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UV ageing of epoxy resin-based glass fiber-reinforced polymer composites incorporating with various curing agents

Yinlong Cao^a, Yanjun Teng^a, Peng Zhang^a, Jiuwen Bao^{a,*}, Peng Feng^b, Rong Li^c, Wenhuan Wang^a

^a School of Civil Engineering, Qingdao University of Technology, Qingdao 266000, China

^b Department of Civil Engineering, Tsinghua University, Beijing 100084, China

^c Central Research Institute of Building and Construction Co. Ltd. MCC Group, China

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ABSTRACT

Improving the mechanical and durability-related properties of the glass fiber-reinforced polymer (GFRP) composites exposed to harsh maritime environments are an ongoing concern. This study comprehensively explored the effect of modified resin systems on the tensile properties of laminates in high ultraviolet (UV) and humidity environments. The UV aging behaviors of resin and GFRP laminates with different curing agents were evaluated, including the tensile properties and colorimetry. The dynamic mechanical properties, Fourier Transform Infrared Spectroscopy (FTIR) analysis and microstructural observations of the GFRP composites were evaluated to further analyze the deterioration mechanism. The results showed that the epoxy resin system with dense chemical structures demonstrated a greater ultimate tensile strength, which can be attributable to its rigid elements and small molecular spacing between reactive functional groups. Laminates comprising 4-ply prepregs facilitated a more effective load transfer across the matrix-fiber boundary, yielding optimal tensile properties of GFRP composites. The yellowing degree of resin incorporating phenolic amine curing agent increased rapidly within 7 d UV exposure. Deeper color of resin matrix reduced UV damage to upper fibers. The use of resin matrix with dense chemical structures and polar functional groups (-OH) can improve the tensile properties of GFRP and keep it at high ultimate tensile strength and toughness after 90 d UV exposure.

1. Introduction

Fiber-reinforced polymer (FRP) composites contain fibers, resin, and an interfacial phase. Each phase's unique characteristics contribute to the mechanical and durability properties of FRP. Glass fiber-reinforced polymer (GFRP) composites are frequently used in maritime applications due to their high strength-to-weight ratio, good corrosive resistance, and chemical stability [1]. However, long-term ultraviolet (UV) irradiation and high humidity conditions have been major factors that cause performance degradation in GFRP under harsh maritime environments. The UV and aggressive medium can synergistically damage the resin matrix and fiber phase. These environmental factors contribute to yellowing, mass loss, and internal defects of GFRP, further causing fiber breakage and interfacial debonding [2,3].

The tensile strength of fibers without attaching a resin matrix decreases significantly after a few hours of UV irradiation exposure [4]. Thus, the resin matrix in FRP has protective and bonding effects on the

fibers. Although the mechanical and UV resistance performances can be improved by adding modified materials (nanomaterials and geopolymers, etc.) into the resin phase or chemically bonding them onto the surface of fibers [5–7]. Poor compatibility between the filler and resin, undefined dosages of modified materials and complex chemical processes largely limit the industrial production of high-performance GFRP. The resins' performance depends highly on its chemical structures [8]. The epoxy resin is usually a better choice for FRP due to its superior mechanical properties and chemical resistance compared to other resin systems [9]. The resin matrix in FRP consists of epoxy resin and curing agents. Curing agents give the resin matrix different molecular structures and modify the FRP properties, including the toughness, chemical resistance, and mechanical and adhesive performances. Previous studies focused on curing agents due to the limited use of GFRPs in aggressive environments [10–12]. Curing agents commonly applied in epoxy resin include acid anhydride and amine curing agents. The curing temperatures of acid anhydride curing agents and epoxy resin are above 80 °C,

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^{*} Correspondence to: No. 777, Jialingjiang Eastern Road, Huangdao District,, Qingdao City, China. *E-mail address:* baojiuwen@qut.edu.cn (J. Bao).

while amine curing agents can react with epoxy resin at room temperature (24 °C). Thus, amine curing agents are widely applicated in the actual projects.

