

Bridging Effect and Efficiency of Partly-Cured Z-pin Reinforced Composite Laminates

Chu Qiyi, Li Yong*, Xiao Jun, Huan Dajun, Zhang Xiangyang

College of Materials Science and Technology, Nanjing University of Aeronautics
and Astronautics, Nanjing 211106, P. R. China

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Abstract: To study the bridging effect of partly-cured Z-pin, Z-pins with different curing degrees are manufactured by controlling pultrusion parameters. A unit cell is selected to analyze the stress of Z-pinned laminates and the quantitative relationship between the maximum bridging force and Z-pin diameter, embedded length, interfacial shear strength and tensile strength is acquired. The Z-pin "bridging law" test and Z-pin tensile test are carried out to study the effect of Z-pin's curing degree on bridging effect, and the bridging efficiency is defined to evaluate the reinforcement effect of Z-pin. The mode I interlaminar fracture toughness (G_{IC}) is measured by the double cantilever beam test. The experimental results show that Z-pin's co-curing with laminate matrix can improve the bridging force significantly and the fitting results show a linear relationship between Z-pin curing degree and interfacial shear strength. The three-dimensional images of the surface of pullout Z-pins indicate that the failure mode changed from totally interfacial debonding to a mixed mode. Finally, the reinforcement by partly-cured Z-pin can be used to further enhance the interlaminar toughness. Compared with completely-cured Z-pin, G_{IC} of Z-pin with 67.6% curing degree increases by 47.0%.

Key words: polymer-matrix composites; through-the-thickness reinforcement; Z-pin; interfacial shear strength; fracture toughness

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0 Introduction

Advanced composites in laminated form have been extensively applied in many industries, especially in aerospace engineering because of their high strength/weight ratio relative to metallic materials^[1]. But a long-standing problem with fiber-reinforced polymer laminates is their low delamination resistance and poor impact damage tolerance due to the lack of through-the-thickness reinforcement. It has limited the application of laminated composites in structures susceptible to impact, in-plane shear or through-thickness tensile loads^[2]. New materials and techniques have been developed to increase the delamination toughness and the impact resistance of laminates,

including toughened resins and through-the-thickness reinforcement techniques, such as stitching, weaving, 3-D braiding and Z-pinning^[3].

Z-pinned laminates are a class of continuous fiber reinforced polymer composite materials which are reinforced in the through-the-thickness direction with fibrous composites or metal rods^[4], called Z-pin. Z-pins can increase the interlaminar fracture toughness^[5-7], impact damage resistance^[8], damage tolerance^[9-10], fatigue resistance^[11-13] and joint properties^[14-15] by inducing crack bridging tractions. This approach has been applied on some military aircraft, including the FA-18 Superhornet, C17-Globemaster III heavy-lift transporter, and other aerospace applications^[16].

* Corresponding author, E-mail address: lyong@nuaa.edu.cn.

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The dominating mechanism of Z-pin reinforcement is the "bridging effect"—when the crack propagates, the reinforcing Z-pin provides a closure force against the opening crack; at the same time, the Z-pin's pull-out from the matrix consumes large amount of energy, consequently improving the toughness of laminates^[17]. Therefore, the reinforcement efficacy of Z-pin through-the-thickness technology largely depends on the interfacial bonding of Z-pin and composites.

Several methods of enhancing the bridging force were proposed. Knaupp et al.^[18] manufactured Z-pins with a rectangular cross-section by changing the shape of mould, and pointed out that different cross-section shapes would affect the performance of laminates reinforced by Z-pin. Knopp and Scharr^[19] utilized surface treatment methods to increase the surface roughness and the number of active groups of Z-pin to enhance the bonding between Z-pin and laminates. Wang and Zhang et al. proposed twisted Z-pin method to achieve an improvement of bridging force by increasing the contact area of interface^[20,21].

The above methods to improve Z-pin bridging force are mainly from the perspective of increasing the contact area between Z-pin and laminates. And the interfacial bonding is decided by the bonding strength of Z-pin and the laminates. If we can appropriately reduce the curing degree of Z-pin on the premise of meeting the stiffness demand during the ultrasonic inserting process, an enhancement of interfacial bonding between Z-pin and laminates can generate because of a larger extent of co-curing between the residual active group in Z-pins and the laminated prepregs.

The purpose of this paper is to improve the reinforcement efficacy of Z-pin based on the strategy of partly-cured Z-pins through the experimental research on the relationship between the bridging force and the curing degree. In this paper, this stress analysis of the bridging Z-pin reveals the quantitative relationship between the maximum bridging force provided by a single Z-

pin and the Z-pin's diameter, embedded length, interfacial shear strength and tensile strength. The Z-pin "bridging law" test is conducted to acquire the Z-pin's bridging force and analyze the bonding situation between Z-pin and the laminates. Finally, the influence of Z-pin's curing degree on the mode I interlaminar fracture toughness is studied by the double cantilever beam test.

1 Material and Methods

1.1 Material

Carbon fiber T300 and 180 cure-type epoxy resin FW-125 for Z-pin pultrusion are supplied by Toray Industries, Inc., Japan and Kunshan Yubo Composite materials Co., LTD, China, respectively. And the performance parameters are shown in Tables 1, 2.

