Research on the influence of humid heat environment on the mechanical properties of multilayer composite structure

W C Wang*, H W Yang, N Li and Y S Kang
Institute of Physical and Chemical Engineering of Nuclear Industry, Tianjin300180, China
E-mail: wangwencai6666@sina.com

Abstract. For resin-based composite materials, the hot and humid environment has a very obvious impact on its performance. Moisture can penetrate into the composite material through diffusion and capillary action, which causes the resin matrix with plasticization, swelling and hydrolysis, and swelling and infiltration of liquid will lead to micro-stress inside the material. Thus, the polymer macromolecular chain will stretch or even break, and it can lead to the weakening of the interface properties of the resin and the fiber, which in turn leads to fluctuations in the mechanical properties of the composite material. In this paper, we carried out damp and heat tests on multilayer composite structures to study the effects of different temperature and humidity environments on the physical and chemical properties and mechanical properties of composite materials. The law of moisture absorption characteristics of composite materials is clarified, and the moisture absorption in the initial stage of moisture absorption is proportional to the moisture absorption time $t^{1/2}$. With time increasing, the moisture absorption gradually tends to balance, and the higher are the damp and heat conditions, the greater the moisture absorption of the composite material will be. The moisture absorption is between $0.13\%$ and $0.78\%$ with different damp and heat environments. The chemical structure of the composite material itself has not changed significantly, and the damp-heat effect will induce the destruction of the fiber-matrix interface and the expansion of cracks along the pores, which weakens the bonding strength of the interface. As a result, the moisture makes the transverse performance and shear performance of the composite material greatly reducing, but has little effect on the longitudinal performance.

Keywords: Composite Materials; Hot and Humid Environment; Moisture Absorption; Mechanical Properties

1. Introduction
As an advanced composite material, carbon fiber composite materials have been widely used in 16 fields including aviation, aerospace, construction engineering, automobiles, medical care, pressure vessels, military products and sports[1]. Take military aircraft as an example. With the continuous improvement of military aircraft performance requirements, the requirements for composite material structure performance are getting higher and higher. Aircraft composite material structures not only have to withstand complex and long-term fatigue loads and unexpected impact loads during service, and they have to withstand harsh external environmental tests such as temperature and humidity. In the strength design phase of composite aircraft structures, static strength design and verification involving the impact of humid and hot environments has become one of the important features of the strength...
specification. The hot and humid environment will not only cause the aging of the phase interface and phase components of the composite material, but also because the thermal expansion coefficient and the wet expansion coefficient of the fiber and resin are very different, it will produce non-negligible wet heat stress inside the structure. This effect is commonly called the damp-heat effect; the damp-heat effect has two main influences on composite materials: one is the change in the internal stress state of the material caused by the hot and humid environment; the second is that the performance of the component material will change due to the hot and humid environment[2]. At the same time, the hot and humid environment will also cause changes in the internal interface bonding strength and micro-destructive morphology of the composite material, resulting in a significant drop in the shear and bending properties of the composite material, which seriously threatens the safety of the structure[3]. Aircraft, spacecraft, etc. will inevitably be exposed to a series of environmental factors such as high and low temperature environment, rainwater soaking, etc. during service. The damp and heat effect will have a certain impact on the physical properties, mechanical properties and failure behavior of composite materials[4]. In the literature[5], some conclusions were obtained through the immersion test at the same temperature and different time: 1) The saturated moisture absorption rate of G827/-5224 and G803/5224 composite laminates are 1.590% and 1.642%, respectively. 2) Soaking and moisture absorption will significantly reduce the interlaminar shear strength and bending strength of the material. With the extension of time, the rate of decline becomes slower and slower (after 25 days). In the literature[6], the immersion test at different temperatures (room temperature, -55℃, 70℃) was used, and the following conclusions were obtained: 1) Temperature has a greater influence on the performance of the resin matrix; 2) The moisture absorption process of carbon fiber composite materials in water follows a certain low in the initial stage of moisture absorption, the diffusion of water molecules conforms to Fick's second law. Literature[7] studied the effect of heat and humidity on the properties of composite materials under different pores. After moisture saturation, the tensile, bending, compression and interlaminar shear properties show a downward trend. It can be seen that, as the carbon fiber composite material absorbs moisture and diffuses, it usually causes changes in the matrix performance, and leads to a decrease in the strength, stiffness, and interface properties of the composite material.