Polyamide amine curing agent is the most widely used due to its lower prices. The resin matrix cured by polyamide amines exhibits higher elongation and better adhesion, but lower tensile strength than other resin systems. In addition, the partial water solubility and greater interstitial free volume space of the resin system provide a site for corrosion media in marine environment, allowing the resin system to swell in humid conditions. The FRP containing this resin system are sensitive to the environment in terms of UV irradiation or interactions with water [13]. Najmi et al. [14] developed nanohybrid unites to bestow the desired multifunctionality to the resin system, increasing the tensile strength by 225 % and improving the UV resistance performance. Wang et al. [15] prepared nanomaterials via etching and a sol-gel technique, reducing the UV transmittance of epoxy/polyamide amine resin system-based composites to less than 1.8 %. Compared with these complex treatment processes, optimizing resin systems via curing agents is more convenient to improve the FRP's mechanical and durability performance. Yang et al. [16] used a novel phosphorus-containing tertiary amine curing agent to cure epoxy resin, improving its strength and elongation at break by 61.2% and 72%, respectively. Raj Shree et al. [17] demonstrated that the cycloaliphatic amine cured epoxy resin system has better mechanical properties in a humidity condition. Deepak et al. [18] studied the mechanical properties of composites made of epoxy resin cured with different curing agents. The composite samples made from different resin systems have their own advantages in tensile and shear properties. The composites with epoxy/phenalkamine resin system have better tensile properties. Many studies have focused on the effects of fibers and fiber-matrix interfaces on the mechanical and durability properties of FRP [19-21]. However, few studies have focused on how the chemical structure of the resin matrix affects the mechanical and UV resistance properties of GFRP.

The significance of this study is to understand the effects of UV and high humidity conditions on the aging behaviors and degradation mechanisms of GFRP made from different resin systems. The tensile properties of the resin and GFRP laminates with varying ply thicknesses (2-, 4-, and 8-ply prepregs) were evaluated using a tensile method. An aging program was implemented to simulate the synergistic effects of UV and high humidity exposures. The UV aging behaviors of the resin and GFRP laminates were evaluated in terms of the ultimate tensile strength (UTS), elasticity modulus, breaking elongation evolution laws, stress-strain curves, and toughness. The colorimetry of the resin and GFRP subjected to different UV exposure times was further conducted. Morphological and elemental changes in the glass fibers were observed through scanning electron microscopy (SEM) and energy-dispersive Xray Spectroscopy (EDX). The dynamic mechanical behaviors, functional group changes and microstructural observation of GFR were further evaluated. This study provided some critical information to support the broad applications of durable GFRP in maritime applications.

2. Experimental

2.1. Raw materials

Epoxy resin systems used in the experiments are composed of two parts: Bisphenol A diglycidyl ether type epoxy resin (E51) and curing agents, including polyamide, alicyclic, and phenolic amine curing agents. The molecular formula and main reaction groups of curing agents are shown in Table 1. The epoxy equivalent of E51 is 185–210 g/ eq. The amine value of the polyamide, alicyclic, and phenolic amine curing agents are 220 ± 20 , 270 ± 10 , and 500 ± 20 mgKOH/g, respectively. The amine equivalent and active hydrogen equivalent are calculated based on the amine value of curing agents. The calculation method is as follows:

Amine equivalent = 56,100/amine value

Table 1
Molecular formula of curing agents.

Curing agents	Molecular formula
PA650 AA	$\begin{array}{c} \text{RCO-NH-(CH2)-2NH-(CH2)-2NH2} \\ \text{H}_{3}\text{C} & \begin{array}{c} \text{H}_{2} \\ \text{H}_{3}\text{C} & \begin{array}{c} \text{C} \\ \text{C} \\ \text{H}_{3} \\ \text{H}_{2} \\ \text{H}_{2} \\ \text{C} \\ \text{H}_{3} \\ \text{C} \\ \text{C} \\ \text{H}_{2} \\ \text{NH}_{2} \\ \text{C} \\ \text{H}_{3} \\ \text{C} \\ \text{C} \\ \text{C} \\ \text{H}_{2} \\ \text{C} \\ \text{C} \\ \text{H}_{2} \\ \text{C} \\ \text{C} \\ \text{H}_{2} \\ \text{C} \\ \text{C} \\ \text{C} \\ \text{C} \\ \text{NH}_{2} \\ \text{C} \\ $
PAA	RNH-CH ₂ - (O)-OH

Active hydrogen equivalent = amine equivalent \times (number of nitrogen atoms in the amine adduct/number of active hydrogen atoms in the amine adduct)

The calculated active hydrogen equivalents in polyamide, alicyclic, and phenolic amine curing agents (i.e. PA650, AA and PAA) are 190 ± 15 , 105 ± 5 and 110 ± 5 g/eq, respectively. The epoxy resin and curing agents were purchased from Hangzhou Wuhuigang Adhesive Co. Ltd., China. Due to uncertainties in the production process, the number of epoxy resin and active hydrogen in these products is not a definite stoichiometric value, but fluctuates within a certain range. The bidirectional glass fiber fabrics were purchased from Taishan Fiberglass Inc. The areal density and thickness of the GF fabrics are 200 g/m² and 0.2 mm, respectively. The raw materials used in this study are shown in Fig. 1.