The carbon fiber/epoxy prepreg in nominal thickness of 0.125 mm supplied by Weihai Guangwei Composites Co., LTD is adopted, and the resin content is approximately 33wt%.

Table 1 Performance parameters of FW-125 epoxy resin

Component	Viscosity/ (Pa · s)	Specific gravity	Gel time/ min
FW125-A	—	1.16	5—8(120 °C)
FW125-B	0.05—0.1	1.20	3—6(130 °C)

Table 2 Performance parameters of T300 carbon fiber

Brand	Tensile strength/ MPa	Tensile modulus/ GPa	Elongation/ %
T300	3 530	230	1.5

1.2 Pultrusion of partly-cured Z-pin

Z-pins with different curing degrees are obtained by pultrusion process; Carbon fibers are impregnated with epoxy resin and with the pultrusion speed, and mould and oven temperatures of post-curing are automated controlled. Z-pins are rolled for inserting after cooling. The curing degrees of Z-pins are measured by the differential scanning calorimeter (DSC) methods.

Z-pins with different curing degrees are ob-

tained by the pultrusion process and the DSC curves of Z-pins with different curing degrees are shown in Fig. 1. The curing degrees of Z-pins with different pultrusion parameters are calculated in Eq. (1) and shown in Table 3.

$$\alpha = (H_u - H_p/w)/H_u \quad (1)$$

where H_u is the specific enthalpy of the curing reaction of the pure uncross-linked resin, J/g; H_p the specific enthalpy of post-curing of Z-pin, J/g; w the resin content of Z-pin, wt%.

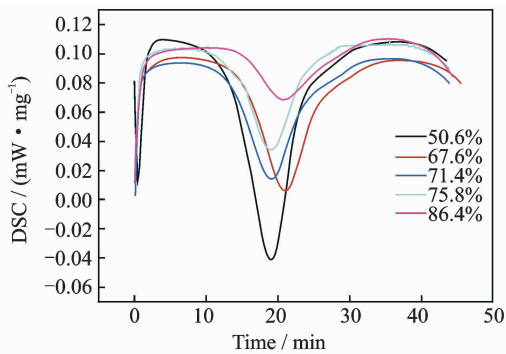


Fig. 1 DSC curves of Z-pin with different curing degrees

Table 3 Results of pultrusion parameter and curing degree of Z-pin

No.	Pultrusion speed $v/(\text{mm} \cdot \text{s}^{-1})$	Mould temperature $T_{\text{mould}}/^\circ\text{C}$	Oven temperature $T_{\text{oven}}/^\circ\text{C}$	Degree of cure $\alpha/\%$
1	3.85	90	125	50.6
2	3.85	90	130	67.6
3	3.85	90	135	71.4
4	3.26	90	135	75.8
5	3.85	90	140	86.4

To study the effect of partly-cured Z-pin on the interlaminar reinforcement, Z-pins with the curing degrees of 67.6%, 75.8% and 86.4% are chosen to conduct the Z-pin "bridging law" test and the DCB test. And the completely-cured Z-pin reinforced specimens are manufactured as the control groups. Z-pins with curing degrees of 50.6% and 71.4% are eliminated because the 50.6% Z-pin has poor stiffness for insertion and the 71.4% Z-pin is close to 75.8%.

1.3 Manufacture of Z-pinned composites

The manufacture of Z-pinned composites consists of three stages: (1) Preparation of preform; (2) Z-pin inserting process; (3) Curing processing. The preparation of preform is conducted with computer numerical control (CNC) inserting machine, and the Z-pins are arranged in a square pattern inside the foam carrier.

Then the Z-pins will be inserted into the prepreg stack by UAZ (Ultrasonically assisted Z-fibre™) method with an ultrasonic tool in Fig. 2.

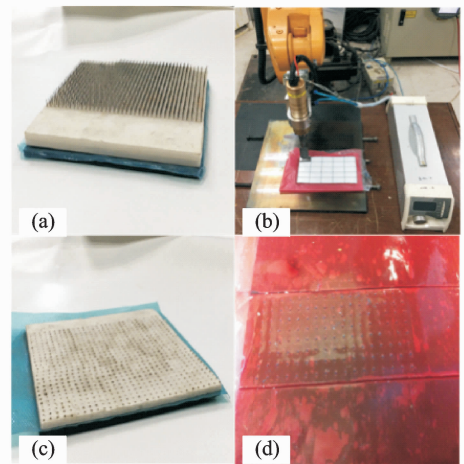


Fig. 2 Ultrasonic inserting process of Z-pin

The process starts by placing a polystyrene foam carrier containing Z-pins over the prepreg (Fig. 2(a)). The Z-pins are arranged in a square pattern inside the foam carrier. The role of the carrier foam is to ensure an even spacing between the Z-pins and to provide lateral support during insertion preventing Z-pins from destabilizing.

Z-pins are driven from the foam carrier into the prepregs using the ultrasonic horn assisted by robotic arm (Fig. 2(b)). High frequency vibration is generated at the ultrasonic horn bottom to heat the prepregs and to soften the resin matrix while the gradually applied pressure drives the Z-pins into the prepregs. Z-pins are inserted progressively by moving the ultrasonic horn over the foam carrier several times until all the pins have penetrated the prepreg stack with the robotic arm

(Fig. 2(c)). Finally, the foam carrier is discarded afterwards and any excess length of Z-pins protruding the prepreg is shaved off by a blade to ensure a smooth surface (Fig. 2(d)).

