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Research Paper

Research progress on interface modification techniques and reinforcement mechanisms for metal-fiber reinforced resin matrix composites

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Abstract. Metal-fiber reinforced resin matrix composites formed by combining metals with fiber reinforced polymers (FRP) represent a new generation of lightweight, multifunctional materials demonstrating significant application potential in aerospace, new energy vehicles, and high-end equipment manufacturing. The interfacial bonding state of this composite is the core factor determining its superior mechanical properties. However, issues such as insufficient wettability between metal and resin matrix, weak chemical bonding interactions, high thermal residual stresses due to differing thermal expansion coefficients, and interfacial debonding failure under thermo-mechanical coupled loads severely limit stress transfer efficiency between cross-scale heterogeneous materials and compromise long-term structural reliability. Interface modification techniques, such as metal surface treatment and functional layer introduction, can significantly enhance the interface bonding strength, stress transfer efficiency, and durability between metals and FRP composites, thereby optimizing the overall performance of composite structures. This paper systematically reviews key technologies and research progress in metal-FRP interface modification and outlines future development trends.

Keywords: *metal-FRP structure; dissimilar material bonding; bond strength; interface modification; surface roughness*

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1 Introduction

In recent years, the rapid development of aerospace, new energy vehicles, and high-end equipment manufacturing has driven composite materials toward lightweight, high specific strength, high specific stiffness, excellent impact resistance, and fatigue resistance [1]. Multi-phase composite structures synergistically composed of metals and FRP materials have emerged, including typical metal-fiber reinforced laminated structures, honeycomb sandwich structures, composite risers [2–3], and other design schemes. These are used as key components such as aircraft skins, wings, and tails, providing critical material support for breakthroughs in aerospace technology [4]. This structure combines the advantages of metals and FRP, offering high specific strength and stiffness, excellent fatigue performance, and high damage tolerance [5–7]. Compared with metal materials, it achieves significant weight reduction, compensates for the poor fatigue performance of traditional metal materials, and improves the shortcomings of FRP such as low fracture toughness, poor impact resistance, and low residual strength. In practical engineering, the efficient and reliable joining of such heterogeneous materials is a key link to ensure the overall structural performance. However, due to significant differences in mechanical properties, thermal expansion coefficients, and chemical properties between metals and FRP, how to achieve high-strength, durable, and controllable interfacial bonding has become a technical bottleneck restricting further applications.

To meet different application scenarios and performance requirements, metal-FRP structures have derived a variety of joining technologies, which can be mainly divided into traditional step-by-step joining and integrated molding joining. Step-by-step joining includes mechanical joining, adhesive bonding, mechanical-adhesive hybrid joining, and hot-melt joining. Among them, mechanical joining is a traditional joining method that fixes metal and FRP through physical fasteners. Common mechanical joining methods include bolted connections [8] and riveting [9]. Their main advantages lie in the detachability of the joint, ease of inspection and maintenance, and the ability to maintain good joint strength under large thicknesses and high loads, with mature processes and strong applicability. However, mechanical joining often introduces geometric damage and stress concentration, leading to damage in composite materials and reduced joint strength. Adhesive bonding uses adhesives to form physical adsorption or chemical bonding on the interface to combine metal and FRP [10]. Adhesive bonding can achieve relatively uniform load transfer, avoiding stress concentration and material damage caused by mechanical fasteners, while also providing good sealing and vibration damping capabilities [11–12]. It is especially suitable for joining large areas and complex curved surfaces, but the performance of adhesive bonding is highly dependent on the adhesive properties and interfacial bonding state. Hot-melt joining is only applicable to thermoplastic resin materials; it uses an external heat source (laser, friction heat, conduction heat) to melt and flow the resin, which closely contacts the metal surface under pressure and forms a mechanical anchorage mixed joint after cooling [13]. Overall, step-by-step joining processes are mature and detachable, and are widely used in the final assembly of large-size components or structural parts that require maintenance and replacement, such as aircraft fuselage splicing, repair nodes, and automobile body frame connections.

Compared with step-by-step joining, integrated molding joining technology synchronizes the component manufacturing process with the interface bonding process, that is, the bonding with the metal substrate is achieved simultaneously during the molding or curing of the composite material. This method can reduce process steps, improve production efficiency, enhance interface continuity and reliability, and avoid defects or damage caused by secondary processing. Common processes include injection overmolding, nano-molding technology, and metal-prepreg integrated molding. Among them, injection overmolding injects molten thermoplastic resin into a mold cavity to directly encapsulate metal inserts; the interface bonding relies on the wetting of the melt to the metal surface and mechanical interlocking generated by cooling shrinkage [14]. Nano-molding technology is a new technology derived from injection overmolding; it first pretreats the metal by pickling, anodizing, etc. to form a nanoporous array, and during injection, the resin penetrates into the pores and cools and solidifies to produce a mechanical interlocking effect [15]. Metal-prepreg integrated molding technology stacks metal sheets with fiber-reinforced prepregs and applies temperature and pressure to simultaneously form the part and the interface bond [16]. Integrated molding joining not only helps to improve interfacial bonding strength and durability but also achieves better mechanical properties and structural integrity. Therefore, integrated molding technology is more suitable for components with complex structures, high lightweight requirements, and the need to ensure interface integrity, such as composite skin-stiffener integral structures, load-bearing cabins, and electronic packaging parts. Although various joining technologies have their own advantages, they also have non-negligible limitations. For example, mechanical joining easily introduces stress concentration and damage; adhesive bonding and hot-melt joining are sensitive to interface state and are significantly affected by factors such as interfacial wettability, chemical reactivity, and surface cleanliness; while integrated molding can improve overall performance, interface bonding is still constrained by the inherent incompatibility between metal and resin. These problems essentially originate from the differences in physical and chemical properties between metal and polymer, such as insufficient wettability, weak interfacial chemical bonding, and high residual stress caused by thermal expansion mismatch, making the interface region a weak link in the structure [17]. Therefore, relying solely on the joining form itself is difficult to fundamentally solve the problem of interface failure. To fully exploit the potential of metal-FRP composite structures and improve interfacial bonding strength, stress transfer efficiency, and durability, it is urgent to optimize the interface at the levels of surface treatment and functional layer introduction through interface modification technologies.

This paper focuses on summarizing the research progress in enhancing interface performance through metal surface treatment technologies, functional layer introduction, etc., and based on the mechanism of interface bonding, deeply elaborates on the action principles of different interface modification technologies, revealing the synergistic mechanisms of physical, chemical, and mechanical effects in improving interface strength, as well as the factors affecting the interface bonding strength between metal and FRP. Finally, the challenges in current research and future development directions are prospected.

2 Interface failure mechanisms of metal-FRP structures

Under the combined action of external loads and service environment, metal-FRP structures are prone to various failure modes, as shown in Fig. 1, mainly including interface delamination damage, metal or matrix fracture, fiber debonding and fracture, etc. [18–19]. However, as a reinforcement phase, fibers themselves have high strength and modulus, and are usually laid in specific directions to bear stress in the main load direction, avoiding direct exposure to complex loads, so they usually do not break or debond; at the same time, the material bulk usually has high strength and toughness, and matrix or metal bulk fracture rarely occurs during actual service. Therefore, the most critical and common failure mode is interfacial debonding between metal and resin matrix [20], which mainly stems from significant differences in thermal expansion coefficient, surface energy, and chemical activity between metal and FRP, leading to interface incompatibility, stress concentration, and insufficient chemical bonding. Therefore, the interface region is the weak link in stress transfer between metal and composite layers and plays a decisive role in the overall structural performance [21]. The interface failure of metal-FRP is affected by multiple factors synergistically. First, there is a mismatch in thermal expansion coefficient between metal and FRP, which easily induces accumulation of interfacial residual stress during thermal cycling, thereby inducing interface cracking. Second, the wettability of molten resin to the metal surface is poor, making it difficult to spread on the metal surface and form a structurally complete, continuous, and uniform interface layer. In addition, the natural oxide film on the metal surface is usually inert, making it difficult to form effective chemical bonds with polymer molecules, resulting in weak interfacial bonding. Finally, when the metal surface roughness is insufficient or the structural design is unreasonable, the interface lacks sufficient mechanical embedding and locking effects. These factors jointly determine the interfacial bonding quality and its stability under external loads.

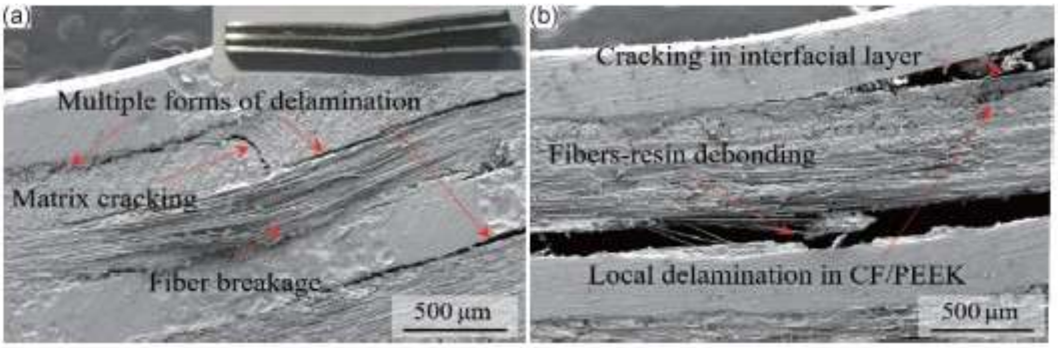

Figure 1 Failure mechanisms of metal-FRP structures [19] (a) matrix fracture and fiber breakage; (b) interface delamination and fiber debonding

It can be seen that the improvement of interface performance requires not only overcoming the differences in physical properties and chemical activity of the materials themselves, but also comprehensively considering the synergistic relationship among various interface action mechanisms. Interfacial bonding force is the result of the combined action of mechanical, physical, chemical, etc. Therefore, in-depth analysis of different action mechanisms and their coupling effects in interfacial bonding is of great significance for scientifically guiding interface modification strategies and improving interfacial bonding strength.

