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Study on the properties of thermoplastic nonwoven interlayer toughened GF/EVE composites, i.e. toughening mechanism

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ABSTRACT

In order to improve the impact toughness and service life of GF/EVE composites, this paper applies the thermoplastic nonwoven fabric structure to the preparation of GF/EVE composites. The thermoplastic polyurethane was used as the raw material, and the meltblown method was used for the preparation of thermoplastic nonwoven fabrics, and then the prepared thermoplastic nonwoven fabrics were used for the preparation of GF/EVE composites through the VARTM device. For the properties of GF/EVE-TPU composites, specific test methods are given to define the moisture absorption rate and the erosion performance based on the consideration of the stress change of its hygrothermal properties, and the determination of the interlaminar fracture toughness is given.The critical damage threshold load of GF/EVE-TPU composites is 1.57kN, and its contact force increases with time, and the composites are aging in After 60 days, its moisture absorption and erosion weight loss in alkaline environment were 0.736% and 81.19%, respectively.The optimum fracture toughness value of 9g/m² thermoplastic nonwoven structure incorporated into GF/EVE composite was 0.97kJ/m², and the GIIC value of GF\EVE-TPU30 was increased compared with the GF/EVE material without interlaminar toughening by 183.83%. Combining the thermoplastic nonwoven fabric structure with GF/EVE composites can enhance the erosion resistance and interlaminar toughness of the composites and improve the service life of GF/EVE composites.

Keywords: thermoplastic polyurethane, nonwoven fabric, VARTM device, GF/EVE composites, interlaminar fracture toughness

1. Introduction

Materials are the foundation and precursor of social development, and new materials are the important standard of social progress [1]. With the continuous progress of aerospace science and technology, advanced composite materials have been developed rapidly [2].

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Carbon fiber reinforced resin matrix composites have become one of the main structural materials used in contemporary aerospace applications due to the advantages of high specific modulus, high specific strength, strong designability of mechanical properties, excellent fatigue resistance [etc., and significant weight reduction benefits compared with traditional metal materials. At present, the post-impact compression strength (CAI) of high-strength medium-model carbon fiber-reinforced high-toughness epoxy resin composites has reached more than 310 MPa and has been successfully applied in the main bearing structure in aerospace field. Nowadays, the mass share of resin matrix composites in aircraft structures has become one of the important symbols to measure the advancement of aircraft [3-4].

Recently, an interlaminar "off-site" toughening technique was first developed by the Beijing Institute of Aeronautical Materials of AVIC (BIMRA), which fundamentally solves the inherent contradiction of the interaction of the two sub-processes. Against this background, the third generation of composites represented by interlayer "off-site" toughening technology has emerged. Interlayer "off-site" toughening technology significantly improves the toughness of composite materials, the key lies in the interlayer toughening materials. The earlier toughening materials are interlayer granular particles, and then interlayer toughening materials in the form of thin film structure have been widely used. However, there are certain problems with thermoplastic resin films as the toughening layer. On the one hand, the presence of the toughening layer may create a certain resistance to the flow of resin [5]. On the other hand, at the injection temperature of the process, the thermoplastic toughened layer may partially dissolve in the resin matrix leading to an increase in the resin viscosity, which reduces the flowability of the resin and thus has an effect on the mold filling process. In order to improve this situation, nonwoven fabrics with high porosity structure as interlayer tensile materials have become a hot research topic in recent years [6].

Vallack, N et al. summarized studies related to interlaminar toughening of fiber-reinforced polymer composites and found that differences in infusion of resin porous structure resulted in different interlaminar toughness of fiber-reinforced polymer composites, as well as differences in fiber type had a limited effect on interlaminar toughness [7]. Wang, Y et al. investigated pathways for interlaminar toughening of composite laminates and contributed to the existing studies on the short fiber toughening frontiers and future development trends, contributing to the performance optimization of composites [8]. Di Boon, Y. et al. reviewed the studies related to the interlaminar failure of fiber-reinforced polymer (FRP) and fiber-metal laminate (FML) composites, including the measurement of interlaminar toughness reinforcement methods as well as the advantages and drawbacks of various treatments [9]. Dikshit, V. et al. attempted to introduce carbon nanotubes into fiber-reinforced polymer composites to improve the interlaminar toughness and inhibit delamination phenomenon, and introduced the current strategies on the reinforcement of interlaminar toughness of composites, and gave an outlook on the application areas and trends of polymer-fiber-nanotube composites [10]. Shao, M et al. discussed the good performance of carbon fiber laminated composites at the level of lightweight and mechanical properties, and explored the problem of interlaminar damage under the impact conditions, and proposed the design and production of a new type of double-sided ring two-dimensional (2D) woven laminated composites (DWLC) by combining RTM molding process, based on the testing experiments, which proved that the DWLC has a good interlayer shear strength [11]. Han, W et al. comprehensively analyzed various aspects of graphene and carbon nanotube (CNT)-reinforced fiber-reinforced polymer (FRP) composites and related research advances, with an emphasis on exploring the fusion principle of carbon nanotubes and graphene, as well as the principle of toughening [12].

In order to enhance the service life of GF/EVE composites and make them adaptable to more scenarios, this paper proposes a method of interlayer toughening of GF/EVE composites with thermoplastic nonwoven fabrics. Firstly, the preparation method of thermoplastic nonwoven fabric is introduced, and the thermoplastic polyurethane is used as the material, and the meltblown method is applied for the preparation, and the prepared thermoplastic nonwoven structure is used to prepare GF/EVE composites using the VARTM device, and for the experiments on the GF/EVE composites, the corresponding test and characterization methods are selected, and the specific calculation methods of the moisture absorption rate and erosion performance of the composites are given. In addition, the hygrothermal properties of the composites are also fully considered, and the determination method of the interlaminar fracture toughness of the composites is given. For the GF/EVE-TPU composites prepared in this paper, they are analyzed in several dimensions, such as FTIR data, low secular impact response, moisture absorption rate, erosion resistance, and interlaminar toughness.

2. Specimen preparation and test methods

In recent years, glass fiber reinforced resin-based (GF/EVE) composites have been widely used in engineering. However, they are affected by erosive wear in many applications. Therefore, how to improve the erosion and wear resistance of composites is of great significance for the improvement and application of the materials. In addition, composite materials are prone to delamination damage between layers, which seriously restricts the service life of the materials. How to inhibit the material delamination damage and improve the delamination resistance of laminates has been of great concern. Thermoplastic polyurethane (TPU) has both plastic processing characteristics and rubber physical properties and strength, and at the same time has excellent wear resistance. By using meltblown method to prepare TPU and adding it into glass fiber reinforced resin matrix composites, the mechanical properties of GF/EVE composites can be effectively enhanced, and the service life of the materials can be greatly enhanced.

