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Preparation and Properties of GFRP with Carbon Nanotube Interface Modification and Tension Control

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Abstract: In response to the problem of interlayer performance degradation caused by insufficient fiber/resin interface bonding and fiber relaxation during the molding process of Glass Fiber Reinforced Polymer (GFRP) composites, a preparation strategy of "nanoscale interface modification molding tension synergy" is proposed. Firstly, a chemical grafting method promoted by silane coupling and coupling agents was used to stably graft aminated carbon nanotubes (CNTs) onto the surface of glass fibers to enhance interfacial bonding; Secondly, design and manufacture a hot press mold that integrates a dual-mode tensioning mechanism (double-sided synchronous displacement tensioning and center guided anti deviation) and a uniform heating scheme to achieve stable tensioning and uniform temperature field control of short fibers during the curing process. Prepare GFRP laminates using the same raw materials and curing system, and conduct short beam shear tests in accordance with JC/T 773-2010. The results showed that the interlaminar shear strength (ILSS) of CNT modified laminates increased from (53.46 ± 2.36) MPa to (68.89 ± 2.90) MPa, an increase of 28.9%. Research has shown that the multi-level interface structure formed by CNT grafting can enhance mechanical interlocking and chemical bonding, while tension forming and uniform heating provide stable process guarantees for interface infiltration and curing. This study provides an engineering implementation path for the controllable molding and interface enhancement of GFRP components for automotive lightweighting.

1. Introduction

Glass fiber reinforced polymer (GFRP) composites are widely used in aerospace, rail transit, and other fields due to their excellent tensile strength, high modulus ratio, and corrosion resistance [1]. However, the mechanical properties of GFRP composites are limited by the intrinsic interface properties between glass fibers and resin matrixes. Due to the weak adhesion between glass fiber and matrix resin, glass fiber is easy to fall off the matrix under pressure, resulting in poor mechanical properties. When delamination damage occurs, cracks in the interlaminar zone continue to develop and propagate due to the brittleness of the matrix [2]. According to the theory of fracture mechanics, the interlayer failure in the practical application of GFRP composites can be divided into two basic modes: mode I. (open type) is dominated by normal tensile stress, and the crack surface is vertically separated; Mode II. (in-plane shear type) is driven by shear stress, and the displacement is located on the plate surface, and the displacement relative to the leading edge of the crack is normal displacement.

In recent years, through the collaborative innovation of nanotechnology, interface engineering and advanced manufacturing processes, the research on the interlayer failure problem of GFRP composites has entered a new stage of multi-scale collaborative design. According to literature studies, the strength and toughness of GFRP composites depend on the fiberSeveral key factors include the type of maintenance epoxy resin, the interface interaction between fibers and epoxy resins, and the interfacial microstructure of GFRP composites [3]. However, for prepregs commonly used in engineering, the fiber type, resin type, and interactions between them are often constant. Therefore, optimizing interface performance is a viable and promising way to enhance resilience. Interlayer toughening of composites is a key research direction to solve the problem of layered failure and promote high-performance applications. Therefore, modifying the fiber surface is one of the effective ways to improve the mechanical properties of fibers. Mechanical properties such as flexural strength and modulus, ILSS, and impact strength can be improved [4-5]. For example, the use of nanofiber felts (NMs) as compartments has been shown to be a cost-effective method to improve the fracture toughness between layers of CFRP composites [6-8]. Several methods to optimize interfacial properties, such as chemical grafting, carbon nanotube sizing, spraying, electrophoretic deposition (EPD), and chemical vapor deposition (CVD), have been used to deposit carbon nanotubes onto fibers and fabrics. Relevant studies have been actively exploring the improvement of the mechanical properties of carbon nanotube (CNT) deposited fiber composites. Godara et al. reported that the IFSS of CNT-sized glass fiber/epoxy composites improved by approximately 90% based on the results of single-fiber roll-out microindentations [9]. Moallemzadeh et al. compared the modification of GFs surfaces with corona, silane, and corona-silane treatments, respectively. The results showed that glass fibers modified with corona silane showed better performance [10]. Luo et al. prepared a glass-fiber-reinforced polypropylene composite with improved properties by using a grafted polypropylene and a nucleating agent to form a thin film on the surface of glass fiber [11]. Yang et al. synthesized a phosphorus-containing silane coupling agent for diverting the surface of glass fibers to prepare composites with better interfacial adhesion [12]. Sever et al. modified glass fibers using γ-glycidyloxypropyltrimethoxysilane to obtain composites with ILSS reinforcement [13]. Wardle and Wicks used a chemical vapor deposition (CVD) method to grow aligned CNTs on alumina fiber woven fabrics [14-15]. Meanwhile, Lv and Jing reported modification methods, including grafting polysiloxane nanowires onto glass fibers and graphene oxide-coated glass fiber surfaces [16-17]Both can effectively enhance the interfacial interaction between organic matrix and inorganic GFs. However, the length of modified glass fibers is limited, and the existing hot-pressed small molds cannot effectively solve the tension problem of shorter glass fibers during the molding process, which can easily cause fiber sagging and affect the interlayer interface properties of composites [18].

