HOT-WET ENVIRONMENTAL PROPERTIES OF Z-PINNED CARBON-EPOXY COMPOSITES

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1 General Introduction

Z-pin laminae are a class of continuous fibre reinforced polymer composite material that are reinforced in the through-thickness direction with fibrous composite or metal pins [1]. The z-pins increase the delamination fracture toughness [e.g. 2,3], impact damage resistance [e.g. 4,5], and joint properties [e.g. 6,7] by generating crack bridging traction loads. Z-pin composites are used on a few types of military aircraft, including the FA-18 Superhornet and C17-Globemaster III heavy-lift transporter, and their aerospace applications may increase in coming years.

An important consideration in the use of z-pin laminae in aircraft structures is their environmental durability. The insertion of z-pins must not adversely affect the physical and mechanical properties when composite materials are exposed to the environmental operating conditions of the aircraft. One of the most important environmental conditions considered in the durability assessment of aircraft composite materials is long-term exposure to water vapour (humidity) at elevated temperature; which is known as the hot/wet environment.

A large body of research into the durability of composite materials exposed to water has been published [e.g. 8-10]. Furthermore, numerous studies into the processes by which water is absorbed into epoxy resins which are used as the matrix phase to aerospace-grade carbon fibre composites have been reported [e.g. 11-14].

While the water absorption properties of polymers and polymer composites have been extensively studied [8-10], nothing has been reported on the moisture absorption properties of z-pin composites. The environmental durability of z-pin composites must be known, particularly when exposed to hot and humid conditions, as part of the certification assessment of structural composite materials used in aircraft.

This paper presents an investigation into the environmental durability of z-pin carbon fibre-epoxy laminae and z-pin T-shaped joints when exposed to hot-wet conditions. Carbon-epoxy was selected because it is the most common material used in aircraft composite structures. Unpinned and z-pin laminae and joints were exposed to hot and humid conditions for increasing periods of time to assess the influence of z-pins on the moisture absorption behaviour. The effect of water absorption by the laminae on the mode I crack bridging traction and interlaminar fracture toughness properties of the z-pins was evaluated as part of the durability assessment. This was performed because the most important reason for z-pinning is to increase the interlaminar fracture toughness and damage tolerance properties of composites, and it is essential to determine whether moisture absorption changes the bridging traction properties of the z-pins. The effect of water absorption on the strength and toughness of z-pin T-joints was also assessed. Work presented in this paper is described in greater detail by Mouritz [15-17].

2 Materials and Experimental Methodology

2.1 Composite Materials and Joints

The composite material used in this study was made from unidirectional T700 carbon fibre-epoxy prepreg tape (VTM264 supplied by Advanced Composites). The uncured prepreg stacks were reinforced in the through-thickness direction with pultruded z-pins of T300 carbon fibre-bismaleimide
The prepreg was reinforced with 280 µm diameter z-pins arranged in a square grid with a fixed spacing of 1.75 mm. The volume content of z-pins was 2%. The z-pins were inserted into the prepreg stack using the ultrasonically-assisted z-pinning process [1]. The process basically involves driving z-pins from a foam carrier into the uncured prepreg using an ultrasonic tool operated at a constant frequency of 20 kHz. The high frequency vibrations generated by the tool gently force the z-pins into the composite without causing severe microstructural damage.

The composites were cured inside an autoclave at 120°C and 620 kPa for one hour. The thickness of the unpinned and z-pinned materials following curing was 4.2 and 4.3 mm, respectively, and their average carbon fibre content was determined by density measurements to be 59% and 58%, respectively.

The geometry and dimensions of the unpinned and z-pinned T-joint specimens are shown in Figure 1. Unpinned and z-pinned T-joint specimens consisted of the skin laminate, web laminate and flange laminate. The z-pins were aligned in straight rows both along and across the skin-flange section. The regions of the T-joint outside of the skin-flange section were not z-pinned. The T-joints were cured and consolidated under the same conditions as the laminates described above.

2.2 Environmental Durability Test

The unpinned and z-pinned composites were conditioned in an environmental chamber (Sunrise SU600, Angelantoni Industries SpA) at elevated temperature (75°C) and humidity (85%) for increasing periods up to about 150 days. Water absorption was monitored by weighing the materials using an And microbalance to within an accuracy of 100 mg. Samples of both the unpinned and z-pinned composites were removed from the chamber at different times to measure their pin pull-out traction properties, interlaminar fracture toughness, T-joint properties.

