Study on the effect of hygrothermal aging on the properties of three-dimensional woven composite materials with damage

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Abstract. This study analyzed the hygroscopic characteristics and mechanical properties of three-dimensional woven composite materials under 70℃/85%RH conditions and with the presence of damage. First, the materials underwent hygrothermal aging tests, including analysis of mass change, moisture absorption rate, SEM microstructure, Fourier-transform infrared spectroscopy (FT-IR), dynamic mechanical analysis (DMA), and subsequent open-hole tensile and compression strength tests under different environmental conditions. Finally, macroscopic failure analysis was conducted. The results showed that as the hygrothermal aging time increased, the moisture absorption rate increased and the fiber surface became smoother, while the degree of debonding between the fiber and matrix increased. The open-hole tensile and compression strength of the composite material decreased as the aging time extended, and the environmental temperature had different effects on open-hole tensile and compression strength.

Keywords: Three-dimensional woven; hygrothermal aging; surface morphology; open-hole.

1. Introduction

3D woven technology is an emerging technique that not only inherits the high specific strength, high specific modulus and other advantages of traditional composite materials, but also ensures the continuity of fibers, superior performance, and high design flexibility. It has been widely applied in aviation, aerospace, and industrial fields[1-2].

Our country has a diverse climate, and the use of composite materials in aircraft operating environments exposes them to high temperature and humidity. The influence of hygrothermal environments on the mechanical properties of composite materials has become a major issue for the stability and reliability of composite structures[3]. The high temperature and humid environment is an important environmental factor that needs to be considered in the study of the mechanical properties of composite materials. At the same time, in practical engineering applications, open-hole damage may be introduced into composite structure components due to assembly, inspection, and disassembly requirements. Therefore, the damage tolerance ability of composite materials during service needs to be considered in the design[4].

In recent years, many domestic and foreign experts and scholars have conducted in-depth research on the hygrothermal aging and open-hole behavior of composite materials.Li Hailin[5] studied the static/dynamic mechanical properties and failure mechanism of carbon fiber reinforced polymer composites (CFRP) in seawater environment. Quasi-static tensile and dynamic mechanical analysis (DMA) tests were performed to evaluate the tensile and damping performance. Scanning electron microscopy (SEM) was used to observe the aging damage and fracture morphology. It was found that the tensile strength of the composite material was sensitive to aging time and environmental temperature, but not to sodium chloride concentration. In addition, the failure mode was also changed by hygrothermal aging. Du Yong[6] found that the moisture absorption curve of CFRP laminates can be divided into three stages. They proposed an improved Fick model to capture the diffusion behavior of Tg800/E207 CFRP laminates and investigated the correlation and comparison among non-Fickian parameters, environmental parameters, and the stacking sequence of CFRP. The results showed that the modified Fickian curve was sensitive to the diffusion coefficients of the first and second stages.Liang[4] conducted experimental research on the mechanical properties of two types of three-dimensional woven composite materials under tensile and compressive loads. The study investigated the effect of open-hole damage on the mechanical properties of the two structures of composite materials and the failure process of the open-hole specimens under tensile and compressive loads. The study found that the fully woven structure composite material exhibited superior mechanical properties.

There is relatively little research on the woven carbon fiber composites with damage under the humid and hot environment at home and abroad. This paper focuses on the study of the aging mechanism and mechanical properties of the composite materials after different aging times in humid and hot environment. The research is of great significance for damage tolerance design of aircraft under typical service conditions.

2. Experimental methods

2.1 Experimental materials

The 3D woven composite material used in the experiment was fabricated by a four-step weaving process, using T700/12K carbon fiber and epoxy resin matrix, and formed by resin transfer molding. After fabrication, the standard open-hole tension specimen was obtained by low-speed cutting with a diamond grinding wheel to the size of 250.00mm × 36.00mm × 4.00mm.

The specimen was drilled with a diamond drill bit at the center using a composite engraving and milling machine[7]. A through-hole with a diameter of 6mm was drilled at the center of the specimen as shown in Figure 1.

