reach the vicinity of the crack tip at a sufficiently fast rate to enable the environmental attack mechanism to occur readily, since the G_c versus crack velocity dependence is controlled by the viscoelastic nature of the epoxy adhesive, not by the RH employed.

The ‘GBD’-Pretreated Joints

In the case of the ‘GBD’-pretreated joints, the intrinsic stability of the adhesive/substrate interface in the presence of an aqueous environment in the long term may be assessed from the thermodynamic arguments advanced by Gledhill and Kinloch [17]. The thermodynamic work of adhesion is defined as the energy required to separate unit area of two phases forming an interface. If only secondary forces (e.g. van der Waals forces) are acting across the interface which is considered to be the main mechanism of adhesion of most epoxy adhesives, then the work of adhesion, W_A , in an inert medium may be expressed by:

$$W_A = \gamma_a + \gamma_s - \gamma_{as} \quad (7)$$

where γ_a and γ_s are the surface free energies of the adhesive and substrate, respectively, and γ_{as} is the interfacial free energy. In the presence of a liquid (denoted by the suffix 'l'), such as water, this expression must be modified and the work of adhesion W_{Al} is now given by:

$$W_{Al} = \gamma_{al} + \gamma_{sl} - \gamma_{as} \quad (8)$$

where γ_{al} and γ_{sl} are the interfacial free energies between the adhesive/liquid and substrate/liquid interfaces, respectively. For an adhesive/substrate interface the work of adhesion, W_A , in an inert atmosphere, for example dry air, usually has a positive value indicating thermodynamic stability of the interface. However, in the presence of a liquid the thermodynamic work of adhesion, W_{Al} , may well have a negative value indicating that the interface is now unstable and may dissociate. Thus, calculation of the terms W_A and W_{Al} may enable the durability of the interface in the long term to be predicted. The values of W_A and W_{Al} for epoxy/steel joints, respectively, have been reported to be +291 and -255 mJ/m² [17]; and for epoxy/aluminium-alloy joints +232 and -137 mJ/m² [18]. These values lead to the conclusion that the epoxy/oxide interfaces will indeed be susceptible to attack and degradation upon exposure to water molecules.

To assist in establishing the mechanisms of failure for the 'GBD'-pretreated joint, the exact locus of failure in 'Region I' was determined using scanning electron microscopy and X-ray photoelectron spectroscopy (XPS). The joints failed visually along the adhesive/substrate interface. Notwithstanding this observation, failure could have occurred within the adhesive layer, or oxide layer, with a very thin layer of adhesive, or oxide, retained on the opposite side of the joint which would be invisible to the naked eye. The substrate beam of a failed joint that visually appeared to have no adhesive left on its surface was referred to as the 'metal' side, whilst the beam that was visually covered with adhesive was termed the 'adhesive' side.

When the ‘metal’ sides of a fractured ‘GBD’-pretreated aluminium-alloy joint and a ‘GBD’-pretreated steel joint were examined using scanning electron microscopy, only a few isolated areas of the ‘metal’ side of the joint appeared to be covered by any retained adhesive. The remainder of the surface appeared to be metallic in nature, implying that interfacial failure had occurred.

The XPS spectra of the control (i.e. unbonded) adhesive and ‘GBD’-pretreated aluminium-alloy materials are shown in Figures 12 and 13, respectively. As expected the aluminium-alloy surface prior to bonding is covered by a thin layer of carbonaceous contamination adsorbed from the atmosphere, as may be seen from the relatively strong C1s peak in Figure 13. However, previous work [19] has established that such contamination is readily absorbed and displaced during the bonding operation.