In summary, composite materials are often affected by factors such as damp heat stress, water molecule diffusion, and plasticizing swelling in a hot and humid environment. However, the current theoretical calculation and analysis of damp heat stress from the perspective of macro-mechanics cannot accurately evaluate the humid and hot environment theoretically. At the same time, the above researches are all based on unidirectional structures, and the influence rules are different for different temperature and humidity environmental conditions, different material systems, and different structural forms. This paper focuses on the multi-layer composite cylindrical shell structure containing the hoop layer and the angle layer of different materials, and conducts the research on the influence of the damp heat environment on its physical and chemical properties and mechanical properties.

2. Humidity and heat aging test of multilayer composite structure

2.1. State of the test piece
Multi-layer composite shell structure: including hoop layer and ±25angle layer, and the two layers use T300 and T700 fiber composite materials, and resin is epoxy resin system. Types of test pieces: NOL ring (Diameter 135mm, thickness 3mm, width 6mm), strip sample(Length 100mm, thickness 3mm, width 10mm), arc sample(Length 15mm, thickness 3mm, width 10mm), shell burst sample(Length 450mm, thickness 3mm, diameter 135mm), The thickness ratio of the hoop layer to the angle layer is 1:1. As shown in Figure 1.
2.2. Test method
Based on the multi-layer composite shell structure forming, processing and use of damp and heat environment, while considering the stricter test conditions, four groups of different damp and heat conditions are designed, the specific groups are shown in Table 1.

Before the test, put the sample in an oven to dry to the engineering dry state (50°C, 24h), and after natural cooling to room temperature, weigh the sample and record the initial mass $W_b$, then put it in a constant temperature and humidity box (model: LRHS-1000-LH), and deionized water (distilled water) is used as test water. Weigh the sample every 24h and write down the mass $W_t$. Before weighing, the sample should be cooled to room temperature (soak test with filter paper to wipe dry surface moisture) and weighing. The calculation method of moisture absorption (percentage) is as follows:

$$c(t) = \frac{(W_t - W_b)}{W_b} \times 100\%$$

(1)

Where: $c(t)$ is the moisture absorption at time $t$; $W_t$ is the mass of the sample at time $t$, and $W_b$ is the initial mass of the dry sample.

![Figure 1. Composite material test piece.](image)

| Groups | Condition | Group 1 | Group 2 | Group 3 | Group 4 |
|--------|-----------|---------|---------|---------|---------|
| Temperature | 40°C | 65°C | 40°C | 80°C |
| Humidity | 80% | 80% | Soak | Soak |

3. Research on moisture absorption characteristics of multilayer composite structure

3.1. Theory of moisture absorption characteristics
In recent years, with the increase in research on the diffusion of water molecules in composite materials, several models have been proposed for the diffusion of water molecules in composite materials. These models are based on diffusion theory and Fick's law. Diffusion theory believes that water molecules undergo a macroscopic material flow process in which a large number of atoms migrate in composite materials. This short- or long-distance migration microscopic process is an irregular Brownian motion. Fick's law is summarized on the basis of diffusion theory [8].

The Fick model can be expressed as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad t > 0, \quad z \in [-h/2, h/2]$$

(2)

Boundary conditions: $C(z,0) = C_0$, $C(-h/2,t) = C(h/2,t) = C_\infty \quad t > 0$ Where $C$ is the humidity concentration; $C_0$, $C_\infty$ is the initial and equilibrium concentration respectively; $D$ is the diffusion coefficient; $t$ is the time; $h$ is the thickness; $z$ is the coordinates along the thickness direction.
The total moisture absorption is:

\[
c(t) = c_e - (c_e - c_0) \frac{8}{\pi^2} \sum_{n=0}^\infty \frac{1}{(2n+1)^2} \exp^{-\frac{(2n+1)^2 \pi^2 t}{h^2}}
\]

(3)

Where: \( c(t) \) is the moisture absorption of the composite material; \( c_0, c_e \) is the initial and equilibrium moisture absorption respectively; when the moisture is absorbed for a long time, \( n \) it is 0.

