Study on single-lap joints tensile properties under fire and thermal conductivity of Z-pin reinforced thermal protection composites

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Abstract. Quartz fiber reinforced phenolic (QFRP) resin composites were often used in thermal protection structures such as the engines and tip of missiles or rockets, but its anti-erosion performance needs to be further optimized. Z-pin technology can improve the anti-erosion performance because Z-pin effectively improved the inter-laminar shear strength of composite materials. However, it will increase the through-thickness thermal conductivity (TC), resulting in a decrease of its thermal protection performance. This paper successfully established the equation about through-thickness TC of Z-pin reinforced composites based on theoretical analysis and experimental results and tested the single-lap joints tensile strength of the samples compared with the blank and Z-pin samples under fire which characterized the interlayer performance of Z-pin reinforced thermal protection composites at high temperatures. Research showed that the through-thickness TC of the composite increases regularly with the TC and content of Z-pin, and this is because the pins act as a thermally conductive pathway. The TC increases by 13.19%, 12.34% and 12.13% when the Z-pin implantation volume fraction is 2.18%, 0.785% and 0.401%, respectively. Z-pin samples have an increase in shear strength of 63.85%, 78.97% and 88.31% compared with blank samples when the ablation time is 20s, 40s and 60s, respectively, indicating that Z-pin technology effectively could reduce the shear strength of single-lap joint with the increase of ablation time. These results prove the controllability of the through-thickness TC enhancement and effectiveness of interlayer strength by Z-pin, and guide the structural design of Z-pin reinforced thermal protection composites.

1. Introduction
The performance and reliability of thermal protection materials is one of the decisive factors for the development of aircraft such as hypersonic aircraft [1], reentry aircraft, and space exploration aircraft [2]. Ablation thermal protection is a common method for returning spacecraft, reentry missile warheads and the inner wall of rocket engines. It is the only feasible thermal protection method under high heat flow conditions. Quartz/phenolic composites are widely used in aerospace fields as ablative thermal resistant materials due to their low density [3], low thermal conductivity, low line ablation rate, and high carbon formation rate [4].

In recent years, rockets, missiles and other aircraft have developed in the direction of high Mach number and lightweight, higher requirements are put forward for thermal protection materials accordingly [5]. The introduction of ablative ceramic powders in resin-based composite systems is a
simple and effective modification method [6-8]. Li et al. [9] investigated the ablation resistance of quartz phenolic composites modified by glass microspheres and ZrB₂. Its high performance of low line ablation and mass ablation rate is related to the "nail-anchor effect" of ZrO₂ in silicon melts.

The principle of the "nail-anchor effect" is very similar to Z-pin technology. The principle of the "nail-anchor effect" is very similar to Z-pin technology. Z-pin has become a fast-developing three-dimensional reinforcement technology due to its advantages such as high efficiency, low cost, good operability, and small in-plane damage [10]. It has been applied in aviation stiffened structures [11]. F/A 18-E/F fighter jet, engine compartment door and other structures. Studies have shown that Z-pin can increase the type I and II inter laminar fracture toughness of composites by 18% [12] and 53% [13] and increase the interlayer bonding strength by 40% [14]. Chang et al. [15] investigated the shear properties of Z-pin reinforced single-lap joints. When the Z-pin volume fractions were 0.5%, 2%, and 4%, the tensile failure loads were increased by 8%, 41%, and 23%, respectively. Z-pin implantation will increase the through-thickness TC of the composites, which has a negative impact on the heat-resistant function of the thermal protection materials. Li et al. [16] considers composites show considerable increase in through-thickness TCs after implanting carbon fiber Z-pins. At present, there is less information about applying Z-pin technology to thermal protection materials, and the effect on interlayer enhancement and through-thickness TC are unknown.

This paper obtained the equation of through-thickness TC by establishing a Z-pin reinforced composites heat conduction model, and the steady-state heat flow method is used to test the through-thickness TC of QFRP with different Z-pin implantation parameters. And in this paper, the tensile strength of single lap joint of Z-pin and blank samples under different ablation conditions was measured, then the failure mode and strength of them were compared, in order to discuss the mechanism of inter laminar reinforcement of Z-pin on thermal materials.