The XPS spectra of the ‘adhesive’ and ‘metal’ sides taken from a failed ‘GBD’-pretreated aluminium-alloy joint, tested at 55%RH at a crack velocity of approximately 0.3 mm/minute, are shown in Figures 14a and b, respectively. The spectrum of the ‘adhesive’ side is rather similar to that of the control adhesive material (see Figure 12) and that of the ‘metal’ side is very similar to that of the control ‘GBD’-pretreated aluminium-alloy material (see Figure 13). This suggests that the failure occurred mainly along the adhesive/substrate interface. However, the presence of aluminium peaks in the spectrum of the ‘adhesive’ side (see Figure 14a) reveals that the fracture occurred also to a small extent in the oxide layer. Further, the increase in the ‘C/O’ ratio in the XPS spectrum of the ‘metal’ failure side (see Figure 14b) compared with that recorded from the control ‘GBD’-pretreated aluminium-alloy (see Figure 13) is indicative of a small amount of adhesive being retained on the ‘metal’ side. This observation is supported by the presence of a small ‘N1s’ signal (at a binding energy of about 400 eV) which is presumably attributable to a curing agent or other, minor, component of the adhesive formulation. Thus, it may be concluded

that the ‘GBD’-pretreated aluminium-alloy joints failed mainly along the adhesive/substrate interface. However, the crack occasionally travelled in the oxide and in the adhesive layer and this might be simply be due to the crack growing through the oxide asperities, and leaving adhesive retained in the ‘valleys’ of the very rough surface, as the crack travelled mainly along the substrate/adhesive interface. Similar conclusions were reached for the ‘GBD’-pretreated steel joints.

The fact that the fracture occurred mainly at the interface is in agreement with the thermodynamic arguments reported above. However, it should be borne in mind that the thermodynamic approach describes the behaviour of the joints at equilibrium (i.e. over a relatively long timescale) and, given the short length of the test (i.e. a few hours), it is unlikely that the failure solely occurred as a result of the presence of water molecules. Thus, it is suggested that the joints failed due to both the application of a stress and the presence of water molecules at the crack tip, a phenomenon similar to stress corrosion cracking which occurs in metals and ceramics (see for example [20]). As the relative humidity was increased, the number of water molecules was higher and the value of the adhesive fracture energy was seen to decrease, as indeed would be expected.

‘GBS’-Pretreated Joints

Silane pretreatments are known to increase the degree of interfacial adhesion, see for example [21-24]. This increase in the intrinsic adhesion has been attributed to the formation of covalent bonds between the metallic substrate and silane primer, and in turn between the silane primer and the adhesive layer; i.e. the silane primer acts as a ‘coupling agent’. Indeed, covalent bonds between the substrates and the silane, based upon GPS, have been detected for steel [21,23] and aluminium [24] using secondary ion-mass spectrometry.

From using scanning electron microscopy, the ‘metal’ side of a ‘GBS’-pretreated aluminium-alloy joint and a ‘GBS’-pretreated steel joint appeared to be predominantly covered with adhesive.

The XPS spectra of the control (i.e. unbonded) adhesive and ‘GBS’-pretreated aluminium-alloy materials are shown in Figures 12 and 15, respectively. The XPS spectra of the ‘adhesive’ and ‘metal’ sides taken from a failed ‘GBS’-pretreated aluminium-alloy joint, tested at 55%RH at a crack velocity of approximately 0.15 mm/minute, are shown in Figures 16a and 16b, respectively. The ratio of the ‘C1s’ and ‘O1s’ peaks in these spectra appear to be of the same order as that for the control adhesive (see Figure 12), which suggests that the failure occurred mainly in the adhesive layer. However, the presence of aluminium and silicon on the ‘adhesive’ side of the ‘GBS’-pretreated aluminium-alloy joint (see Figure 16a) suggests that fracture also occurred to a certain extent in the silane and oxide layers. This is presumably due to the asperities on the grit-blasted substrate surface being pulled off during failure and indicates a complex fracture path. Similar conclusions were reached for the ‘GBS’-pretreated steel joints.

The fact that the failure occurred mainly in the adhesive layer is consistent with the presence of covalent bonds being formed across the adhesive/substrate interface when a silane coupling agent is used, as widely reported in the literature. As for the ‘GBD’-pretreated joints, it appears that the ‘GBS’-pretreated joints failed as a result of both the application of a stress and the presence of water molecules at the crack tip. And as the relative humidity was increased, the number of water molecules at the crack tip increased and the adhesive fracture energy decreased as a result, possibly due to the interfacial covalent bonds being attacked and ruptured. Although there is a clear suggestion that a critical concentration of water molecules may have to be attained in the case of the ‘GBS’ surface-treated joints before any such environmental attack occurs.