2.2. Resin specimen preparation and GFRP laminate fabrication

The calculation method of the amount of curing agent in epoxy resin is as follows:

Amount of curing agent = active hydrogen equivalent/epoxy equivalent \times 100 %

Three epoxy resin systems were selected based on the content of epoxy and active hydrogen equivalent in the resin systems [22,23]: (i) E51 and polyamide amine curing agent (PA650) with a mass ratio of 1:1, (ii) E51 and phenolic amine curing agent (PAA) with a mass ratio of 2:1, and (iii) E51 and alicyclic amine curing agent (AA) with a mass ratio of 2:1. These cured epoxy resin specimens were termed as EPA650, EPAA, and EAA, respectively. The mass of resin system is approximately 100 g per preparation to ensure the quality of the resin. Resins were cured in silicon molds at room temperature $(22\pm2 \ ^{\circ}C)$ for 24 h. Based on GB/T 2567 [24], the standard length for the resin tensile specimens was set at 50 mm. The GFRP laminates were fabricated using the hand layup technique. Mild steel molds with dimensions of $350 \times 350 \times 5$ mm, vacuum compressed bags, and a vacuum pump were utilized during production. The two-dimensional size of self-made laminates was



Fig. 1. Raw materials: (a) GF fabric, (b) epoxy resin, (c) polyamide amine, (d) alicyclic amine, and (e) phenolic amine.

 300×300 mm with varying thicknesses based on the number of GF fabric layers and the resin matrix. The mass ratio of resin matrix to glass fiber fabrics is 6:4.

The GFRP composites were sectioned for various tests. According to ASTM D3039 [25], the standard length for the GFRP laminate tensile specimens was 100 mm. The production process, detailed shapes, and dimensions of resin and GFRP laminates are presented in Fig. 2. The laminate specimens were named based on the resin system type and the number of prepreg layers. For example, EPAA-2 L denotes GFRP laminates with an EPAA resin system and two prepreg layers.

2.3. Aging exposure conditions

A UV radiation accelerated weathering tester produced by Guangdong Grande Automatic test equipment Ltd., China simulated the maritime exposure conditions of high UV radiation and humidity. Fig. 3 (a) shows that the machine consists of UV lamps, a humidifier, a water tank, and a condensing unit. The UV radiation is continually produced using eight UV lamps. Water in the tank provides humidity to the tester through a humidifier. Then, the backflow of water vapor by the condensing unit enables circularity. A controller adjusts the radiation intensity, humidity, and temperature. The aging exposure conditions were performed according to ISO 4892 [26]. The representation of the aging cycles was given in Fig. 3(b). The UV wavelength was 340 nm at an irradiation of $0.76 \text{ W} \cdot \text{m}^{-2} \cdot \text{nm}^{-1}$, and the humidity was maintained at 95 %. The aging tests were operated under a repeated aging cycle of 8 h UV exposure at 30 °C, followed by a 4 h condensation cycle at 25 °C without UV radiation. The temperature under illumination was 5 °C greater than condensation conditions due to the lamps. The exposure times were 7, 14, 30, 60, and 90 days.

2.4. Test methods

2.4.1. UV aging behaviors of resin systems and GFRP laminates

The tensile properties of the resin and GFRP specimens were tested on a universal testing machine at a displacement rate of 2 mm/min. The specimen deformations were measured with an extensioneter. Five samples were prepared for each resin and GFRP laminate type to obtain average values under each condition. The color variations of the resin and GFRP specimens after UV aging were further analyzed according to the ASTM D2244 standard [27]. The observed color variations were measured using a colorimeter with a CMOS image sensor. Samples sized at 10×4 mm were cut from the aged resin and GFRP laminates. Three samples were prepared for each resin and GFRP laminate type to obtain the average color difference under each condition. The images were collected using the 8 °/d measuring mode of an integrating sphere. The RGB information was converted to tristimulus values (X, Y, and Z) and then into color coordinates for CIE L * a * b with a reference white of D65/0°. The total color difference (ΔE) was calculated as:

$$\Delta L = L1 - L2, \ \Delta a = a1 - a2, \ \Delta b = b1 - b2 \tag{1}$$

$$\Delta E = \sqrt{\left(\Delta L\right)^2 + \left(\Delta a\right)^2 + \left(\Delta b\right)^2} \tag{2}$$

where *L*, *a*, and *b* represent the lightness, redness, and yellowness, respectively.