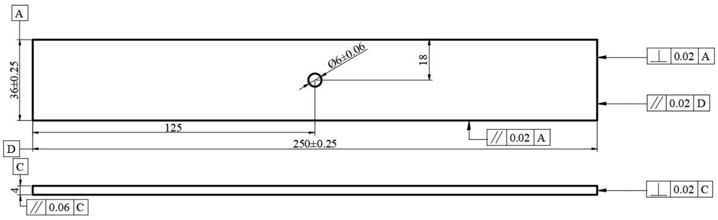


Fig.1 Specimen diagram

2.2 Hygrothermal aging test

The composite specimens were subjected to humid-heat aging in a constant environment with a temperature of 70℃ and a relative humidity of 85% according to ASTM D 5229-2014[8]. Aging time durations were 30 days, 60 days, and 90 days.

2.3 Scanning electron microscope（SEM）

SEM was conducted using a Hitachi Su3500 scanning electron microscope to obtain the microstructures of the specimens before and after humidity exposure at different aging times, in order to analyze the reasons for the change in properties. The working voltage of the scanning electron microscope was 10 kV.

2.4 Dynamic mechanical analysis（DMA）

Dynamic mechanical analysis (DMA) was performed using a DMA Q800 instrument, in accordance with ASTM D7028-2007[9], to obtain DMA curves at different aging times. The single cantilever mode was adopted with an amplitude of 20 μm and a frequency of 1Hz. The temperature was raised at a rate of 5℃/min, and the testing temperature ranged from 20℃ to 250℃ under nitrogen protection. The sample size was 36mm × 12mm × 2.24mm.

2.5 Fourier Transform Infrared Spectroscopy Analysis(FTIR)

The infrared spectra were obtained using a Bruker Tensor 27 Fourier transform infrared (FT-IR) spectrometer in diffuse reflection mode, with a resolution of 100 cm^{-1} and a range of 500 – 4000 cm^{-1}. The spectra were recorded after 5 scans, and the chemical functional groups of the specimens in different environments were analyzed and compared with those of dry specimens.

2.6 Open-hole mechanical properties

Using Instron 5982 electronic universal testing machine,conducted according to ASTM D 6484/D 6484M-2014[10] and ASTM D 5766/D 5766M-11(2018)[11] standards, the open-hole compress and tensile tests were performed at a loading rate of 2 mm/min. tests were conducted in three different temperature environments: low temperature (-25℃), room temperature (23℃), and high temperature (60℃). The temperature was controlled by the Instron environmental chamber.

3. Experimental Results and Analysis

3.1 Moisture absorption analysis

Before the hygrothermal aging, the composite specimens were weighed to obtain the original mass m_0, and then placed in a constant temperature and humidity chamber at 70℃/85%RH for hygrothermal aging. During the experiment, the samples were taken out every 12 hours, wiped clean of surface moisture, and weighed on an electronic analytical balance to obtain the mass m_t. The moisture uptake was calculated according to formula (1):

$$M_t = \frac{m_t - m_0}{m_0} \times 100\% \quad (1)$$

In the formula, M_t is the mass change rate of the specimen at time t, m_t is the mass of the specimen at time t (in grams), and m_0 is the mass of the specimen before moisture absorption (in grams).

The variation curves of the moisture uptake rate (M_t) and the square root of the moisture uptake time ($t^{1/2}$) of the composite material under 70℃/85%RH are shown in Figure 2.

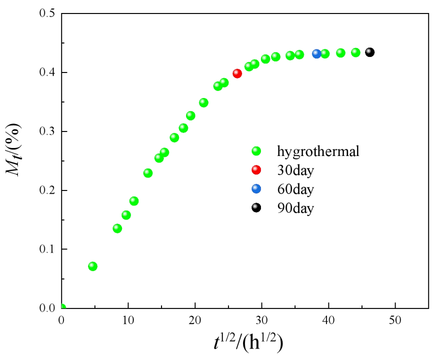
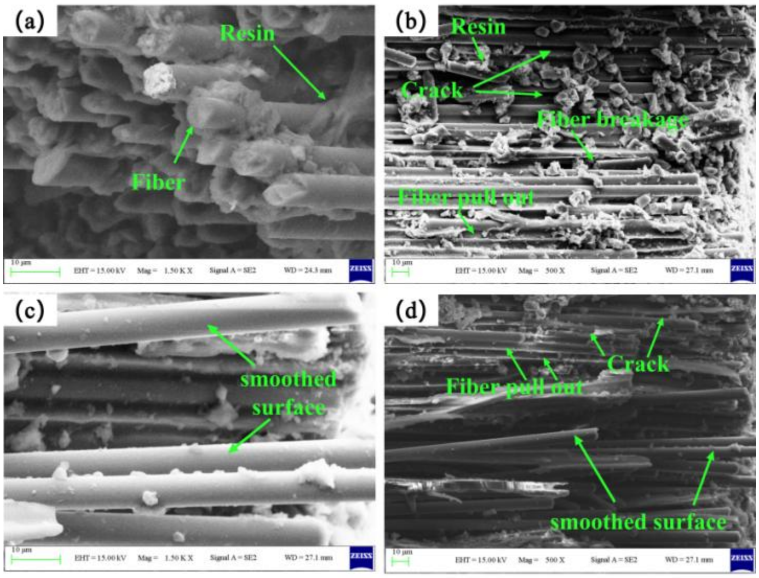