2. Experimental

2.1. Materials

Three kinds of fibers, T300 and M60J carbon fibers manufactured by Toray and B Type Quartz fibers manufactured by Suzhou Donghua Fiber Material Products Co., Ltd. They were used to fabricate pins denoted as T-pin, M-pin and Q-pin [17-19], respectively. Both phenolic resin and quartz/phenolic prepreg were supplied by Honggang Machinery Factory of Inner Mongolia. Phenolic resin was used to fabricate pins, and prepreg turn into laminated composites after hot pressing. table 1 shows the density and axial or through-thickness TC of these materials.

| Material               | Density/(g·cm⁻³) | TC/(W·m⁻¹·K⁻¹) |
|------------------------|------------------|-----------------|
| T300-Carbon fibers     | 1.76             | 4.00            |
| M60J-Carbon fibers     | 1.93             | 7.00×10         |
| B-Quartz fibers        | 2.20             | 1.40            |
| Phenolic resin         | 1.13             | 0.02            |
| Quartz/phenolic composites | 1.49           | 0.47            |

2.2. Measurement on through-thickness TC of Z-pinned QFRP composites

The volume content and axial TC of Z-pin will change the state of heat transfer path in the direction of composite laminate thickness. Therefore, the effects of different reinforcing fiber materials of Z-pin, the spacing of Z-pin implantation, and the diameter of Z-pin on the through-thickness TC of QFRP composites were studied, respectively. The detailed test plan is shown in table 2.
Table 2. TC test plan of Z-pinned QFRP composites.

| Number | Type of fibers in Z-pin | Diameter/mm | Spacing of implantation/(mm × mm) |
|--------|-------------------------|-------------|----------------------------------|
| Blank  | None                    | 0           | 0                                |
| T-1    | T300-Carbon fibers      | 0.5         | 5 × 5                            |
| T-2    | M60J-Carbon fibers      | 0.5         | 5 × 5                            |
| T-3    | B-Quartz fibers         | 0.3         |                                  |
| D-1    | T300-Carbon fibers      | 0.7         |                                  |
| D-2    | T300-Carbon fibers      | 0.3         |                                  |
| D-3    | T300-Carbon fibers      | 0.5         | 3 × 3                            |
| S-1    | T300-Carbon fibers      | 0.5         | 5 × 5                            |
| S-2    | T300-Carbon fibers      | 0.5         | 3 × 3                            |
| S-3    | T300-Carbon fibers      | 0.5         | 7 × 7                            |

The composite laminates were shaped to round samples with diameter of 30mm and thickness of 4mm for through-thickness TC measurement. A DRL-II Thermal Conductivity Tester was used to record the temperature at four points on the upper and lower surfaces. Hot and cold poles temperatures are set to 60°C and 10°C, respectively. Both hot and cold poles have two temperature sensors separated by an axial distance, and TC of poles’ materials is known, so the respective heat flow values can be calculated. Figure 1 shows the experimental sample and equipment. Heat flow value flowing through the sample is equal to the average of heat flow values from the hot and cold pole.

Figure 1. Experimental sample and equipment.

The through-thickness TC of composite laminates can be calculated by a functional relationship:

$$ \lambda = \frac{L \cdot Q}{A \cdot \Delta T} $$

where L and A is sample thickness and area, Q is heat flow value flowing through the sample, $\Delta T$ is temperature difference on both sides of the sample.

2.3. High-temperature single-lap joint tensile test
In order to study the high-temperature performance of QFRP single-lap joint, tensile experiments were performed on blank and Z-pin reinforced single lap joints. A flame-spray gun achieves the high-temperature environment, and a point-type thermocouple is set on the front and back of the sample. When the sample’s temperature is eligible, the timing is beginning. When the timing reaches 20s, 40s, and 60s, the tensile test is performed respectively and the results are compared. The Z-pin material is
quartz fibers reinforced phenolic resin with a diameter of 0.5mm, an implanted spacing of 5mm×5mm, and an implanted depth throughout the entire overlap thickness. The joint was designed with reference to ASTM D3039/D 3039M-07. The sample length is \( l \), the lap length is \( l_0 \), the width is \( b \), the joint thickness is \( h \), and the thickness of reinforcement is \( n \). The geometric dimensions of single-lap joint are shown in figure 2.

![Figure 2. Geometric dimensions of single-lap joint specimen.]

Figure 3 shows a schematic illustration and equipment of tensile test. The centerline of the muzzle of the flame spray gun is at the same level as the centerline of the overlap of the sample. The front temperature of the sample can reach 900 °C and remain stable when the muzzle is 10 cm away from the sample. This test was performed on a Sans Universal Testing Machine with a tensile speed of 0.5 mm/min.

![Figure 3. Schematic illustration and equipment of tensile test.]

When the front temperature is 900 °C, the back temperature of blank and Z-pin sample reach 750°C and 780°C, respectively. At this point, the temperature at the overlap is considered to be 830°C, which reaches the target experimental temperature. After single-lap joint tensile tests, the failure surfaces were analyzed by Three-dimensional Topography Instrument (Leica DVM6), in order to analyze its failure mode better.