3 Interface bonding mechanisms

The interface bonding mechanism of metal-FRP structures is complex and diversified, which can be mainly attributed to physical action, chemical action, mechanical action, and synergistic action of multiple mechanisms. Different bonding mechanisms often do not exist in isolation in actual interfaces, but are superimposed and work together, determining the interface strength, durability, and service stability, as shown in Fig. 2.

Understanding these action mechanisms is crucial for reasonably selecting and designing interface modification processes.

3.1 Mechanical interlocking theory

The mechanical interlocking theory is one of the earliest proposed views in bonding mechanisms, originating in the 1920s. McBain and Hopkins [22] believed that the interfacial bonding strength mainly comes from the meshing and locking effect formed by the adhesive filling the pores, grooves, and other irregular structures on the surface of the adherend during the curing process, namely mechanical interlocking. The ups and downs, cracks, pores, pits, grooves, inverted cone holes, and other microstructures on the surface of the adherend help the liquid adhesive to deeply penetrate into them during wetting, infiltration, extrusion, and curing, forming an embedded structure similar to a "lock" or "barb", showing high mechanical bonding strength. This theory simply and intuitively explains the influence of factors such as roughness, porosity, and wettability on interfacial bonding performance, and is especially suitable for bonding scenarios of porous or rough-surfaced materials, such as wood, paper, foam, etc. The mechanical interlocking theory well explains that interfaces treated by surface roughening or porous treatment usually obtain better bonding performance than smooth surfaces. However, because it cannot explain the phenomenon of high bonding strength on smooth or dense surfaces, this theory is usually regarded as a part of the interface bonding mechanism rather than a complete mechanism.

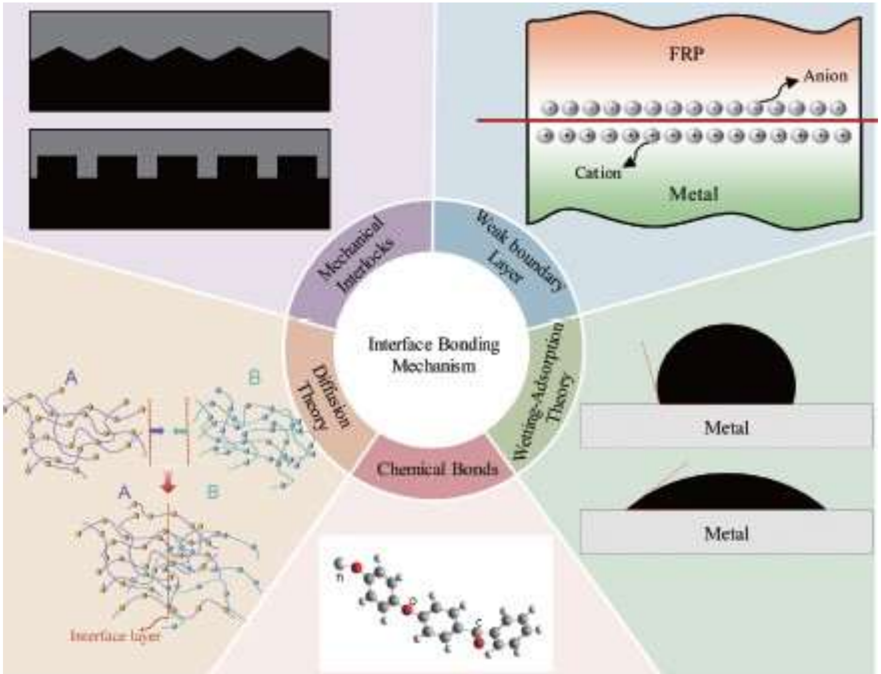

Figure 2 Interface bonding mechanism

3.2 Wetting-adsorption theory

The surface wetting and adsorption theory is one of the most widely used thermodynamic theories in bonding research, proposed by Sharpe and Schonhorn [23]. This theory emphasizes that the wetting effect of the adhesive on the substrate surface is the prerequisite for interface bonding and an important factor determining the magnitude of interfacial force. The wetting effect is determined by thermodynamic parameters such as contact angle, surface tension, and surface energy. When wetting is sufficient, the adhesive can fully contact the substrate surface and fill micro-irregularities, improving the interface contact area and bonding force. On the basis of wetting, adhesive molecules diffuse to the substrate surface through Brownian motion and further approach substrate molecules, and adsorption occurs under the action of intermolecular forces to form a stable interface bond. Intermolecular forces such as van der Waals forces and hydrogen bonds are the main sources of adsorption, and their strength is also closely related to interfacial free energy. Therefore, this theory points out that good wettability and strong intermolecular interaction jointly determine the interfacial bonding strength [24]. However, the wetting-adsorption theory still has certain limitations; it attributes the bonding effect entirely to the intermolecular force at the interface, and cannot explain the phenomenon that the bonding strength exceeds the strength of the adhesive itself in some cases. In addition, this theory believes that the work required to overcome molecular force should be independent of the separation speed, but experimental results show that the bonding strength is significantly affected by the peeling speed, which is also beyond the explanation scope of this theory.

3.3 Chemical bonding theory

The chemical bonding theory holds that the adhesive and the substrate surface form high-strength chemical bonds such as covalent bonds and ionic bonds through chemical action [25], thereby improving the adhesion between the two materials. The formation of chemical bonds is closely related to the chemical reaction activity of the adhesive and the substrate. The higher the reaction activity, the more active functional groups are generated on the interface, and the greater the number of chemical bonds formed, thereby significantly improving the bonding performance and medium resistance. The chemical bonding force is 1 to 2 orders of magnitude higher than van der Waals force, but chemical bonding requires close contact at the interface, and defects, cracks, and bubbles that may exist on the interface will seriously reduce the interfacial bonding strength.

3.4 Other theories

The electrostatic adsorption theory was proposed by Derjaguin et al. [26]. This theory regards the bonding interface as a double-layer capacitor structure. Because the two materials have different affinities for electrons, charge transfer occurs, causing positive and negative charges to be generated on both sides of the interface, thereby generating electrostatic attraction. This electrostatic attraction helps to enhance the interfacial bonding strength between the adhesive and the adherend, and the interface strength depends on the charge density formed on the interface. However, in practical applications, the surface charge density of the substrate is usually low, so the electrostatic effect contributes little to the overall bonding strength and usually works together with other mechanisms described by other bonding theories.

The diffusion theory was proposed by Voyutskii [27] to explain the bonding mechanism between two polymer materials. Its core view is that at the interface, polymer chains undergo molecular motion and interdiffuse to form an interpenetrating transition layer, thereby enhancing the bonding strength. The realization of this mechanism depends on a certain compatibility and fluidity of the adhesive and the adherend, so it is mainly suitable for explaining the bonding phenomenon between polymer chain polymers. At the same time, adjusting the concentration of the adhesive can enhance molecular motion and interfacial diffusion rate, thereby improving the mechanical properties of the bonded joint. However, this theory cannot fully explain the bonding of adhesives to inorganic materials such as metals or ceramics. But studies have shown that in special cases metals can diffuse into the polymer [28].

Bikerman et al. [29] improved the weak boundary layer theory in 1961. This theory is closely related to other bonding mechanisms and points out the preconditions for achieving strong bonding from the perspective of failure. This theory believes that bonding failure often does not occur at the ideal adhesive-substrate interface, but is triggered by a weak boundary layer on the surface of the adherend. Under the combined action of adherend contamination and environmental moisture absorption and oxidation, low molecular substances precipitate, adsorb, and aggregate on the adherend surface to form a low molecular enrichment zone, weakening the interfacial stress transfer capacity and causing poor bonding effect of the adhesive at the interface. To solve this problem, various surface pretreatment technologies remove or destroy the weak boundary layer to expose a fresh and clean substrate surface. The physical structure and chemical activity of the treated surface are important prerequisites for the effective functioning of mechanisms such as mechanical interlocking, wetting-adsorption, and chemical bonding. Therefore, the weak boundary layer theory not only reveals the root cause of interface failure but also provides necessary support for other bonding theories.

It can be seen that the existing interface theories explain the interface bonding mechanism from different levels of mechanical, physical, and chemical aspects, each with its own focus and complementing each other, as shown in Table 1 [22–23, 25–27, 29]. However, due to the diversity of materials, complexity of interfaces, and different research scales, it is difficult for these theories to fully explain complex interface behaviors alone, and a unified theoretical framework has not yet been formed to fully explain all bonding phenomena [30]. In practical engineering applications, the interface state is often affected by the coupling effect of multiple factors, making it difficult for interfacial bonding strength and durability to meet requirements. Therefore, on the basis of deep understanding of interface bonding mechanisms, effective interface modification technologies should be adopted to actively regulate and optimize the interface structure and performance, and ultimately improve bonding quality and service reliability.