2.1. Preparation of GF/EVE composites

2.1.1. Thermoplastic Nonwoven Fabric Preparation. In order to achieve the delamination resistance of laminates of glass fiber reinforced resin matrix composites, in this paper, thermoplastic polyurethane was used as the raw material for the preparation of thermoplastic nonwoven fabrics using the meltblown method, so that it can provide support for the enhancement of interlaminar toughness of GF/EVE composites [13]. The materials involved in the preparation of thermoplastic nonwoven fabrics were mainly thermoplastic polyurethane selected from G Company, whose model is 1175A, sodium dodecyl sulfate from T City ZY Chemical Reagent Co. Multi-walled carbon nanotubes with a diameter of 15-25 nm and a length of 10-20 μm, with a purity higher than 90% and a catalyst residue lower than 0.15% were from S Nanotechnology Co. Anhydrous ethanol, analytically pure was selected from T City TL Chemical Reagent Co. and conductive copper adhesive was from DY Tape Co.

TPU was used as raw material to prepare TPU meltblown nonwoven fabric by meltblown spinning technology. Before meltblown, the raw material was dried in an oven at 95°C for 12 h. The meltblown process parameters were 165, 210, 220, 230°C for screw extruder one to four zones, 220°C for metering pump temperature, 235°C for head temperature, 240°C for hot air temperature, 0.5 MPa for air pressure, 30 cm for receiving distance, and 0.42 m-min for screen speed -1.

Sodium dodecyl sulfate was used as the dispersant, and anhydrous ethanol was used as the solvent to formulate the multi-walled carbon nanotubes (MWCNTs) with the mass concentrations of 0.4, 0.8, 1.2, 1.8, 2.4, and 3.2 mg-mL-1 dispersions, respectively. The above dispersions were placed in an ultrasonic cleaner and ultrasonically dispersed at 80°C for 3 h. Two pieces of nickel mesh were cut and placed at the bottom of the Brinell's funnel, and TPU nonwoven fabrics of suitable size were cut and placed on the nickel mesh. The above MWCNTs dispersion was quickly poured into the Brinell funnel for filtration, so that the carbon nanotubes were uniformly loaded on the surface of the nonwoven fabric. After filtration, the TPU nonwoven was vacuum dried at 75°C for 2h to obtain TPU/MWCNTs thermoplastic nonwoven fabrics with different conductivity.

2.1.2. Composite material preparation process. After the thermoplastic nonwoven fabrics were successfully prepared, they were utilized in the VARTM device for the preparation of GF/EVE composites [14]. The flow of the VARTM molding process is shown in Fig. 1, which is as follows:

Step1 Lay layers on the stainless steel flat mold in the order of anti-adhesive film, TPU non-woven fabric, release cloth, high porosity permeable film, and perforated anti-adhesive film, and finally lay the vacuum bag film, seal the vacuum bag film and the mold around the mold with a sealant, and connect a vacuum pump to vacuum the whole device through the external conduit to check the airtightness of the device.

Step2 Weigh epoxy resin LT5072A and curing agent LT5071B according to the mass ratio of 100:25, mix evenly and then degas in a vacuum oven for 20-25min.

Step3 Under the negative vacuum pressure, the resin is injected from one end of the device, turn off the vacuum pump when the TPU nonwoven fabric is completely infiltrated, and seal the mouth of the infusion tube.

Step4 The device was cured at room temperature (26°C) for 20h and then post-cured in a 75°C oven for 8h.

Step5 Demolding to obtain GF/EVE composites based on TPU nonwoven fabric.

To prepare the pure epoxy samples, the degassed resin was directly cast into polytetrafluoroethylene (PTFE) molds, and then demolded after curing at room temperature (26°C) for 20h and post-curing in a 75°C oven for 8h.

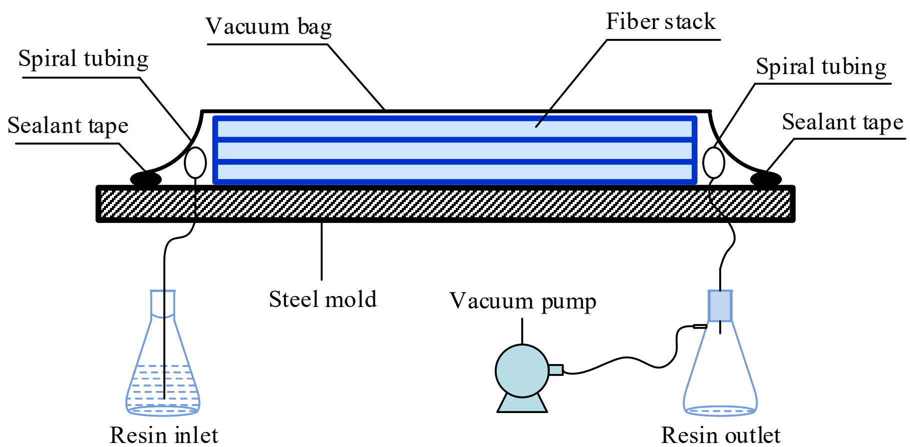


Fig. 1. Diagram of VARTM device

In this experiment, 0/90° carbon fiber woven fabric was used and layered according to the instructions in Step1. The TPU nonwoven fabric was located in the surface layer when the solid particle erosion and wear performance test was conducted, and the TPU nonwoven fabric was located in the middle layer when the mechanical properties and interlayer toughness test was conducted. The thickness of the experimentally obtained GF/EVE composite was 1.55 mm, and the content of TPU nonwoven was 50 wt%.

2.2. GF/EVE composite material test

2.2.1. Test methods and characterization:

1) Infrared spectroscopy test (FTIR). A Nicolet 18XB infrared spectrometer was used, and the resin was cured and ground into powder, which was tested after being pressed using the potassium bromide pressing method, with an instrumental resolution of 5 cm-1 and a wavelength range of 400 cm-1 to 5000 cm-1, and the presence of characteristic peaks was judged according to the wavelengths of vibrational peaks.