Based on the above research status, existing interface enhancement methods such as CNT deposition/grafting have been shown to significantly improve the interface properties of fibers/resins, but in engineering molding, short fibers or short prepregs are prone to relaxation and deflection during the hot press curing stage, resulting in uneven infiltration and interlayer defects, thereby weakening the interface enhancement effect. To this end, the following work is carried out:

(1) an interface reinforcement route for CNT chemical grafting on the surface of glass fiber is proposed to construct a stable multi-level reinforcement structure; (2) Design and process GFRP hot pressing mold integrating dual-mode tensioning and uniform heating to achieve repeatable displacement tensioning and anti-bias guidance of fibers during the molding process; (3) Modified and unmodified GFRP laminates were prepared under the same curing system, and the short beam shear test was carried out according to JC/T 773-2010 to evaluate the interface enhancement effect and molding consistency.

2. Mold structure design

2.1 Overall structure design

The GFRP composite molding mold designed in this paper is mainly composed of the lower base and the upper cover. A molding groove is provided in the middle of the lower base for laying fibers and resin films, while the upper cover is installed on top of the lower base to form a closed cavity. In order to fix and apply tension to facilitate the forming of the prepreg, the side of the mold is equipped with a first fixing notch and a matching upper fixing block for clamping the starting end of the fiber. On the opposite side, a movable tensioning mechanism is designed: it consists of a rotating adjustment bolt connected to the lower base, a moving slot that is threaded to it, and a down-pressure retaining block mounted in the second retaining notch at the top of the moving slot to hold the end of the fiber. The rotating adjustment bolt can drive the moving slot and the down-pressure fixing block to generate linear displacement to achieve tension or release of the fiber. In addition, there are heating holes evenly distributed on the upper cover and lower base body, which are used to insert the heating rod to provide the required heat energy for the molding process, and the physical drawing of the mold and the three-dimensional structure are shown in Figures 1 and 2.