Table 1 Common interface bonding theories

Interface bonding theory	Proposer/Year	Applicable scope	Limitations
Mechanical interlocking theory	McBain & Hopkins/20th century [22]	Interfaces with significant surface roughness, grooves, or porous structures.	Difficult to account for strong adhesion on smooth interfaces; chemical and physical interactions are neglected
Wetting-adsorption theory	Sharpe & Schonhorn/1965 [23]	Heterogeneous interfaces such as polymer-metal and polymer-ceramic interfaces	Unable to explain cases where the interfacial strength exceeds that of the adhesive bulk; rate-dependent effects are not considered
Chemical bonding theory	Lewis/1916 [25]	Interfaces containing functional groups capable of chemical reactions with active groups on the substrate surface, such as hydroxyl, carboxyl, and amino groups	Chemical bonding requires intimate interfacial contact, which is not always achievable
Electrostatic adsorption theory	Derjaguin/1967 [26]	Metal/non-metal interfaces with significant differences in electron affinity	Actual surface charge densities are generally low; electrostatic interactions contribute only marginally to the overall adhesion strength
Diffusion theory	Voyutskii/1963 [27]	Polymer/polymer interfaces require a certain degree of molecular compatibility and chain mobility	Not applicable to metal or ceramic interfaces; diffusion rates are strongly limited by temperature and viscosity
Weak boundary layer theory	Bikerman/1961 [29]	Interfaces affected by contamination, oxide layers, or moisture-induced degradation	Emphasizes interfacial failure mechanisms rather than adhesion formation; cannot independently explain the development of strong interfacial bonding

4 Interface modification technologies

Based on the understanding of interface bonding mechanisms, to address the problems of insufficient interfacial bonding strength, easy peeling and debonding, and poor durability between metal and FRP, researchers have developed a variety of interface modification technologies to optimize interface performance and improve service reliability [31], as shown in Fig. 3. They can be mainly divided into two categories: one is to improve the interfacial morphology, chemical activity, and wettability by surface treatment of metal (such as mechanical, physical, chemical, electrochemical methods, etc.) [32]; the other is to introduce functional layers (such as coating coupling agents, nanostructure layers, coordination bond bridging, etc.) to enhance interfacial chemical bonding, mechanical interlocking, and molecular chain entanglement effects.

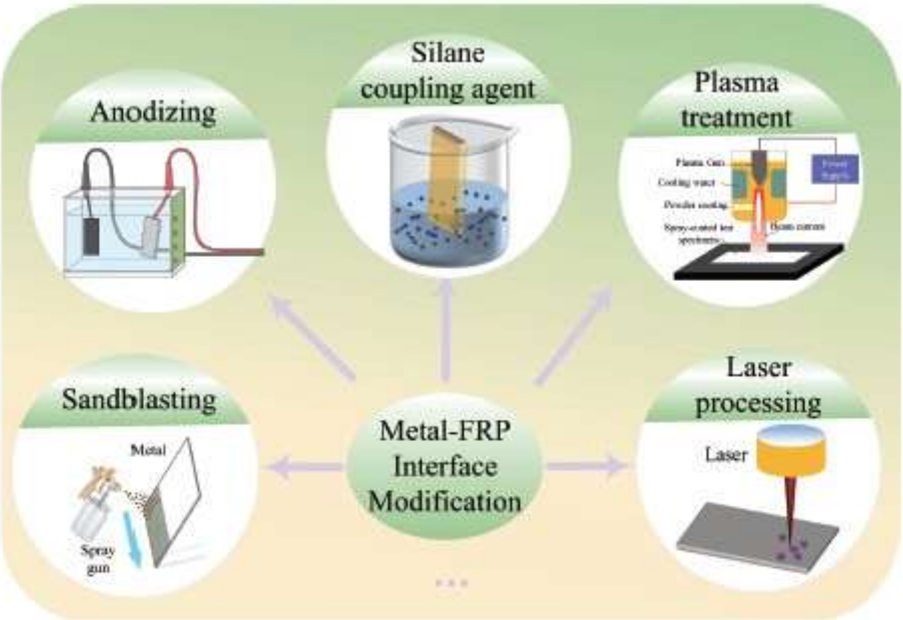

Figure 3 Metal-FRP interface modification technology

4.1 Metal surface treatment

As a basic means of interface modification technology, metal surface treatment mainly improves the wettability and bonding performance between metal and FRP by changing the physical morphology and chemical properties of the metal surface. The roughness and active functional groups of the metal surface have a significant impact on the interfacial bonding strength. Common metal surface treatment methods include mechanical treatment, physical treatment, chemical treatment, and electrochemical treatment, etc. These methods improve interfacial bonding performance by increasing the effective contact area, removing surface oxide layers, and introducing active functional groups.

4.1.1 Mechanical treatment

Mechanical treatment is a simple and efficient metal surface modification method. By changing the surface roughness and texture of the metal and removing loose oxide layers, it improves the wettability and mechanical interlocking effect between metal and FRP, thereby enhancing the interfacial bonding strength. Common methods include sandpaper grinding, sandblasting, etc. Before surface treatment of metal, it is often necessary to degrease and clean the metal surface to remove oil and contaminants [33–34].

Metals and their alloys rapidly form a dense oxide film in air, which acts as a weak boundary layer and reduces interface bonding capacity. Mechanical treatment can not only remove loose surface oxides but also form a rough morphology with a "peak-valley" structure on the surface, increasing the actual contact area and surface free energy of the two materials, thereby improving the wettability and adsorption capacity of the resin to the metal [35–36]. Sandpaper grinding is the most basic mechanical treatment method, and the surface roughness and surface energy can be adjusted through different grit sizes. Zhang et al. [37] used 120-grit and 3000-grit silicon carbide sandpaper to grind magnesium alloy plates, forming obvious rough surfaces, significantly increasing the actual contact area and liquid adsorption capacity, and improving surface energy. As the sandpaper grit increased, the surface roughness and surface energy further increased. To improve the efficiency of surface treatment and adapt to complex geometries or large-area workpieces, sandblasting has become a better choice [38]. The principle is to use fine abrasive particles carried in high-speed airflow to impact the metal surface to remove contaminants, forming irregular micron-scale pits and anisotropic surface textures, thereby significantly improving the interfacial bonding strength [36]. Multiple processing parameters usually need to be considered, including sandblasting coverage, sandblasting intensity, and sandblasting media type [39–41]. Harris et al. [42] explored the effects of different types and particle sizes of alumina abrasive sandblasting on the surface characteristics and bonding properties of low-carbon steel and aluminum alloy substrates, and deeply discussed the relationship between changes in surface texture, surface energy, and chemical properties during sandblasting and bonding performance. Ho et al. [43] used silicon-coated alumina blasting media with the same diameter to study the effects of different sandblasting distances and angles on the roughness of titanium surface, and determined the sandblasting parameters to achieve the best interfacial bonding effect between titanium and resin. Among them, the sandblasting angle is a key factor affecting the interfacial bonding strength, while the sandblasting distance has no significant effect on the strength. In addition to traditional processes, constructing regular surface structures through machining is also an important way to improve interface performance. Guo et al. [44] used wire cutting to cut groove structures with a depth of 0.4 mm and an oblique angle of 45° on steel plates to enhance mechanical interlocking between metal and CFRP. Similarly, Lv Yingying et al. [45] used a milling machine to mill parallel grooves on the steel plate surface to obtain a uniform rough surface with parallel equal depth, and compared it with steel plates ground by sandpaper. The results showed that grooves that were too deep were not easily filled by adhesive, which 反而 reduced the interfacial bonding strength.

From the perspective of failure mode transition, mechanical treatment has a significant effect on the failure path of metal-FRP interface. Without treatment, the metal surface is smooth and has an oxide film, and the interfacial bonding force mainly depends on weak intermolecular forces, and the failure mode is mostly manifested as interface debonding or peeling. After mechanical treatment, the interface strength is significantly improved, and the failure mode changes from interface debonding to resin matrix cohesive failure or even fiber fracture, which indicates that the interfacial bonding strength has exceeded the strength of the resin bulk, and is a direct manifestation of the effectiveness of mechanical modification.

Overall, mechanical treatment significantly improves wettability and mechanical interlocking effect through roughening, and can effectively suppress peeling and interlayer cracking failure caused by insufficient wetting or stress concentration. However, the treatment effect is greatly affected by process parameters; insufficient sandblasting will lead to insufficient surface roughness and insufficient formation of active surface, which cannot significantly improve the interface and cause interface failure; while excessive sandblasting may cause damage to the metal surface or form holes that cannot be filled, leading to bubbles and defects at the interface and affecting interface durability [46]. To overcome the shortcomings of unpredictable surface morphology, uneven treatment, and difficulty in precise control after mechanical treatment, researchers have proposed physical treatment methods, such as laser ablation, plasma spraying, etc., to more accurately regulate the metal surface morphology and chemical state to improve interface performance.

4.1.2 Physical treatment

Physical treatment methods have become a common and efficient surface modification means due to their advantages of clean process, simple operation, and no obvious damage to the substrate. Among them, laser ablation and plasma treatment are widely used in the field of metal-FRP interface enhancement.