2) Heat loss analysis (TGA). Mettler TGA/SDTA425 thermogravimetric analyzer was selected, and the samples had to be dried in the oven before testing, and after drying was completed, 5mg~10mg of samples were taken in an aluminum crucible, compacted, and then tested at a nitrogen flow rate of 40mL/min, a temperature increase rate of 22℃, and a temperature range of 35℃~900℃.
3) Dynamic Mechanical Analysis (DMA). METTLER DMA861 Dynamic Thermo-mechanical Analyzer was selected, the sample size was 35mm×5mm×3mm, the heating rate was 5℃/min, and the temperature range was 40℃~300℃.
4) Bending strength test. Instron5567AR223 electronic universal testing machine was used, the cured material with reference to GB/T2567 three-point bending mode of bending strength test requirements, the sample size of 60mm × 12mm × 5mm, the loading rate is 3mm/min, the span is 50mm. composite material with reference to GB/T9341-2005 standard test, the size is 50mm × 14mm × 3mm, the rate is 1.5mm/min, the span is 36mm, and 10 samples are tested in each group.
5) Impact strength test. Select XCJ-4 type simply supported beam testing machine, in accordance with GB/T 1843-2005 standard for notched impact strength test, the sample size of 50mm × 14mm × 3mm, each group of 10 samples.
6) Tensile strength test. Thermoplastic nonwoven GF/EVE composites tensile performance test specimens cut into strips, in the electronic universal testing machine for testing. The length of the specimen is 60mm*20mm*3mm.The tensile specimen of thermoplastic nonwoven GF/EVE composites is cut into I-beam shape, 50mm in length, 2mm in width, 1.5mm in thickness, and the radius of chamfer is 5mm.5 specimens are tested for each proportion of the fibers, and then the average value of the specimens is taken as the final tensile strength. The test temperature was room temperature and the experiment was conducted at a rate of 1.5mm/min.
7) Corrosion resistance test. The method of weighing after immersion in corrosive liquid is adopted, the sheet specimen is completely immersed in the liquid state, and the samples are taken at intervals of three days, and then cleaned with water first, and then weighed with absorbent paper to absorb the dry surface. Each material under three specimens, take the average value as the final test results. The corrosion liquids were water, 10% hydrochloric acid solution, 18% sodium hydroxide solution, 2.5% sodium chloride solution and motor oil.

2.2.2. Moisture absorption and erosion properties:

1) Hygroscopic properties of composite materials. The GF/EVE composites of thermoplastic nonwoven fabrics have a wide range of applications, and the purpose of adding thermoplastic nonwoven fabrics is to enhance their service life, and the hygroscopic properties of the composites will be affected to a certain extent with the aging of the materials [15]. In this paper, the moisture absorption property of GF/EVE composites is defined, and the moisture absorption rate R of the specimen at the moment of aging t can be expressed as:

$$R_t = \frac{M_t - M_0}{M_0} \times 100\% \tag{1}$$

Where M_1 is the mass of the specimen after immersion t moments (g), M_0 is the reference mass of the specimen (g).
2) Erosion performance of composites. Most of the application fields of GF/EVE composites belong to wind power generation, and the erosion performance of the composite material should take into full consideration of the composite material application of the wind speed of the geographical area of the impact, but also by the sand and gravel carried in the wind. Therefore, in this paper, the erosion performance test, choose the erosion speed of 10m/s, according to the distribution of sand particles in the air to select the sand parameters of the jump layer and the suspension layer as the experimental parameters, the erosion particles for the 0.35 ~ 0.55mm spherical sand particles, the erosion angle of 60 ° C, the mass of sand particles used for erosion for each time for 0.35kg, before weighing the

ultrasonic cleaner to clean the sample, and after cleaning the sample using a drying box to clean the sample, and after weighing the sample, the sample was cleaned using a drying box. Before weighing, the specimen was cleaned by ultrasonic cleaner, after cleaning, the specimen was dried in drying oven, and weighed by electronic balance with precision of 1/10,000 at intervals until the quality was stable.

The weight loss by erosion R_c (g/kg) is given in the following equation:

$$R_c = \frac{m_c}{m} \tag{2}$$

Where m_c is the loss of specimen mass before and after erosion (g), m is the mass of sand grains used for each erosion (kg).

3. Mechanism of GF/EVE composite properties

GF/EVE composites have the advantages of light weight, high strength, corrosion resistance, good vibration damping and strong process designability, etc., which have been widely used in the wind power industry, but the current wind power generation equipment are in the working environment of the more severe areas. Therefore, GF/EVE composites should not only consider the mechanical performance requirements, but also the influence of environmental factors in the actual engineering application process. These environmental factors will accelerate the decline of material properties through different damage mechanisms, leading to early failure of the material. Therefore, it is of great engineering value and theoretical significance to study the performance mechanism of composite materials in typical environments.

3.1. Hygrothermal properties of composites

In hot and humid environments, the anisotropy of the composites is more significant due to the different coefficients of thermal expansion of the fibers and matrix materials in the composites and the different water absorption rates. When the composite is not subjected to external loads. The thermal expansion strain of the plywood is when the temperature change is ΔT:

$$\begin{bmatrix} \varepsilon_1^{\mathrm{T}} \\ \varepsilon_2^{\mathrm{T}} \\ \varepsilon_{12}^{\mathrm{T}} \end{bmatrix} = \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ 0 \end{bmatrix} \Delta T \tag{3}$$

where $\varepsilon_1^{\mathrm{T}}$, $\varepsilon_2^{\mathrm{T}}$ and $\varepsilon_{12}^{\mathrm{T}}$ are the thermal strains in the fiber direction and vertical fiber direction, respectively, and λ_1 and λ_2 are the coefficients of thermal expansion in the fiber direction and vertical fiber direction, respectively.

The composite material absorbs water in a humid environment, let the mass of the composite material in the dry state be M. After the material absorbs water, the mass increases by ΔM. The water absorption rate is $SI = \frac{\Delta M}{M}$ and the wet expansion strain is:

$$\begin{bmatrix} \varepsilon_1^{\mathrm{H}} \\ \varepsilon_2^{\mathrm{H}} \\ \varepsilon_{12}^{\mathrm{H}} \end{bmatrix} = \begin{bmatrix} \xi_1 \\ \xi_2 \\ 0 \end{bmatrix} I \tag{4}$$

where $\varepsilon_1^{\mathrm{H}}$, $\varepsilon_2^{\mathrm{H}}$ and $\varepsilon_{12}^{\mathrm{H}}$ are the wet strains in the fiber direction and vertical fiber direction, respectively, and ξ_1 and ξ_2 are the wet expansion coefficients in the fiber direction and vertical fiber direction, respectively.

Under positive axial loading, considering the deformation generated in the hot and humid environment, the stress-strain relationship of the single-ply plate is:

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \end{bmatrix} = \begin{bmatrix} Q_{xx} & Q_{xy} & 0 \\ Q_{yx} & Q_{yy} & 0 \\ 0 & 0 & Q_{cc} \end{bmatrix} \begin{bmatrix} \varepsilon_1 & -\lambda_1 \Delta T & -\xi_1 I \\ \varepsilon_2 & -\lambda_2 \Delta T & -\xi_2 I \\ \gamma_{12} & 0 & 0 \end{bmatrix} \tag{5}$$

Where σ_1 and ε_1 are the total stress and strain in the fiber direction of the composite laminate, σ_2 and ε_2 are the total stress and strain in the vertical fiber direction of the composite laminate, τ_{12} and γ_{12} are the tangential stress and tangential strain in the fiber direction and vertical fiber direction, respectively, and Q_{xx}, Q_{yy}, Q_{cc}, Q_{xy}, and Q_{yx} are the elastic modulus and the product of the shear modulus and Poisson's ratio in the fiber direction and vertical fiber direction, respectively.