After knowing the D and equilibrium moisture absorption of the material system, the moisture absorption at any moment can be calculated. It is also possible to calculate the diffusion coefficient with two moisture absorptions at different times:

\[
D = \pi \left[ \frac{h}{4(c_e - c_0)} \right]^2 \left[ \frac{c(t_1) - c(t_2)}{\sqrt{t_1} - \sqrt{t_2}} \right]^2
\]

(4)

Among them: \( \sqrt{t_1} - \sqrt{t_2} \) is the slope of the initial straight line segment of the moisture absorption curve, defined as the moisture absorption rate, expressed by \( k \).

In the initial stage of moisture absorption, the moisture absorption equation can be simplified as:

\[
c(t) = c_0 - \frac{4}{\pi^2} \left( \frac{Dt}{h^2} \right)^{1/2}
\]

or

\[
c(t) = k t^{1/2}
\]

(5)

Calculate the diffusion coefficient of water molecules and the moisture absorption rate constant of the material during the moisture absorption process, so as to more accurately study the moisture absorption behavior of the composite material.

3.2. Analysis of moisture absorption characteristics

According to the four sets of damp and heat conditions, the samples were respectively subjected to a damp and heat aging test for nearly 2500 hours.

It can be seen from the Figure 2 that the growth trend of the moisture absorption curve of the composite material under different damp and heat conditions is consistent. The moisture absorption rate increases with the extension of the soaking time. As shown in Figure 3, in the initial stage of moisture absorption, the moisture absorption is approximately linear with the test time. It shows that the composite material conforms to Fick’s second law in the initial stage of the moisture absorption process, which is in good agreement with the theoretical model. With the further diffusion of water molecules, the rate of moisture absorption gradually slows down, and the square root linear relationship between moisture absorption and moisture absorption time no longer holds. A stable platform appears on the moisture absorption curve. Deviating from Fick’s second law, moisture absorption no longer increases rapidly. With the extension of time, the adsorption and desorption process of water molecules reach a dynamic equilibrium.

Figure 2. The relationship between moisture absorption of different groups of composite materials and time.
It can be seen from Figure 2 that the water absorption rate of the composite material is obviously different under different damp and heat conditions. With the extension of time, the moisture absorption is basically stable between 500h and 750h, and the subsequent moisture absorption increases slowly, and the moisture absorption balance is basically reached after 2000h. At the same time, using formula (2.3), the water molecule diffusion coefficient and composite material moisture absorption rate under four different test conditions were calculated. The specific results are shown in Table 2.

![Figure 3](image3.png)

**Figure 3.** The relationship curve between the initial stage moisture absorption and time of different groups of composite materials.

Table 2. The equilibrium moisture absorption, diffusion coefficient and moisture absorption rate of composite materials under different conditions.

| Groups | Parameter                  | Balance moisture absorption /% | Diffusion coefficient /mm²/h | Moisture absorption rate /h¹/₂ |
|--------|----------------------------|-------------------------------|-----------------------------|-------------------------------|
| Group 1| Balance moisture absorption | 0.13                          | 2.51×10⁻⁶                   | 0.43×10⁻⁴                    |
| Group 2| Balance moisture absorption | 0.24                          | 8.12×10⁻⁶                   | 1.05×10⁻⁴                    |
| Group 3| Balance moisture absorption | 0.32                          | 1.10×10⁻⁵                   | 1.42×10⁻⁴                    |
| Group 4| Balance moisture absorption | 0.78                          | 1.52×10⁻⁵                   | 2.73×10⁻⁴                    |

It can be seen from the test results that the higher the humidity and heat conditions, the greater the moisture absorption rate of the composite material in the initial stage and the saturated moisture absorption when reaching equilibrium, and the greater the water molecule diffusion coefficient.

4. Research on the physical and chemical properties of multilayer composite structures

4.1. Microstructure changes

During the test, it was found that when the harsh fourth group test (80°C, soak) was carried out to 2100h, the composite material test piece appeared inside folds and local delamination of the section. The specific results are shown in the Figure 4.

At the same time, the X-ray non-destructive testing method is used to observe the internal micro-morphology of the samples before and after the damp heat test. The specific results are shown in Figure 5.

![Figure 4](image4.png)

**Figure 4.** Wrinkles and delamination in the test piece.
Figure 5. The internal micro morphology of the test piece before and after the damp heat test (left: before the test, right: after the test).

It can be seen from the figure that after a long period of high temperature soaking, the performance of the fiber and matrix interface decreases, microcracks appear inside the composite material, and crack growth appears at the interface between the angle layer and the circumferential layer, which further weakens the bonding strength of the interface, and finally leads to delamination and debonding of fiber and resin.