Laser ablation is a physical surface treatment method that uses laser energy to regulate the surface properties of materials. Because of its high efficiency and controllability, it has been widely used in metal-FRP interface modification in recent years. Laser modification uses the absorption of laser energy by the metal surface, rapid heating, short-term melting, and then rapid cooling and solidification to form specific rough structures, reorganized microstructures, and chemically active layers on the surface, improving interfacial bonding performance through mechanical interlocking and interfacial wettability. A large number of studies have shown that the process parameters of laser ablation, the formed surface patterns, and geometric features all have important effects on interface performance. The mechanism is mainly reflected in two aspects: on the one hand, laser acts as a heat source to rapidly heat the metal surface and transfer heat to the interface, so that the resin melts and fully wets the metal and fills the surface micropores, forming a flat and firm bonding interface after cooling, which is similar to thermal welding. Laser process parameters such as laser power [50], scanning speed [51–52], defocus amount [53–54], and energy density [55] have a great influence on the heat input of the interface, thereby affecting the interfacial bonding performance of metal and FRP [56]. Therefore, reasonable selection and optimization of laser process parameters to ensure sufficient wetting and mechanical interlocking of the metal surface while avoiding excessive thermal damage to the resin is the key to improving the interface performance of metal-FRP [57–59]. On the other hand, laser ablation forms microstructures such as pits, grooves, or grids on the metal surface (as shown in Fig. 4 [60–63]), significantly increasing the specific surface area and roughness, enhancing interfacial mechanical interlocking and resin penetration capacity, thereby further improving interfacial bonding strength and durability [60, 64–65].

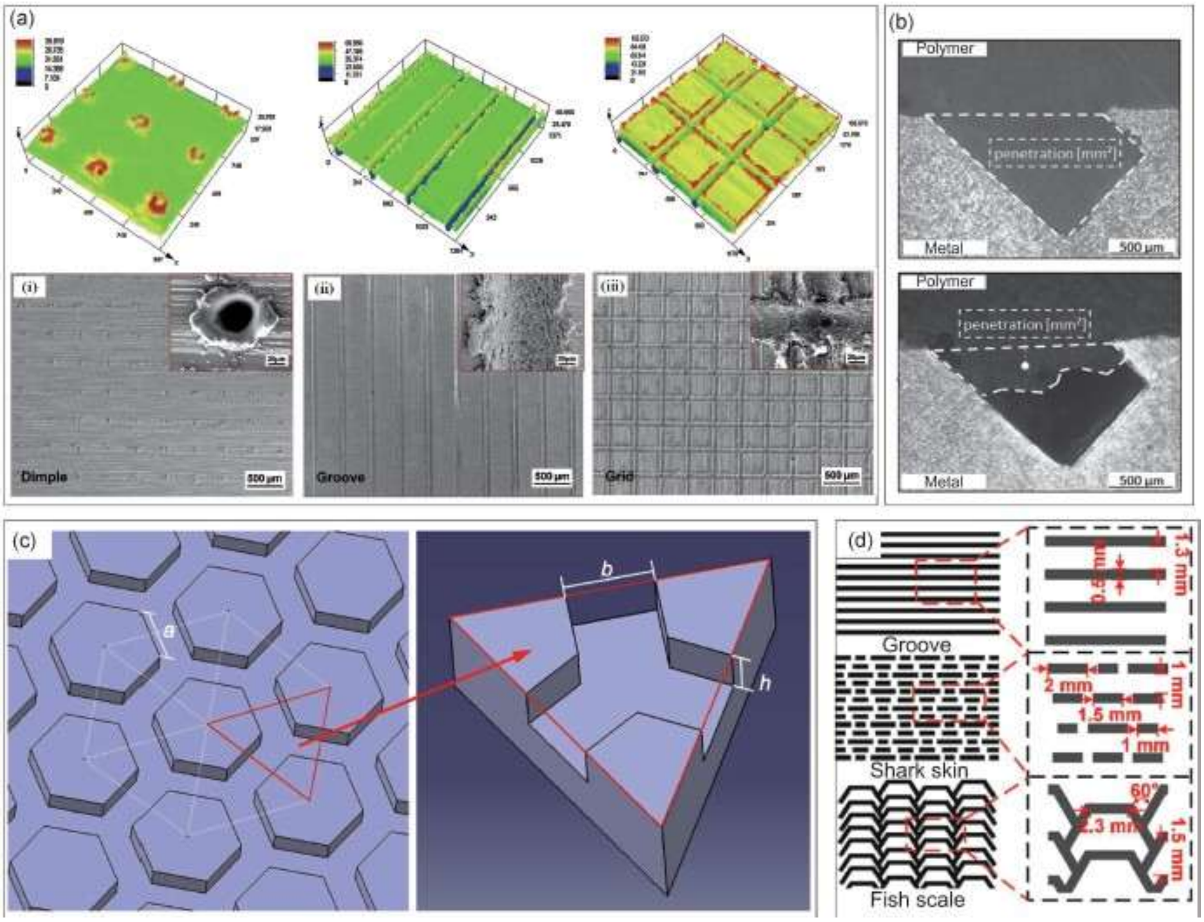

Figure 4 Surface microstructure morphology of laser ablation (a) dimple, groove, and grid patterns [60]; (b) −45° inclined groove arrangement [61]; (c) hexagonal grooves [62]; (d) shark skin and fish scale textures [63]

A large number of studies have been carried out around the morphology design of surface microstructures, and the results show that the morphological characteristics and arrangement of surface microstructures have an important impact on the interface failure mode. Maressa et al. [64] prepared three textures of depression, grid, and disorder on the surface of titanium alloy by laser, and the results showed that the grid texture had the best mechanical interlocking effect, and the interface damage was mainly cohesive failure of the adhesive; the depression texture had partial interface failure due to insufficient hole filling; while the disordered texture caused surface tearing of the substrate due to the generation of brittle oxides, and the interface performance was poor. Similarly, Feng et al. [60] used laser treatment to prepare different microstructure patterns (dots, grooves, grids) on the surface of 30CrMnSiA high-strength steel, and found that the grid pattern significantly improved the surface roughness and wettability, enhanced the mechanical interlocking of the interface, and changed the fracture mode from interface damage to cohesive damage. And under high temperature and high humidity conditions, it still maintained high strength and toughness. In addition, in addition to the morphological characteristics of the texture, the geometric dimensions (such as depth, width, spacing) of laser ablation grooves also significantly affect the interface performance [65–66]. Schricker et al. [61] further studied the influence of groove arrangement angle on interface performance, and the results showed that arranging the grooves at an inclination angle of −45° could significantly improve the bearing capacity of the interface. Compared with traditional parallel or vertical arrangement, this structure formed a more favorable stress distribution and resin penetration path under shear load, effectively enhancing the mechanical interlocking and overall stability of the interface. In addition to simple surface textures, some scholars have designed more complex microstructures from the perspective of bionics. Wang et al. [62] constructed a surface texture with a hexagonal groove shape inspired by the toe-end morphology of tree frogs, which enhanced the wettability and mechanical embedding of resin on the metal surface, and significantly improved the interface performance. Li et al. [63] constructed two bionic textures of shark skin and fish scales, increasing the surface roughness and improving the mechanical interlocking at the interface, while the bionic texture hindered crack initiation and propagation, thereby improving the bonding strength of the joint. However, some studies believe that in the mechanism of laser etching to improve interface performance, the change of chemical properties plays a more critical role, not just mechanical interlocking. Alfano et al. [67] used low-power fiber laser to ablate the surface of aluminum alloy and stainless steel, and the results showed that when the ablation power was higher than the threshold, the surface roughness increased significantly and micro-patterns were formed; the original Al_2O_3 layer on the aluminum alloy surface was replaced by an AlO layer, and C—O polar bonds were generated on the stainless steel surface, and the chemical properties of both were improved. After treatment, the shear strength of aluminum alloy and stainless steel increased by 100% and 25%, respectively. Among them, the improvement of interface strength of aluminum alloy was mainly attributed to surface chemical modification, while the enhancement effect of stainless steel mainly came from mechanical interlocking.

In addition, plasma spraying is also an effective physical surface modification technology, with the advantages of environmental protection, no pollution, low cost, high efficiency, and strong adaptability, and is widely used to improve the interface bonding performance between metal and resin [68]. This method excites gas molecules through an electric field to generate plasma rich in ions, electrons, and free radicals, which bombard the material surface or introduce functional groups under pressure [69–70], improving surface energy and wettability, thereby enhancing interface performance [71–72]. Its significant advantage is low operating temperature, controllable process, and no macroscopic thermal damage, especially suitable for temperature-sensitive resin-based composites. Pike et al. [73] sprayed an alumina ceramic layer on the surface of aluminum alloy to form a microstructure with 8%–10% porosity, thereby enhancing the permeability and mechanical interlocking of the adhesive. It enhanced the wettability and mechanical interlocking between metal and epoxy resin, and the shear strength was enhanced. Process parameters during plasma spraying [74] (such as spraying distance, spraying time, etc.) also have a significant impact on the density, roughness, porosity, and residual stress distribution of the coating, thereby determining the plasma treatment effect and interfacial bonding performance.

Physical treatment alleviates the problem of interface debonding failure caused by thermal expansion mismatch and insufficient wettability by synergistically regulating the microstructure, chemical state, and thermal stress distribution of the metal surface. Among them, surface microstructures and bionic textures can not only increase mechanical interlocking but also induce crack deflection, promote energy dissipation, and prevent crack propagation along the interface. On the other hand, the rapid heating and instant cooling process of laser can generate a stress field in the metal layer, which helps to offset the thermal residual stress generated during hot-press molding, thereby reducing the risk of interface cracking. In addition, laser etching and plasma spraying can reconstruct the chemical state and bonding structure of the metal surface, significantly improve the interfacial bonding strength, and change the failure mode from interface debonding to resin layer fracture or fiber pull-out.