Under the action of off-axis loading and considering the deformation generated in the hot and humid environment, the intrinsic relationship of the single-layer plate is:

$$\begin{bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{bmatrix} = \begin{bmatrix} Q_{11} & Q_{12} & Q_{16} \\ Q_{21} & Q_{22} & Q_{26} \\ Q_{61} & Q_{62} & Q_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_x & -\lambda_x \Delta T & -\xi_x I \\ \varepsilon_y & -\lambda_y \Delta T & -\xi_y I \\ \gamma_{xy} & -\lambda_{xy} \Delta T & -\xi_{xy} I \end{bmatrix} \tag{6}$$

$$\begin{cases} \lambda_x = \lambda_1 \cos^2\alpha + \lambda_2 \sin^2\alpha \\ \lambda_y = \lambda_1 \sin^2\alpha + \lambda_2 \cos^2\alpha \\ \lambda_{xy} = 2(\lambda_1 - \lambda_2)\cos\alpha \sin\alpha \end{cases} \tag{7}$$

$$\begin{cases} \xi_x = \xi_1 \cos^2\alpha + \xi_2 \sin^2\alpha \\ \xi_y = \xi_1 \sin^2\alpha + \xi_2 \cos^2\alpha \\ \xi_{xy} = 2(\xi_1 - \xi_2)\cos\alpha \sin\alpha \end{cases} \tag{8}$$

where σ_y and ε_y are the longitudinal stresses and strains of the composite laminate, σ_x and ε_x are the transverse stresses and strains of the composite laminate, τ_{xy} and γ_{xy} are the shear stress and strain of the composite laminate, λ_x, λ_y and λ_{xy} are the thermal expansion coefficients of the composite laminate, ξ_x, ξ_y and ξ_{xy} are the wet expansion coefficients of the composite laminate, Q_{ij} are the product of the elastic modulus and shear modulus and Poisson's ratio in the abscissa system, and a is the winding angle, that is, the angle between the fiber direction and the transverse direction.

Considering the deformation in the humid and hot environment, the constitutive relationship of the laminate is as follows:

$$\begin{bmatrix} B_x \\ B_y \\ B_{xy} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{16} \\ C_{21} & C_{22} & C_{26} \\ C_{61} & C_{62} & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \gamma_{xy} \end{bmatrix} \tag{9}$$

where B_x, B_y and B_{xy} are the combined stresses in the plywood in the longitudinal and transverse coordinate systems, and C_{ij} is the in-plane modulus of the plywood.

3.2. Determination of interlaminar fracture toughness

Type I interlaminar fracture toughness tests of thermoplastic nonwoven GF/EVE composites were carried out on an Instron 5524 universal materials testing machine, and the test method was performed according to ASTMD 5568. During the molding of the thermoplastic nonwoven GF/EVE composite laminates, TNF was placed in the middle layer and a PTFE film (thickness ~25 μm) was laid on one side for the creation of prefabricated cracks. The molded thermoplastic nonwoven GF/EVE composite laminate was cut into sample strips of 140 mm in length and 30 mm in width. The schematic diagram of the test sample is shown in Fig. 2. The loading rate of the carrier head was 1.5 mm/min. During the testing process, the crack length as well as the corresponding loading point loads and displacements needed to be recorded, and the number of test samples was not less than 10.

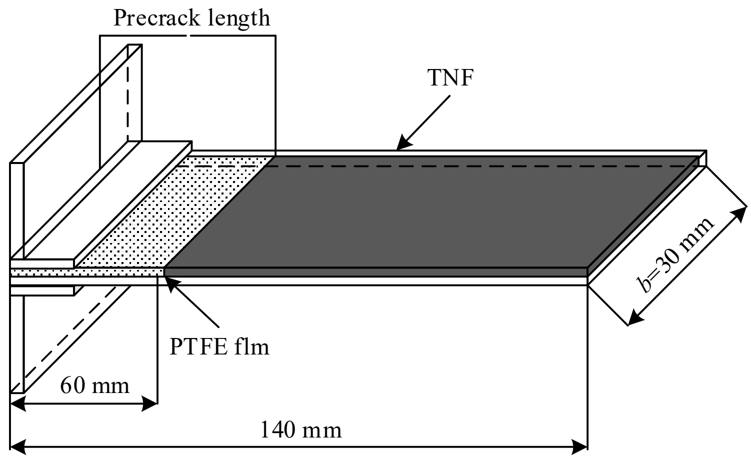


Fig. 2. Ⅰ-type layer discontinuous fracture toughness test

Type I energy release rate G_{IC} is calculated by Modified Beam Theory (MBT), then:

$$G_{IC} = \frac{3P\delta}{2b(a+\Delta)} \tag{10}$$

where b is the width of the specimen, a is the crack length, δ is the displacement at the loading point, P is the load, and Δ is the intercept on the x axis of the cubic root of flexibility versus crack a relationship curve.

The test method for composite type II interlaminar toughness test is based on the HB7403-48 standard. The molded composite sheet was cut into sample strips of 150 mm in length and 30 mm in width, and the schematic diagram of the test sample is shown in Fig. 3. The loading rate of the load head during the test was 1.5mm/min, and the number of test samples was not less than 10.

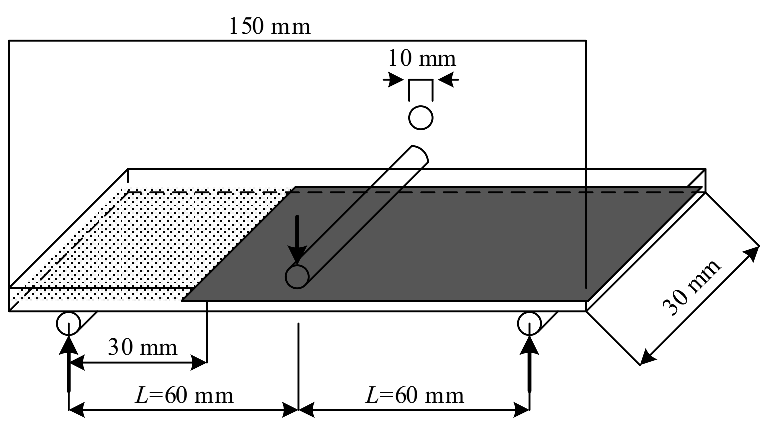


Fig. 3. Ⅱ-type layer discontinuous fracture toughness test

Type II interlaminar fracture toughness can be expressed as:

$$G_{IIC} = \frac{9P\delta a^2}{2w\left(2l^3 + 3a^3\right)} \times 10^3 \tag{11}$$

where G_{IIC} is the type II interlaminar fracture toughness, a is the effective crack length, P is the critical load for crack extension, δ is the deflection at the P corresponding specimen loading point, w is the specimen width, and $2l$ is the span.