MECHANISMS OF FAILURE IN ‘REGION III’

‘Region III’ was observed at relatively high rates of displacement. In this region, the crack grew in a stick-slip manner, mainly cohesively in the adhesive layer, and the adhesive fracture energy, G_c , was relatively high. Indeed, as mentioned previously, the crack velocity was estimated to be equal to approximately 20 km/minute. Furthermore, the values of the adhesive fracture energy did not depend on the test environment, but only on the surface pretreatment.

The fact that G_c was independent of the test environment and that the crack velocity was relatively high suggests that ‘Region III’ corresponds to the situation when the rate of flow of water molecules to the crack tip is substantially slower than the rate of crack advance. Thus, the concentration of water molecules reaching the crack tip is below that needed for environmental attack on the interphase to occur. Hence, a relative high value of G_c is recorded with the locus of joint failure being mainly cohesively in the adhesive layer. This suggested mechanism is in agreement with similar work which has been previously reported on glass [7] and thermoplastic polymers [13, 14].

In ‘Region III’, the ‘GBS’-pretreated joints had a relatively high G_c value at crack initiation of $1010 \pm 100 \text{ J/m}^2$, compared with the GBD joints where the value of G_c was $780 \pm 100 \text{ J/m}^2$. However, it should be noted that the ‘GBS’-pretreated joints always failed completely in the adhesive layer. This is in contrast to the ‘GBD’-pretreated joints, where many of the joints exhibited some fraction of interfacial failure at the very point of crack initiation; with completely cohesive failure in the adhesive occurring as the crack propagated, at a relatively high velocity, down the TDCB specimen. However, the value of G_c for the ‘GBD’-pretreated joints was not significantly dependent upon the details of the locus of failure. This suggests that the difference in the values of the G_c for the ‘GBD’- and ‘GBS’-pretreated joints was not due to any minor

difference in the locus of failure at crack initiation. The underlying reason for these intriguing observations are discussed below.

THE TRANSITION FROM ‘REGION I’ TO ‘REGION III’ BEHAVIOUR

Maugis [25] has reviewed the transition from stable to stick-slip crack growth that occurs in brittle materials as the crack velocity is increased. To model the transition between stable (i.e. our ‘Region I’ behaviour) and unstable crack growth (i.e. our ‘Region III’ behaviour), he assumed that the $\log G_c$ versus $\log \dot{a}$ curve observed experimentally was the result of the superposition of two curves, as shown schematically in Figure 17:

- (a) A curve corresponding to stable crack growth, i.e. curve ‘CAD’: which shows an increase in G_c with crack velocity governed by viscoelastic losses, followed by a decrease in G_c . The reason for this decrease is not clear, although this has been the subject of much debate. Maugis [25] has attributed the decrease in G_c after point ‘A’ has been reached to a significant reduction in the loss modulus, occurring when the crack propagates sufficiently fast that the material tends to behave in a more elastic fashion. On the other hand, Williams [14] has speculated that, for poly(methyl methacrylate), the decrease in G_c reported to occur between 1.5 m/minute and 6 m/minute (see [26-29]) corresponded to the case where the heat generated at the crack tip is not dissipated, resulting in a softening of the polymer and a decrease in the fracture energy. Notwithstanding, other workers [26] have suggested that the decrease in G_c is associated with a $\tan\delta_R$ peak, and that this $\tan\delta_R$ peak is governed by the β process, i.e. the viscoelastic relaxation corresponding to localised main-chain motions.

- (b) A second curve corresponding to purely ‘brittle’ fracture with dynamic effects, i.e. curve ‘CDB’. In this region, the crack velocity cannot exceed the Rayleigh velocity, which is the velocity of propagation of a stress wave travelling along a stress-free surface.