4.1.3 Chemical treatment

Chemical etching uses acidic or alkaline chemical reagents to treat the metal surface to remove contaminants and oxide layers, improve surface roughness and activation degree [75], and form a structure conducive to bonding on the surface [76], thereby enhancing the interfacial bonding strength. This method is suitable for various metal materials, especially when treating large areas or geometrically complex surfaces, it can achieve a uniform modification effect. Common chemical etching includes acid etching, alkaline peroxide etching, and phosphate fluoride etching. Among them, acid etching methods usually use chromic-sulfuric acid etching [77–78], nitric-hydrofluoric acid [79], chromic acid-sodium dichromate solution [80], etc. to treat the metal surface, which can effectively improve roughness and initial bonding strength. However, chromate etching solution has large environmental pollution and health risks, and more environmentally friendly non-chromium acid etching agents have been proven to provide good adhesion [30, 81]. Although acid etching can improve shear strength, its durability is poor and there is a hydrogen embrittlement problem [82]. This problem can be improved by alkaline treatment [80, 83]. He et al. [3] placed titanium plates in a 60°C alkaline peroxide $NaOH$-H_2O_2 solution for 24 h, forming a stable oxide layer with a thickness of about 2 μm, which still maintained good bonding performance in high temperature and high humidity environments, but the reaction rate of this method is slow and the treatment cycle is long, limiting its wide application in engineering practice.

Phosphate fluoride etching can not only change the surface morphology of the metal but also introduce polar groups on the interface. Xu Lining et al. [84] used fluoride phosphate to phosphating treat the metal surface. The results showed that the phosphating treatment formed a rough structure and polar groups on the interface, significantly improving wettability and interfacial chemical bonding capacity, thereby significantly enhancing the interfacial bonding strength and fatigue resistance. Drozdziel et al. [85] further compared the effects of two different etching processes for aluminum alloy and titanium alloy on interface performance. The results showed that P2 etching (concentrated sulfuric acid-ferric sulfate solution) treated aluminum alloy at 63–65°C for 11 min, which could form a low-roughness, uniformly porous structure on its surface, conducive to adhesive penetration and mechanical interlocking, and improved interfacial bonding strength. For titanium alloy, using a phosphate fluoride solution containing sodium phosphate and potassium fluoride at 24°C for 1.5–2.5 min, a surface with clear grain boundaries and depressions was obtained, but it still needed to be combined with other surface modification methods to further enhance interface performance.

From the perspective of interface failure mechanism, chemical etching can significantly improve the wettability and chemical reactivity between metal and resin by removing inert oxide layers, introducing polar functional groups, and reconstructing surface roughness, inhibiting interface peeling and debonding failure. The metal surface after etching is more likely to form stable chemical bonds and mechanical interpenetration with the resin, changing the interface failure mode from debonding to resin cohesive failure, significantly improving the load transfer capacity and durability of the structure. However, when selecting chemical etching methods, factors such as environmental impact, operation cycle, and potential effects on metal material properties need to be comprehensively considered to achieve the best modification effect.

4.1.4 Electrochemical treatment

Electrochemical treatment is an interface modification method that generates a functional oxide film on the metal surface through an applied electric field, mainly including anodizing and micro-arc oxidation (MAO). By regulating the film structure and chemical composition, it can effectively improve the wettability, mechanical interlocking capacity, and chemical reaction activity between metal and resin matrix, thereby enhancing interfacial bonding strength and durability.

(1) Anodizing treatment

Anodizing is widely used for metal surface treatment. Its principle is to generate a dense, porous oxide film on the metal surface through electrolysis under an applied electric field to enhance interfacial bonding [86]. The oxide surface produced by anodizing mainly depends on the electrolyte, anodizing voltage [87], time [88], and temperature [89–91]. According to the electrolyte, common systems include acidic (such as phosphoric acid, sulfuric acid) [92], alkaline (such as NaOH) systems [3], and fluoride systems [93]. Among them, alkaline electrolytes are widely used because of their good environmental protection and low corrosiveness [84].

For aluminum alloys, common anodizing methods include chromic acid anodizing (CAA) [94], phosphoric acid anodizing (PAA), and sulfuric acid anodizing (SAA) [95]. However, due to the harm of chromic acid electrolyte to the environment, it has been gradually replaced in recent years [76, 96]. Critchlow et al. [76] carried out a systematic optimization study on the standard boric-sulfuric acid anodizing (BSAA) process. By adjusting parameters such as deoxidizer, anodizing parameters, and post-treatment process, they developed the best treatment scheme for high-temperature boric-sulfuric acid anodizing (HTBSAA). The aluminum alloy surface treated by this method formed an open pore structure similar to that produced by CAA. The initial shear strength, fatigue life under humid and heat aging, and corrosion resistance were close to those of CAA, making it an ideal environmentally friendly alternative to CAA. Zhang et al. [97] explored a novel phosphoric-boric-sulfuric acid anodizing (P-B-SAA) process, which formed an oxide film with a thickness of about 5 μm and high and uniform porosity on the aluminum alloy surface (Fig. 5(a)). The surface structure is conducive to resin penetration and mechanical interlocking at the bonding interface. The shear strength test results showed that the shear strength after P-B-SAA treatment reached 20 MPa, close to the traditional CAA process (23 MPa), showing excellent interfacial bonding performance. To achieve more excellent interfacial bonding performance, researchers began to explore other electrolyte systems. Chen et al. compared the effects of oxalic acid system and phosphoric acid system anodizing on the lap joint performance of aluminum alloy and glass fiber reinforced polypropylene composites. The results showed that phosphoric acid anodizing could generate larger holes and higher roughness on the aluminum alloy surface, thereby enhancing the interfacial mechanical interlocking effect and increasing the single-lap shear strength by about 65.8%. In addition, Fiore et al. [99] used tartaric acid-sulfuric acid composite system to anodize aluminum alloy. The results showed that the joint shear strength of aluminum alloy and basalt FRP increased by 50%–60% compared with traditional sandpaper grinding. Then, the anodic oxide film was etched with NaOH solution, which could significantly amplify the surface pore structure and roughness, further improve the interfacial bonding capacity, and increase the shear strength by about 83% compared with the original state. Different from aluminum alloy, titanium and its alloys can form different surface structures when anodized in different types of electrolytes. In acidic (chromic acid, sulfuric acid, etc.) or alkaline (NaOH, etc.) electrolyte systems, an oxide titanium film can be formed on its surface; while in specific fluoride-containing electrolyte systems, an ordered TiO_2 nanotube array structure will be generated. These oxide structures not only improve the roughness and specific surface area of the titanium surface but also significantly enhance wettability and chemical reaction activity, thereby effectively improving interfacial bonding strength.

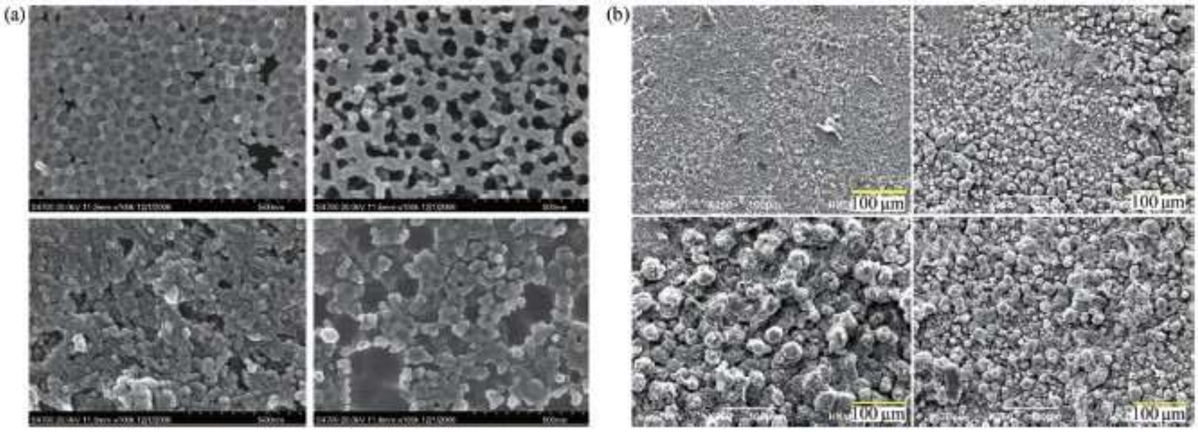

Figure 5 Surface morphology of electrochemistry treated surfaces (a) anodic oxidation [97]; (b)MAO[114]

To evaluate the effects of different electrolytes on interface performance, Schulze et al. [100] compared the surface morphology and bonding performance with polyetheretherketone (PEEK) resin after anodizing titanium alloy plates in 5 mol/L NaOH solution (15 V, 10 min), 1 mol/L H_2SO_4 solution (40 V, 3 min), and 1 mol/L H_3PO_4 solution (60 V, 3 min) based on laser treatment. The results showed that NaOH treatment could form a highly structured oxide layer, H_2SO_4 treatment was the second, and H_3PO_4 treatment only generated a slightly structured oxide film at the edge, showing poor interface enhancement effect. Therefore, alkaline anodizing system has greater potential in interface enhancement between titanium and resin. Mertens et al. [101] expanded the alkaline anodizing system and used NaTESi electrolyte to anodize titanium metal, showing good bonding strength and long-term durability between titanium and polymer. To further optimize the treatment effect of NaTESi system, Xu Fei et al. [102] used orthogonal experiments to optimize the voltage, time, and temperature of anodizing. After treatment, the roughness test, scanning electron microscopy observation, and XRD crystal analysis of the titanium surface showed that a uniformly distributed nanoparticle structure was formed on the titanium surface after anodizing under optimized process, with a roughness of about 1.34 μm, which helped to enhance the mechanical embedding and resin wettability of the interface, significantly increased the shear strength, reaching 26 MPa. In addition, He et al. [89] prepared a composite alkaline electrolyte composed of sodium hydroxide (7.5 mol/L), ethylenediaminetetraacetic acid (0.1 mol/L), and sodium tartrate (0.2 mol/L), and obtained a honeycomb-like porous structure on the titanium alloy surface by regulating the anodizing temperature, which enhanced the surface roughness and wettability, greatly improved its interfacial bonding capacity with resin, and the shear strength increased by up to 317.2%. Researchers further explored the preparation of TiO_2 nanotube array structures with high specific surface area and high interface activity in specific electrolyte systems, which has become a research hotspot in metal/resin interface enhancement. Different from traditional acid and alkaline systems, the preparation of TiO_2 nanotubes is mainly achieved by anodizing in fluoride-containing electrolytes, and its size and morphology can be precisely controlled by electrolyte composition, voltage, pH, oxidation time, and temperature [103–104].