Fig.2 Mass change curve

During hygrothermal aging, water molecules are attracted to the internal voids and bubbles of the composite material due to capillary action, resulting in a relatively fast initial moisture absorption rate. During this period, water molecules enter the composite material uniformly and stably. As shown in Figure 2, the moisture absorption rate and the square root of time show almost linear growth at this stage. The diffusion law of moisture absorption in the early stage conforms to Fick's second law[12]. At 30 days, the equilibrium moisture absorption rate of the composite material is 0.398%. After a certain period of time, water molecules gradually fill the internal voids of the specimen[13], and the moisture absorption of the matrix gradually reaches saturation, resulting in a slow increase in the rate of mass change. At 60 days of aging, the equilibrium moisture absorption rate of the composite material is 0.431%. Finally, the rate of mass change enters the stage of relative saturation, and at 90 days, the equilibrium moisture absorption rate of the composite material reaches a saturated state of 0.434%.

3.2 Surface morphology analysis

As shown in Figure 3, micrographs of different hygrothermal aging times are presented.



(a) Unaged; (b) 30 days; (c) 60 days; (d) 90 days
Fig.3 SEM images under different ageing time

From Figure 2, it can be seen that the carbon fibers in the unaged sample were tightly combined with the resin matrix, and a large amount of resin was attached to the fiber surface. No obvious damage occurred at the carbon fiber/matrix interface. After 30 days of hygrothermal aging, the resin surface became smoother but still attached to a large number of matrix particles, and visible cracks began to appear between the matrix and fibers. Water molecules entered the woven composite material, weakening the adhesive strength between resin and resin and resin and fibers, causing resin swelling and separation from fibers[14].

When hygrothermal aging proceeded to 60 days, fewer and fewer matrix particles were attached to the fiber surface, the fibers became smoother, and more fibers were pulled out from the matrix. At this time, the swelling amount of resin increased, and the significant difference in expansion between the resin and non-swelling carbon fibers led to internal stress at the carbon fiber/resin interface[15]. Internal stress occurs in the initial stage of water absorption and increases with increasing water absorption time. When the internal stress exceeds the adhesion strength between the fiber and the matrix, debonding occurs at the fiber/matrix interface, eventually leading to cracks inside the material.

After 90 days of aging, the fiber surface was very smooth, and the number of pulled-out fibers increased. The internal cracks further expanded because the previously generated cracks provided channels for water vapor to diffuse into the material. With the increase of hygrothermal aging time, the number of cracks in the composite material also increased, which would reduce the mechanical properties and shorten the service life of the material.

3.3 Infrared spectroscopy analysis

The infrared spectra of three-dimensional woven composite materials aged for 30, 60, and 90 days at a temperature of 70 ℃/85%RH (relative humidity) are shown in Figure 4. Compared with the infrared spectra of the unaged samples, the spectra of the aged samples show no significant changes in peak position or intensity, and no new characteristic peaks appear, indicating that only physical changes occur during hygrothermal aging and no chemical changes or new substances are formed.

