



Review Research Status of Graphene Polyurethane Composite Coating

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Abstract: Graphene material has a variety of excellent properties and applications in energy storage, biomaterials, photoelectric devices, and other fields. With the progress of nanotechnology, graphene nanomaterials have shown their advantages in the field of new nano-corrosion coatings with their high barrier structure. In addition, polyurethane is also widely used in the field of anticorrosion coatings due to its excellent chemical resistance, mechanical properties, and weathering resistance. The preparation of composite coatings by combining graphene nanomaterials with traditional polyurethane (PU) coatings has opened up a new way for the research and development of new anticorrotic coatings. In this paper, graphene polyurethane composite coating was first used as the research object, and the mechanism of graphene material in the new composite coating was analyzed. Then, graphene oxide (GO), a commonly used precursor material, was used as an entry point for a detailed study of the properties of GO materials and the advantages and disadvantages of its application in composites, and two types of modifications, covalent and non-covalent, were analyzed. In addition, the preparation methods and processes of graphene polyurethane composite coatings were summarized. Finally, the future research directions and research focus of GO were prospected.

Keywords: graphene oxide; polyurethane; composite coating; corrosion protection



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1. Introduction

Corrosion is a worldwide problem that causes huge economic losses every year, and it is estimated that for industrialized countries, losses due to corrosion can be as high as 7–8% of the gross national product [1], and the average annual economic loss due to metal corrosion in countries around the world is as high as \$250 million [2]. In addition, corrosion will lead to a number of potential safety problems and pollution problems, which will cause huge losses, so scholars around the world are trying to explore new anti-corrosion strategies [3]. The main methods of preventing metal corrosion are improving the corrosion resistance of metals, improving the corrosive environment, electrochemical protection methods, or the application of isolators on metal surfaces [4]. Among them, the isolation method of applying anti-corrosion coatings to metal surfaces is by far the most effective and widely used anti-corrosion measure.

The mechanism of action of the coating is barrier protection. As an external layer, the coating prevents direct contact of corrosive ions with the surface of the substrate. The role of anti-corrosion coating on the metal substrate is mainly reflected in the following aspects. Firstly, the anti-corrosion coating hinders the contact between the corrosive medium and the protected metal, and delays the penetration of the corrosive medium through the anti-corrosion coating to the metal/coating interface, which is called the shielding effect. Secondly, when the corrosive medium diffuses to the metal/coating interface through the micro-pores of the anticorrosive layer, the strong bonding force between the anticorrosive layer and the metal limits the accumulation of corrosive medium at the interface and slows down the spread of corrosion. Therefore, the strength of the coating bonding force is one of the decisive factors affecting the good or bad corrosion resistance of the coating. Third, anti-corrosion coating in the production, transportation, and use of the process, will

inevitably be due to inclusions of impurities or scratches and local defects and damage, thus making the metal matrix exposed. At this time, the external environment of the corrosive medium will take advantage of the virtual entry in these exposed places and the metal matrix direct contact, and in some cases even the formation of local chemical

corrosive medium will take advantage of the virtual entry in these exposed places and the metal matrix direct contact, and in some cases even the formation of local chemical cells, in order to accelerate the corrosion. This corrosion is called electrochemical corrosion and is caused by local defects; the application of metal anti-corrosion coating is used since it is more difficult to solve a practical problem. Barrier protection will fail if defects such as pinholes, bubble inclusions, poor inter-pigment adhesion, or mechanical damage to the coating are present [5]. Therefore, the coating must have ionic impermeability, inherent durability, good adhesion to the substrate, and sufficient flexibility and toughness to withstand impact and cracking, while being able to maintain integrity under pressure, swelling, mechanical damage, or weathering [6]. Obviously, traditional coatings can no longer meet the increasing performance requirements under actual working conditions, and there is an urgent need to develop and apply new high-performance coatings, and relevant researchers are constantly making technological innovations to prepare new coatings.

As a functional coating, PU coating has been widely used in construction engineering, transportation, military defense, and other fields due to its good corrosion resistance, mechanical properties, and wear resistance [7]. PU coatings have the advantages of strong acid and alkali resistance, excellent weather resistance, and strong mechanical properties in terms of corrosion protection. However, the traditional PU coatings cannot meet the application requirements of the new era, so researchers are constantly exploring various ways to improve PU coatings to prepare new PU coatings in line with the requirements of the new era.

With the development of nanotechnology, researchers have tried to combine nanomaterials with traditional PU coatings to enhance their performance or make up for their shortcomings. Among them, graphene nanomaterials can form highly herringbone paths on other substrates to block corrosive media, and graphene materials have excellent properties such as gas impermeability, which makes graphene materials very promising in the field of coatings. Therefore, the application of graphene materials in the field of coatings has attracted the attention of many researchers. GO, an oxide of graphene, has been widely used in related research due to its many convenient properties.

The graphene polyurethane composite coating has good mechanical properties and corrosion resistance. It is a promising corrosion protection method to modify PU coating with GO. This paper firstly introduces the application characteristics of graphene as anticorrosion coatings and analyzes and compares the advantages and disadvantages of graphene and GO in composites. Then the limitations of GO in PU coatings are pointed out, and covalent and non-covalent modification methods for preparing functionalized GO are presented. In addition, the preparation methods of graphene polyurethane composites and of coatings are analyzed. Finally, the research directions and research priorities of GO are prospected.