The curing process of Z-pinned laminates is also the key process of its manufacture during which the interfacial bond between Z-pin and laminates formed. The Z-pinned laminates are cured in the autoclave with the curing process curves shown in Fig. 3.

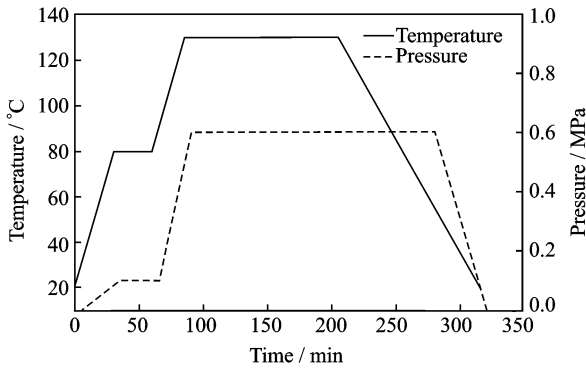


Fig. 3 Autoclave curing process curves of USN12500 prepreg

1.4 Z-pin "bridging law" test

According to Ref. [17], the bridging effect of Z-pin can be characterized by the "bridging law", which is the functional relationship between the delamination crack-opening displacement and the closure force from a single pin. The bridging force increases with the increment of the displacement until the peak while the interfacial debonding occurs, and then the bridging force drops suddenly. The maximum bridging force is determined by the bonding condition of the interface between Z-pin and the laminates. Therefore, the bridging force is assumed to be influenced by Z-pin co-curing with the matrix resin.

In order to confirm this assumption, four different curing degrees of Z-pin with the diameter of 0.3 mm are employed for the Z-pin "bridging law" test and the inserting pattern is 3×3 . The specimen is a 40 mm long and 20 mm wide block from stacked prepreps in $[0/90]_{12s}$. A Teflon film with the thickness of $10 \mu\text{m}$ is placed be-

tween the upper and lower laminates to avoid any adhesive bonding (Fig. 4). Two T-shaped tabs are glued by epoxy grouting agent to the laminates and stalled in the universal material testing machine with a cross-head speed of 1 mm/min.

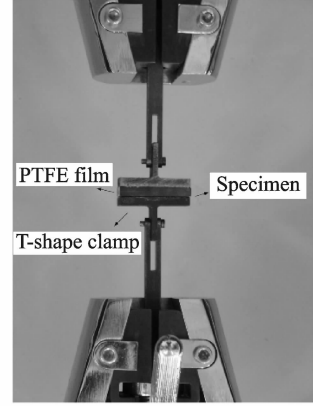


Fig. 4 Illustration of Z-pin "bridging law" test

1.5 Partly-cured Z-pin tensile test

The partly-cured Z-pin will undergo a post-curing process during the curing process of Z-pin reinforced laminates, which may cause the reduction of Z-pin's axial tensile property. Then Z-pin will rupture before the interfacial debonding of Z-pin and laminates so as to affect the bridging effect of Z-pin. Therefore, it is necessary to study the influence of the curing degree on the tensile properties of post-curing Z-pin.

The curing of Z-pin can be divided into two stages: (1) Part-cured during the pultrusion; (2) Post-curing during the co-curing with laminates. Therefore, the post-curing of partly-cured Z-pin can be simulated by the $130 \text{ }^\circ\text{C}$ isothermal-curing for 120 min. The Z-pin tensile test configuration is shown in Fig. 5. The free length of Z-pin is 250 mm. The universal material testing machine moves in tension at a speed of 0.5 mm/min. The ultimate strength and the axial tensile modulus of Z-pin are calculated by

$$\sigma_{p,u} = \frac{4P_{\max}}{\pi d^2} \quad (2)$$

$$E_{p,l} = \frac{4\Delta P \cdot l_g}{\pi \Delta l \cdot d^2} \quad (3)$$

where P_{\max} is the peak load of the load-displace-



Fig. 5 Fixture of partly-cured Z-pin tensile test

ment curve, N; d the diameter of Z-pin, mm; l_g the gauge length of extensometer, mm; $\Delta P/\Delta l$ the slope of load-deformation curve, N/mm.

1.6 Double cantilever beam (DCB) test

Quasi-static mode I interlaminar toughness tests are performed employing DCB specimens according to ASTM D 5528 standard test method, and performed at 20 °C. The laminated beams are stacked in $[0]_{24}$ with the thickness of 3 mm and 180 mm in length, 25 mm in width. A 50 mm long Teflon film is inserted between the upper and lower beams to create a pre-existed crack. Two T-shaped tabs are glued to the top and bottom surfaces of the laminates and firmly gripped for testing in the universal material testing machine at a cross-head speed of 2 mm/min. The load-displacement curves are recorded during the tests (Fig. 6).