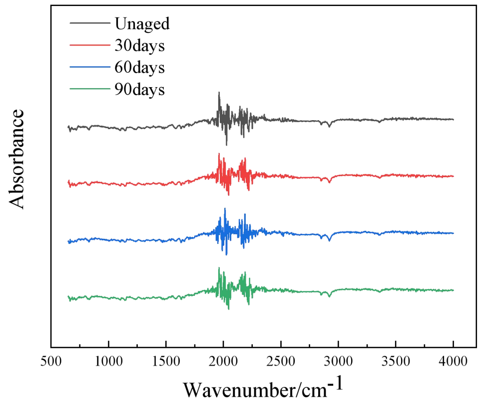
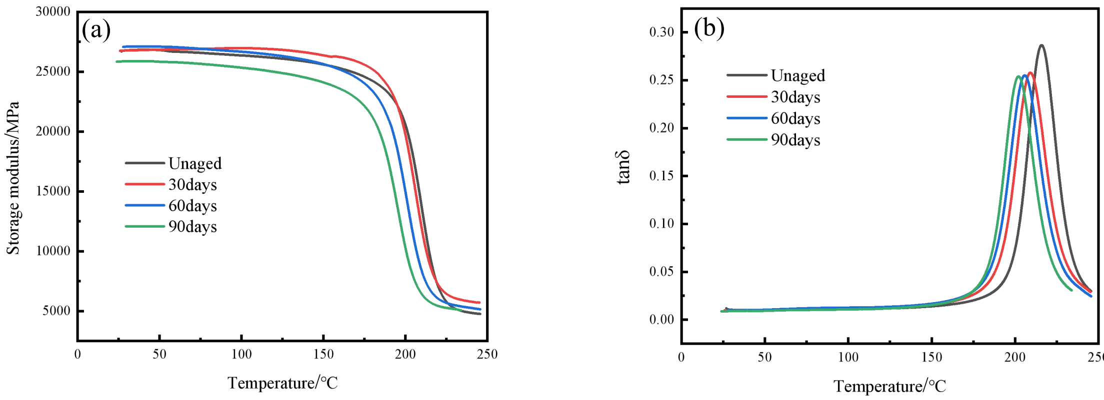


Fig.4 Infrared spectrum under different ageing time

3.4 Dynamic mechanical analysis

As shown in Figure 5, the DMA storage modulus and tanδ curves of the three-dimensional braided composite samples before and after hygrothermal aging for 30 days, 60 days, and 90 days at 70℃/85%RH are presented.



(a) storage modulus (b) tanδ

Fig.5 DMA curves of 3D woven composite materials at different aging periods.

With the increase of hygrothermal aging time, the peak of the loss factor tanδ shifted towards lower temperatures, and the glass transition temperature (Tg) gradually decreased from 215.9 ℃ to 209.2 ℃, 205.9 ℃, and 202.0 ℃ after 30, 60, and 90 days of aging, respectively. The decrease in Tg did not exceed 6% of the Tg of the unaged sample, indicating good dynamic mechanical properties of the three-dimensional woven composite after aging.

Hygrothermal aging has an impact on the glass transition temperature (Tg) of the composite material. Under the same environment, with the increase of aging time, the tanδ curve continues to move towards lower temperatures and the storage modulus continues to decrease, because hygrothermal aging can increase the free volume and decrease the structural density of the composite material, leading to a decrease in Tg[16]. In addition, hygrothermal aging may also cause changes in the micro-porous structure of the composite material, increase the movement space of polymer chain segments, cause cross-linking point fractures, and affect the measurement results of

Tg. At the same time, water molecules in the hygrothermal environment can cause hydrolysis of polymer chain ends, resulting in the loss of polymer chains and a decrease in Tg[17].

3.5 Mechanical properties testing

3.5.1 Open-hole tensile property analysis

The open-hole tensile test aims to investigate the capability of composite materials with damage introduced in engineering design to bear defects and damage. The open-hole tensile strength of carbon fiber composite specimens with hole damage at different hygrothermal aging times is shown in Figure.6 under three test temperatures of -25 ℃, 23 ℃, and 60 ℃.