Now, for relatively low crack velocities, the initial dependence of fracture energy on crack velocity is governed by viscoelastic losses, and the portion ‘CA’ of the curve ‘CAD’ is appropriate, i.e. the portion of the curve ‘CA’ is equivalent to ‘Region I’ behaviour. However, when the rate of test is now increased by a small increment and the fracture energy becomes slightly greater than G_c^{crit} (point ‘A’ on Figure 17), the crack is forced to jump to the curve ‘CDB’, and hence the crack velocity jumps suddenly from $\dot{a}_c$ to $\dot{a}_1$ (i.e. point ‘B’ is now attained). Thus, the essential argument is that the portion of the two curves ‘ADB’ is not experimentally accessible: so that ‘Region I’ behaviour is seen (curve ‘CA’) and is followed by ‘Region III’ (point ‘B’).

However, in the present experiments, a further complication is that the transition from ‘Region I’ to ‘Region III’ behaviour is also accompanied by a change from visually interfacial failure to cohesive fracture through the adhesive layer. There are two factors which need to be considered to that may possibly explain this accompanying change in the locus of failure. Firstly, that except at 0%RH, this change in the locus in failure upon going from ‘Region I’ to ‘Region III’ will arise, at least in part, from the lack of environmental attack, and hence lack of associated interfacial weakening, that occurs in ‘Region III’. However, from Figure 8, it may be seen that this change in the locus of failure is also seen for the joints tested at 0%RH. Thus, secondly, it is noteworthy that several groups of workers [e.g. 30-32] have clearly shown that the locus of joint failure is not necessarily located where the joint may be at its weakest; e.g. the plane where the value of G_c may be at its lowest. Instead, the locus of joint failure is governed by such factors as the values of G_c for the various potential failure paths coupled with the local strain-energy release

rates, G , and stress fields available to initiate and propagate failure along these potential failure paths. For example, the above workers have shown that an increase in the shear stress component (i.e. Mode II (in-plane shear) component) at an interfacial crack tip would tend to favour the crack kinking towards the centre-line of the adhesive layer. This arises since cracks always tend to favour growing along a pure Mode I (tensile) path. Now, interfacial cracks between materials possessing very different moduli and Poisson's ratios do have a significant shear stress component. In particular, Fleck et al. [31] have shown that for a crack in an adhesive joint a relatively very small change in the Mode I/Mode II ratio in the stress field at the crack tip can result in a change in the locus of failure from interfacial to cohesive in the adhesive layer. Thus, it is suggested that, as the value of G_c increases in the present TDCB joints upon going from 'Region I' to 'Region III' behaviour, the shear stress component at the interfacial crack will increase and so cause the change from a visually interfacial to a cohesive (in the adhesive layer) locus of failure which is observed to accompany this change in behaviour.

Finally, we need to explain why the value of the adhesive fracture energy for stick-slip crack growth (i.e. 'Region III') is higher for the 'GBS'-pretreated joints than for the 'GBD'-pretreated joints, as was noted earlier. According to Maugis [25], the G_c value on the 'dynamic effects curve', i.e. at point 'B', is dependent upon the G_c value in the stable regime of crack growth prior to the instability occurring (i.e. the value of G_c at point 'A'). Thus, if the portion of the curve 'CA', corresponding to 'Region I' stable crack growth, is shifted upwards, then the G_c value corresponding to point 'B' (i.e. 'Region III' behaviour) will also increase.

CONCLUSIONS

In the present study the adhesive fracture energy, G_c , of aluminium-alloy and steel joints, bonded using a rubber-toughened epoxy, has been measured via a fracture-mechanics approach employing tapered double-cantilever beam (TDCB) tests which were loaded monotonically. The

substrates were either (a) grit-blasted and degreased ('GBD') or (b) silane ('GBS') pretreated. The monotonically-loaded tests were undertaken over a wide range of constant rates of displacement, $\dot{y}$, of the crosshead and at different levels of relative humidity. The adhesive fracture energy, G_c , was determined as a function of the crack velocity, $\dot{a}$. When the data were plotted in the form of $\log_{10} G_c$ versus $\log_{10} \dot{a}$, three clearly different regions of crack growth behaviour could be identified and these have been labelled 'Region I', 'Region II' and 'Region III',