2. Graphene Material

Graphene is a carbon heterostructure. It is a monolayer of flat plates of carbon atoms with sp2 hybridization orbitals, densely packed in a honeycomb structure [8]. Its structure is shown in Figure 1. The graphene material has ultra-high strength with a Young's modulus of about 1 TPa [9]. It also has a high thermal conductivity of about 5300 W/m/K [10] and an ultra-high surface area of 2630 m²/g [11]. Graphene materials have many excellent properties such as chemical inertness [12], thermal stability [13], gas impermeability [14], and toughness. Researchers have used these properties to try to use graphene materials for various applications. Among them, scholars in the field of protective coatings have started to experiment with graphene as part of protective coating systems and have initially demonstrated that graphene and its derivatives can improve the physical properties of polymeric nanocomposites [15,16]. Graphene nanocomposite



coatings have great potential for application in material corrosion protection and will lead to the development of new coatings.

Figure 1. Schematic diagram of graphene structure.

At present, reduced graphene (G), reduced graphene oxide (RGO), GO, functional group-modified graphene, and composites based on the above graphene are often applied in organic anti-corrosive coatings. GO is an oxide of graphene. Compared with pure graphene, GO has more oxygen-containing functional groups. In addition, GO has many properties such as being more active than graphene, easy to chemically modify, low production cost, and can be mass produced. GO contains four main oxygen-containing functional groups: hydroxyl, epoxide, carbonyl, and carboxyl groups. In addition, it contains small amounts of esters, ethers, and phenols [17]. The hydroxyl and epoxy groups are mainly distributed on the sheet of GO, while the carbonyl and carboxyl groups are mainly located at the edges of GO [18]. Its molecular structure is shown in Figure 2. GO can remain stable in aqueous solutions and polar solvents due to the presence of a large number of oxygen-containing groups. Compared with graphene, GO has higher chemical stability and can be used as a precursor and support carrier for the synthesis of graphene composites. It is characterized by easy functionalization and high controllability.



Figure 2. Molecular structure of GO.

The molecular structure differences between GO and graphene are a double-edged sword, with both advantages and disadvantages. Graphene consists almost entirely of sp2 hybridized carbon atoms, but GO contains not only sp2 hybridized regions, but also a large number of sp3 hybridized regions. Structurally, GO has oxygen-containing groups on its edges and surfaces, but it also brings certain defects. It is completely different from graphene in terms of mechanical properties, electrical properties, thermal conductivity,

and surface properties. The excellent properties of graphene are due to its highly conjugated structure. However, the oxygen-containing functional groups and damaged pores in GO severely disrupt this highly conjugated structure, making GO less capable than graphene [19,20].

As an important oxygen-containing derivative of graphene, GO has many lattice defects in its structure, leading to degradation of its electrical conductivity, thermal conductivity, and other properties. Therefore, it is difficult to apply it in the preparation of nanocomposites that have strict requirements for its structural integrity. However, GO still has great advantages in the preparation of nanocomposites with excellent mechanical properties, wear resistance, adsorption properties, etc. The presence of a large number of oxygen-containing groups gives GO a significant advantage in terms of water dispersibility, amphiphilicity, degree of modifiability, and compatibility with a polymer matrix.

RGO is obtained by treating GO using a series of methods such as reductant reduction, thermal reduction, and electrochemical reduction. In this process, the structural damage caused by oxidation is partially repaired during the reduction of GO, making the reduced GO stronger than GO. The process of reducing GO is actually a process of repairing the conjugated structure of graphene to restore the properties of GO [21]. Therefore, in order to overcome the structural defects of GO, researchers usually use GO as a precursor material in the preparation of graphene-based composites and prepare RGO by chemical reduction. Then, the composites are prepared by mixing with other substrates. The reduction process of GO is shown in Figure 3. The RGO prepared by GO reduction retains various rich oxygen-containing functional groups at the edges and surfaces, which makes it easier to be chemically modified than pure graphene materials, thus improving its compatibility with other substrates.



Figure 3. Reduction of GO.

3. Anti-Corrosion Mechanism of Graphene Nanocomposites

Currently, graphene-polymer nanocomposites are generally prepared by the physical or chemical mixing of graphene and its derivative nanocrystals with polymers. The effect of graphene nanomaterials on polymers is achieved by lengthening the path of motion of ions and improving the bending of the path of motion of molecules, thus reducing the permeability of the composite coating [22,23]. The mechanism of action is shown in Figure 4.

Kamal et al. [24] showed that graphene has a significant effect on the impermeability of discrete molecular HO. In the study by Tong et al. [25], the impermeability of graphene and its derivatives can lead to distorted path effect and nano-barrier wall effect of diffusing molecules in polymer matrix. In addition, the main factors affecting the degree of bending of the corrosion ion diffusion path are proposed, including the degree of exfoliation and dispersion of the filler in the polymer matrix, the aspect ratio of graphene, and the orientation of the graphene sheet.



Figure 4. Schematic diagram of graphene corrosion protection mechanism.