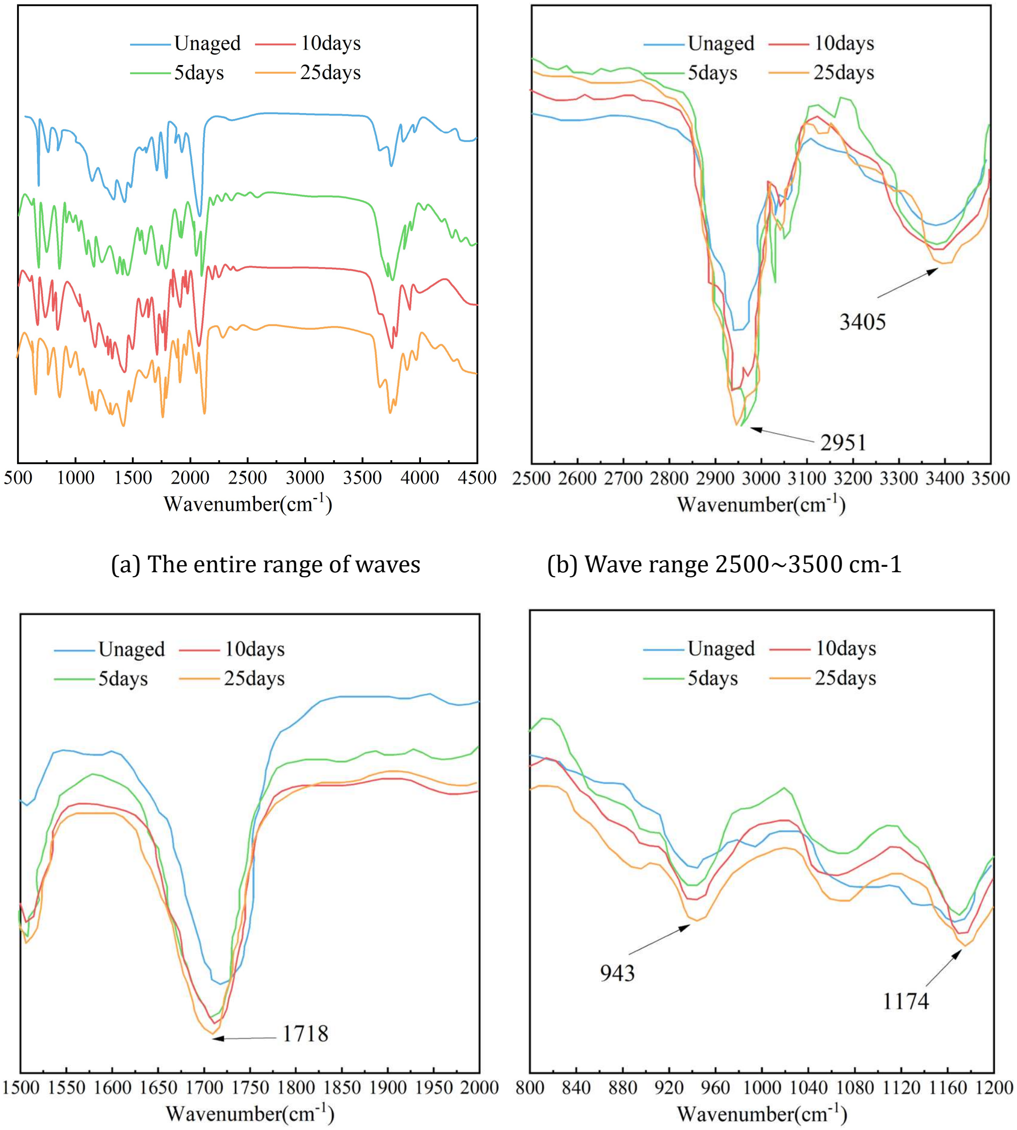
4. Performance analysis of GF/EVE composites

GF/EVE composites are composites made of glass fiber reinforcing material and resin matrix prepared by appropriate reinforcing technology and molding process, which have superior mechanical properties.GF/EVE composite components in engineering service will inevitably be subjected to light, temperature, oxygen and rainfall and other aging and corrosive media, which will lead to degradation of composite macro mechanical properties, which further aggravates the material inhomogeneity and ultimately leads to the decline of the bonding capacity between the fibers and the resin in the composites. This will lead to the degradation of the macroscopic mechanical properties of the composites, which will further exacerbate the inhomogeneity of the materials, and ultimately lead to the decline of the bonding ability between the fibers and the resin in the composite. This chapter focuses on the toughening mechanism of GF/EVE composites based on thermoplastic nonwoven fabrics as interlayer toughness materials prepared in the previous section, aiming to improve the service life of GF/EVE composites.

4.1. FTIR analysis and low velocity impacts

4.1.1. FTIR data analysis. The material spectra of the thermoplastic nonwoven interlayer toughness GF/EVE composites prepared in this paper were analyzed using an infrared spectrometer, and the changes in the intrinsic group structure of the GF/EVE composites during aging can be analyzed according to the changes in the peak positions in the infrared spectra, and the absorption peaks can be attributed. Fig. 4 shows the FTIR spectra of GF/EVE composites in different wave number ranges, where Fig. 4(a), (b), (c), (d) shows the FTIR spectra of the whole wave number range, wave number range of 2500~3500 cm-1, wave number range of 1500~2000 cm-1 and wave number range of 800~1200 cm-1, respectively.

Based on the FTIR spectra of GF/EVE composites with different aging times, it can be seen that the absorption band near 3405 cm-1 corresponds to the hydroxyl group O-H telescopic vibration, and its intensity increases with time, indicating that the composite material undergoes oxidation to form alcohols or acids during the aging process.2951 cm-1 corresponds to the asymmetric telescopic vibration of the methylidene-CH2 group, respectively, and its intensity increases firstly and then decreases with aging time. and then decreases, the results indicate that the oxidation of hydrogen placed on the tertiary carbon in the position of the ester with its associated finite chain breakage can lead to the formation of various carbonyl groups, especially ketone and ester groups.The adsorption band near 1718 cm-1 after aging at 100°C for 5 d is the vibration of the C=O group in the characteristic ester group of the telescopes, and it is observed that the intensity of it increases with time. It is well known that curing of curing agents accelerated with accelerators results in the production of ester groups in epoxy resins, and thus the increase in the intensity of the peak at 1718 cm-1 is due to the post-curing reaction of the epoxy resin at the beginning of thermo-oxidative aging. After aging at 100 °C for 10 d, the absorption band of the C=O group at 1718 cm-1 of the ester group shifted to a lower wave number and increased with aging time due to the oxidation of the hydroxyl group to form a carbonyl group.The absorption band near 1174 cm-1 corresponded to the -C-O-C-stretching vibration, and that near 943 cm-1 corresponded to the perovskite structure. The absorption bands around 1174 cm-1 correspond to -C-O-C-stretching vibration, and the absorption bands around 943 cm-1 correspond to -C-O-C-stretching vibration of the peroxide structure.