3. Through-thickness TC of Z-pin reinforced QFRP composites

3.1. Simplified heat conduction model of Z-pin reinforced composites

According to Fourier's law, the thermal resistance \( R \) of a homogeneous material has the relationship:

\[
R = \frac{L}{A \cdot \lambda}
\]  

where \( L \) and \( A \) are the length and area of the heat flow channel, \( \lambda \) is the TC of the channel materials. For composites, the equivalent thermal resistance \( R_e \) is introduced, corresponding to the equivalent TC \( \lambda_e \), which also has:
According to the law of equal specific TC, periodic unit body of composites has equal specific equivalent thermal resistance when the composites are homogeneous macroscopically. When only heat conduction is considered, the unit body has the same equivalent TC as the overall. Therefore, the calculation of TC of composite material can be simplified to the calculation of equivalent thermal resistance of element. Heat transfer in solids follows the law of least resistance in nature. Some people compare the thermal resistance to resistance, and simplify the composites unit body into a corresponding equivalent thermal resistance network. The equivalent thermal resistance is calculated by using the calculation method of resistance.

When the Z-pin in the composites is uniformly distributed with the same specifications, a periodic unit body containing one Z-pin can be taken as the calculation unit of the equivalent thermal resistance of the Z-pin reinforced composites, as shown in figure 4.

![Figure 4. Unit body of Z-pin reinforced composites.](image)

Z-pin reinforced composites are purely parallel models (as shown in figure 5).

From the pure parallel model of Z-pin and composites, the equivalent thermal resistance of Z-pin reinforced composite material is:

$$\frac{1}{R} = \frac{1}{R_c} + \frac{1}{R_p}$$

Substituting formulas (1) and (2) into (4):

$$\lambda = \frac{A_p \lambda_c}{A} + \frac{A \lambda_p}{A}$$

When Z-pin is implanted vertically, Z-pin volume fraction $V_p = \frac{A_c}{A}$, Then the equivalent TC is:

$$\lambda = (1-V_p)\lambda_c + V_p\lambda_p$$

Consistent with the mixing rules of composite materials. Z-pin is a unidirectional fiber reinforced composites. The equivalent TC $\lambda_p$ of Z-pin can be obtained by parallel equivalent method:

$$\lambda_p = (1-V_{pf})\lambda_{pm} + \lambda_{pf}V_{pf}$$

where $\lambda_{pf}$ and $\lambda_{pm}$ is TC of fiber and resin in Z-pin, $V_{pf}$ is the volume fraction of the fiber in the Z-pin.

Substituting formulas (7) into (6):
\[
\lambda = (1 - V_p)\lambda_c + \left[ (1 - V_{pf})\lambda_{pm} + \lambda_{pf}V_{pf} \right] V_p
\]  

(8)

From the above formula, three important factors affecting the through-thickness TC of Z-pin reinforced composites are obtained: the Z-pin volume fraction, the TC of the fibers in the Z-pin and its volume fraction.

3.2. Test result of TC on QFRP composites with different Z-pin

The through-thickness TC of sample without Z-pin is 0.47 W m\(^{-1}\) K\(^{-1}\). TC will increase to varying degrees after Z-pin implantation. On the one hand, the fiber in Z-pin directly forms continuous through-thickness conductive path. On the other hand, Z-pin possess higher TC than composites, and it is a component that improves the through-thickness TC.

Figure 6 shows the relationship between axial TC of fibers in Z-pin and through-thickness TC of QFRP composites.

![Figure 6. Variation of TC with fibers’ TC in Z-pin.](image)

![Figure 7. Variation of TC with Z-pin volume fraction.](image)

The through-thickness TC of composites has a linear growth with the axial TC of fibers in Z-pin. In addition, the larger Z-pin implantation volume fraction, the greater growth rate. The implantation of quartz/phenolic Z-pin has little effect on TC. When the volume fraction of quartz/phenolic Z-pin implantation is 2.18%, the TC increases by 0.062 W m\(^{-1}\) K\(^{-1}\), which is 13.19%, relative to the blank sample. The Z-pin made of M60J/phenolic with a large TC significantly increases the TC of the composites. When the volume fraction of M60J/phenolic Z-pin implantation is 2.18%, the TC increases by 1.05 W m\(^{-1}\) K\(^{-1}\), which is 224.0%, relative to the blank sample.

Figure 7 shows the relationship between volume fractions of Z-pin and through-thickness TC of QFRP composites. It can be seen that when the Z-pin is made of quartz fiber, the TC hardly increases with the increase of the volume fraction. Therefore, the Z-pin made of the same heatproof material is used to strengthen the thermal protection structure, which will not cause too much effect to TC. You can rest assured to use Z-pin technology.