2.3 Mechanical Testing

Z-pin pull-out tests were performed to assess the influence of environmental ageing on the crack bridging traction properties of the pins. Details of the test are provided in [18]. The mode I interlaminar fracture toughness properties of the unpinned and z-pinned cross-ply composites were measured before and after exposure to the hot-wet environment using the double cantilever beam (DCB) test, as described in [16]. The structural properties of the unpinned and z-pinned joints were determined under tensile (web pull-off) loading, as described by Koh et al. [6].

3  Results and Discussion

3.1 Water Absorption Properties

The effect of increasing exposure time to the hot-wet environment on the percentage weight gain to the unpinned and z-pinned composites is shown in figure 2. Both composites display Fickian diffusion behaviour with the mass increasing at a linear rate with exposure time (expressed as $t^{\text{time}}$), and then reaching a constant weight when the materials become saturated with water. Z-pinning increased slightly (~10%) the water absorption rate of the composite, although it did not change the maximum weight gain at saturation. This small increase to the absorption rate is attributed to the z-pins providing a diffusion pathway which accelerated water ingress into the composite. The z-pins, which are unidirectional composite rods of carbon fibre-bismaleimide, were aligned in the same direction as the moisture diffusion path, as shown schematically in figure 3. The diffusion rate of water in composites is much higher (typically 5-10 times) in the fibre direction than in the anti-fibre direction (i.e. 90° to the diffusion direction) [19]. Therefore, water will diffuse more quickly into the composite along the z-pins than in those regions that are not z-pinned where the fibre direction is transverse to the diffusion direction. As a result, the weight gain due to water absorption was increased by the z-pins. Using rule-of-mixtures, the effect of z-pinning on the water diffusion rate of the composite ($D_p$) can be determined using:
The first and second terms on the right hand side refer to diffusion in the unpinned region of the composite and the z-pins, respectively. The subscripts \( o \) and \( p \) refer to the unpinned composite and z-pin, respectively. The subscripts \( \perp \) and II refer to the diffusion direction being in the anti-fibre and fibre directions, respectively. \( V_o \) and \( V_p \) are the volume fractions of the composite without and with z-pins, respectively. \( D_{o\perp} \) is the diffusion coefficient of the unpinned composite in the anti-fibre direction and \( D_{pII} \) is diffusion coefficient in the fibre direction of the z-pins. The composite had a z-pin volume content of 2% (i.e. \( V_o = 0.98 \) and \( V_p = 0.02 \)). The diffusion coefficient for water in bismaleimide is similar or slightly higher than epoxy resin (depending on the exact type of resin).

Assuming that the axial diffusion coefficient \( (D_{pII}) \) of the z-pins is 5-10 times higher than the transverse diffusion coefficient \( (D_{o\perp}) \) of the unpinned composite, then it is estimated (using equation 2) that the z-pins will increase the water absorption rate by 8% to 18%. The measured increase in the absorption rate due to z-pins (~10%) is within this range, suggesting that the pins provide a pathway for the accelerated ingress of water.

3.2 Z-Pin Traction Properties

Z-pin pull-out tests were performed to determine whether water absorption from the hot-wet environment affected the traction load generated by the pins embedded in the carbon-epoxy composite. Figure 3 presents traction load-crack opening displacement (P-\( \delta \)) curves measured for the z-pinned composite in the original (dry), partially saturated (120 hours), close to saturation (980 hours), and beyond saturation (1320 hours) conditions. The P-\( \delta \) curves are characterised by an initial linear response due to elastic stretching of the z-pins. The curves reach an ultimate traction load \( (P_{\text{max}}) \), and this value decreased with increasing exposure time to the hot-wet environment. The ultimate traction load fell by about 60% when the composite was saturated with water. The abrupt drop in the P-\( \delta \) curves immediately following the ultimate load was due to debonding of the z-pins from the composite. Both the crack opening displacement to cause z-pin debonding \( (\delta_{db}) \) and load drop \( (\Delta P_{db}) \) caused by debonding were reduced by hot-wet conditioning. The P-\( \delta \) curves show that increasing the crack opening displacement beyond the point of z-pin debonding \( (\delta_{db}) \) resulted in a gradual reduction to the traction load. This load was generated by friction stress caused by sliding of the z-pin as it was pulled from the composite.