2.4.2. Dynamic mechanical thermal and FTIR analysis

The thermal response of the GFRP after UV aging was determined using a dynamic mechanical analysis (DMA) instrument (Model: Q800, produced by TA Instruments, USA) according to ASTM D4065 [28]. The two-dimensional size of the samples cut from GFRP laminates after 90 d of UV aging was 30×10 mm. The prepared samples were then tested in cantilever beam mode with a frequency of 1 Hz. The testing temperature increased from 20 to 120 °C at a rate of 2 °C/min. The thermomechanical properties, including the glass transition temperature (T_g) , storage modulus, loss modulus, and loss factor (tan δ) were measured. The T_g was determined by the intersection point of two tangent lines from the storage modulus. The first tangent line was selected at the temperature before the transition. The second tangent line was built at the inflection point to approximate the midpoint of the storage modulus drop. The glass transition temperature was determined according to ASTM D7028 [29]. The functional groups of GFRP before and after UV aging were characterized by ATR mode of FTIR. The two-dimensional size of the samples cut from GFRP laminates was 10×10 mm.

2.4.3. Characterization

The microscopic topography of the GFRP after UV aging was analyzed and compared using optical microscopy. Before characterization, the GFRP laminates were polished using an automatic polisher with



Fig. 2. Production process of the resin and GFRP laminates: (a) hand layup technique for GFRP laminates and (b) detailed shapes and dimensions of the resin and GFRP laminates.



Fig. 3. The UV aging exposure conditions: (a) UV radiation accelerated weathering tester and (b) 24 h representation of aging cycles.

silicon carbide grinding paper (400–2000 mesh). The morphological and elemental changes of aged glass fibers (GFs) in accelerated weathering tester were analyzed via SEM and EDX. The microstructural observations allowed for visualizing the GFs and resin matrix. Thus, the effect of high UV and humidity on the morphology and failure modes of the GFRP were well assessed.

3. Results and discussions

3.1. Tensile properties of different epoxy resin systems and GFRP laminates

3.1.1. Tensile properties of different epoxy resin systems

The tensile properties of three epoxy resin systems are illustrated in Fig. 4, including the UTS, elastic modulus, and breaking elongation. The resin systems with different curing agents exhibited distinct chemical and cross-linking structures, contributing to differences in their tensile properties. Notably, the EPA650 demonstrated high breaking elongation (4.80–5.18 %) due to its flexible chain structure, while the EPAA and EAA exhibited superior UTS (31.60–36.53 MPa and 37.82–41.43 MPa) and elastic modulus (3.61–3.72 GPa and 3.20–3.67 GPa). The EPAA and EAA resin systems possess a dense cross-linked structure with more rigid segments (benzene and carbon rings), enhancing the tensile strength and rigidity [30]. However, it is challenging for these resin systems to balance high strength and ductility. The UTS and elastic modulus of the resins generally increased as the breaking elongation decreased, mainly because of variations in their chemical structures.



Fig. 5. Stress-strain curves and toughness of different epoxy resin systems.

The range of stress-strain curves and toughness values of different epoxy resin systems are depicted in Fig. 5. Compared with EPA650, the EPAA and EAA failed at higher stress and lower strain. Numerical integration based on the trapezoid method was used to calculate the toughness of different resin systems as the area under the stress-strain curves shown in Fig. 5 [31]. The EPA650 showed better deformation than the other resin systems. As a result, it has the highest toughness value. Conversely, the toughness of the EPAA and EAA markedly decreased due to their rigid structures.



Fig. 4. Tensile properties of different epoxy resin systems: (a) ultimate tensile strength and (b) elastic modulus and breaking elongation.