4.2. Changes in chemical structure
The problem of whether the composite material has chemical structure changes under damp and hot conditions is analyzed by infrared spectroscopy. In this paper, the composite material structure is selected for analysis before the test and after 1900h under 80℃ and soak conditions. The infrared spectroscopy test results before and after the test as shown in Figure 6.

Figure 6. Comparison of infrared spectra before and after the damp heat test of composite materials.

It can be seen from the Figure 6 that after the damp heat aging test, there aren’t new absorption peaks and absorption peaks disappearing, but the absorption intensity of -OH (wave number 3435cm⁻¹) and C=C (wave number 1631cm⁻¹) peaks with a slight weakening indicate that a certain degree of molecular chain breakage has occurred in the material. However, absorption peaks don’t appear in the absorption curve, which indicates that no new groups are produced, and the chemical structure of the composite material has not changed significantly.
5. Research on the mechanical properties of multilayer composite structures

5.1. Shear performance of structural parts

Refer to the GB/T14618-88 fiber-wound reinforced plastic ring sample shear test method, each group has 9 samples, and the HY-5080 composite material three-point bending tester is used for testing.

Under different damp and heat conditions, the shear strength and retention rate of composite materials are shown in the Table 3. It can be seen from the above table that the heat and humidity conditions have a greater impact on the shear performance of the composite material. The harsher the heat and humidity conditions, the more the shear performance decreases. When the composite material is in a hot and humid environment, moisture not only causes the swelling and plasticization of the resin matrix, but also causes the resin matrix to soften, weaken the support of the matrix to the fiber, reduce the ability to transmit shear loads, and the difference in the thermal expansion coefficient of the material under high temperature conditions, which makes the interface debonding more serious, and finally leads to a significant decrease in the shear strength of the composite material.

| Number of groups | Parameter | Initial state | Group 1 | Group 2 | Group 3 | Group 4 |
|------------------|-----------|--------------|--------|--------|--------|--------|
|                  | Shear strength /MPa | 25.5±1.5 (5.8%) | 23.2±1.4 (6.0%) | 22.6±1.5 (7.1%) | 22.4±1.3 (5.8%) | 13.7±1.0 (7.3%) |
|                  | Retention rate | 91.0% | 88.6% | 87.8% | 53.7% |

5.2. Circumferential performance of structural parts

Refer to GB/T14582-2008 fiber-wound reinforced plastic ring sample mechanical performance test method, each group has 7 samples, and Shimadzu AG100KG material testing machine is used for testing. There is one blasting test for each group, using the FST5000-AZ2-36/323 blasting test bench.

Under different damp and heat conditions, the hoop tensile modulus, strength and retention rate of composite materials are shown in Table 4. It can be seen from the Table 4 that the soaking conditions have a greater impact on the hoop modulus and strength of the multilayer composite shell. The hoop modulus retention rate is about 94%-96%, and the hoop strength retention rate is about 89%-92%; the hoop modulus and strength change little under other damp and heat conditions. Through research and analysis, the hoop performance of the composite shell is mainly determined by the hoop layer (the longitudinal performance of the composite material). On the one hand, the penetration of moisture causes the resin matrix to plasticize and hydrolyze, which weakens the interface performance of the composite material. The above will lead to the reduction of the hoop tensile strength and tensile modulus; on the other hand, the temperature rise may further solidify the resin matrix, which improves the tensile strength and tensile modulus of the composite material; at the same time, the composite material performance is dispersible larger features. Based on the above analysis, the damp and heat...
conditions have relatively little effect on the longitudinal properties of the composite material. The circumferential tensile strength and tensile modulus of the shell will show certain fluctuations. In the case of harsh damp and heat conditions, the effect of post-curing is much less than that of moisture absorption. The effect caused by the effect, therefore, the final performance degradation.

5.3. Axial performance of structural parts

Refer to GB/T3354-1999 oriented fiber reinforced plastic tensile performance test method, each group has 6 styles, using Shimadzu AG-100KG material testing machine to test. Under different damp and heat conditions, the axial tensile modulus and retention rate of the composite shell are shown in Table 5.

| Groups | Initial | Group 1 | Group 2 | Group 3 | Group 4 |
|--------|---------|---------|---------|---------|--------|
| Axial tensile modulus (GPa) | 73.3 | 70.4 | 71.8 | 72.6 | - |
| Retention rate (%) | 96.0% | 98.0% | 99.0% | - | - |

Table 5. Axial tensile modulus and retention rate of composite materials.