The maximum z-pin traction load and the elastic pin traction energy were reduced by moisture absorption, as shown in figure 4. The elastic traction energy was determined by the area under the z-pin traction load-displacement curve up to the peak load, over which phase of the pull-out test the pin reacted elastically to the applied tensile force. Both the elastic traction load and energy decreased with increasing exposure time before reaching low and constant values when the laminates were fully saturated with water. Figure 4 shows that the elastic traction load and energy were reduced by 60-70%, which indicates significant weakening of the mode I interlaminar toughening generated by z-pinning. Both the peak traction load and elastic traction energy were reduced by hot-wet conditioning, and this is attributed to water-induced plasticization of the interface between the z-pin and composite. Water weakened the interfacial shear strength which in turn reduced the traction load and crack opening displacement at which the z-pin debonded from the composite.

Following z-pin debonding, the traction properties for the pull-out stage were not degraded by water absorption. Both the traction load to initiate z-pin pull-out and the pull-out traction energy did not change significantly with increasing hot-wet conditioning times.

Based on the results, water absorption reduced the elastic traction properties of the z-pins due to softening of the interfacial shear strength. Once the z-pins had debonded from the composite, however, the traction properties during the pull-out stage were not affected by the absorbed water. This weakening of the elastic z-pin traction properties is attributed to a loss in the interfacial shear strength between the z-pin and laminate due to moisture absorption.
3.3 Delamination Fracture Toughness Properties

The effect of hot-wet conditioning time on the mode I steady-state interlaminar fracture toughness ($G_{IC}$) of the unpinned and z-pinned composites is shown in figure 5. The fracture toughness of the unpinned composite was relatively high (~1 kJ/m$^2$) due to the presence of a fibre bridging zone along the delamination crack. The fracture toughness of the unpinned material remained unaffected by the absorption of moisture, even after long period of exposure to the hot-wet environment.

As expected, the toughness values were increased by z-pinning, and this was due to the formation of a bridging traction zone along the delamination by the z-pins. Within the bounds of scatter, water absorption did not change the interlaminar fracture toughness of the z-pinned composite, although the average toughness value was reduced slightly.

The fracture toughness of the z-pinned composite remained unchanged, despite the z-pin pull-out test revealing that water absorption reduced the ultimate traction load and elastic traction energy. The z-pin bridging zone formed along the delamination crack consisted of two distinct regions as shown schematically in figure 6. A short bridging zone occurred immediately behind the crack front where the z-pins were elastically deformed due to the low crack opening displacement (i.e. $\delta < \delta_{eb}$). A much longer bridging zone occurred further behind the crack front where the z-pins were pulled from one of the arms of the DCB specimen due to the increased opening displacement (i.e. $\delta_{eb} \geq \delta \geq \delta_f$). The length of the bridging zone involving elastic deformation of the z-pins was only a small percentage (<10%) of the entire bridging zone, which was dominated by z-pin pull-out. Because water absorption only reduced the bridging traction properties during elastic deformation, and does not alter the properties during pull-out, overall there is a small loss in the total traction energy generated by the z-pins along the delamination crack. As a result, water absorption by the z-pinned composite does not significantly reduce the mode I delamination resistance.

3.4 T-Joint Properties

The effect of hot-wet conditioning on the mechanical response of the unpinned and z-pinned joints when subjected to tensile (web pull-off) loading is shown in Figure 7. Load-displacement curves are presented for joints in their original (dry) condition and after exposure to hot-wet conditions which caused partial and complete saturation. The response of the two types of joint to the hot-wet environment was different. The unpinned joint in the dry condition initially showed an elastic response under increasing load until it reached ultimate load, at which point the skin-flange bond-line failed catastrophically. Figure 8 shows an unpinned T-joint specimen following failure. Finite element analysis of the unpinned joint revealed that failure initiated in the Δ-fillet [20], where the interlaminar tensile and shear stresses are highest due to the geometric stress concentration in this region. Delamination cracks propagated from the Δ-fillet region along the skin-flange bond-line which caused the joint to fail catastrophically. The unpinned joint in the partially saturated condition showed the same load response and failure mode as the dry joint. However, the mechanical behaviour of the unpinned joint changed abruptly once it was saturated with water. The ultimate load decreased suddenly whereas the failure displacement increased when the unpinned joint became saturated.