Fig. 6. Stress-strain curves, toughness, elastic modulus and breaking elongation of (a) and (b) EPA650-based GFRP laminates, (c) and (d) EPAA-based GFRP laminates, and (e) and (f) EAA-based GFRP laminates.

3.1.2. Tensile properties of GFRP laminate based on different epoxy resin systems

The thickness of the plies in the laminates notably influences their mechanical properties [32]. The tensile properties of the GFRP laminates containing different glass fiber fabric layers (2, 4, and 8) are depicted in Fig. 6. Specimens utilizing the EPA650 exhibited better tensile properties with increasing ply thicknesses. Due to EPA650's high breaking elongation, GFs in EPA650-2 L could undergo more extensive deformation at lower UTS. As shown in Fig. 6(a) and (b), EPA650-2 L exhibited the greatest strain and breaking elongation. The GFs primarily bear the tensile load in laminates [33]. The UTS and elastic modulus of EPA650-4 L and EPA650-8 L improved with the glass fiber fabric layers. However, the low UTS of EPA650 limited the development of the tensile properties. The enhanced UTS in EPA650-4 L and EPA650-8 L caused the resin matrix to break down and lose its binding effect on GFs, reducing the GFRP's breaking elongation. Fig. 6(d) and (f) demonstrate that the breaking elongations of EPAA-2 L and EAA-2 L remained low. The rigid structures of EPAA and EAA caused early-stage breakage of the resin matrix and diminished its restraining effect on the GFs. As shown in Fig. 6(c) and (e), EPAA and EAA based laminates with 4- and 8-ply prepregs demonstrated stable tensile properties. However, the anisotropy of the multiphase structure induced varying stress levels in each laminate. The highest stress was observed in the top and bottom layers [34]. Different from composites made by other manufacturing processes, the loads were transmitted through resins phase in the laminates. The thicker ply laminates may fail due to interlaminar delamination between layers and surface cracking [35]. Fibers determine the final UTS of the laminates. However, the probability of defects increased with the increase of laminate volume. The defects in the structure and differences in failure modes of laminates can lead to a loss of strength. Thus, the UTS and toughness of the 8-ply prepreg laminates were slightly inferior to the 4-ply prepregs.

The above results indicated that GFRP laminates comprising 4-ply prepregs achieved stable tensile properties. Thus, the tensile properties of GFRP laminates with a 4-ply thickness are displayed in Fig. 7. The ultimate strain and stress of the laminates can be enhanced by the use of resin matrix with dense chemical structures. Besides, interfacial adhesion between the GFs and resin matrix was enhanced due to reactive functional groups (-OH), further improving the tensile properties of GFRP. The toughness value of the EPAA-4 L was the greatest due to its high UTS and deformation. Meanwhile, the EAA-4 L with less polar

groups had a greater elastic modulus, resulting in a lower breaking elongation and interfacial bonding. As the ductility and UTS of the resin matrix and interfacial adhesion between the GFs and resin matrix increased, the tensile load was transferred more effectively across the matrix-fiber boundary [36]. The expansion of the damaged bond zone in the laminates with enhanced tensile properties indicates that each GFRP phase can fully bear the tensile load.

3.2. UV aging behaviors of different epoxy resin systems and GFRP laminates

3.2.1. UV aging behaviors of different epoxy resin systems

The UTS evolution laws of different resin systems are displayed in Fig. 8(a). At early UV exposure stages, UV radiation reactivates the molecular bonds in the EPAA and EAA, contributing to an increased resin UTS. Unlike EAA, the EPAA has a plateau because it has more reactive groups, enabling a brief equilibrium between the degradation and enhancement of the UTS. Meanwhile, the UTS of the EPA650 continually decreased during UV exposure. After 90 d of UV aging, the UTS of the EPA650 and EAA decreased, while the UTS of EPAA remained higher than the unaged specimens. Thus, the EPAA had the best UV resistance.

As shown in Appendix A, the tensile stress-strain curves of the EPA650 had a strong yield stage, while the EPAA and EAA exhibited brittle failure modes without a descending stage. The EPA650 mainly contains primary amine, which reacted with the epoxy groups to form secondary amine. The secondary amine groups then continued to react with the epoxy groups to form tertiary amines. The reaction process between the epoxy resin and PA650 takes considerable time, resulting in unactivated functional groups in the EPA650 not being able to fully react with the epoxy resin under high UV and humidity conditions. The hydrophilic groups (amides) in EPA650 accelerate the water invasion process [37]. As shown in Fig. 8(b), these factors contributed to the decreased elastic modulus of EPA650. In contrast, there were few variations in the elasticity modulus for EPAA and EAA as they have more stable chemical structures (Fig. 8c and d). Notably, the breaking elongation of the three resin systems increases and then decreases. The increased EPA650's breaking elongation is attributed to its softening in the simulated environment, whereas the other two resin systems are due to the enhanced post-cure phase performance.