Fig. 6 Experiment fixture of DCB test

2 Result and Discussion

2.1 The maximum bridging force of Z-pin

The failure mode of Z-pin in the mode I load includes the pullout of Z-pin from laminates and the rupture of Z-pin itself. Therefore, the maximum bridging force provided by Z-pin $F_{p,max}$ which determines the reinforcement capacity of Z-pin can be calculated by

$$F_{p,max} = \begin{cases} \pi dl\tau_{p,s} & \text{Z-pin pullout} \\ \pi d^2\sigma_{p,u}/4 & \text{Z-pin rupture} \end{cases} \quad (4)$$

where l is the embedded length of Z-pin, mm, and $\tau_{p,s}$ the interfacial shear strength, MPa.

The maximum bridging force provided by Z-pin depends on the diameter, embedded length of Z-pin and the relative value of interfacial shear strength and the Z-pin tensile strength. With the increase of the embedded length of Z-pin, the axial stress of Z-pin increases. Then Z-pin will rupture once the axial stress reaches the tensile strength of Z-pin. Z-pin cannot continue to provide more bridging force by continuing to increase the embedded length. There exists a critical embedded length l_c .

Stress analysis is conducted by a unit cell reinforced by a single Z-pin (Fig. 7). From the equilibrium equation, we can deduce the relationship of Z-pin axial tensile stress σ_p and interfacial shear stress τ between Z-pin and laminates

$$\pi kd \cdot \Delta x = \frac{\pi d^2}{4} \cdot \frac{\partial \sigma_p}{\partial x} \cdot \Delta x \quad (5)$$

$$\frac{\partial \sigma_p}{\partial x} = \frac{4\tau}{d} \quad (6)$$

where $\partial \sigma_p/\partial x$ is the stress gradient along the Z-pin axial direction, MPa/mm.

The maximum axial stress $\sigma_{p,max}$ of Z-pin can be calculated by

$$\int_0^{\sigma_{p,max}} \partial \sigma_p = \int_0^l \frac{4\tau_{p,s}}{d} \partial x \quad (7)$$

$$\sigma_{p,max} = \frac{4l}{d}\tau_{p,s} \quad (8)$$

Therefore, the critical embedded length of Z-pin can be calculated by

$$l_c = \frac{\sigma_{p,u}}{\tau_{p,s}} \cdot d \quad (9)$$

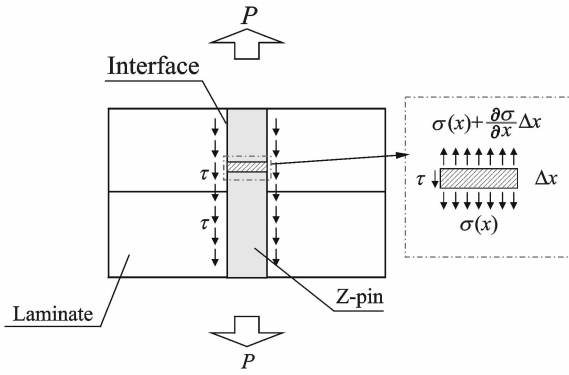


Fig. 7 Stress analysis of Z-pin in the laminates

When the embedded length l is lower than the critical embedded length of Z-pin l_c , the failure mode is interfacial debonding and being pulled-out, otherwise the Z-pin fails in rupture.

The relationship between Z-pin curing degree α and interfacial shear strength $\tau_{p,s}$ and the tensile strength $\sigma_{p,u}$ can be acquired by Z-pin "bridging law" test and tensile test. Therefore, the relationship between the maximum bridging force $F_{p,max}$ and Z-pin curing degree α can be determined.

2.2 Effect of Z-pin's curing degree on bridging force

Fig. 8 shows the typical load-displacement curve of Z-pinned laminates in the "bridging law" test. The total process can be divided into three stages: (1) The bridging force increases linearly with the displacement while Z-pin deforms elastically. The slope is determined by the axial tensile module of Z-pin. (2) When the bridging force reaches P_{max} , debond occurs and the force drops to P_f . (3) Z-pin is gradually pulled out from the matrix while the friction can contribute energy absorption.

Therefore, the interfacial shear strength $\tau_{p,s}$ can be calculated by

$$\tau_{p,s} = \frac{P_{max}}{n\pi dl} \quad (10)$$

The bridging effect provided by Z-pin depends on many factors such as Z-pin properties, residual stress at the interface between the Z-pin and the composite due to the mismatch of coefficient of thermal expansion (CTE)^[22], and the

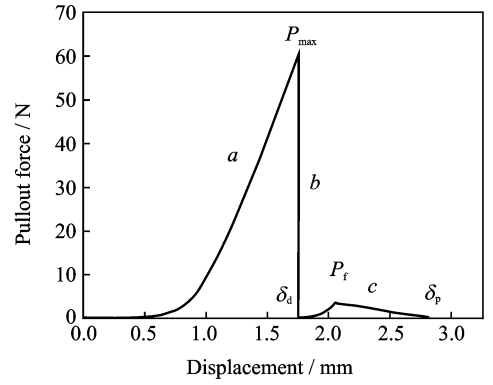


Fig. 8 Typical load-displacement curve of Z-pin "bridging law" test

frictional effect during the pullout process. The co-curing between Z-pin and laminates may improve the interfacial bonding and reduce the interfacial crack caused by the CTE mismatch. Therefore, the decrease of Z-pin curing degree will enhance the bridging effect.