(2) MAO treatment

MAO is further developed on the basis of conventional anodizing process. It generates local high temperature and high pressure through high-voltage spark discharge on the metal surface, and interacts with the electrolyte solution to induce the in-situ generation of a thicker, harder, and more uniform ceramic-type porous oxide film on the metal substrate surface [86, 105–106]. This process is suitable for metals and their alloys such as titanium, aluminum, and magnesium. It enhances the interface bonding strength while also being more corrosion-resistant and wear-resistant. During MAO, process parameters such as electrolyte composition, power type, voltage, current density, and processing time have a significant impact on the oxide film structure [107–111], thereby determining the degree of interfacial mechanical interlocking and chemical bonding with the resin matrix [112–113]. After MAO treatment, the metal surface usually forms a double-layer ceramic film structure with a porous outer layer and a dense inner layer. Among them, the outer porous zone provides a larger specific surface area, which is conducive to resin penetration and mechanical embedding; while the inner dense zone provides a good barrier performance and attachment foundation, which helps to enhance interfacial bonding stability and durability. Tang et al. [112] found that during MAO, an increase in duty cycle would significantly increase the porosity of the outer porous zone. These porous structures provide more space for epoxy resin penetration, thereby enhancing the mechanical embedding between interfaces and improving interfacial bonding strength. At the same time, the presence of MgO in the oxide film can induce the formation of hydroxyl groups on the surface, further promoting hydrogen bond formation and strengthening the chemical bonding of the interface. In addition, the appropriate pore structure also optimizes stress distribution and energy dissipation paths, enhancing the overall toughness of the interface. Studies have shown that at a duty cycle of 40%, the porosity of the oxide film and MgO content reach a better level, achieving a maximum lap shear strength of 24.5 MPa. In addition to electrical parameters such as duty cycle, the regulation of electrolyte composition also affects the film structure.

Gao et al. [113] studied the effect of Na_2SiO_3 concentration change in the electrolyte during MAO on the interfacial bonding performance between magnesium alloy and epoxy resin. The results showed that when the Na_2SiO_3 concentration was low, the presence of MgO in the oxide film helped to generate hydroxyl groups on the surface, enhance the wettability and hydrogen bonding of the interface, thereby improving the shear strength of magnesium alloy and epoxy resin. As the Na_2SiO_3 concentration increased, the Mg_2SiO_4 content increased, and the MgO content in the oxide film gradually decreased, and the shear strength decreased. In addition to magnesium alloy, MAO has also achieved remarkable results in the interface modification of titanium alloy. Logesh et al. [114] compared the differences between single-step MAO treatment and traditional multi-step anodizing process (including sandblasting, anodizing, etching, and annealing) in improving the interfacial bonding performance between titanium alloy and thermoplastic resin (Fig. 5(b)). The results showed that the single-step MAO treatment was more effective, mainly attributed to the formation of a higher porosity, larger pore size, and thicker oxide layer on the surface, which was conducive to full resin penetration and interfacial mechanical interlocking, thereby enhancing the interfacial bonding strength.

Electrochemical treatment builds a porous oxide film and functional structure on the metal surface, and realizes precise regulation of the microscopic morphology and chemical composition of the metal surface without introducing mechanical damage, thereby effectively improving the interfacial bonding strength and service durability with the resin matrix. Among them, the porous film structure formed by anodizing helps resin penetration and mechanical interlocking, while polar functional groups in the oxide film enhance chemical bonding capacity, changing the failure mode from interface debonding to resin cohesive failure or fiber pull-out. MAO improves stress transfer at the interface and inhibits crack propagation along the interface by regulating the porosity, thickness, and composition of the oxide film, thereby improving interface toughness and fatigue life. Therefore, electrochemical treatment not only improves the initial bonding strength of the interface but also shows excellent failure inhibition effect in complex service environments. As a green, controllable, and highly adaptable surface modification method, electrochemical treatment has become an important direction in the current research on interface enhancement of metal-resin composites.

4.2 Functional layer introduction

Different from directly treating the metal substrate, the construction of an interfacial functional layer is to introduce one or more intermediate layers with specific structures and chemical activities on the metal surface to provide a better interfacial transition zone between metal and FRP. It can not only improve the mechanical embedding and chemical bonding at the interface but also realize multiple functions such as barrier, buffer, and corrosion resistance. Among them, the typical mechanisms of common interfacial functional layer introduction methods are shown in Fig. 6. In the construction of interfacial functional layers, silane coupling agent (SCA) treatment is a common and effective strategy. Its mechanism of action is to form a stable functionalized intermediate layer (i.e., a dense silane film) between the two materials through the bifunctional groups (X group and Y group) in the coupling agent molecules, which react with the metal substrate surface and the resin matrix respectively, thereby enhancing the interface connection between the two materials [115–117]. The interfacial enhancement effect of SCA is closely related to the chemical structure of the polymer and the surface active groups. When the resin matrix contains active functional groups such as hydroxyl, amino, and carboxyl groups, it can form chemical bonds or hydrogen bonds with the Y group in the coupling agent, significantly improving the interfacial bonding strength. Ji et al. [116] used SCA to modify the titanium surface and explored the effects of coupling agent concentration, curing temperature, and time on the interfacial bonding performance between titanium and FRP. The results showed that a uniform and complete silane film was formed on the titanium surface, and there was a Si—O—Ti covalent bond, verifying the interfacial enhancement effect of SCA. Compared with sandblasting treatment, the interlaminar shear strength of the treated sample increased by 132.6%. Similarly, Guo Yimin [118] used KH560 to treat AA6061-T4 aluminum alloy and C/PA6 composite, forming Al—O—Si, Si—O—Si covalent bonds and Si—N, Si—O—Si covalent bonds, respectively, effectively improving the interfacial bonding performance. Although SCA has achieved remarkable results in improving the interfacial bonding performance of heterogeneous materials, due to the lack of active groups in some resins, the probability of chemical reaction with SCA is low, and the interface enhancement effect is limited. To further improve the interface strength, researchers began to explore the construction of nanostructured functional layers to achieve better interface performance.

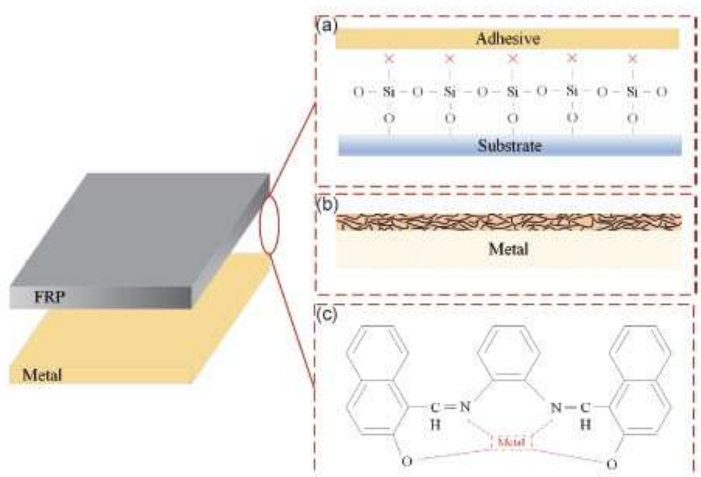

Figure 6 Schematic of typical mechanisms introduced by the functional interface layer (a) SCA bridging; (b)network enhancement by nano-functional layers; (c) Schiff base metal complex coordination bridging

Pan et al. [119] used electrophoretic deposition (EPD) to deposit graphene oxide (GO) on the titanium alloy surface to build a nano-functional interface layer to improve its bonding performance with PEEK. During EPD, negatively charged GO sheets deposited on the titanium alloy anode surface under electric field driving to form a uniform and dense coating. GO is rich in polar functional groups such as carboxyl, hydroxyl, and epoxy groups, which can produce intermolecular forces such as hydrogen bonds and van der Waals forces with PEEK molecules, thereby realizing molecular-level interface bridging. This intermediate layer not only improves the wettability of the metal surface but also enhances the mechanical interlocking, significantly improving the interfacial bonding strength. Similarly, Ji et al. [19] used EPD process to construct a carbon nanotube (CNT) network structure layer between the titanium layer and CF/PEEK composite. Studies have shown that the density and thickness of the deposited layer are mainly regulated by CNT concentration and deposition time, and this network structure can significantly improve the bonding strength of heterogeneous materials with weak interfacial bonding. Coordination bond bridging, as an important mechanism for constructing interfacial functional layers, can also effectively improve the bonding strength between metal and polymer. Pan et al. [120] used Schiff base ligands (Schiff) to form stable complexes with titanium ions (Ti^{4+}). The complexes bridged the titanium alloy surface through coordination bonds. Ti^{4+} as the central ion formed coordination bonds with nitrogen and oxygen electron-donating atoms in the Schiff base. The complexes self-assembled and adsorbed on the metal surface to build an ordered interface layer. Although this functional layer reduced the wettability and apparent surface energy of the material, it effectively enhanced the interfacial bonding capacity through multiple mechanisms such as coordination bonds, hydrogen bonds, mechanical interlocking, and molecular chain entanglement. The single-lap shear strength of TC4 plate and PEEK increased by 53.89% compared with anodizing treatment alone. In summary, the introduction of interfacial functional layers can not only realize chemical coupling between metal and resin matrix but also regulate the interfacial energy state and micro-morphology at the nanoscale, providing a multi-dimensional enhancement mechanism for improving the interfacial performance between metal and FRP.