(a) The entire range of waves (b) Wave range 2500~3500 cm-1

(c) Wave range 1500~2000 cm-1 (d) Wave range 800~1200 cm-1

Fig. 4. FTIR spectra of the 100 ℃ aged epoxy samples

4.1.2. Low-speed shock response. In order to analyze the response of the thermoplastic nonwoven fabric-based GF/EVE composites in this paper when subjected to impact, the uninterlaminate toughened GF/EVE material, the materials in this paper, GF/EVE-TPU, GF/EVE-PA, and GF/EVE-EVA, were compared. Figure 5 shows the contact force-time curves of the drop hammer impact at 30°C for the uninterlaminated toughened and interlaminated toughened GF/EVER composites.

It can be seen that the contact force of the GF/EVE composites increases with time and decreases steeply when the load reaches 1.57 kN. It is generally believed that the load at 1.57 kN is the critical damage threshold load, indicating that the laminate produces damage at this point, such as cracking of the impact front surface matrix resin. Subsequently, when the force value is reduced to 1.01kN, the contact load increases again on the shock. When the contact force reaches a maximum value of 7.39 kN, the contact force starts to fall back until the punch bounces off the composite surface. The contact force-time curve has obvious fluctuations in the ascending section, while the descending section is relatively smooth, indicating that the damage to the composite material mainly occurs in the impact loading stage rather than in the unloading stage. In addition, the peak load and the slope of the curve of the GF/EVE composites without interlayer toughening are smaller than those of the interlayer-modified GF/EVE composites, and compared with the other types of composites, the overall impact response of the composites based on thermoplastic nonwoven GF/EVE in this paper is stronger. It indicates that the enhanced load bearing capacity of the modified GF/EVE composites is related to the increased thickness of the modified plywood in addition to the effect of the interlaminar toughening material.

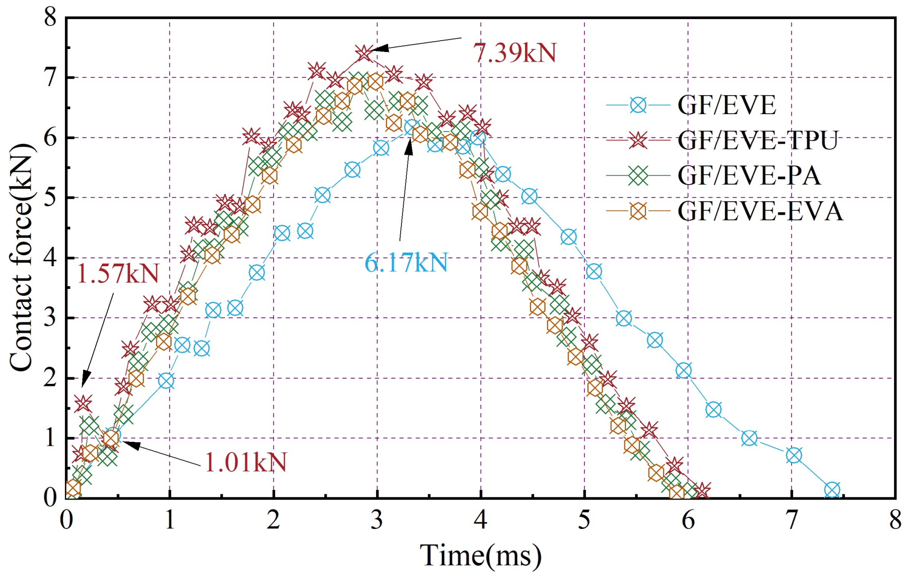


Fig. 5. The contact force - time curve of the gf/eve composite material at 30℃

4.2. Moisture absorption and erosion resistance

4.2.1. Moisture absorption rate of materials. In order to analyze the moisture absorption rate of GF/EVE composites based on the interlayer toughness of thermoplastic nonwoven fabrics under different aging environments, this paper set up two environments of hygrothermal and alkaline, respectively, and based on the method of calculating the moisture absorption rate given in the previous section, the curves of moisture absorption rate of the specimens of GF/EVE composites with the change of time were obtained as shown in Fig. 6.

It can be seen that the water absorption rate of the specimen under the humid-heat and alkaline aging environments has basically the same trend, and the early aging stage is the rapid moisture absorption stage, when the moisture absorption rate of the specimen is in a linear relationship with the aging time, which is due to the defects of the composite material itself as well as the absorption of water by the resin matrix. As the aging time is prolonged, the internal defects of the composite material and other physical or chemical changes gradually reach saturation, so that the moisture absorption rate becomes slower and tends to stabilize, but the overall trend is rising. And under the same aging time, the water absorption rate of composites in alkaline environment is larger than that in hot and humid environment. When the aging time reaches 60 days, the moisture absorption rate in alkaline environment reaches 0.736%, which is 24.96% higher than that in hot and humid environment, indicating that the alkaline medium promotes the improvement of the moisture absorption rate of GF/EVE composites.

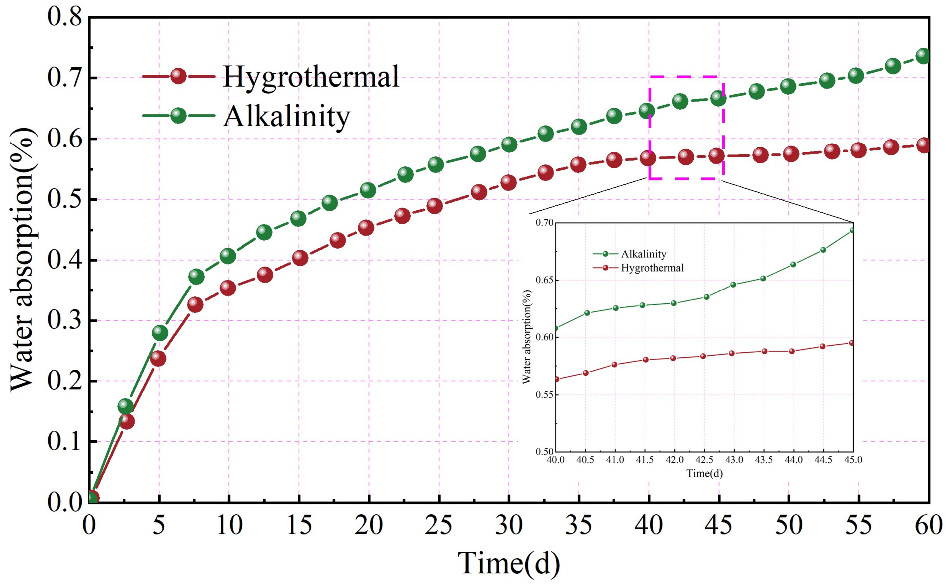


Fig. 6. Composite material moisture absorption curve

4.2.2. Material erosion resistance. Fig. 7 shows the variation curves of the erosion weight loss rate of GF/EVE specimens aged for different times in humid heat and alkaline environments. It can be seen that the changes in the erosion weight loss curves of composites in moist heat and alkaline solution are basically the same, and the overall trend is increasing, and after aging for 5 days, the erosion weight loss rate decreased by 16.29% and 5.98%, respectively. This is mainly due to the fact that water molecules in humid heat and alkali solution will make the resin matrix undergo hygroscopic swelling effect, which makes the spacing of the resin macromolecules become larger, leading to an increase in the activity of the rigid groups, and hygroscopic plasticization of the resin matrix occurs. At the same time, the increased flexibility of the resin matrix will enhance the rigidity of the composite specimen, which will lead to an increase in the erosion resistance. The erosion resistance of GF/EVE composites gradually decreased with the aging time, and the erosion weight loss of the specimens increased by 60.61% and 81.19% respectively after 60 days of aging in both environments. The reason for the decrease in the erosion resistance of GF/EVE composites is that with aging, the diffusion of water molecules will lead to a decrease in the performance of the resin and fiber/matrix interfaces, and at the same time, the water molecules leaching into the composites through cracks or defects in the resin matrix as well as the substances leaching out of the matrix will lead to a decrease in the performance of the glass fibers.