The relationship of interfacial shear strength and Z-pin curing degree is shown in Fig. 9. It is found out that the shear strength of Z-pin/laminates' interface increases with the decrease of Z-pin curing degree. Compared with the 100% Z-pin, the interfacial shear strength of Z-pin with 67.6% curing degree is improved by 30.7%. According to the results of the linear fitting, the interfacial shear strength $\tau_{p,s}$ shows a linear relation with curing degree of Z-pin α , namely

$$\tau_{p,s} = 44.44 - 21.1\alpha \quad R^2 = 0.9773 \quad (11)$$

The metallograph of interface of laminates and Z-pin with different curing degrees is shown in Fig. 10. There exists obvious crack along the completely-cured Z-pin/laminates' interface. This is due to the interfacial residual stress caused by CTE mismatch. Rare obvious interfacial crack can be observed while the Z-pin is 67.6% cured, which ensures a better interfacial bond. Therefore, the partly-cured Z-pin can provide better bridging effect.

To explain the reinforcing mechanism further, the Leica DVM5000 three-dimensional video microscopy is adopted to observe the surface morphology of Z-pin after pullout (Fig. 11). Com-

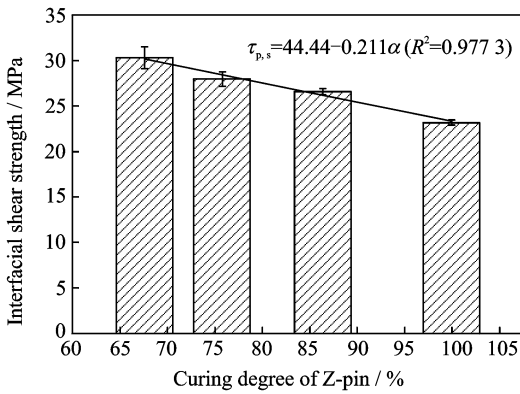


Fig. 9 Interfacial shear strength and Z-pin curing degree

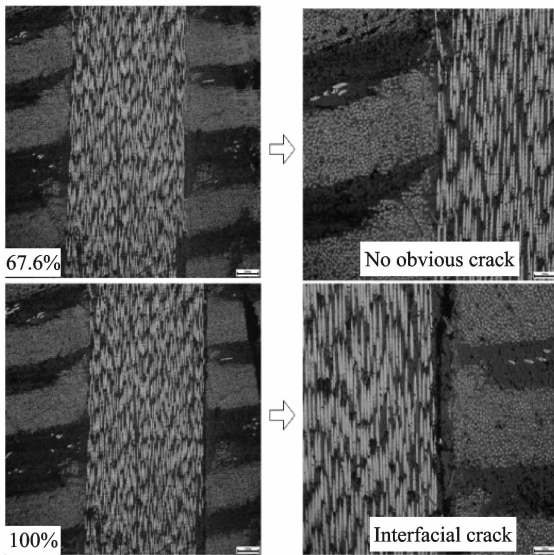
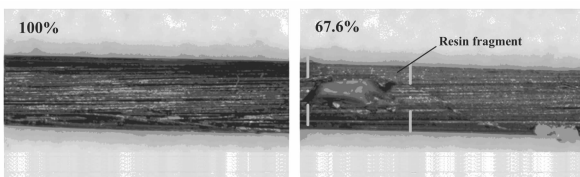


Fig. 10 Interfacial bonding situation of Z-pinned laminate



(a) Surface of completely-cured Z-pin (b) Surface of partly-cured Z-pin

Fig. 11 Surface morphology of Z-pin after pullout

pared with the completely-cured Z-pins, the partly-cured Z-pins with 67.6% curing degree are much rougher; The surface of Z-pin with 67.6% curing degree has obvious resin fragments. This indicates that the failure mechanism changes from interfacial debonding to a combined failure of in-

terface and cohesive failure. Therefore, we can conclude that the decrease of Z-pin's curing degree can improve the bridging effect by on one hand eliminating micro cracks during manufacture and on the other hand enhancing the co-curing effect between Z-pin and laminates matrix.

2.3 Effect of Z-pin's curing degree on tensile strength

The results of the Z-pin tensile test are shown in Fig. 12, and we can see that Z-pin curing degree has marginal effect on the tensile module. It suggests that the axial elastic property is mainly up to the reinforcement fiber. However, the axial tensile strength shows a negative correlation with Z-pin curing degree. With the reduction of Z-pin's curing degree, the tensile strength shows an obvious decrease: The average tensile strength of Z-pin with 67.6% curing degree is only 81.4% of completely-cured Z-pin. This is because secondly curing will reduce the bonding situation between resin and carbon fiber inside Z-pins.