3.3. Comparison of theory and experiment result

The comparison between TC calculated theoretically and TC measured experimentally is listed in table 3.
Table 3. Comparison between TC calculated theoretically and TC measured experimentally.

| Number  | Difference /W m⁻¹ K⁻¹ | Test value /W m⁻¹ K⁻¹ | Theoretical value /W m⁻¹ K⁻¹ |
|---------|------------------------|------------------------|-----------------------------|
| Blank   | 0                      | 0.470                  | 0.470                       |
| 0.5Q-3×3 | 0.058                  | 0.532                  | 0.474                       |
| 0.5Q-5×5 | 0.057                  | 0.528                  | 0.471                       |
| 0.5Q-7×7 | 0.056                  | 0.527                  | 0.471                       |
| 0.5T-3×3 | 0.073                  | 0.584                  | 0.511                       |
| 0.5T-5×5 | 0.071                  | 0.555                  | 0.485                       |
| 0.5T-7×7 | 0.069                  | 0.547                  | 0.478                       |
| 0.5M-3×3 | 0.150                  | 1.520                  | 1.380                       |
| 0.5M-5×5 | 0.140                  | 0.941                  | 0.796                       |
| 0.5M-7×7 | 0.140                  | 0.780                  | 0.636                       |
| 0.7T-5×5 | 0.072                  | 0.571                  | 0.500                       |
| 0.3T-5×5 | 0.075                  | 0.550                  | 0.475                       |

Table 3 shows that the theoretical value of the through-thickness TC of the Z-pin reinforced QFRP composites is smaller than the experimental value, because the theoretical model only considers the heat transfer of the Z-pin along its own axis, and ignores the Z-pin to the laminate. The heat transfer is shown in figure 8.

![Figure 8. Heat transfer diagram.](image)

Because the axial TC of the Z-pin is higher than the through-thickness TC of the laminate, during the heat transfer process, the temperature of the Z-pin in the same cross-section is higher than the temperature of the surrounding laminate. This causes the Z-pin not only to transfer heat from the high-temperature surface to the low-temperature surface along its axis, but also to transfer heat to the surrounding laminate through the bonding interface, thereby increasing the overall TC of the laminate.

Considering the cause of the difference, the axial TC of fibers in Z-pin is the main cause of the difference. Figure 9 shows the relationship between difference and axial TC of fibers in Z-pin.
Figure 9. Relationship between difference and axial TC of fibers in Z-pin.

From Figure 9, the equation of the difference $\lambda_D$ between the theoretical value and the experimental value can be expressed by:

$$\lambda_D = 0.0012\lambda_{pf} + 0.06$$

Correct formula 8 and add the difference $\lambda_D$ to the theoretical value to get the true TC $\lambda_T$ expression:

$$\lambda_T = (1-V_p)\lambda_c + [(1-V_{pf})\lambda_{pm} + \lambda_{pf}V_p] + 0.0012\lambda_{pf} + 0.06$$

The calculation results of the Equ.10 are considered to be consistent with the actual measurement results after theoretical analysis and experimental verification. Equ.10 can be used to calculate the through-thickness TC of the Z-pin reinforced composites, and provide the basis for the three-dimensional reinforcement design with restriction of thermal conductivity.

4. Single-lap joints tensile strength under high temperature
The tensile action of the single-lap joints sample is equivalent to shearing the bonding surface, which can effectively characterize the interlayer strength of the sample.

4.1. Effect of different ablative time on QFRP composites tensile strength of single-lap joints
In the same ablation time, two groups of blank and Z-pin enhanced samples were compared. Observing the experimental process, it was found that at the same ablation temperature (section 2.3), when the ablation time reached 15s, the sample would start to burn resin, and the combustion continued for about 20s. Figure 10 shows the morphology of the ablation surface and tensile failure surface at an ablation time of 60S, where (a) and (b) are the ablation surfaces of the blank sample and the Z-pin enhanced sample, respectively, (c) and (d) The tensile failure surfaces of the blank specimen and the Z-pin reinforced specimen, respectively.
Figure 10. Morphology of ablative and tensile-failure surface.

In figure 10, the ablation surface of the blank sample almost completely shows the white color of the quartz fiber, and there is a little bit of residual carbon. However, the failure surface is mainly black, which is formed by the carbon remaining after the resin burns. At the same time, the Z-pin sample has a lower burning degree than the blank sample. It may be that the Z-pin provides a path for heat transfer, prevents heat accumulation, and slows down the carbonization of the resin.