Through research and analysis, the multi-layer composite shell is composed of an angle layer and a hoop layer. The axial modulus of the shell is mainly composed of the comprehensive superposition of the angle layer longitudinal modulus, the shear modulus and the hoop layer transverse modulus. As a result, the longitudinal modulus of the angle layer mainly depends on the fiber properties, while the shear and transverse properties mainly depend on the resin. The moisture absorption of the composite material is mainly the moisture absorption of the resin. The changes in the matrix and the interface will cause the shear performance and the transverse performance to decrease greatly. However, the angle layer (longitudinal) plays a leading role in the axial modulus of the shell structure, while the damp and heat conditions have a relatively small effect on the longitudinal performance of the composite material, so the axial performance of the shell structure will eventually decrease slightly.

6. Conclusions

This article carried out the damp and heat aging test of the multilayer composite shell under different damp and heat conditions, and reached the following conclusions:

(1) In terms of moisture absorption characteristics: In the initial stage of moisture absorption, the moisture absorption of the composite material has a linear relationship with the moisture absorption time $t^{1/2}$. The greater the temperature and humidity, the greater the diffusion coefficient and moisture absorption rate. With the extension of time, the rate of moisture absorption slowed down after 500h to 750h, and the moisture absorption process basically reached dynamic equilibrium after 2000h, and the equilibrium moisture absorption under different damp and heat conditions was between 0.13% and 0.78%.

(2) In terms of physical and chemical properties: After the composite material and the resin reach the moisture absorption balance, the infrared spectrum shows that the $-\text{OH}$ and $\text{C}=\text{C}$ bonds change slightly, but there is no absorption peak generation or disappearance, and the overall chemical structure has not changed significantly. However, under long-term damp and heat conditions, the damp heat stress will induce the destruction of the fiber-matrix interface and the expansion of cracks along the layers, weakening the bonding strength of the interface, macroscopically manifested as the appearance of wrinkles and local delamination of the shell.

(3) Mechanical properties: damp and heat conditions mainly have a greater impact on the mechanical properties closely related to the interface and matrix properties of the composite material. After different damp and heat conditions absorb moisture and balance, the interlayer shear strength retention rate is 53.7%-91.0%; Under the soak condition (temperature 40°C and 80°C), the hoop
strength and modulus of the shell showed a downward trend, and the retention rate was 92.2%, 95.9% and 88.7%, 93.9%, and under 80% humidity (40°C and 65°C), the performance is slightly reduced, and individual increases; Damp and heat conditions have little effect on the axial modulus of the shell, and the retention rate is above 96%. At the same time, the influence of damp and heat conditions on the strength and performance of composite materials is greater than that on the modulus.

References
[1] Zhou H 2017 Sixteen main application fields of carbon fiber and recent technological progress
Industrial Textiles 35(5) 1
[2] Liu S F, Cheng X Q and Bao J W 2014 Analysis of the influence of heat and humidity on the properties of resin matrix composites Polym. Mater. Sci. Eng. 30(9) 184
[3] Gong T C, Zou T C and Feng Z Y 2016 Research Progress in the Influence of Humid and Heat Environments on the Properties of CFRP Composites Mater. Rev. 30(27) 320
[4] Zheng L, Chang X L and Zhao F 2007 Research on the moisture absorption characteristics of composite materials in hot and humid environments Fiber Composite Materials 2 37-9
[5] Zhang J, Zhang Q, Ma H P, Lu X J, Li X F and Xiang M 2008 Research on G827/5224 and G803/5224 carbon fiber reinforced epoxy resin moist heat Equip. Environ. Eng. 5(3) 16-20
[6] Wang S M 2011 Research on the influence of temperature and humidity environment on the mechanical behavior of carbon fiber composites (Nanjing: Nanjing University of Aeronautics and Astronautics)
[7] Tao S 2010 Research on the effect of pores on the mechanical properties of CFRP in hot and humid environment (Harbin: Harbin Institute of Technology)
[8] Yi X S, Du S Y and Zhang L T 2009 Handbook of Composite Materials (Beijing: Chemical Industry Press)