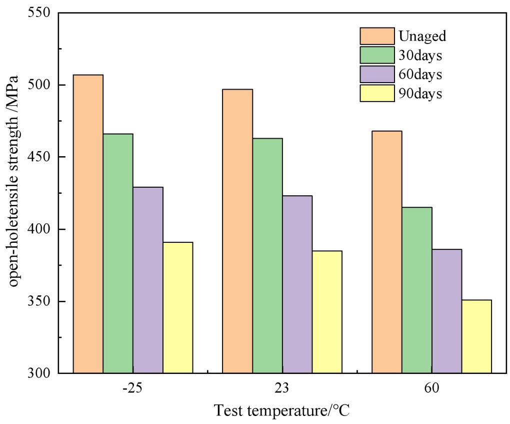


Fig.6 open-hole tensile strength distributions under different aging times and test environments.

From Figure 6, it can be observed that the higher the test temperature, the lower the open-hole tensile strength of the three-dimensional woven composite material. For samples aged for the same duration, the open-hole tensile strength gradually decreases with the increase of test temperature. Under the same experimental conditions, the longer the aging time, the lower the open-hole tensile strength. As the test temperature increases, the decrease in open-hole tensile strength of the unaged samples is smaller than that of the aged samples in the hygrothermal environment[18].

3.5.2 Open-hole compress property analysis

The open-hole compression strength of carbon fiber composite material specimens with holes after hygrothermal aging at different test temperatures (-25 ℃, 23 ℃, and 60 ℃) is shown in Figure.7.

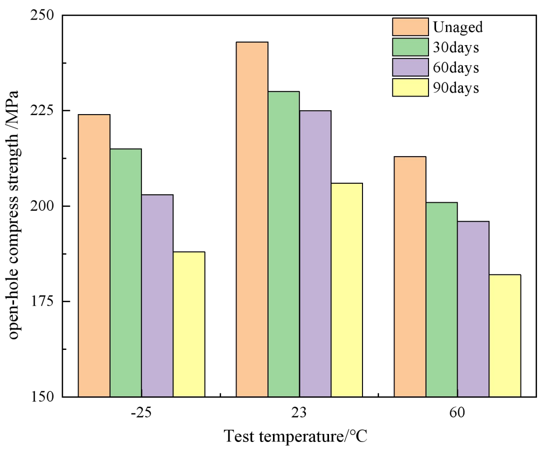


Fig.7 open-hole compress strength distributions under different aging times and test environments.

The compression performance of the composite material after the introduction of an opening is an important evaluation criterion for the sensitivity of the composite material to defects and thickness-direction defects.

During hygrothermal aging, water molecules penetrate the internal structure of three-dimensional woven carbon fiber composite samples through various defects, causing swelling and plasticization of the resin matrix, which in turn reduces the performance of the resin matrix and leads to a decrease in the compressive strength of the composite material with damage. At the same time, water molecules infiltrate the carbon fiber/resin interface of the composite material sample, reducing the bonding ability between the carbon fiber and matrix, further leading to a decrease in the compressive strength with damage[19]. In the same experimental environment, the longer the aging time, the lower the compressive strength with damage. The lowest mechanical properties of the material are observed under the combined effects of hygrothermal aging and high temperature.

4. Conclusion

(1) During the hygrothermal aging of the composite material at 70° C/85%RH, the moisture absorption rate increased rapidly in the early and middle stages and gradually slowed down in the later stages, with a final moisture absorption rate of 0.434%.

(2) The scanning electron microscopy (SEM) observation showed that there were plenty of resin bodies around the fibers on the surface of the unaged sample. After the hygrothermal aging, the surface of the samples became smooth, and some resin fell off, and the cracks between the fibers and the matrix became larger with the increase of aging time.

(3) Before and after the hygrothermal aging, the characteristic peaks of the infrared spectrum did not show significant changes, indicating that no new substances were generated and no chemical changes occurred during the aging process of the material.

(4) The longer the hygrothermal aging time, the greater the decrease in the material's glass transition temperature (Tg). The main reason is that water molecules penetrate into the epoxy resin and break the van der Waals forces and hydrogen bonds between polymer chains, reducing the intermolecular forces between the large polymer chains.

(5) In the open-hole tensile test, the mechanical properties of the composite material decrease with increasing aging time at the same test temperature. At the same aging period, the mechanical properties decrease with increasing test temperature. In the open-hole compression test, the mechanical properties of the composite material decrease with increasing aging time at the same test temperature, with the strongest mechanical properties at room temperature, followed by low temperature and the weakest at high temperature.

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