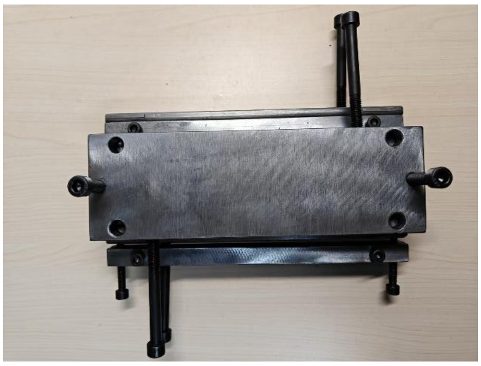

Figure 1 Overall physical drawing of the mold

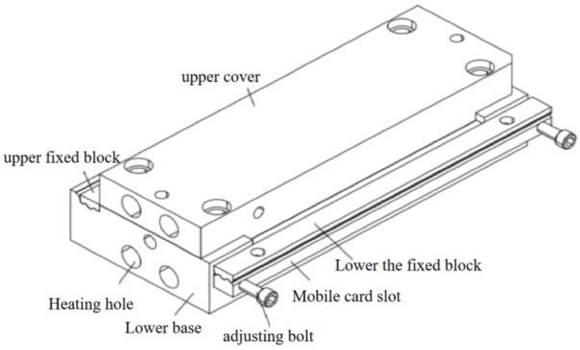

Figure 2 Three-dimensional structure of the mold

2.2 Tensioning mechanism design

In order to maintain the uniform tension state of the fiber and prevent its relaxation and skewing during the hot compression molding process, a set of tensioning mechanism based on screw drive (shown in Fig. 3) was designed in this study. The mechanism mainly consists of an adjusting bolt, a moving slot and a downward-pressing fixing block. The rotating bolt can drive the slot to move linearly along the axial direction of the mold, thus applying controllable tension to the fibers fixed at one end. A guide bar and holes are integrated into the mechanism to strictly limit the translation of the slot only along a predefined path, ensuring that the fibers are not deflected during the tensioning process. The mechanism supports two modes of synchronous tensioning and center-guided adjustment, providing high-precision, stable and reliable tension control, which is an effective guarantee for the core process.

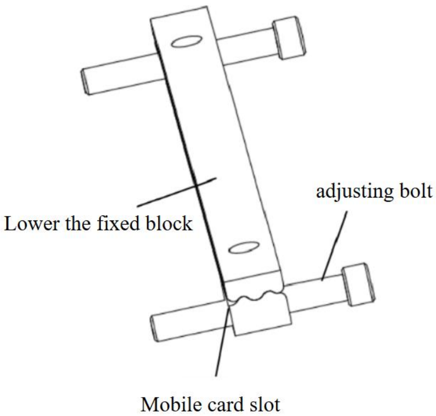

Figure. 3 Schematic diagram of the three-dimensional structure of the tensioning mechanism

2.3 Auxiliary system

In order to ensure the full melting, flow and curing of the resin of GFRP composites in the hot compression molding process, this mold integrates the design of an efficient and controllable auxiliary system, the core of which is the heating and temperature control system (shown in Figure 2). The system adopts a dual-mode heating architecture that combines built-in and external heating to provide a uniform and stable thermal environment for the mold cavities. The built-in mode is achieved by symmetrically and uniformly machining heating holes and inserting heating rods in the top cover and bottom base of the mold, while the external mode supports heating the mold as a whole in an oven. The temperature control system is based on PID algorithm and real-time monitoring of the cavity temperature by thermocouples, which realizes precise program control of the heating rate, target temperature and holding time. As verified by the no-load test, the temperature difference between the working area of the mold and the target temperature interval can be controlled within ± 2℃, which meets the requirement of high-quality molding.

3. Workflow and performance advantages

3.1 Workflow

The workflow of prepreg molding using this mold is shown in Figure 4: First, glass fiber (various micro-modified glass fibers) and resin film are placed in the forming groove of the lower base; One end of the fiber is fastened to the first fixing notch by the upper fixing block, and the other end is preliminarily fixed to the second fixing notch of the moving clamping groove by pressing down the fixing block. Subsequently, the two-sided configuration of the rotary adjustment bolt requires the simultaneous operation of the bolts on both sides, and the single-bolt center scheme uses the middle bolt) to drive the moving slot to move in a straight line (without deflection under the constraints of the guide rod), thereby applying precise and uniform preset tension to the fibers. Next, the tense fiber layer is covered with a resin film and the top cover is closed to complete the mold closure. Finally, the heating rod is inserted into the heating holes evenly distributed on the upper cover and lower base, and the temperature control system is activated to heat the mold to the target curing temperature range of 80-90 ℃. Under this condition, the resin melts and flows and fully infiltrates the fibers in the tension state, and is cured under the action of hot pressing to form the final GFRP composite product.