At present, research on the barrier properties of graphene-based polymer nanocomposites is very limited. The study by Cui et al. [14] showed that the permeability of osmotic fluid in nanocomposites is greatly affected by pressure gradient. The pressure gradient is an important factor affecting the diffusion solubility mechanism of nanocomposite membranes. In general, permeability is related to diffusivity and solubility. However, in the case of graphene nanocomposites, the existence of dispersed graphene nanocrystals can construct zigzag paths and significantly improve the barrier properties of the polymer nanocomposites, which leads to the reduction of the diffusion coefficient.

Huang et al. [26] suggested that curvature is the main factor affecting the barrier properties of polymeric nanocomposites, while the orientation and stacking behavior of the graphene filler will affect the distance between the penetrant and the substrate. Taking the structures of horizontal stacking and random stacking as examples, the relatively large curvature of graphene nanosheets in horizontal stacking can significantly improve the barrier properties of nanocomposites. In a study by Dan et al. [27] it was demonstrated that the orientation and shape of the filler affects the corrosion resistance and tribological properties of the epoxy resin coating.

In addition, graphene and its derivatives in the coating can also act to prevent metal corrosion reactions. The high electrical conductivity of graphene materials can transfer the electrons lost from metallic materials to the surface of the coating, and by forming a passivation film on the surface of the base material, the corrosion rate can be effectively reduced. It also absorbs the corrosive medium Cl⁻ to avoid corrosion caused by its contact with metal surfaces and provides effective electrochemical protection for the substrate material [28,29].

Graphene can fundamentally change the morphology of the coating; as the particles are close to or even smaller than the pores, they can fill the pores and embed themselves in the coating structure. As a result, the graphene-coated coatings are dense and have low porosity. Arash et al. [30] showed that during plasma electrolytic oxidation (PEO) treatment, graphene is embedded in the inner layer to form a denser and thicker PEO coating, and when immersed in a corrosive medium, the graphene in the coating prevents the corrosive medium from penetrating the inner layer, thus improving the corrosion behavior of magnesium alloys.

4. Polyurethane Anticorrosive Coating

PU, known as polycarbonates, are polymers made from polyisocyanates and either polyether polyols, polyester polyols, small molecule polyols, polyamines, or water and other chain extenders or crosslinkers. The general formula of the synthesis reaction is shown in Figure 5. By changing the type of raw material and composition of synthetic PU, the morphology and properties of the product can be greatly changed to obtain end products of different softness and hardness. The film formed by PU is tough and glossy, with strong adhesion, water resistance, abrasion resistance, excellent corrosion resistance, etc. PU is widely used for high-grade wooden furniture and metal surfaces. In addition,

according to the different raw materials used and different product performance, PU can generally be divided into two categories: polyester type and polyether type.



Figure 5. PU synthesis reaction formula.

The macromolecular structure of PU resins contains a large number of repeating carbamate chains that are formed by the reaction of polyisocyanates with polyols, including oligomers containing hydroxyl groups. PU is a block polymer with a molecular structure consisting of hard and soft segments. The soft segment of the molecular structure is formed by the polymerization of high molecular weight polyols with polyisocyanates, while the hard segment is formed by the polymerization of small molecular weight diols (chain extenders) with polyisocyanates [31]. The structure of the hard and soft segments of PU is shown in Figure 6. The properties of PU materials depend to a large extent on the phase structure of the hard and soft segments and the degree of microphase separation. A moderate degree of phase separation is beneficial to improve the properties of the polymer. From the viewpoint of microstructure, in PU materials, carbamate groups with strong polarity and rigidity can form hydrogen bonds between molecules due to their large cohesion energy and gather together to form hard segment microphase regions. At room temperature, these microregions exhibit glassy subcrystalline or microcrystalline forms. Polyether or polyester segments with weak polarity are clustered together to form soft segment phase regions [32]. Although there is some miscibility between the soft and hard segments, the hard and soft segments are thermodynamically incompatible. In this case, microphase separation occurs, and the soft and hard microzones exhibit their respective glass transition temperatures. The soft phase region mainly affects the elasticity and low temperature properties of the material. The chain segment attraction between the hard segments is much greater than that between the soft segments. The hard phase does not dissolve in the soft phase, but is distributed in it, forming a discontinuous microphase structure. At room temperature, it acts as a physical cross-linking point for the soft segments and acts as a reinforcement. Therefore, the hard segment has an important influence on the mechanical properties of the material, especially tensile strength, hardness, and tear resistance. This is why PU elastomers exhibit high strength and elasticity at room temperature, even without chemical cross-linking. The mechanical properties of PU elastomers are directly influenced by the degree of microphase separation and the uniformity of the distribution of the hard phase in the soft phase.