Fig. 7. Tensile properties of the GFRP laminates with different epoxy resin systems: (a) Stress-strain curves and toughness, and (b) elastic modulus and breaking elongation.



Fig. 8. UV aging behaviors: (a) UTS evolution laws of different resin systems, and elastic modulus and breaking elongation of (b) EPA650, (c) EPAA, and (d) EAA.

3.2.2. UV aging behaviors of GFRP laminates based on different epoxy resin systems

The UTS evolution laws of GFRP laminates with different resin systems are illustrated in Fig. 9(a). In the early UV aging stage, a stable development phase for the UTS of GFRP occurred due to EPA650's longer curing cycles and EAA's fewer polar groups. However, the UTS of EPAA-4 L can still be developed due to its additional reactive groups. After 30 d of UV exposure, the UTS of the GFRP with EPAA and EAA decreased. This is attributed to fiber damage caused by the high light transmission of the resin systems and the accumulation of surface resin matrix damage [38]. In contrast, the GFRP with EPA650 is darker and has a lower UV transmittance. Fiber fabrics also block out moisture and UV rays, allowing residual cross-linking within the resin [39]. The UTS of the GFRP with EPA650 improved after 30 d of UV exposure but was still lower than the GFRP with functional amine curing agents.

Fibers usually exhibit brittleness and mainly play the role of enduring force in the GFRP. Distinct from the resin samples, GFRP laminates exhibit abrupt brittle damage patterns (Appendix B). As shown in Fig. 9(b)-(d), UV radiation has little effect on the modulus of elasticity, regardless of the applied curing agents. This is because the fiber fabrics provide the primary rigidity of the GFRP [40]. The enhanced internal structure of the EPA650 increases the breaking elongation of EPA650–4 L in the late UV aging stages. However, the peak strain of EPA650 (4.80–5.18 %) is greater than that of EPA650–4 L (1.34–1.38 %). Both the deformation incompatibility of the GFs and EPA650 and the poor UTS of the EPA650 worsened the tensile properties of EPA650–4 L. The residual UTS of the EPAA-4 L remains higher than the other resins despite a 7.5 % decrease in the UTS after 90 d of UV exposure. It also has good toughness (210.68–247.92 J/m³) after 90 d UV aging. These results indicate that the EPAA resin system has an outstanding protective and cohesive effect on GFs.

3.2.3. Yellowing degree

The relationship between total color difference (ΔE) and UV aging time is shown in Fig. 10. Yellowing of the EPAA and EAA deepened with the aging time. At the same time, there were few color variations in the EPA650 after UV aging due to the deeper color of the curing agent (PA650). The EPAA had a rapid color change after 7 d, but the rate of color change decreased significantly from 7–90 d. The color variation rate of the EAA remained relatively stable over the entire aging period.



Fig. 9. UV aging behaviors: (a) UTS evolution laws of GFRP laminates based different resin systems, and elastic modulus and breaking elongation of (b) EPA650–4 L, (c) EPAA-4 L, and (d) EAA-4 L.



Fig. 10. Yellowing of (a) resin and (b) GFRP laminates after UV exposure.



Fig. 11. DMA and FTIR analysis of the EPAA-4 L: (a) Storage and loss modulus, (b) Tan δ and (c) infrared spectrogram.

As shown in Fig. 10(b), the GFRP laminates exhibited a similar trend as the resin from a global perspective, but the surface showed a greater color variation due to the barrier from the fiber fabrics. Yellowing of the EPA650–4 L can be perceived only on the lighter surface due to the deeper color after curing.