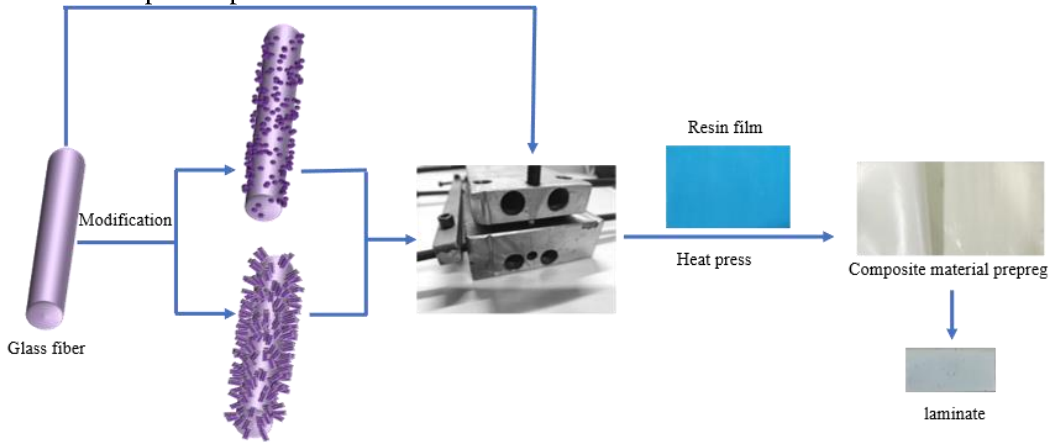

Figure.4 GFRP composite molding workflow

3.2 Advantages of molds

The core advantages of this mold are: the tensioning mechanism of the mold effectively eliminates fiber relaxation and significantly improves the interlayer interface performance; Modular design and intuitive operation steps (clamping, tensioning, clamping, heating) for easy implementation; Distributed heating and precise temperature control ensure flexible adaptability and consistent molding quality for different resin systems. The design principle of the tensioning mechanism is based on the principle of spiral transmission, which transforms the rotational motion into a linear motion of the moving slot by rotating the adjustment bolt, so as to exert uniform tension on the glass fiber.

The tensioning mechanism is designed with the guide rod and guide hole, which has a better effect, which can effectively solve the tensioning problem of glass fiber in the molding process, avoid fiber relaxation, and improve the interlayer interface performance of composite materials. The mold structure is reasonably designed, easy to operate, easy to achieve automated production, and improves production efficiency. The mold heating method is flexible, and the heating temperature can be adjusted as needed to adapt to the molding needs of different materials.

4. Laminate preparation and interface performance testing

In order to ensure the effectiveness of the designed dual-mode tension-controlled GFRP mold in practical application, the preparation and interface performance test of the laminate are systematically carried out in this chapter. The glass fiber electron microscopy before and after modification is shown in Figure 5 and Figure 6. The advantages of the mold in improving the interface properties of the composite materials were verified by comparing and analyzing the interlayer shear strength of GFRP laminates before and after modification.

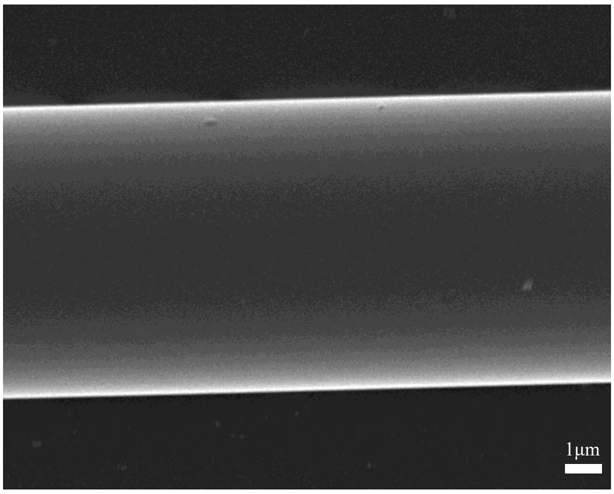

Figure. 5 Original glass fiber electron microscopy

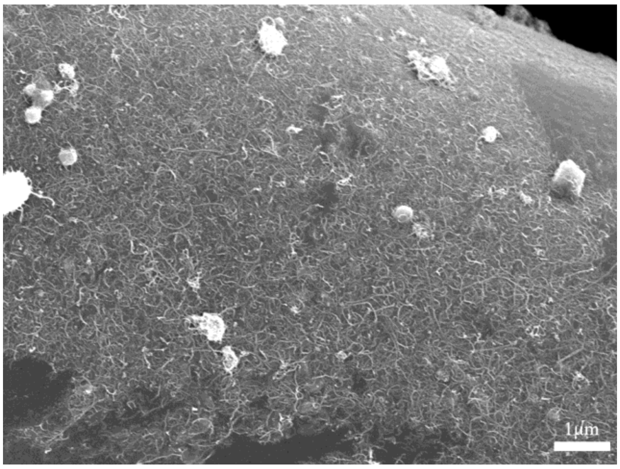

Figure.6 Glass fiber electron microscopy of grafted carbon nanotubes

4.1 Laminate preparation

In this study, chopped glass fiber (length 100-120 mm) was used as the reinforcement and epoxy resin as the matrix, and the fiber-to-resin mass ratio was 1:1. The prepreg was prepared by the designed dual-mode tension control mold and further thermoformed into GFRP laminates. The fiber raw material is selected from E-glass fiber, and the interface modification is carried out by aminoated CNTs, and the specific modification steps are as follows:

4.1.1 Surface pretreatment of glass fiber

Shear 100-120mm long pure glass fibers immersed in acetone solution, sonicated and soaked overnight to remove wetted substances from the fiberglass surface. After drying, the prepared glass fibers were added to the concentrated sulfuric acid/hydrogen peroxide mixture (volume ratio of 7/3) and stirred overnight to thoroughly expose the silicon hydroxyl groups.

4.1.2 Amination modification of glass fiber

Add the surface pretreated glass fibers to the toluene solution of the silane couplant (KH-550) in a volume ratio of 1:50 (KH-550:toluene) and reflux overnight (12-14 h) at 110 ℃ (round-bottom flask condenser oil bath heating). After completing the reaction, the amination glass fibers are washed with toluene and then dried in an oven.

4.1.3 Carboxylation modification of glass fiber

Add the ammoniaized glass fibers and 50 mL DMF described above to a 250 mL flask and sonicate for 30 minutes. Then transfer to an oil bath, add 50 mL of 0.5 mol/L succinic anhydride drop by drop, and stir at 60 ℃ for 24 h. After the reaction, the glass fibers were washed with DMF and anhydrous ethanol and then dried in a vacuum drying oven.

4.1.4 Carboxylated glass fiber grafted amination carbon nanotubes

Dissolve 5 mg HATU and 50 mg aminoated carbon nanotube ultrasound into 30 ml of DMF for 1 h to obtain CNT/DMF solution; Next, the carboxylated glass fibers were soaked in the prepared CNT/DMF solution at about 25 ℃ for 4 h, during which the magnetic rotor was stirred continuously to obtain the target CNT/GF multi-stage reinforcement structure.

4.1.5 Hot press forming process

Separate glass fibers before and after modification are used for hot press molding. The fibers and epoxy resin film are laid in the mold grooves in a unidirectional layup. The fibers were fixed at one end and clamped at the other end by a tensioning mechanism, with a preset tension applied by rotating an adjusting bolt and a guiding structure to ensure that the fibers were not deflected. The resin film was then covered and the mold was closed, and the temperature was ramped up to 80 ℃ at 5 ℃/min. When the temperature reached 60 ℃, a pressure of 1.0 MPa was applied and the mold was held for 60 min to allow the resin to fully cure, after which it was cooled slowly at 2 ℃/min to below 40 ℃. The final product was prepared in each group in five sizes. Five laminate specimens with dimensions of 20 mm × 10 mm × 2 mm were finally prepared for each group for comparative performance analysis.

4.2 Interface performance test

In order to evaluate the effect of mold tension control on the interlayer interface properties of composite materials, ILSS test was carried out on GFRP laminate samples prepared according to the building materials industry standard "JC/T 773-2010 Shear Strength Test Method for Fiber-Reinforced Plastic Short Beams". ILSS is a key index for evaluating the interlayer properties of composites, which directly reflects the interfacial bonding quality between fibers and resin matrix.

4.2.1 Test methods and equipment

The test was conducted at room temperature. Test equipment for universal material testing machine, the diameter of the support roller is 6 mm, and the diameter of the loading roller is 10 mm. The span is set to 10 mm (span-to-thickness ratio 5:1) and the loading rate is set to 1 mm/min. The specimen size was 20 mm × 10 mm × 2 mm, and the number of specimens in each group was 5, and the average was taken as the final result. Before testing, the actual width and thickness of each specimen were accurately measured using digital calipers with a measurement accuracy of 0.01 mm.