Calculation formula of shear strength $\tau_b$ of lap surface:

$$\tau_b = \frac{F_b}{bL_0}$$

(11)

where $F_b$ is the peak load at the time of single-lap joints failure.

The shear strength of the lap surface gradually decreases with the increase of ablation time. Figure 11 shows the relationship between them.

Figure 11. Relationship of tensile strength or growth rate and ablation time.

With the increase of the ablation time, the tensile strength of the single-lap joint is greatly reduced, but the reduction of the Z-pin specimen is significantly smaller than that of the blank specimen. That is, under the same ablative condition, the strength retention rate of Z-pin sample is better. For example, when the ablation time is 60s, the strength retention rates of the Z-pin and blank samples are 32.36%
and 22.75%, respectively. In addition, as the ablation time increases, the growth rate of the tensile strength of the Z-pin sample relative to the tensile strength of the blank sample increases logarithmically. Based on the analysis of the ablation process, the resin adhesion between the sample layers is the main source of resistance to tensile failure before the lap surface is ablated. As the ablation progresses, the resin bonded to the lap surface gradually being carbonized, the bonding force is getting smaller and smaller, and the bonding between the Z-pin and the composite material, in addition to the resin bonding force, also has mechanical forces that are not affected or less affected by ablation. When the resin is gone, the proportion of Z-pin's share force reaches the maximum. Therefore, Z-pin can effectively delay the tendency of the interlayer strength of the heat-resistant structure to decrease during the ablation process.

4.2. Morphological properties of tensile failure surfaces of single-lap joints

Figure 12 shows morphological properties of tensile failure surface of blank specimen.

![Figure 12. Tensile failure surface of blank sample.](image)

We can found the fiber broken in the Figure 12. This proves that during the stretching process of the blank sample, in addition to the shear failure of the resin bonding layer, it was also accompanied by the tensile failure of some fibers. During the hot-press curing of the prepreg, the fibers on the bonding surface are affected by pressure and resin flow, and some of the fibers are entangled, resulting in final damage during stretching. Fibers that undergo tensile failure are uncontrollable and in small numbers. Therefore, the failure mode of tensile test of blank single-lap joints sample is mainly based on the shear failure of the resin bonding layer.

During the tensile process of the Z-pin sample, in addition to the shear failure of the resin bonding layer, there is also resistance caused by the Z-pin. The specific morphological of failure surface of Z-pin sample is shown in figure 13.
Figure 13. Tensile failure surface of Z-pin sample.

Figure 13 (a) shows the morphology of the Z-pin with pullout failure, and the resin in Z-pin also ablated. The interface between Z-pin and laminate are losing adhesive force after ablated and only mechanical force remained. With stretching continued, the Z-pin shows the behaviors of pull out. From the 3D images of Z-pin pull out, it shows that with the increasing of height, Z-pin becomes thinner, and more and more fibers are lost. This should be attributed to that some of the fibers in Z-pin are combined with the laminated plate, when Z-pin is pulled out, the fibers are pulled by a large tension, thus fibers are teared off. (b) is the morphology of Z-pin of shear failure. The shear plane and failure plane are almost at the same horizontal plane. Both sides of the Z-pin have a strong binding force with the laminated plate respectively. During the tensile test, Z-pin is destroyed along with the shear failure of the resin bonding surface. (c) is the hole after Z-pin was removed. It can be clearly observed that the fiber in the laminated plate in the stress direction of Z-pin has been cut off. Therefore, in addition to the shear failure of the basic resin bonding layer, the tensile failure of Z-pin samples is accompanied by the tensile failure of the fibers in Z-pin and the shear failure of the fibers in laminated plates.

5. Conclusion

The following conclusions can be drawn by testing the TC of the samples and testing the tensile properties of the single-lap joints samples at high temperature:

The implantation of Z-pin increases the through-thickness TC of the composite laminate, and the axial TC of the fibers in the Z-pin is the main reason. Generally speaking, the material of the Z-pin is the same as the material of the laminate to be reinforced. Therefore, the use of Z-pin three-dimensional technology in the thermal protection structure will not have a large impact on its through-thickness TC.

After theoretical analysis and modification combined with experimental results, the expression formula of through-thickness TC of Z-pin reinforced composites is obtained, which can provide references for Z-pin reinforced composites.

The shear strength of the overlap surface of the single-lap joints decreases with the increase of the ablation time. The Z-pin technology effectively slows this downward trend. When the ablation time is 60s, Z-pin samples have an increase in shear strength of 88.31% compared with blank samples.

These results strongly prove the effectiveness of the application of Z-pin technology in the field of thermal protection structures, and provide a design basis for Z-pin reinforced composites.
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