The molecular chain of the resin matrix breaks due to the long-term UV exposure, and the chromogenic groups in the resin accumulate on the GFRP surface. The yellowing degree of the GFRP depends on the molecular structure of the resin matrix. The EPAA contains large amounts of amino groups, forming the single bonded amino group and causing color variations [41]. Both the formation carbonyl group due to breaking of the phenolic hydroxyl groups and the epoxy groups in EPAA contribute to the yellowing [42]. In short, EPAA-4 L has the greatest color change due to the altered molecular structure of the GFRP surface, while the chromaticity of the EAA-4 L has significant advantages. The chromaticity of the EPA650–4 L remains stable because it has the deepest color before UV aging, making it difficult for UV radiation to penetrate the inner parts of the GFRP laminates. However, the deeper color of the EPA650 before aging and the greater color variation of the EPAA may limit its engineering application.

3.3. Deterioration mechanism analyses

3.3.1. Dynamic thermomechanical and FTIR analysis of GFRP

DSC is the standard method for curing degree of resin, allowing the evaluation of the time-temperature dependence of the epoxy polymer. Glass transition temperature T_g can be used as a bridge to evaluate the curing degree of resin [43,44]. However, post-curing and deterioration of GFRP occurred simultaneously during UV aging. The curing degree, temperature dependence and damage of GFRP after UV aging also can be evaluated by DMA, such as T_g , storage modulus, loss modulus, and loss factors tan δ . Besides, the molecular chain changes of GFRP can be revealed by FTIR. Unaged and aged EPAA-4 L were chosen to conduct DMA and FTIR as it had the greatest UV resistance.

Fig. 11 illustrates the thermal responses of the GFRP, which has three phases at different temperatures: glass stage, glass transition, and rubber-elastic plateau. The T_g is obtained by the intersection of two tangent lines from the storage modulus. After 90 d of UV exposure, the T_g of the EPAA-4 L decreased by 8.11 %, from 69.4 to 63.77 °C. Additionally, the storage and loss modulus of aged specimen increased by 21.76 % and 17.81 %, respectively. In the UV exposure environment,



a)

(0)

Fig. 12. SEM images and EDX of (a) unaged and (b) aged GFs.



(a)

(b)



(c)

Fig. 13. Microscopic morphology of (a) EPA650-4 L, (b) EPAA-4 L, and (c) EAA-4 L after 90 d UV exposure.

secondary curing enhancement and performance degradation of the GFRP were concurrent. The increased GFRP's storage modulus at room temperature indicated greater resin cross-linking.

Besides, the GFRP spectra were normalized based on the C=C bonds of the aromatic rings due to its high molecular bond energy (611 kJ/ mol) [45]. The peaks at 826 cm⁻¹ were characteristics of benzene ring C-H out-of-plane bend. An insignificant absorption peak at 928 cm⁻¹ represents the C-H stretching vibration of the epoxy groups. Peaks at 2921 cm⁻¹ were assigned to saturated alkane C-H stretching. The absorption peaks of N-H/O-H in PAA curing agent at 3348 cm⁻¹ decreased (see Fig. 11c) [46]. It indicated that the curing agent (PAA) is consumed while the reaction with epoxy resin and GFs. At the same time, the GFRP surface is embrittled due to UV radiation, increasing the stiffness and brittleness. As shown in Fig. 11(b), the ratio of the loss modulus to the storage modulus is measured as the mechanical loss factor (tan δ). After 90 days of UV exposure, the tan δ of the EPAA-4 L increased by 14.17 %. This indicates that UV damage to the GFRP is greater than its residual cross-linking-promoting effect on the resin [47].

3.3.2. Morphological properties

E-glass fibers are mainly made of SiO₂, Al₂O₃, B₂O₃, MgO and CaO. The Al-O, Ca-O, and Mg-O bonds in the GFs were susceptible to change under high UV and humidity condition. The bonds can absorb UV radiation at specific wavelengths, leading to the destruction of GFs' molecular structure [48]. The surface structure and elemental composition of the GFs were analyzed via SEM and EDX. The SEM examination concentrated on observing the topography of the GF surface, employing thermal emission electron optics. From Fig. 12, the unaged GF surfaces

are smooth, while the surface morphology of aged GFs exhibits cracks and recessed areas. The EDX was employed to conduct a chemical elemental analysis of the GFs, capitalizing on the fundamental spectroscopy principle that each element possesses a unique atomic structure. This manifests as a distinct series of peaks in its electromagnetic emission spectrum. The silane and oxygen contents in unaged and aged GFs were quantified via EDX. The untreated glass fibers showed the relative amount of silicon and oxygen content as 38.33 and 46.18 wt%. After 90 d UV exposure, the relative amount of oxygen decreased by 5.13 % which was attributed to the decomposition of the oxygen-containing compounds. Then, cracks and defects appeared on the fiber surface, resulting in the decrease of mechanical properties. Both changes in the surface morphology and decreased oxygen content indicate UV damage to the GFs.