PU material has the characteristics of low temperature resistance, high tensile strength, high elongation, high hardness and modulus variation, good adhesion, wear resistance, oil resistance, and chemical medium corrosion resistance. PU coating is made of isocyanate or isocyanate reaction products. It is a coating composed of PU resin as the main film-forming substance, plus color filler, solvent, catalyst, and other auxiliary materials. PU polymers contain a large number of carbamate bonds (–NH–CO–O–R). In addition, the formed coating also contains a large number of ester bonds, ether bonds, unsaturated oil esters of the double chain, diurethane-formate bonds, etc. PU coating has a variety of excellent properties. PU coating has good adhesion; high toughness; strong abrasion resistance; high elasticity and high gloss; and has excellent corrosion resistance to acids, alkalis, salts, oils, and organic solvents. It also has good weather resistance and can be dried at high temperatures and cured at low temperatures. PU coating not only has a strong protective function, but also has beautiful decorative properties [33].



Figure 6. PU soft and hard segment structure diagram.

PU coating can be divided into solvent-based polyurethane and water-based polyurethane according to the different dispersion media. Solvent-based polyurethane uses organic solvents such as xylene and acetone as the dispersing medium. Water-based polyurethane is a new type of polyurethane system, also known as water disperse polyurethane, water polyurethane, or water-based polyurethane, which uses water instead of organic solvents as the dispersing medium. In the field of corrosion protection, the two different types of polyurethane coatings have their own characteristics. The solvent-based polyurethane technology is relatively more mature, with excellent performance and wider application. Waterborne polyurethane uses water as the solvent, which has the advantages of no pollution, safety and reliability, excellent mechanical properties, good compatibility, and easy modification. In addition, waterborne polyurethane is also environmentally friendly and pollution-free, which is more in line with the concept and development trend of environmental protection in today's world [34]. Therefore, water-based polyurethane coatings have a broader development prospect. With the continuous development of the times, the traditional polyurethane coatings can no longer meet the growing performance requirements. It still has a lot of room for improvement in terms of versatility and high performance. Researchers are also trying to modify traditional PU with many different methods to improve its performance and make it more multifunctional. However, the modification method of incorporating graphene nanomaterials as nano-fillers in PU matrix has attracted the attention of many researchers and made great progress.

5. Modification of Graphene Nanomaterials

Graphene is a typical sheet structure whose excellent mechanical, electrical, and thermal properties are derived from the large periodic conjugated structure of sp2-hybridized carbon atoms [35]. Currently, graphene materials are mostly prepared by chemical vapor deposition and micromechanical dissection. The prepared graphene surface lacks hydrophilic oxygen-containing functional groups and is highly chemically inert. Moreover, the van der Waals forces between the sheets make them prone to agglomeration and difficult to disperse effectively in solvents. The compatibility and dispersion of graphene in other substrates are important factors limiting the wide application of graphene materials. To solve this problem, the researchers tried to prepare nanocomposites using GO as a precursor based on the characteristics of GO with a large number of oxygen-containing functional groups on its surface and edges.

The molecular structure of GO makes it stable in aqueous solutions and polar solvents. Adding GO to the PU matrix not only improves the corrosion resistance of PU, but also improves its electrical conductivity. Since GO has good miscibility in polar materials, it can be added directly to the PU matrix as a reinforcing filler [36]. However, due to the

strong interaction between GO and PU, the mechanical properties of the GO-modified PU anticorrosion coatings decreased [37]. With the development of surface modification technology, researchers have tried to modify GO with different surface modification techniques to prepare functionalized GO to promote the application of GO in PU coatings. The active oxygen-containing functional groups on the surface and edges of GO can interact with other molecules to achieve non-covalent and covalent modification of GO. In this way, the dispersion properties of the nanocomposites in the PU matrix are improved and the interfacial interaction between GO and PU matrix is improved, resulting in a functional nanocomposite.

5.1. Noncovalent Modification of GO

The non-covalent modification of GO mainly involves the adsorption of the modifier onto GO surface by π – π bonds, hydrogen bonds, or van der Waals forces. This process does not destroy the structure of GO, but changes its properties.

The GO structure contains a large number of covalent bonding systems, which can interact with some molecules containing benzene ring, pyridine ring, or imidazole ring in the molecular structure and adsorb them on the GO surface, realizing the non-covalent modification of GO. Wei et al. [38] used the π - π interaction between the benzene ring and sulfonated RGO in the polymer structure of water-based styrene-acrylic emulsion to enhance the interfacial bonding between sulfonated RGO and styrene-acrylic emulsion, and significantly improved the mechanical properties of the composite. Because the π - π interaction is weak, it fails when confronted with a stronger force. For example, under strongly alkaline conditions, the function of π - π is easily damaged, resulting in its limitations in practical applications.

The oxygen-containing functional groups on GO sheets can interact with polymers with certain polarity, such as polyaniline, polyamide, and PU, to achieve non-covalent modification of GO. For example, polyvinyl alcohol or polymethyl methacrylate, which can be cross-linked with GO sheets through hydrogen bonding interactions, can improve the tensile strength and Young's modulus of the composite.

The carboxyl and hydroxyl groups on GO sheets can statically interact with some charged substances to achieve non-covalent modification of GO. Yan et al. [39] used electrostatic force to adsorb Fe₃O₄ nanoparticles on the surface of GO nanosheets to make them magnetically responsive, providing the possibility of their subsequent ordered arrangement in the composite.

5.2. Covalent Modification of GO

The covalent modification of GO can also be referred to as chemical covalent modification. The principle is to functionalize GO by introducing a modification group at the active site of GO. In addition, according to the different modified functional groups, the functionalization of GO mainly includes hydroxyl functionalization, carboxyl functionalization, epoxy functionalization, and so on.