4.3 Interfacial modification adaptability of different metal substrates

Different metal materials have significant differences in physical and chemical properties, surface energy, and oxide layer characteristics, and their surface modification strategies must be targeted. Titanium alloy surface oxide film is dense and chemically inert, making it difficult to form strong chemical bonds with resin. Therefore, it is suitable to use laser ablation, anodizing, or SCA and other modification methods to form a porous layer or nanotube array with high specific surface area on the surface, and introduce Ti—O—C chemical bonds or polar functional groups, thereby realizing mechanical interlocking and chemical bonding. Aluminum alloy is easy to oxidize, but the surface energy is low, and its natural oxide film (Al_2O_3) has a loose structure and is easy to hydrolyze in a hot and humid environment, forming a weak boundary layer, which is the main reason for interface failure. Therefore, laser ablation or anodizing is often used to remove the natural oxide film and build a dense, porous, and hydrolysis-resistant new oxide layer to improve interfacial wettability and surface activity, thereby improving interfacial bonding strength and durability.

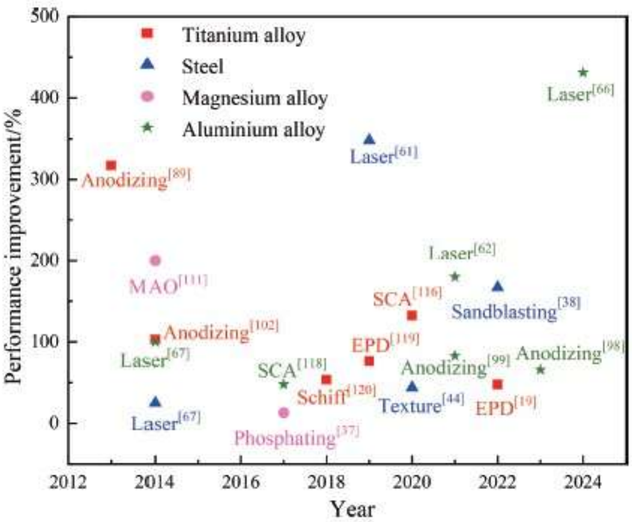

Figure 7 Performance improvement effect of interface modification methods for different metal materials

Magnesium alloy has active chemical properties but poor corrosion resistance. MAO is often used to in-situ generate a porous and dense ceramic layer structure on the magnesium surface, which can not only provide excellent corrosion resistance but also achieve firm mechanical interlocking with FRP. Stainless steel and other high-density metals have low surface energy and are prone to rust. Sandblasting or laser ablation can be used to improve surface roughness, enhance interfacial wettability and mechanical interlocking, thereby obtaining high interfacial bonding strength. As shown in Fig. 7, for different metal materials, various modification methods show differentiated performance optimization effects, providing a variety of interface modification technology choices for the application of metal-FRP structures in different engineering scenarios.

Although different metals have significant differences in modification strategies, a single mechanism is often difficult to comprehensively consider interface strength, toughness, and durability. Therefore, multi-mechanism synergy has become a key direction to improve the interface performance of metal-FRP.

4.4 Multi-mechanism synergy

The bonding strength of metal-FRP interface is not determined by a single interface bonding mechanism, but is the result of the synergy of multiple mechanisms at different scales. Although mechanical interlocking, wetting-adsorption, and chemical bonding theories are each established, they are often coupled with each other in engineering applications, jointly affecting interface performance. In recent years, researchers have gradually recognized the importance of multi-mechanism synergistic design and significantly improved interfacial bonding strength and service stability through composite modification processes. Jiang et al. [121] proposed a composite enhancement strategy combining mechanical treatment and coordination functional interface layer introduction. First, sandblasting was used to build a micro-rough morphology on the titanium alloy surface to improve the mechanical interlocking and wettability of the interface; then a coordination layer with rare earth Ce^{3+} was introduced to form stable coordination bonds with oxygen atoms on the surface of PEEK and TiO_2, building a chemically active interface layer on the metal surface. This coordination structure promoted stress transfer and energy dissipation while enhancing chemical bonding, increasing the interface shear strength by about 178% compared with sandblasting alone, reflecting the synergistic enhancement effect of mechanical treatment and functional layer introduction. Hao et al. [122] proposed a dual modification interface enhancement strategy based on UV/ozone oxidation and SCA for Cu/PEEK interface. Studies have shown that UV/ozone treatment can induce the formation of a Cu_2O oxide layer on the copper foil surface, and then SCA treatment is used to obtain a silane coupling film on the copper foil or copper oxide foil surface, and finally the copper foil and PEEK film are connected by nanosecond laser. This composite modification strategy effectively improved the interfacial stress transfer efficiency, and the peel strength of the Cu/PEEK joint increased by about 95% compared with the untreated sample. Tan et al. [123] used MAO-SCA combined modification process to achieve synergistic enhancement of interface performance when studying the bonding performance of TC4 titanium alloy and CFRTP. MAO treatment built a porous structure on the TC4 surface, which not only improved surface roughness and wettability, enhanced the penetration and mechanical interlocking of molten resin, but also effectively adsorbed —OH functional groups, providing reaction sites for subsequent chemical bonding. The subsequently introduced KH550 coupling agent retained the porous structure and introduced $—NH_2$ polar groups, thereby forming hydrogen bonds and significantly enhancing the interfacial bonding strength, with the bonding force increased by about 29.96%. In addition, Liao et al. [124] proposed a multi-mechanism surface modification strategy combining CNT coating and laser bionic texture to address the insufficient interfacial bonding between AA6060 aluminum alloy and PEEK laminates. Studies have shown that the CNT coating enhanced the interfacial stress transfer capacity while forming Al—O—C chemical bonds with the aluminum oxide layer, thereby enhancing the chemical bonding of the interface; while the laser-induced wavy transverse bionic texture effectively improved the surface roughness and actual contact area, reduced stress concentration, and changed the crack propagation path, achieving better mechanical interlocking effect. Under the synergistic action of the two, the interfacial shear strength increased to 18.8 MPa, and the failure mode changed from interface debonding to aluminum substrate fracture, fully reflecting the cross-scale synergy of mechanical interlocking, chemical bonding, and nano-bridging in interface enhancement.

In summary, metal-FRP interface modification is changing from single-mechanism regulation to multi-mechanism collaborative optimization. By reasonably combining various modification methods such as mechanical, physical, chemical, electrochemical, and functional layer introduction, synchronous improvement of roughness, surface energy, and chemical activity can be achieved at macro-micro-nano scales, thereby realizing high-strength, high-toughness, and high-stability interface bonding. This multi-mechanism collaborative design concept provides a new theoretical basis and technical path for interface modification of high-performance metal-FRP composite structures.

Table 2. Performance Comparison of Interface Modification Methods for Different Metal Substrates

Metal Substrate	Recommended Modification Method	Key Process Parameters / Structural Features	Interface Performance Improvement	Primary Enhancement Mechanisms	Reference
Titanium alloy	Laser ablation (grid pattern)	Grid-like microstructure	Significant increase in shear strength; failure mode shifted from interfacial debonding to cohesive failure	Mechanical interlocking + improved wettability	Feng et al. [60]
	Anodizing (alkaline system)	NaOH solution, 15 V, 10 min	Formation of highly structured oxide layer with excellent bonding strength	Mechanical embedding + chemical bonding	Schulze et al. [100]
	Anodizing (composite alkaline electrolyte)	NaOH 7.5 mol/L + EDTA + sodium tartrate	Shear strength increased by **317.2%**	Honeycomb-like porous structure → roughness↑ + wettability↑	He et al. [89]
	Micro-arc oxidation (MAO)	Optimized duty cycle 40%	Maximum lap shear strength **24.5 MPa**	Outer porous zone promotes resin penetration + MgO-induced hydroxyl formation for hydrogen bonding	Tang et al. [112]
	Silane coupling agent (SCA)	KH series	Interlaminar shear strength increased by **132.6%** vs. sandblasting	Si–O–Ti covalent bonds + chemical coupling	Ji et al. [116]
	Electrophoretic deposition (CNT network)	CNT concentration & deposition time controlled	Significantly enhanced bonding strength of dissimilar materials	Nano-bridging + mechanical interlocking	Ji et al. [19]
Aluminum alloy	Phosphoric–boric–sulfuric acid anodizing (P-B-SAA)	Novel electrolyte system	Oxide film ~5 μm thick with uniform porosity; shear strength **20 MPa** (close to chromic acid method: 23 MPa)	Resin penetration + mechanical interlocking	Zhang et al. [97]
	Tartaric–sulfuric acid anodizing + NaOH post-etching	Anodizing followed by alkaline etching	Shear strength increased by **~83%** vs. original state	Amplified surface porosity + roughness↑	Fiore et al. [99]