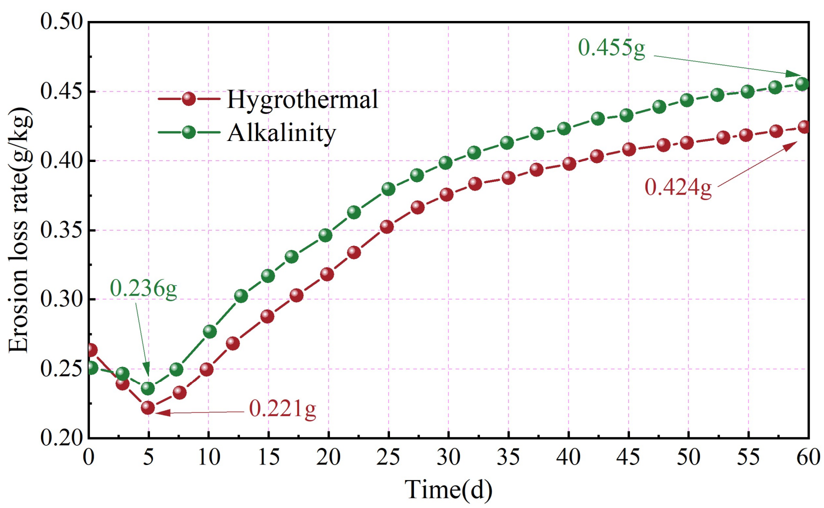
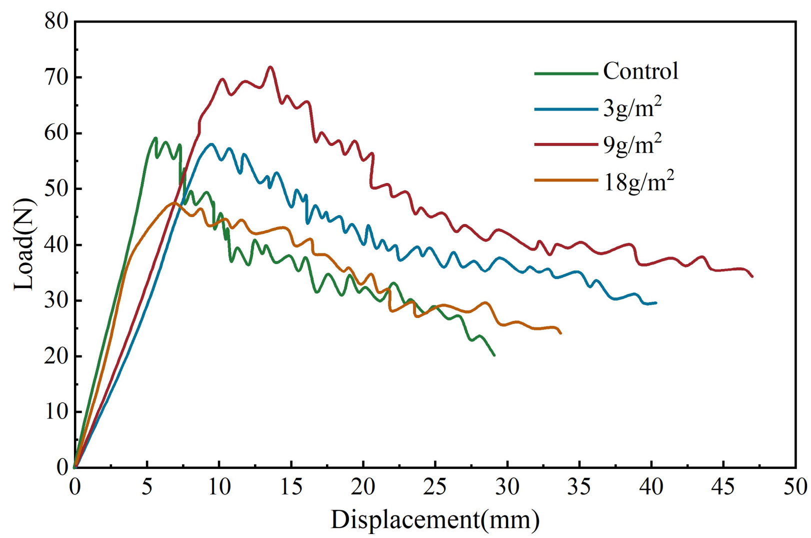


Fig. 7. Erosion loss rate after different aging time

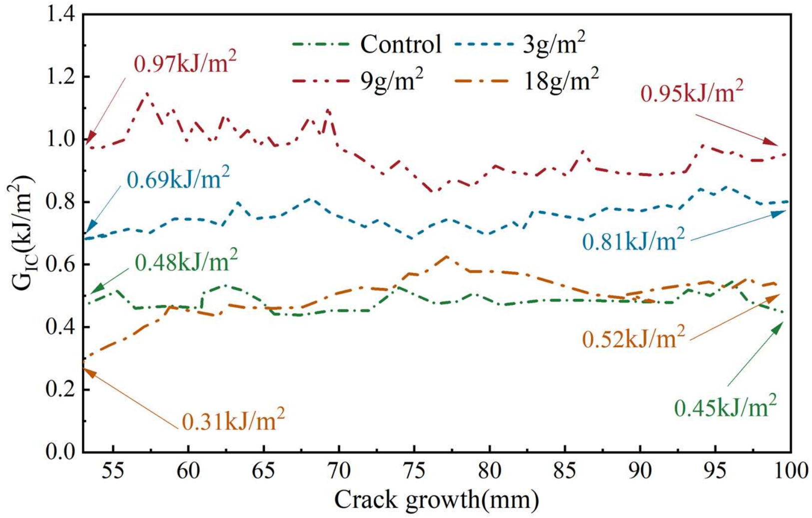
In addition, the specimen erosion resistance in alkali solution decreased more seriously than the hot and humid environment, mainly because the alkali corrosion medium in addition to water molecules caused by the attenuation of composite material performance, the presence of hydroxide in the solution will accelerate the hydrolysis of ester groups in the resin matrix. At the same time, water molecules immersed in the fiber surface so that the glass fiber hydrolysis, resulting in the destruction of the molecular chain of the resin matrix, resin and fiber interface debonding, glass fiber exposure, making the interface properties further decline. And water molecules into the matrix so that the molecular structure of the resin network cross-linking density is reduced, the resin matrix intermolecular stress transfer is weakened, all will lead to a decline in the erosion performance of the composite material.

4.3. Composite interlayer toughness

4.3.1. Type I interlaminar fracture toughness. Fig. 8 shows the type I interlaminar fracture toughness data of several different composite laminates, where Figs. 8(a) and (b) show the typical load-displacement curves and R curves, respectively. It can be seen that the addition of the thermoplastic nonwoven fabric structure can effectively slow down the decreasing trend of load and increase the maximum displacement distance, which indicates that the thermoplastic nonwoven fabric structure can effectively play a role in toughening the GF/EVE composites. In the control group, the GIC was 0.48kJ/m^2, and when the thermoplastic nonwoven structure with a surface density of 9g/m^2 was added, it showed the best fracture toughness value, with a GIC of 0.97kJ/m^2, which was 102.08% higher than that of the control group, and after adding the thermoplastic nonwoven structure with a surface density of 3g/m^2, the GIC was 0.69kJ/m^2, which was 43.75% higher. However, when the density of the added thermoplastic nonwoven structure was 18g/m^2, its GIC decreased compared to the control group, which was 0.31kJ/m^2, a decrease of 35.42%. This is mainly due to the fact that when the surface density increases, the thickness also increases, so when the surface density is too large, it will affect the resin infiltration, which leads to the toughening effect is not obvious or even play a negative effect.