Zhang et al. [36] proposed the synthesis of RGO modified by aminoethyl (AERGO) by grafting aminoethyl to the hydroxyl group of RGO. The prepared material has thermal stability, acid stability, and alkali stability, and is also an effective and reusable adsorbent. The specific process of preparation was firstly to treat GO with ammonium persulfate to increase the content of hydroxyl groups. Then bromoethylamine was added to make it react with GO to form amino functionalization.

Jing et al. [40] prepared a composite coating based on PU as a polymer matrix by a simple method. Gallic acid modified graphene oxide (FGO) flakes and acidified multi-walled carbon nanotubes (FMWCNTs) were used as nanofillers, and the presence of FMWCNTs improved the dispersion of FGO in PU. The dispersion of GO and MWCNTS was improved by direct and effective chemical modification. The functionalized MWCNTS improved the compatibility and dispersion of GO in PU resin. The results showed that the synergistic effect of FMWCNTs and FGO in PU substrates significantly improved the corrosion resistance of PU coatings compared to pure PU, FGO/PU, and FMWCNT/PU coatings. In addition, the composite coating had good impermeability, indicating that the simultaneous action of FMWCNT and FGO nanomaterials greatly extended the penetration path of corrosive media. The effect of the composite coating is shown in Figure 7.



Figure 7. FGO and FMWCNTs in the PU matrix that act as shields within the coating. Reprinted with permission from [40].

Najafabadi et al. [41] prepared PU/GO nanocomposite films by adding GO to PU matrix and PU/CS–O nanocomposite films by adding chitosan-modified GO nanosheets to the PU matrix. The modification process of GO is shown in Figure 8. The results showed that the chitosan-modified GO nanocrystals had better dispersion quality in the PU matrix compared with the unmodified GO nanocrystals. In addition, the modification of GO nanosheets by chitosan not only improved the dispersion quality of the nanosheets and the thermomechanical properties of the nanocomposites, but also improved the bioavailability of carbon nanotubes, resulting in PU nanocomposites with enhanced biocompatibility and antibacterial activity.



Figure 8. The schematic illustration of the modification of GO nanosheets with chitosan. Reprinted with permission from [41].

Du et al. [42] designed and synthesized a typical multifunctional GO/PU composite material (dPTD-mFGO) containing reversible selenium bonds. The results of fourier transform infra-red (FT-IR), thermal gravity analysis-differential thermal gravity (TG-DTG), X-ray diffraction (XRD), Raman, X-ray photoelectron spectroscopy (XPS), and scanning electron microscope-energy dispersive spectrometer (SEM-EDS) showed that the functionalization of mFGO was successful. In addition, covalently grafted polymer chains on mFGO sheets can improve the dispersion and compatibility of mFGO in the dPTD matrix. The research results showed that the films prepared by introducing 2 wt% mFGO into dPTD matrix had been improved in terms of toughness, shape memory, self-healing, flame retardancy, and water resistance. Bera et al. [43] used p-phenylenediamine (PPD), hexamethylenediamine (HMD), and liquid NH₃ functionalized GO. The results showed that the functionalization of amines had positive effects on the thermal, mechanical, and other properties of composites. The cyclic tensile load-unload curve was used to evaluate the resilience of PU. The addition of GO or amine functionalized GO improved the resilience of PU, while amine-functionalized GO improved more significantly.

Mohammadi et al. [44] prepared SC4A-GO nanosheets (SGO) and BC4A-GO nanosheets (CGO) by modifying GO respectively with p-tert-butyl calixarene (BC4A) and sulfonated arene (SC4A), and prepared a new type of environmental friendly aqueous dispersion of PU nanocomposites. The specific preparation process is shown in Figure 9. The covalent surface modification of nanosheets was confirmed by FTIR, XRD, thermal gravity analysis (TGA), SEM, and wettability analysis. The modification of GO nanosheets not only overcame the flocculation problem of Water-borne Polyurethane/graphene oxide (WPU/GO) nanocomposite dispersion, but also improved the mechanical properties of WPU/CGO and WPU/SGO nanocomposite membranes. In addition, WPU/CGO was proved to have the best anti-corrosion activity by corrosion experiments, and corrosion inhibition rate could reach 99.8%.



Figure 9. Schematic diagram of specific process. Reprinted with permission from [44].

By comparing different modification methods of GO, it can be found that non-covalent modification can basically retain the structure and properties of GO itself. However, the interaction between modified molecules and GO is weak, the functionalization is not stable, and the requirements for modified molecules are high. Covalent modification can form a stable covalent bond between the reactants and GO to stabilize the existence of modified GO in the solvent and give it excellent properties. Therefore, the covalent modification of GO has been extensively studied.

6. Preparation Method of Graphene PU Composite Material

In the process of preparing graphene polyurethane nanocomposites, the surface modification of GO by various modification methods can effectively improve its dispersion in the PU matrix. In addition, the preparation method of composites is also a key factor. The preparation methods have a direct and important effect on the dispersion of modified GO, and then affects the properties of composites. At present, the preparation methods of graphene polyurethane composites mainly include six methods: solution blending, melt blending, in-situ polymerization, photopolymerization, sol-gel, and self-assembly. The six methods can be used to prepare graphene polyurethane composites, and each has its own merits.