'Region I': At slow crack velocities, the value of the adhesive fracture energy, G_c , was relatively low and the crack grew visually along the adhesive/substrate interface. The value of G_c was almost constant with increasing crack velocity and the dependence of G_c upon the crack velocity, $\dot{a}$, was controlled by the viscoelastic nature of the epoxy adhesive. The low dependence of the value of G_c upon the crack velocity was attributed to the low value of the viscoelastic loss factor of the epoxy adhesive in this range, arising from the highly cross-linked structure of the epoxy polymer. The G_c value was observed to decrease linearly with the relative humidity, since water molecules were readily able to reach the crack tip and to attack the interface. Although, especially for the 'GBS'-pretreated joints, one could infer that a critical RH, below which interfacial attack and weakening of the joints did not occur, might well exist. Further, the use of the silane pretreatment was clearly successful in increasing the value of the adhesive fracture energy, G_c . The improvement in joint durability observed in this 'Region I' when using the silane primer was considered to arise from the formation of covalent bonds between the substrates and the adhesive.

'Region III': The crack velocity was constant and estimated to be equal to approximately 20 km/minute. The crack grew in a stick-slip manner, with relatively high values of fracture energy at crack initiation. No water molecules were considered to be able to reach the crack tip, since the environment had no effect on the value of G_c . The crack grew mainly cohesively in the adhesive

layer, possibly because the shear stress component of the local stress field at the crack tip was sufficiently high so as to force the crack to kink towards the centre of the adhesive layer. In this region, the 'GBS'-pretreated joints had a higher G_c value at crack initiation than the 'GBD'-pretreated joints, due to the higher intrinsic adhesion achieved when employing the silane pretreatment.

'Region II': Between 'Region I' and 'Region III', two types of transition region were observed, termed either 'Region IIa' or 'Region IIb'. In 'Region IIa', the crack grew stably along the interface and the value of G_c increased sharply before the crack propagated cohesively in the adhesive layer in a stick-slip manner (i.e. 'Region III' was attained). The crack velocity (corresponding to the sharp increase in G_c) was considered to equivalent to the rate of water molecules flowing to the crack tip. When the crack velocity was somewhat higher than the rate of the flow of water molecules to the crack tip, then the concentration of water molecules at the crack tip would be insufficient to cause interfacial attack and weakening. Hence, the value of G_c now increased sharply to give 'Region III' behaviour. In 'Region IIb', only a change in the type of crack growth was observed (i.e. from stable (interfacial) crack growth in 'Region I' to unstable, slip-stick (cohesively in the adhesive) crack growth in 'Region III'), with no sharp increase in G_c being observed as in 'Region IIa'.

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Table 1 Chemical composition of BS 970 070M55 steel (by weight).

C	Mn	Si	S	P	Fe
0.5-0.6 %	0.5-0.8%	0.15-0.35%	0.04% max	0.04% max	balance

Table 2 Chemical composition of BS 7075 aluminium-alloy (by weight).

Zn	Mg	Cu	Cr	Fe	Si	Ti	Al
5.1-6.1 %	2.1-2.8%	1.2-2.0%	0.18-0.4%	0.7% max	0.50% max	0.20% max	balance

Table 3 **Expected and measured relative humidities (RHs) obtained**
from using the saturated salt solutions.

Saturated salt solution	Expected RH	Measured RH
CaHPO ₄ ·2H ₂ O	95%	96-98%
Na ₂ SO ₄	93%	88-94%
(NH ₄) ₂ SO ₄	81%	78%
NaNO ₂	66%	58-72%
KNO ₂	45%	48-50%
CaCl ₂	32%	36-38%
CH ₃ COOH	20%	19-22%
ZnCl ₂	10%	10-13%
P ₂ O ₅	0%	1-5%