Load-displacement curves for the z-pinned joint in the dry, partly saturated and fully saturated conditions are presented in Figure 7b. The loading response of the z-pinned joint was not changed significantly by the hot-wet environment, even when saturated with water. Regardless of the hot-wet conditioning time, the curve for the z-pinned joint was characterised by a series of load drops followed by load recoveries until final failure occurred at a displacement value (in the range of 15-20 mm) that was much higher than the unpinned joint. Large-scale cracking along the skin-flange bond-line to the z-pinned joint did not occur irrespective of the hot-wet conditioning time. Cracks initiated in the Δ-fillet region, but failed to propagate more than ~15 mm along the skin-flange bond-line before being arrested by the z-pins. Large-scale cracking was suppressed by the z-pins generating crack bridging traction loads along the bond-line. With bond-line cracking suppressed, the z-pinned joint failed in the clamped region of the skin laminate, as shown in Figure 9. Final failure occurred in the skin regardless of
whether the z-pinned joint was dry, partially saturated or fully saturated with water. Figure 8 shows the effect of hot-wet exposure time on the ultimate load, maximum displacement, and absorbed energy of the unpinned and z-pinned joints. The absorbed energy was determined from the area under the load-displacement curve, and defines the total amount of strain energy needed to completely fracture the joints. The mechanical properties of the unpinned joint remained unchanged with increasing exposure to the hot-wet environment until complete saturation occurred at about 900 hours (30 hours $0.5$). Close to saturation, the ultimate load of the unpinned joint dropped whereas both the maximum displacement and absorbed energy increased. This change to the properties corresponded to the time taken for water to diffuse from the external surfaces of the joint to the skin-flange bond-line where failure occurred. The property change also corresponded with degradation of the epoxy matrix and the carbon fibre-epoxy interface at the bond-line. Figure 9 compares the microstructure of the composite material at the bond-line of the unpinned joint in the dry and saturated conditions. The carbon fibres are bonded to the epoxy matrix in the dry composite whereas many of the carbon fibres have debonded from the matrix in the saturated material, due presumably to weakening of the fibre-epoxy interface. Other studies have shown that the interface between carbon fibres and epoxy is weakened by water [8,21,22]. The weakening of the fibre-epoxy interface due to water resulted in extensive fibre bridging along the bond-line during fracture of the saturated joint. It is believed that once water reached the bond-line it weakened the fibre-matrix interfaces, resulting in the sudden loss in ultimate strength of the unpinned joint. The interfacial weakening also caused carbon fibres to partially detach from the crack surfaces during delamination growth between the skin and flange. This led to the formation of a fibre bridging zone in the unpinned joint when fully saturated. It is well known that fibre bridging increases the interlaminar fracture toughness, and this caused the maximum failure displacement and absorbed energy to increase suddenly when the unpinned joint became saturated. The structural properties of the z-pinned joint were not changed by the hot-wet environment. This occurred despite the reduction to the elastic bridging traction properties of the z-pins caused by water absorption. The retention of the structural properties is attributed to the geometry of the short bond-line crack that developed in the z-pinned joint, which is shown schematically in Figure 10. The crack opening displacement increases from the delamination tip towards the $\Delta$-fillet region, where damage initiated. The first row of z-pins nearest the crack front experienced elastic stretching due to the small opening displacement. That is, crack opening displacement caused the z-pins to elastically deform, but the opening was too low to cause debonding and pull-out (i.e. $\delta < \delta_{db}$). The crack opening displacement beyond the first rows of z-pins exceeded the limit required to activate the pin pull-out process. Therefore, along the bond-line crack (which was less than ~15 mm long), the majority of z-pins experienced partial pull-out with a small number of pins (closest to the crack tip) being elastically deformed. The z-pin pull-out testing revealed that water absorption only reduced the peak traction load and elastic traction energy, and does not affect the friction traction load and traction energy generated during the z-pin pull-out stage. Because most of the z-pins along the bond-line crack are in the pull-out stage of the bridging process, and because the friction-induced load and energy during pin pull-out was not affected by water absorption, the total bridging traction load was not reduced significantly. Some weakening of the traction load occurred within the first rows of z-pins, although this accounts for a relatively small proportion of the total load generated by all the z-pins. Consequently, the z-pins retained their high resistance to bond-line cracking and this resulted in the structural properties of the z-pinned joint being unaffected by water absorption.