6.1. Solution Blending Method

The blending method is usually divided into solution blending method and melt blending method. Solution blending method refers to dissolving the polymer with an appropriate solvent, then dispersing graphene nano materials by ultrasonic dispersion, and further making composites in solution. Sun et al. [45] prepared graphene/polyurethane composites by solution blending method. A certain amount of modified graphene was added to solvent polyurethane and fully stirred. The dispersion was obtained after ultrasonic crushing. After air drying, it was placed in the oven until the adhesive film was formed. Solution blending method more easily prepares molecular dispersed graphene polyurethane composites than melt blending method, but it will produce some polluting waste liquid after preparation, which will cause environmental pollution and so on.

6.2. Melt Blending Method

Melt blending method mixes graphene into the molten polymer matrix at a high temperature and makes composites by extrusion. Compared with the solution blending method, the melt mixing method is considered to be more economical because it does not use any solvent, and it is the easiest to realize for industrial production. It can not only avoid environmental pollution, but also save cost. However, when the melting point of polymer materials is high, it needs to be operated at high temperature, and this method cannot provide the same level of filler dispersion as solution mixing method and in-situ polymerization method. In addition, the thermal instability of graphene during melting will have a certain impact on the quality of extruded composites [46]. However, if the melting point of polymer is not high, it is easy to degrade when preparing polymer composites by melt blending.

6.3. In Situ Polymerization

In situ polymerization is the most commonly used preparation method of composites composed of nanoparticles and polymer materials. The reaction process fills the nano layered materials with reactive monomers, and the two undergo polymerization, that is, the fillers are directly added to the liquid monomers in the polymerization state. In situ polymerization is widely used at the experimental level. It can not only control the filling amount, but also operate easily. Dong et al. [47] added isophorone diisocyanate and polycarbonate glycol into GO dispersion to prepare PU/GO composite prepolymer under the condition of water bath of 70~80 °C, and prepared PU/GO composite through a series of chain expansion reactions. Through analysis and testing, the PU/GO composites prepared by polymerization were found to have good mechanical properties, thermal stability, and water resistance

6.4. Photopolymerization

Photopolymerization is a method of polymerization of monomers by photochemical reaction. Monomers can be polymerized directly by light excitation, or by photosensitizers and photoinitiators. The latter is also called photosensitive polymerization. This method has the characteristics of low polymerization temperature, high reaction selectivity, and easy control. It can produce reactions that cannot be carried out by ordinary molecules, and expands the means of obtaining polymers. The light sources used in photopolymerization are mainly high-pressure or medium pressure mercury lamp (discontinuous light) and xenon lamp (continuous light). Photopolymerization is widely used in coatings, paints, surface treatment, and other fields. Seda Akhan et al. [48] prepared polyurethane graphene nanocomposites with self-healing properties by photopolymerization and polymerized

the free films under a high pressure UV lamp. Electrochemical analysis showed that the microencapsulated films had high polarization resistance and low corrosion current.

6.5. Sol-Gel Method

Sol-gel method is a method for preparing composite materials by means of sol and gel process of inorganic salts [49]. The sol gel method has low requirements for reaction conditions and can be carried out under mild conditions. Moreover, the sol-gel method does not require a lot of organic solvents to prepare composite materials, which will not cause much harm to the environment and human body. Wang et al. [50] prepared functionalized graphene-reinforced polyurethane nanocomposite coatings by sol-gel method. When the mass fraction of graphene was 2.0%, the tensile strength of the nanocomposite was 71% higher than that of pure aqueous polyurethane due to the uniform dispersion of functionalized graphene in the PU matrix and the strong interfacial interaction between them.

6.6. Self-Assembly

Self-assembly is a technology in which basic structural units (molecules, nano materials, materials of micron or larger scale) spontaneously form ordered structures. In the process of self-assembly, the basic structural units spontaneously organize or aggregate into a stable structure with regular geometric appearance under the interaction of non-covalent bonds. Shi Zet al. [51] prepared RGO-coated PU composite foam by self-assembly method. The GO was coated on the foam skeleton by self-assembly of hydrogen bonds between GO and the oxygen groups on the PU foam.

7. Coating Preparation Processes

7.1. Laser Cladding Technology

Laser cladding technology is the simultaneous, instantaneous melting and rapid solidification of the required alloy powder with the very thin surface of the substrate, forming a dense metallurgical bonded clad alloy layer on the substrate. Laser cladding offers a wide choice of cladding materials due to the fine organization of the cladding layer, which can be used to achieve high corrosion resistance, high wear resistance, high hardness, and other performance requirements. The main production methods of laser cladding are divided into the pre-set cladding method and the simultaneous powder feeding method [52]. The pre-setting method has a long process flow, complex procedures, poor coating uniformity, high laser power requirements, and the decomposition of the bonding agent can easily cause contamination of the clad layer, which may form defects such as porosity and cracking. The advantage of synchronous powder feeding is that the process is relatively simple and can be controlled automatically with high efficiency, which has been popularized and applied in many enterprises. Currently, ultra-high speed laser cladding technology is very popular. Compared with ordinary laser cladding technology, ultra-high speed laser cladding technology forms finer tissues; however, there are defects caused by unmelted particles and uneven heat distribution of the spot on the surface of the clad layer during the cladding process. To improve the surface quality of the cladding layer, post-treatment is required. Bai et al. [53] prepared iron-based coatings by high-speed laser melting and strongly spun the outer surface of the coatings, and the results showed that the strongly spun coatings exhibited higher corrosion resistance than the untreated coatings. Zhang et al. [54] prepared graphene-reinforced Ti6Al4V composite coatings with good bonding of graphene to the Ti6Al4V substrate.