	Silane treatment (KH560)	AA6061-T4 + C/PA6	Formation of Al–O–Si, Si–O–Si covalent bonds	Chemical bonding	Guo Yimin [118]
Magnesium alloy	Alkaline–peroxide treatment	60°C, 24 h	Stable oxide layer ~2 μm; maintained good bonding under high-temp & high-humidity	Chemically active layer + environmental durability	He et al. [3]
	Micro-arc oxidation (MAO)	Na_2SiO_3 concentration controlled	Higher shear strength at low Na_2SiO_3 (MgO-rich); decreased with increasing concentration due to Mg_2SiO_4 formation	Ceramic barrier layer + mechanical interlocking + hydrogen bonding	Gao et al. [113]
Stainless steel / high-density steel	Sandblasting	Alumina abrasive, optimized angle	Significantly increased shear strength	Roughness↑ + mechanical interlocking	Harris et al. [42]; Ho et al. [43]
	Laser ablation (bionic texture)	Shark-skin / fish-scale patterns	Hindered crack initiation and propagation; improved joint strength	Mechanical interlocking + crack deflection	Li et al. [63]
Steel	Wire-cut grooving	Groove depth 0.4 mm, 45° inclination	Enhanced mechanical interlocking (excessively deep grooves reduced strength)	Macroscopic mechanical locking	Guo et al. [44]

Table 3. Performance Comparison of Multi-Mechanism Synergistic Modification Strategies

Composite Modification Strategy	Target Materials	Single/Baseline Treatment Effect	Synergistic Improvement	Synergistic Mechanism Analysis	Reference
Sandblasting + Ce^{3+} coordination functional layer	Ti alloy / PEEK	Sandblasting alone: limited interface shear strength	**~178%** increase vs. sandblasting alone	Sandblasting builds micro-roughness + Ce^{3+} forms coordination bonds with PEEK/TiO_2 → chemically active interface promotes stress transfer & energy dissipation	Jiang et al. [121]
UV/ozone oxidation + silane coupling agent	Cu / PEEK	Untreated: low peel strength	Peel strength increased by **~95%**	UV/ozone generates Cu_2O layer + SCA film + laser joining → stress transfer efficiency↑	Hao et al. [122]
MAO + SCA (KH550)	TC4 / CFRTP	MAO alone already effective	Bonding force further increased by **~29.96%**	MAO porous structure adsorbs –OH providing reaction sites + KH550 introduces $–NH_2$ for	Tan et al. [123]

				hydrogen bonding	
CNT coating + laser bionic texture	AA6060 / PEEK laminates	Individual treatments: lower strength	Interfacial shear strength reached **18.8 MPa**; failure mode shifted to aluminum substrate fracture	CNT forms Al–O–C bonds + laser-induced wavy texture → roughness↑, stress concentration↓, crack path altered	Liao et al. [124]

Table 4. Performance Comparison and Applicability of Common Interface Bonding Theories

Theory	Proposer / Year	Type of Bonding Force	Applicable Scenarios	Limitations	Contribution to Interface Strength
Mechanical interlocking theory	McBain & Hopkins / 1920s	Macroscopic mechanical meshing	Rough/porous surfaces (sandblasting, laser pits)	Cannot explain high bonding on smooth surfaces	Foundational contribution; often superimposed with chemical mechanisms
Wetting-adsorption theory	Sharpe & Schonhorn / 1965	Van der Waals forces, hydrogen bonds	Polymer–metal/ceramic heterogeneous interfaces	Cannot explain strength exceeding adhesive bulk; rate-dependent effects not considered	Determines contact area and initial adsorption
Chemical bonding theory	Lewis / 1916	Covalent & ionic bonds (1–2 orders of magnitude stronger than van der Waals)	Interfaces with active functional groups (–OH, –COOH, $–NH_2$)	Requires intimate interfacial contact; defects reduce strength	Highest strength contribution; excellent environmental durability
Electrostatic adsorption theory	Derjaguin / 1967	Double-layer electrostatic attraction	Metal/non-metal interfaces with large electron affinity difference	Actual surface charge density is generally low; marginal contribution	Auxiliary enhancement; synergistic with other mechanisms
Diffusion theory	Voyutskii / 1963	Polymer chain interpenetration	Polymer–polymer interfaces (requires compatibility & chain mobility)	Not applicable to metal/ceramic interfaces	Limited to polymer blend systems
Weak boundary layer theory	Bikerman / 1961	N/A (explains failure)	Interfaces affected by contamination, oxide layers, moisture-induced degradation	Focuses on failure rather than bonding; cannot independently explain strong bonding	Guides surface pretreatment to expose clean, active surfaces

Table 5. Quick-Reference Comparison of Surface Treatment Technologies: Process Characteristics and Performance Impact

Treatment Category	Typical Method	Efficiency	Environmental Friendliness	Substrate Damage	Strength Improvement	Suitable Metals
Mechanical	Sandpaper grinding, sandblasting	High	Medium (dust)	Minor	Medium–High (parameter-dependent)	All metals
Physical	Laser ablation	High (controllable)	Excellent (no chemical waste)	Minimal	High (designable textures)	Ti, steel, Al
	Plasma spraying	Medium	Excellent	None	Medium–High	Al, Ti
Chemical	Acid etching (chromic/phosphoric)	Medium	Poor (high pollution)	Possible H_2 embrittlement	Medium (poor durability)	Al, Ti
	Alkaline–peroxide etching	Low (long cycle)	Excellent	None	High (humid-heat resistant)	Ti, Mg
	Phosphate–fluoride etching	Medium	Medium	Minor	Medium–High	Al, Ti
Electrochemical	Anodizing	Medium	Medium–Excellent (Cr-free processes)	None	High (20–23 MPa level)	Al, Ti
	Micro-arc oxidation (MAO)	Medium	Excellent	None	High (24.5 MPa level)	Mg, Ti, Al
Functional layer	Silane coupling agent	High	Excellent	None	High (132.6%↑)	Ti, Al
	Electrophoretic deposition (GO/CNT)	Medium	Excellent	None	High (nano-bridging)	Ti

5 Conclusions and prospects

The interface performance of metal-FRP directly determines the reliability and service life of the structure. This paper reviews the interface failure modes, interface bonding mechanisms, and typical modification strategies of such structures. Studies have shown that interface bonding depends on multiple mechanisms such as mechanical interlocking, wetting adsorption, and chemical bonding, and presents a complex synergistic coupling relationship in the actual interface. In response to the problem of insufficient interfacial bonding strength, metal surface mechanical, physical, chemical, electrochemical treatment, and functional layer construction have all achieved improvement in interface strength and stability to a certain extent. However, current interface modification technologies still face many challenges, such as insufficient understanding of multi-mechanism synergy at the interface, limited applicability of modification processes, and insufficient precision in interface performance regulation. Future research can focus on the following directions:

5.1 Multifunctional nano-enhanced interface

Introduce nanoparticles (such as nano-SiO_2, carbon nanotubes, graphene, etc.) into the interface region. Based on the high specific surface area and high surface energy of nanoparticles, enhance the interface interaction with metal substrates and FRP resins, and promote the synergy of mechanical embedding and chemical bonding; at the same time, nanoparticles can also fill interfacial micro-voids, inhibit micro-crack initiation and propagation, thereby improving the shear resistance and durability of the interface. On this basis, interface modification is gradually moving toward multifunctionalization. For example, introducing nanoparticles with conductivity (such as graphene) and shape memory function at the interface can achieve the dual goals of high-performance load-bearing and multifunctional service of metal-FRP structures.

5.2 Cross-scale synergy of multiple modification methods

A single modification method often has limitations. Different interface action mechanisms can be combined to explore the synergy of various modification methods. For example, electrochemical deposition (building micron-scale metal coating), nanoparticle introduction (filling coating voids), silane coupling agent treatment, and other modification methods can be combined with macro-interface morphology control (such as sandblasting, laser engraving) to achieve micro-nano multi-scale synergistic enhancement and complementarity and coupling of mechanical, physical, and chemical effects. At the same time, it is necessary to avoid interface performance degradation caused by mutual interference between different methods, and ultimately achieve improvement in interfacial bonding strength and durability.

5.3 Multi-scale modeling of interface

Adopt multi-scale modeling methods to analyze chemical bonding and intermolecular interactions at the micro-scale, study microstructural morphology and stress distribution at the meso-scale, and evaluate overall mechanical properties and failure behavior at the macro-scale. Through cross-scale correlation, accurate prediction of interfacial bonding strength, stress distribution, and failure mode under different modification schemes can be achieved.

5.4 Machine learning to optimize interface modification parameters

Based on experimental data and multi-scale simulation data (such as molecular dynamics, finite element simulation, etc.) of interface modification, combined with data-driven methods such as machine learning, an intelligent prediction model of process parameters (such as nanoparticle doping ratio, sandblasting roughness, electrochemical deposition time) - microstructure (such as nanoparticle dispersion, microstructural size) - interface performance (such as interfacial shear strength, humid and heat aging life) is constructed. The model is used to reversely optimize the modification parameters, and under the premise of meeting engineering service requirements, precise control of key parameters and prediction of interface service performance are achieved.

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