4 Conclusions

Through-thickness reinforcement of carbon-epoxy composite with fibrous z-pins accelerated slightly the water absorption rate during exposure to the hot-wet environment. The absorption rate increased because the fibres within the z-pins are aligned parallel to the diffusion pathway of the water. While z-pins increased the absorption rate, they had no effect on the water saturation limit of the carbon-
epoxy composite. Water absorption from the hot-wet environment softened the interfacial region between the z-pins and surrounding composite material. This reduced the ultimate traction load, crack opening displacement to cause pin debonding, and elastic traction energy. These z-pin properties decreased progressively with increasing hot-wet conditioning time as water diffused along the pin-composite interface until it was completely softened when the material reached saturation. Following z-pin debonding, however, the traction load and energy generated during pin pull-out were not affected by absorbed water. The water also caused physical damage to the z-pins, with the surface carbon fibres debonding from the BMI matrix. The mode I interlaminar fracture toughness of the z-pinned composite was not affected significantly by water absorption, even at long hot-wet conditioning times which caused complete saturation. The large-scale bridging zone along the delamination was dominated by traction forces generated by pin pull-out. A short region immediately behind the crack front involved elastic deformation of the z-pins, and this made a relatively small contribution to the total toughening effect. Because the traction load and energy during pin pull-out was not affected by absorbed water there was no significant degradation to the mode I interlaminar fracture toughness. The structural properties of carbon-epoxy T-joints were increased by through-thickness reinforcement of the skin-flange region with z-pins. Bridging traction loads generated by z-pins along the skin-flange bond region restricted crack growth and thereby increased the ultimate strength and toughness (absorbed energy) of the T-joint under web pull-off loading. The z-pins also had an important influence on the structural properties of T-joints in hot-wet environment. The structural properties of the unpinned T-joint were not changed by hot-wet conditioning until water reached the skin-flange bond-line. At this point the ultimate load of the unpinned joint dropped sharply (by about one-third) due to softening of the epoxy matrix and weakening of the carbon fibre-epoxy interface at the bond-line. The absorbed energy of the unpinned joint increased abruptly when water reached the bond-line, and this was because weakening of the carbon fibre-epoxy interface promoted fibre bridging along the bond-line crack between the skin and flange. In contrast, the structural properties of the z-pinned joint were not changed by hot-wet conditioning, even when the bond-line was saturated with water. Strengthening and toughening of the z-pinned joint was due mostly to the traction properties generated during z-pin pull-out (with the elastic traction properties being less important). Because the z-pin pull-out traction properties were not altered by water absorption the properties of the z-pinned joint did not change with increasing hot-wet conditioning time up to and beyond saturation.

References


Fig. 3. Effect of hot-wet conditioning time on the mode I z-pin traction load-crack opening displacement curves.

Fig. 4. Effect of hot-wet conditioning time on the peak mode I traction load and elastic traction energy of the pins.

Fig. 5. Effect of hot-wet conditioning time on the mode I interlaminar fracture toughness of the unpinned and z-pinned laminates.

Fig. 6. Schematic of the bridging zone along the delamination crack in a z-pinned laminate showing it is dominated by pin pull-out.

Fig. 7. Load-displacement curves for the (a) unpinned joint and (b) z-pinned joint in the original (dry), partially saturated (hot-wet conditioning time of 144 hours) and fully saturated (hot-wet time of 3360 hours) conditions.
Fig. 8. Failure mode of the unpinned joint involved debonding of the skin and flange due to delamination cracking.

Fig. 9. Failure mode of the z-pinned joint involved skin failure with large-scale cracking between the skin and flange suppressed by the pins.

Fig. 8. Effect of hot-wet conditioning time on the (a) ultimate load, (b) maximum failure displacement and (b) absorbed energy of the unpinned and z-pinned T-joints. The error bars indicate one standard deviation.
Fig. 9. Carbon-epoxy composite material in the (a) dry and (b) saturated conditions. Note the high degree of fibre-epoxy bonding in (a) and high degree of interfacial debonding between the fibres and epoxy in (b).

Fig. 10. Schematic of the bridging zone along the skin-flange bond-line to the z-pinned joint. The length of the bridging zone involving elastic deformation of the z-pins is short in comparison to pull-out of the pins.