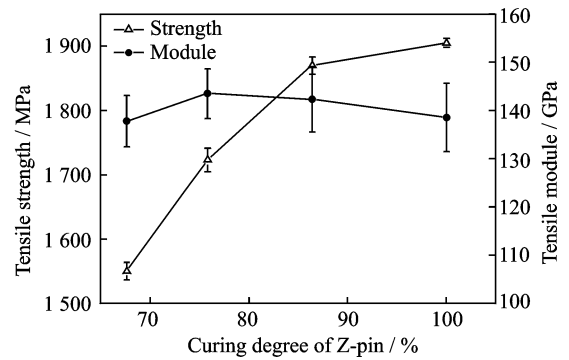


Fig. 12 Z-pin tensile properties and Z-pin curing degree

2.4 Optimization of Z-pin bridging efficiency

According to Eqs. (4), (11), the relationship between Z-pin maximum bridging force $F_{p,max}$ and the curing degree α , diameter d and embedded length l of Z-pin can be expressed by

$$F_{p,max} = \begin{cases} \pi dl(44.44 - 21.1\alpha) & l < l_c \\ \pi d^2 \sigma_{p,u} / 4 & l \geq l_c \end{cases} \quad (12)$$

The critical embedded length of Z-pin can be calculated by

$$l_c = \frac{d}{177.76 - 84.4\alpha} \times \sigma_{p,u} \quad (13)$$

Fig. 13 shows the relationship between the maximum bridging force of Z-pin $F_{p,max}$ with different curing degrees and embedded length for the Z-pin with the diameter of 0.3 mm. The results of Fig. 13 indicate that the interfacial bonding can be enhanced by the co-curing effect which improves the bridging force of Z-pins fail by pull-out. However, when Z-pins fail by rupture, due to the adverse effect of partly-cure on the tensile strength of Z-pin, the maximum bridging force provided by partly-cured Z-pin is lower than that by completely-cured Z-pin.

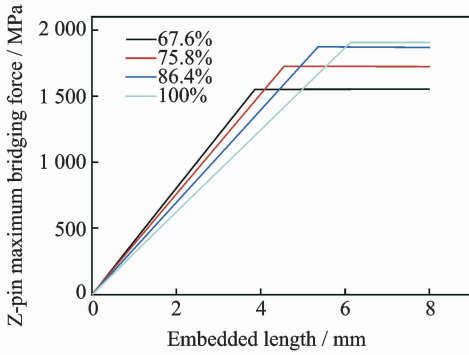


Fig. 13 Z-pin maximum bridging force and embedded length

In order to compare the interlaminar reinforcement of Z-pin with different curing degrees reasonably, the Z-pin bridging efficiency ϕ is defined by the specific value of the maximum bridging force per embedded length between the partly-cured and the completely-cured Z-pins, namely

$$\phi = \frac{F_{p,max}(\alpha)/l}{F_{p,max}(100\%)/l} \times 100\% \quad (14)$$

The bridging efficiency of Z-pin with different curing degrees is shown in Fig. 14. It can be observed that the bridging efficiency increases with the reduction of Z-pin curing degree within the critical embedded length. The efficiency of Z-pin with 67.6% curing degree is improved by 29.0% compared with the completely-cured Z-pin. When the embedded length reaches the critical value l_c , the bridging efficiency of Z-pin starts to decline. For the 67.6% curing degree of Z-pin,

when the embedded length reaches 4.98 mm, the efficiency is 100%. With the embedded length increasing continuously, although the bridging force still increases, the bridging efficiency of Z-pin is lower than that by completely-cured Z-pin. Therefore, the reinforced laminates thickness is also an important consideration when we seek the maximum interlaminar reinforcement of Z-pins by utilizing the Z-pin/laminate co-curing effect.

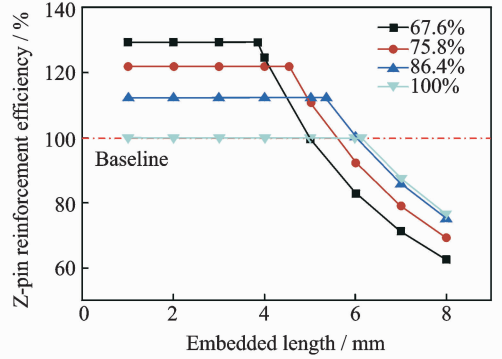


Fig. 14 Bridging efficiency of Z-pin with different curing degrees

2.5 Mode I interlaminar fracture toughness G_{IC}

Five specimens of each degree of cure are tested to study the influence of the co-curing effect on G_{IC} , namely

$$G_{IC} = \frac{3P\delta}{2b(a + |\Delta|)} \quad (15)$$

where P is the measured load, N; δ the crack-open displacement, mm; b the width of the specimen, mm; and a the crack length, mm. Δ is the correction factor of the crack length a , and is determined experimentally by generating a least squares plot of the cube root of compliance $(\delta/P)^{1/3}$. The intercept between this intersection point and the origin of coordinates is defined as the Δ -value.

The R -curves of the Z-pins with different curing degrees are shown in Fig. 15. The comparison between G_{IC} v. s. crack length a of the samples indicates that the critical energy release rate decreases with the increase of Z-pin's curing degree. The results of DCB test are shown in Fig. 16, and it is found that the average G_{IC} of specimens reinforced with the completely-cured

Z-pins is $1\,105\text{ J/m}^2$ and the average G_{IC} of the partly-cured Z-pins reaches up to $1\,628\text{ J/m}^2$ with an increment of 47.0% . The toughening effect is significant.