7.2. Electron Beam Melting Technology

Electron beam cladding technology uses high energy electron beam into the material; the energy is instantly deposited on the surface of the coating, generating heat to make the coating material melt, the substrate partially melts, and the substrate and coating combine to form a coating, improving the surface properties of the material. Electron beam coating is applied to the surface of the coating material by thermal spraying, binder, press, and other processing methods; pre-coating a layer of alloy powder coating with thickness ranging from a few microns to a few millimeters and with special physicochemical properties; and then using high energy density electron beam to irradiate and scan the surface of the coating material. The treated coating instantly melts and fuses with the substrate to form a new alloy layer, thus obtaining the structure and properties compatible with the design requirements. The structure and properties of the coating are compatible with the design requirements, i.e., a coating with wear resistance, corrosion resistance, and high temperature oxidation resistance [55]. Wang et al. [56] prepared single-, double-, and triple-layer WC-40Co coatings by electron beam cladding and analyzed the wear resistance and corrosion resistance of the coatings, which showed that the wear resistance of the coatings increased with the number of cladding layers and could reach 11.5 times the wear resistance of the substrate. The corrosion resistance of the single- and double-layer coatings was better than that of the substrate, however, the surface of the triple-layer coating was significantly damaged by cracks.

7.3. Thermal Spraying Technology

Thermal spraying technology includes flame spraying, plasma spraying [57], laser spraying [58], etc. The use of a heat source to atomize the material with the help of high-speed gas will be sprayed on the surface of the substrate and quickly cooled and deposited into a certain function of the coating technology. Thermal spraying technology can generally prepare anti-oxidation, corrosion resistance, wear resistance, and other coatings. Thermal spraying technology has been widely used in aerospace, marine field, automotive field, petrochemical field, etc. The coating materials for thermal spraying can be chosen from metals, alloys, ceramics, and composites. Thermal spraying technology can be used for a wide range of substrates and coatings, with no restrictions on size and shape and little deformation of the workpiece. In the spraying process, the influence on the performance of the substrate is small, the coating thickness control range is large, and the coating thickness usually reaches 100–400 µm, but in the spraying of smaller areas of the parts, the economy is poor. When preparing coatings by thermal spraying, the cleanliness and roughness of the substrate surface affects the bonding properties, so the substrate is usually subjected to surface cleaning and roughening processes before spraying. Muzika Lukáš et al. [59] prepared metal coatings using three different spraying methods: twin-wire arc spraying (TWAS), flame spraying (FS), and high-speed oxygen fuel spraying (HVOF). Forati Tahmineh et al. [60] used atmospheric plasma spraying and high speed oxygen fuel as a Cu-graphene nanosheet composite coating to develop a multifunctional and scalable surface engineering technique. The results showed that the corrosion resistance of Cu with the coating was improved by 89% compared to the Cu surface without the coating.

7.4. Brazing Technology

Brazing is a material joining method that enables a tight metallurgical bond to be formed between the base material and the additive material. Compared with other welding methods, brazing technology is more suitable for the preparation of coatings on single crystal high temperature alloys. The most important feature of brazing is that the welding temperature is low and the base material does not melt, reducing the possibility of recrystallization and warming; the brazing process uses the wetting and solidifying effect of the molten brazing material to connect with the base material, so the strength is higher than that of spray coatings [61]. However, the diffusion and reaction of C and Si elements at the interface during the brazing process can destabilize the structure. Wang et al. [62] improved the performance of vacuum brazed NiCr-Cr3C2 coatings on single crystal high temperature alloys by adjusting the Cr content to control the amount of Si or C diffusion into the base material.

7.5. Vapor Deposition Technology

Vapor deposition technology is divided into physical vapor deposition (PVD) and chemical vapor deposition (CVD), and as a new green coating technology, PVD is widely used in mechanical, electronic, and optical industries because of its high hardness, good wear resistance, low friction coefficient, stable chemical properties, and heat and oxidation resistance. To protect the substrate against corrosion by PVD technology, the coating must be well shielded and isolated from the corrosive medium and the substrate material, and the coating itself must be stable in the corrosive medium and maintain a low corrosion rate. The corrosion resistance of coatings can be improved by selecting the appropriate chemical composition, reducing the growth and preparation defects to obtain a dense and uniform coating structure, increasing the coating thickness, using a multilayer film structure, pretreating the coating, and adding a transition layer [63]. Jiang et al. [64] laminated pure Mg films onto hot-dip coated Zn-55Al-1.6Si steel by PVD, varying the Ar gas pressure and deposition. It was found that the lamination of Mg film enhanced the corrosion resistance, which was significantly affected by the thickness of Mg film, especially for the cross section by a factor of 2–10.