4.2.2 Test results and analysis

Five groups of composite laminates made of modified glass fiber before and after were tested and passed the formula:

$$\tau_{\text{ILSS}} = \frac{3F_{\max}}{4bh}$$

The ILSS was calculated, where τ_{ILSS} the interlayer shear strength unit (MPa) was the $F_{\max}$ maximum compressive load recorded, *and b and h were the width (*mm) and thickness (mm) of the specimen, respectively.

The average ILSS of the glass fiber composite laminate before modification was 53.46 MPa, and the average ILSS of the glass fiber composite laminate after modification was 68.89 MPa. Compared with the modification, the average ILSS value after modification increased by about 28.9%, indicating that the surface modification of glass fiber significantly improved the interlayer interface performance. This result clearly shows that the interfacial bonding between glass fibers and epoxy resin matrix after aminoated CNT modification is significantly enhanced. The mechanism may lie in the fact that CNTs form a multi-level reinforcing structure on the fiber surface through chemical grafting, which increases the mechanical interlocking and chemical bonding between the fiber and the matrix, thereby effectively transmitting shear stress and inhibiting interface failure.

At the same time, the dual-mode tension control mold designed in this study effectively avoids fiber relaxation during the preparation process, ensures the uniform arrangement of fibers in the tension state, further promotes the infiltration of resin to fibers and interface bonding, and provides a process guarantee for the improvement of ILSS.

4.3 Discussion

In this study, modified and unmodified GFRP laminates were successfully prepared by tension-controlled molds, and their interlayer shear properties were systematically evaluated. The test results show that the synergistic effect of fiber surface modification and mold tension control significantly improves the ILSS of composites. Firstly, after the modification of glass fibers by aminoated CNTs, their surface activity and specific surface area increased, and the physical anchoring and chemical bonding formed with the epoxy resin matrix were enhanced, which effectively inhibited the interfacial slip and delamination. This is consistent with the conclusion reported by Godara et al. that CNTs enhance interface performance [10]. In addition, the dual-mode heating of the mold built-in heating system and external oven ensures the uniformity and controllability of the curing temperature, further reducing the internal stress and pore defects caused by the temperature gradient, and contributing to the complete formation of the interface area. Although this study has achieved significant results in improving the interlayer performance, there are still some areas that can be further optimized. For example, the current fiber modification process is complex and difficult to apply to large-scale production; In the future, more efficient surface treatment processes (such as corona treatment, plasma treatment, etc.) can be explored. At the same time, the tension control of the mold has not yet realized digital feedback adjustment, and sensors and closed-loop control systems can be introduced to realize real-time monitoring and dynamic adjustment of tension. In conclusion, this study effectively improves the interlayer interface performance of GFRP composites through the dual optimization of mold structure and fiber modification, and provides a feasible technical scheme and experimental basis for the high-quality preparation of automotive lightweight composite components.

5. Conclusion

In order to solve the problem of interlayer performance degradation caused by fiber relaxation during the molding process of GFRP composites, a special mold integrating dual-mode tension control and uniform heating system was designed, and the following conclusions were drawn through the preparation and testing of glass fiber reinforced composite laminates before and after modification.

1) The developed dual-mode tension control mold has two working mechanisms: bilateral synchronous tensioning and center-guided anti-deviation, which can achieve high-precision and unbiased tensioning of the fiber, effectively avoid fiber relaxation, and ensure that the fiber is in a uniform and controlled tension state during the molding process.

2) Combined with the built-in heating hole and the dual heating mode of the external oven, the mold can provide a uniform and stable curing temperature field in the range of 80–90 ℃, which is conducive to resin flow, infiltration and curing, and reduces the formation of pores and other defects.

3) The results of short beam shear test showed that the average interlayer shear strength (ILSS) of glass fiber composite laminate modified by aminoated carbon nanotubes reached 68.89 MPa, which was 28.9% higher than that of the unmodified sample (53.46 MPa), indicating that the fiber surface modification significantly enhanced the interfacial bonding performance between the fiber and the resin matrix.

4) The mold has the characteristics of modular structure, easy operation and wide applicability, which can provide effective technical means for high-quality and controllable preparation of lightweight composite components of automobiles, and has a good engineering application prospect.

In future research, the digitalization and intelligent improvement of tension control can be further carried out, and more efficient and environmentally friendly fiber surface modification processes can be explored to promote the application of this technology on an industrial scale.

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