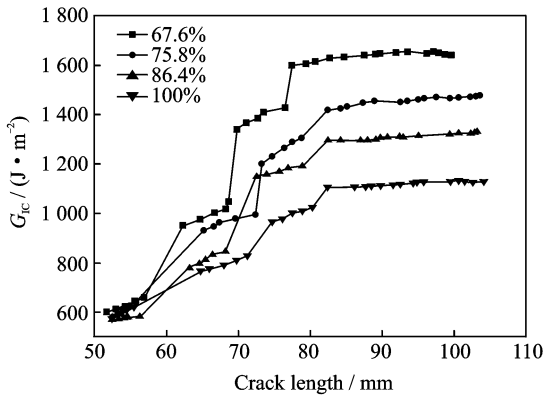


Fig. 15 Delamination resistance curves (R -curves) of different curing degrees Z-pins with DCB specimens under mode-I crack opening

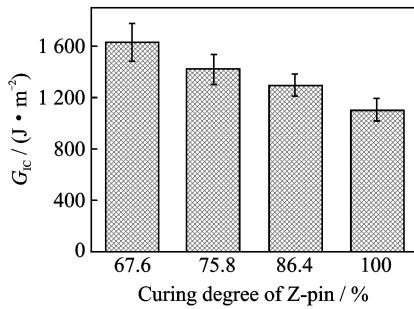


Fig. 16 Comparison of average values of the critical energy release rate of specimens with different Z-pins' degrees of cure

According to Refs. [4-6], inserting Z-pin can improve the mode I interlaminar fracture toughness significantly. The reinforcement mechanism is that when the crack propagates into the Z-pinned zone, on one hand the bridging of Z-pins begins to suppress the propagation of crack, and on the other hand the pullout of Z-pin consumes a great amount of energy. Based on it, we assume that the interlaminar fracture toughness of Z-pinned laminates G_{IC} can be divided into the following two parts

$$G_{IC} = G_c + G_{pin} \quad (16)$$

where G_c represents the interlaminar toughness of the laminates without Z-pin, J/m^2 ; and G_{pin} the

interlaminar toughness provided by the Z-pins which is related to Z-pin's interfacial bonding situation with laminates and equal to the energy consumed by Z-pin's pullout, J/m^2 .

According to Eq. (16), when the interfacial bonding situation is improved, the energy consumed by Z-pin will increase, and consequently G_{IC} will be improved. Compared with the completely-cured Z-pins, the active groups of the partly-cured Z-pins can set off more chemical reaction with the prepregs and occur secondary cross-linking, forming covalent bonds, which leads to the more energy consumed in the process of Z-pin's pullout.

3 Conclusions

Z-pins with different curing degrees are manufactured by pultrusion and measured by DSC method. The Z-pin "bridging law" test and double cantilever beam test are carried out to study the influence of curing degree of Z-pin on the interlaminar reinforcement of laminates. From the present results, several conclusions are drawn as follows:

(1) The oven temperature and pultrusion speed are the main factors to control the curing degree of Z-pin by isothermal curing kinetics analysis. Z-pin's curing degree decreases by reducing the oven temperature and increasing the pultrusion speed.

(2) The results of the stress analysis show that the maximum bridging force of Z-pin is determined by the Z-pin's diameter, embedded length, interfacial shear strength and tensile strength. Results of "bridging law" test indicate an approximately linear relationship between Z-pin curing degree and interfacial shear strength. Compared with completely-cured Z-pin, the interfacial shear strength of Z-pin with 67.6% curing degree is improved by 30.7%. A change of Z-pin pullout's mechanism from interfacial failure to a mix mode of interfacial and cohesive failure is observed by three-dimensional video microscopy.

Besides, the tensile strength of Z-pin decreases with the reduction of Z-pin's curing degree.

(3) Z-pin bridging efficiency is defined taking the interfacial reinforcement and reduction of Z-pin's axial properties into consideration. Compared with completely-cured Z-pin, the efficiency of Z-pin with 67.6% curing degree is improved by 29.0%. When the embedded length increases to the critical value, all the Z-pin bridging efficiency starts to fall down with the further increase of length.

(4) The critical energy release rate of Z-pinned laminates under mode I increases with the reduction of Z-pin's curing degree. Compared with completely-cured Z-pin, G_{IC} of Z-pin with 67.6% curing degree enhances by 47.0%.

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References:

- [1] WO D Z. Encyclopedia of composites[M]. Beijing: Chemical Industry Press, 2000: 2-3.
- [2] MOURITZ A P. Review of Z-pinned composite laminates[J]. Composites Part A: Applied Science & Manufacturing, 2007, 38(12):2383-2397.
- [3] MOURITZ A P, BANNISTER M K, FALZON P J, et al. Review of applications for advanced three-dimensional fibre textile composites[J]. Composites Part A: Applied Science & Manufacturing, 1999, 30(12):1445-1461.
- [4] PARTRIDGE I K, CARTIÉ D D R. Delamination resistant laminates by Z-fiber® pinning: Part I manufacture and fracture performance[J]. Composites Part A: Applied Science & Manufacturing, 2005, 36(1):55-64.
- [5] BYRD L W, BIRMAN V. Effectiveness of Z-pins in preventing delamination of co-cured composite joints on the example of a double cantilever test[J]. Composites Part B: Engineering, 2006, 37(4):365-378.
- [6] LIU H Y, YAN W, YU X Y, et al. Experimental study on effect of loading rate on mode I delamination of Z-pin reinforced laminates[J]. Composites Science & Technology, 2007, 67(7/8):1294-1301.
- [7] PEGORIN F, PINGKARAWAT K, DAYNES S, et al. Influence of Z-pin length on the delamination fracture toughness and fatigue resistance of pinned composites[J]. Composites Part B: Engineering, 2015, 78:298-307.
- [8] ZHANG X, HOUNSLOW L, GRASSI M. Improvement of low-velocity impact and compression-after-impact performance by Z-fibre pinning[J]. Composites Science & Technology, 2006, 66(15):2785-2794.
- [9] KOH T M, ISA M D, FEIH S, et al. Experimental assessment of the damage tolerance of Z-pinned T-stiffened composite panels[J]. Composites Part B: Engineering, 2013, 44(1):620-627.
- [10] FREITAS G, MAGEE C, DARDZINSKI P, et al. Fiber insertion process for improved damage tolerance in aircraft laminates[J]. Journal of Advanced Materials, 1994, 25(4):36-43.
- [11] ZHANG A Y, LIU H Y, MOURITZ A P, et al. Experimental study and computer simulation on degradation of Z-pin reinforcement under cyclic fatigue[J]. Composites Part A: Applied Science and Manufacturing, 2008, 39(2):406-414.
- [12] WARZOK F, ALLEGRI G, GUDE M, et al. Experimental characterisation of fatigue damage in single Z-pins[J]. Composites Part A: Applied Science & Manufacturing, 2016, 91(7):461-477.
- [13] MOURITZ A P, CHANG P. Tension fatigue of fibre-dominated and matrix-dominated laminates reinforced with Z-pins[J]. International Journal of Fatigue, 2010, 32(4):650-658.
- [14] KOH T M, FEIH S, MOURITZ A P. Strengthening mechanics of thin and thick composite T-joints reinforced with Z-pins[J]. Composites Part A: Applied Science & Manufacturing, 2012, 43(8):1308-1317.
- [15] LI M, CHEN P, KONG B, et al. Influences of thickness ratios of flange and skin of composite T-joints on the reinforcement effect of Z-pin[J]. Composites Part B: Engineering, 2016, 97:216-225.
- [16] MOURITZ A P, CHANG P, ISA M D. Z-pin composites: Aerospace structural design considerations[J]. Journal of Aerospace Engineering, 2011, 24(4):425-432.
- [17] DAI S C, YAN W, LIU H Y, et al. Experimental

- study on Z-pin bridging law by pullout test[J]. *Composites Science & Technology*, 2004, 64(16):2451-2457.
- [18] KNAUPP M, BAUDACH F, FRANCK J, et al. Impact and post-impact properties of CFRP laminates reinforced with rectangular Z-pins[J]. *Composites Science & Technology*, 2013, 87(9):218-223.
- [19] KNOPP A, SCHARR G. Effect of Z-pin surface treatment on delamination and debonding properties of Z-pinned composite laminates[J]. *Journal of Materials Science*, 2014, 49(4):1674-1683.
- [20] WANG Xiaoxu, CHEN Li, JIAO Yanan, et al. Experimental study on interfacial adhesive properties between twisted Z-pin and laminates[J]. *Journal of Solid Rocket Technology*, 2014, 21(4):615-631. (in Chinese)
- [21] ZHANG Xiangyang, LI Yong, CHU Qiyi, et al. Pultrusion and properties of the twisted carbon fiber/phenolic resin Z-pin [J]. *Journal of Aerospace Power*, 2015, 30(7):1638-1644. (in Chinese)
- [22] SWEETING R D, THOMSON R S. The effect of thermal mismatch on Z-pinned laminated composite structures[J]. *Composite Structures*, 2004, 66(S1/2/3/4):189-195.

Mr. **Chu Qiyi** received B. S degree in Materials Processing Engineering from Nanjing University of Aeronautics and Astronautics in 2011. From 2012 to present, he has been with the College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics (NUAA), where he is currently a Ph. D. candidate. His research is focused on through-the-thickness reinforcement technology and low-cost manufacture technology of fiber reinforced resin matrix composites.

Prof. **Li Yong** received his B. S. and Ph. D. degrees in Materials Processing Engineering from Nanjing University of Aeronautics and Astronautics, in 1993 and 2010, respectively. From 2010 to present, he has been with College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics (NUAA), where he is currently a full professor. His research has focused on through-the-thickness reinforcement technology and manufacturing processes of advanced composites.

Prof. **Xiao Jun** received his B. S. and M. S. degrees in Materials from Harbin Institute of Architecture, in 1982 and 1985, respectively. From 1985 to present, he has been with College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics (NUAA), where he is currently a full professor. His research has focused on low-cost manufacturing processes of advanced composites and automation.

Dr. **Huan Dajun** received his B. S. and Ph. D. degrees in Materials Processing Engineering from Nanjing University of Aeronautics and Astronautics, in 2003 and 2010, respectively. From 2010 to present, he has been with College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics (NUAA), where he is currently a lecturer. His research has focused on manufacturing processes of advanced composites.

Ms. **Zhang Xiangyang** received her B. S. degree in Materials Processing Engineering from Nanjing University of Aeronautics and Astronautics, in 2010. From 2011 to present, she has been with College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics (NUAA), where she is currently a Ph. D. candidate. Her research has focused on through-the-thickness reinforcement technology of fiber reinforced resin matrix composites.

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