Chemical vapor deposition (CVD) is a technique in which various gases are introduced into a reaction chamber where a chemical reaction occurs on the surface of a substrate and the resulting solid products are deposited on the surface to form a thin film. These gases include gaseous reactants or vapors of liquid reactants that can form thin film elements, as well as other reaction gases. In order to obtain specific thin films by CVD, it is necessary to select the appropriate reaction method and to determine parameters such as temperature, gas composition, concentration, and pressure [65]. Nadeem Aamir et al. [66] deposited boron nitride-based coatings on mild steel substrates by chemical reaction of boron powder and ammonia gas in a CVD apparatus at 1200 °C. It was shown that the salt resistance of the boron nitride nanosheet coating was six times higher than that of bare mild steel. Samira Naghdi et al. [67] performed chemical vapor deposition of graphene on molybdenum and platinum at atmospheric pressure and showed that graphene exhibited good protective properties and could be used as a corrosion barrier.

7.6. Surface Composite Ion Treatment Technology

Surface composite ion treatment is a surface treatment process that combines two or more surface technologies to prepare composite coatings, film layers, and composite modified coatings. It includes ion implantation compounded with coating technology, laser or electron beam compounded with vapor deposition technology, and plasma spray compounded with laser technology. In ion-beam-assisted deposition processes, ion bombardment can increase the density of the film, eliminate or reduce the inherent stresses in the film layer, and improve the properties of the film layer, and a wide transition zone between the film atoms and the substrate atoms can be obtained by ion bombardment, which is extremely beneficial for improving the film/substrate bond. Xu et al. [68] deposited in situ graphene/silicon carbide composite coatings with <111> orientation by laser chemical vapor deposition using hexamethylsilane as a precursor. The study of the growth mechanism showed that the photolytic effect of the laser played an important role in the deposition process.

The coating preparation process is not only related to the characteristics of the coating itself, but also influenced by a variety of factors, such as the type of substrate, the performance of the coating, the type of application environment, and the functional requirements of the coating. With the advancement of science and technology, the coating preparation process and technology are developing rapidly in the direction of intelligence, efficiency and advancement. All the preparation processes introduced above can prepare anti-corrosion coatings, and at present, thermal spray technology, laser cladding technology, and vapor deposition technology are more widely used.

8. Conclusions and Prospect

Graphene materials have great application potential in the coating field. GO, as a nano-filler, can effectively improve the mechanical properties and anti-corrosion properties of PU coatings. Due to the large number of oxygen-containing functional groups on the surface of GO, it can be directly added to the PU matrix as a nano-filler. However, the performance of the composite will be reduced because of their strong interaction. Therefore, modification of GO is essential. Modified GO can react better with the PU matrix and have better dispersion in the PU matrix, so the performance of the composite material will be significantly improved. Considerable progress and development has been made in the application of GO, which mainly includes the following aspects:

- (1) Further research should be carried out on the optimization of the modification mode of GO. The non-covalent modification retains the complete structure and properties of graphene materials, but the relationship with the substrate is unstable and prone to being destroyed. While covalent modification can effectively improve the reaction and compatibility between GO and polymer, it will inevitably destroy the internal structure, thus affecting the performance of graphene materials. Therefore, it is an important research direction to study a new modification method that can modify GO without destroying its structure.
- (2) Among the currently adopted modification methods, a large part of the research is to prepare RGO by reducing GO as precursors and using reducing agents to repair the GO structure and restore its properties. However, most of the previous reducing agents are toxic substances, which cannot meet the environmental requirements in the new era, so it is necessary to try to develop the use of new, green, and non-toxic reducing agents to restore GO. Second, restoring the structure and properties of GO by reduction reaction is also an important research direction. It is necessary to strengthen the research on the mechanism of structural changes of graphene materials and use it as a guide to explore new and more effective reducing agents that can restore the structure of GO to the maximum.
- (3) The application mechanism of graphene materials in coating is mainly the barrier effect generated by its lamellar structure. When the graphene nanomaterials are arranged horizontally in the layer, that is, parallel to the surface of the substrate, they have the best barrier performance. Therefore, the directional arrangement of graphene materials in coatings plays an important role in the performance of graphene nanomaterials. In the future, researchers should pay more attention to the directional arrangement of graphene nanomaterials.
- (4) The superior and inferior properties of graphene polyurethane composites are closely related to their dispersion properties, and the preparation processes such as mechanical stirring time, ultrasonic dispersion degree, graphene content, and type of solvent added directly affect the dispersion properties of graphene. Therefore, optimization of the preparation process can improve the performance of composites to some extent. At present, for the characterization of the dispersity of composites, electron microscopy is mainly used to observe the morphology and structure of the particles. Although possessing the advantage of being intuitive analysis of the dispersity of materials. Therefore, using a quantitative way of characterization to precisely evaluate the dispersion performance of composites, establishing the link between individual preparation processes and dispersion performance, is a future research direction.

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