LIST OF FIGURE CAPTIONS

- FIGURE 1 The tapered double-cantilever beam (TDCB) joint. (Dimensions are in mm.)
- FIGURE 2 Relationship between the fracture energy, G_c , and the crack velocity, $\dot{a}$, for the ‘GBD’- and ‘GBS’-pretreated aluminium-alloy joints. (In these figures the solid or dashed lines ending with an arrowhead indicate that no results could be obtained in this range, since the type of crack growth changed from stable to unstable, as discussed in the text. Filled points: ‘GBS’ pretreated; open points ‘GBD’ pretreated.)
- FIGURE 3 Relationship between the fracture energy, G_c , and the crack velocity, $\dot{a}$, for the ‘GBD’- and ‘GBS’-pretreated steel joints. (In these figures the solid or dashed lines ending with an arrowhead indicate that no results could be obtained in this range, since the type of crack growth changed from stable to unstable, as discussed in the text. Filled points: ‘GBS’ pretreated; open points ‘GBD’ pretreated.)
- FIGURE 4 Typical load, P , versus displacement, y , curve associated with stable crack growth, as seen in ‘Region I’ (and ‘Region II’). The specimen was a ‘GBD’-steel joint tested at 0.1 mm/minute at 55%RH.
- FIGURE 5 Relationship between crack length, a , and time, t , as seen in ‘Region I’. The specimen was a ‘GBD’-steel joint tested at 0.05 mm/minute at 55%RH.
- FIGURE 6 Relationship between crack velocity, $\dot{a}$, and rate of displacement, $\dot{y}$, as seen in ‘Region I’ for (a) the aluminium-alloy joints and (b) the steel joints. (For each type of substrate: ♦: experimental points; and x: points given by Equation (3). The straight line plotted represents the best statistical fit for the experimental data, as obtained via a linear regression analysis.)

- FIGURE 7 Typical load, P , versus displacement, y , curve associated with stick-slip crack growth, as seen in 'Region III'. The peaks correspond to crack initiation and the valleys to crack arrest. The specimen was a 'GBS'-pretreated aluminium-alloy joint tested at 0.1 mm/minute at 55%RH.
- FIGURE 8 Relationship between the fracture energy, G_c , and the crack velocity, $\dot{a}$, for the 'GBD'-pretreated aluminium-alloy joints obtained at 0%, 55% and 100%RH. (Filled circles: 0%RH; open circles: 55%RH and open diamonds: 100%RH.)
- FIGURE 9 Relationship between the fracture energy, G_c , and crack velocity, $\dot{a}$, as a function of the relative humidity for the 'GBD'-pretreated aluminium-alloy joints (Δ : joints exhibiting stick-slip crack growth; $\blacklozenge$: joints exhibiting stable crack growth).
- FIGURE 10 Relationship between the fracture energy, G_c , and the relative humidity for the 'GBS'-pretreated aluminium-alloy joints (Δ : joints exhibiting stick-slip crack growth; $\blacklozenge$: joints exhibiting stable crack growth).
- FIGURE 11 Comparison between the relationships between the fracture energy, G_c , and the relative humidity obtained for the 'GBD'-pretreated aluminium-alloy joints and the 'GBS'-pretreated aluminium-alloy joints for the stable crack growth regime, 'Region I'.
- FIGURE 12 XPS spectrum of the cured adhesive.
- FIGURE 13 XPS spectrum of the 'GBD'-pretreated aluminium-alloy surface.

FIGURE 14 XPS spectra of a failed ‘GBD’-pretreated aluminium-alloy joint: (a) ‘adhesive’ side, (b) ‘metal’ side. (Tested at 55%RH at a crack velocity of approximately 0.3 mm/minute.)

FIGURE 15 XPS spectrum of a ‘GBS’-pretreated aluminium-alloy surface.

FIGURE 16 XPS spectra of a failed ‘GBS’-pretreated aluminium-alloy joint: (a) ‘adhesive’ side, (b) ‘metal’ side. (Tested at 55%RH at a crack velocity of approximately 0.15 mm/minute.)

FIGURE 17 Schematic diagram showing the relationship between the fracture energy and crack velocity. The curve corresponding to stable (viscoelastic-controlled) crack growth is in light grey, whereas that corresponding to ‘brittle’ fracture with dynamic effects is in black. (Note: in this diagram the viscoelastic losses are schematically shown as being relatively large, to highlight the transition, which is not the case for the present adhesive and is not a necessary requirement.)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

(a)

(b)

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17