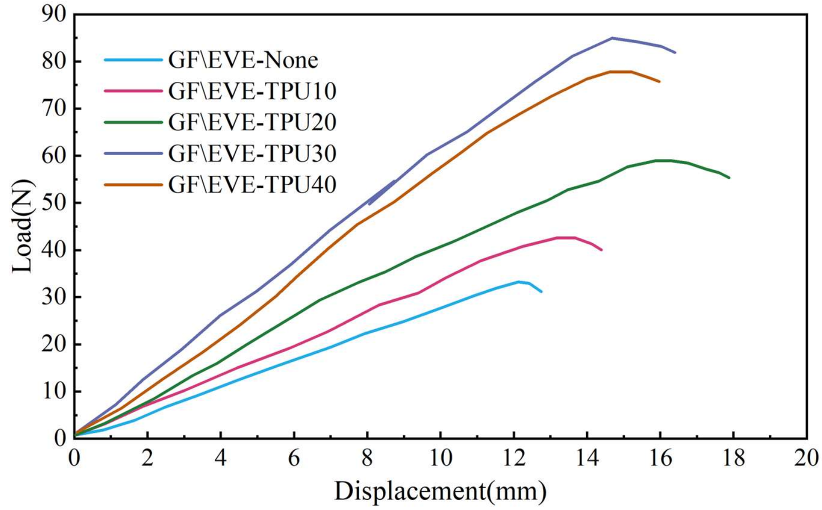
(a) Typical load-displacement curve



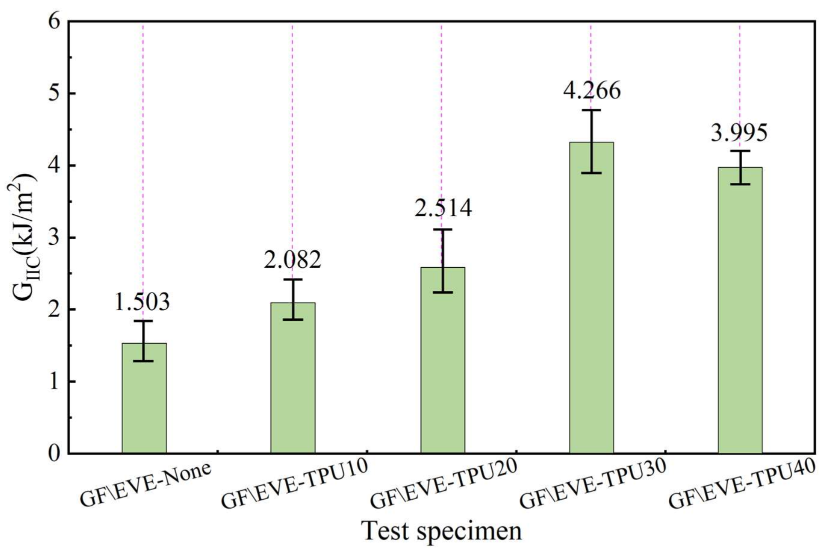
(b) R curve

Fig. 8. Analysis of the fracture test of different laminar I

4.3.2. Type II interlaminar fracture toughness. Fig. 9 shows the type II interlaminar fracture toughness data of GF/EVE composite specimens before and after modification, where Fig. 9(a)(b) shows the typical load-displacement curves versus the GⅡC values, respectively. As can be seen from the figure, the interlaminar crack starts to expand as the displacement at the loading point increases, the load increases accordingly, and the experiment is terminated when the peak load is reached with a sudden drop in the load value. Compared with the GF\EVE-None specimen, the peak loads of GF\EVE-TPU10, GF\EVE-TPU20, GF\EVE-TPU30, and GF\EVE-TPU40 specimens were increased by 29.51%, 79.06, 158.16%, and 136.37%, respectively. This indicates that the resistance to delamination extension of the material was significantly increased after the interlayer modification with TPU nonwoven fabric. After synergistic toughening of the TPU nonwoven fabric, the resistance to delamination extension of the composite material is significantly increased. Compared with the CFRP-None samples, the GIIC values of GFEVE-TPU10 and GFEVE-TPU20 samples increased by 38.52% and 67.27%, respectively, while the GIIC values of GFEVE-TPU30 and GFEVE-TPU40 samples increased by 183.83% and 165.80%, respectively, indicating that the synergistic modification of TPU non-woven fabrics has a significant effect on the improvement of type II interlaminar fracture toughness. Therefore, the interlaminar toughening of GF/EVE composites based on thermoplastic nonwoven fabrics in this paper has high effectiveness, which can significantly enhance the interlaminar fracture toughness of GF/EVE composites, and provide data support for enhancing the application range and service life of GF/EVE.



(a) Typical load-displacement curve



(b) Compare of GⅡC value

Fig. 9. The load-displacement curve of the gf/eve composite material

5. Conclusion

In this paper, based on the preparation of thermoplastic nonwoven fabrics, they were applied to the interlayer toughness material of GF/EVE composites, and the GF/EVE-TPU composites were successfully prepared. The composites were experimentally analyzed for their toughening properties, moisture absorption rate, erosion resistance and low-speed impact. The conclusions are as follows:
1) The strength of GF/EVE-TPU composites changes significantly with different aging times, and the absorption band of C=O groups at 1718 cm-1 of ester groups moves to a lower wavelength after aging at 100°C for 10 d and is enhanced with the increase of aging time.
2) The contact force of the GF/EVE-TPU composites increased with time and decreased steeply when the load reached 1.57 kN. After the contact force reaches a maximum value of 7.39 kN, the contact force of the composite begins to fall back until the punch bounces off the surface of the composite.
3) When the aging time of GF/EVE-TPU composite is 60 days, its moisture absorption rate in alkaline environment is 0.736%, and the anti-punching performance of GF/EVE composite gradually decreases,

and the weight loss rate of the punch in humid-heat and alkaline environments increases by 60.61% and 81.19%, respectively.

4) The best fracture toughness value was exhibited when a thermoplastic nonwoven structure of 9 g/m^2 was added to the GF/EVE composites, with a GIC of 0.97 kJ/m^2, which is an improvement of 102.08% compared to the control, and the GIIC value of GF\EVE-TPU30 was increased by 183.83% compared to the GF/EVE material without interlayer toughening.

In conclusion, the modification of GF/EVE composites by utilizing thermoplastic nonwoven structure can enhance the fracture toughness of the composites, and also effectively ensure the moisture absorption rate and erosion resistance of the materials, which can provide support for the enhancement of the application areas and service life of GF/EVE composites.

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