As illustrated in Fig. 13, the outermost layer of the EPA650–4 L yellowed and showed minor defects. The EPA650's darker color and blocking from the GF fabrics created residual cross-linking of the internal resin. The good ductility and lower UTS endows the EPA650–4 L with improved tensile properties under high UV conditions. In contrast, all resins on top of the GF fabrics yellowed, including the EPAA-4 L and EAA-4 L. Furthermore, the EPAA-4 L surface exhibits significant embrittlement and has more defects, while the EAA-4 L has less visible defects. Due to greater light transmission of the EPAA and EAA resins, UV rays damage the external resins and fibers, making them more susceptible to destruction when stressed. The tensile properties of GFRP with EPAA and EAA are reduced after UV exposure. However, the EPAA-4 L retains its high UTS, elastic modulus, and breaking elongation after 90 days of UV exposure due to the EPAA's excellent performance.

4. Conclusions

An aging program was implemented to simulate the synergistic effects of UV and high humidity exposure conditions. The aging behaviors and deterioration mechanism of GFRP with different curing agents were comprehensively investigated. Under the mix ratios of epoxy resin and curing agents in this study, the resin system (EPA650) with long molecular chain achieved a greater ductility. Its breaking elongation and toughness value is 4.80–5.18 % and 91.24–119.21×10⁴ J/m³, respectively. Conversely, the resin system with rigid elements and smaller molecular spacing between reactive functional groups (EPAA and EAA) showed a larger UTS (31.60–36.53 MPa and 37.82–41.43 MPa. The 4-ply prepreg laminates facilitated a more effective load transfer across the matrix-fiber interface, resulting in the best tensile properties for the GFRP. More reactive functional groups (-OH) enhanced the bonding between the GFs and resin matrix, leading to further improvements in UTS, deformation, and toughness of GFRP.

Under high UV and humidity conditions, the resin system with long curing times (EPA650) deteriorated severely due to the presence of hydrophilic amide groups. In contrast, resin systems with dense chemical structure (PAA and AA) had a post-curing phase. The UTS of the EPAA-4 L can still be improved due to its more reactive groups at the early stages of UV exposure. After 30 d UV exposure, the UTS of the EPAA-4 L and EAA-4 L decreased, which is attributed to fiber damage caused by the high light transmission of the resin and accumulation of surface resin matrix damage. The yellowing degree of the EPAA and EAA increased significantly with the aging time, while the GFRP's yellowing was only observed above the fiber fabrics. The darker EPA650 and fiber fabrics block out moisture and UV rays, allowing residual cross-linking to occur within the resin under the fiber. The UTS of the EPA650–4 L improved after 30 d of UV exposure, but the tensile properties of the EPAA-4 L remained greater than that of the GFRP with the other resin systems, despite a 7.5 % decrease in the UTS after 90 d of UV exposure.

Finally, the deterioration mechanism of the GFRP under UV conditions is elucidated through the DMA, FTIR, SEM, and EDX analyses. After 90 d of UV exposure, the T_g of the EPAA-4 L decreased by 8.11 %, from 69.4 to 63.77 °C. The tan δ of the EPAA-4 L increased by 14.17 %, and the absorption peaks of N-H/O-H in resins at 3348 cm⁻¹ decreased. It indicated that UV damage to the GFRP is greater than its residual cross-linking promotion effect on the resin. Due to the decomposition of the oxygen-containing compounds, cracks and defects appeared on the fiber surface, reducing fiber mechanical properties. The deterioration mechanisms of the GFRP include fiber breakage and outermost resin matrix damage.

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CRediT authorship contribution statement

Yinlong Cao: Writing – original draft, Methodology, Data curation. Yanjun Teng: Investigation. Peng Zhang: Supervision, Conceptualization. Jiuwen Bao: Writing – review & editing. Peng Feng: Validation, Supervision. Rong Li: Visualization, Supervision. Wenhuan Wang: Validation, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

Appendix A



Stress-strain curves of (a) EPA650, (b) EPAA, and (c) EAA





Stress-strain curves of (a) EPA650-4L, (b) EPAA-4L, and (c) EAA-4L

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