Proceedings of the 2nd International Conference on Functional Materials and Civil Engineering
DOI: 10.54254/2755-2721/89/20241049

Application of bio-based modified graphene oxide in epoxy composite coatings

Yang Zhang

Faculty of Civil Engineering, Central South University, Changsha, Hunan, 410083, China

8406210214@csu.edu.cn

Abstract. This study focuses on the application of bio-based modified graphene oxide epoxy composite coatings and analyzes the coating properties, such as anticorrosive ability, hydrophobicity and self-healing properties, through experimental studies of modified graphene oxide using substances such as cashew nut phenol, lignin and glutamic acid. Summarizing the latest research progress, it is found that the materials such as cardanol, lignin and glutamic acid are from a wide range of sources, are green and have a wide range of application prospects, and it is also shown in the results of EIS analysis that the modified graphene oxide epoxy compliant coatings exhibit higher impedance values at low frequencies, and have good protective properties and barrier properties. The cashew phenol-modified graphene oxide epoxy coating has high densification, high barrier capacity and high hydrophobicity in addition to good coating healing ability using GO modification. The glutamate-modified graphene oxide epoxy coating can be desorbed by using HCL solution to make L-Glu/GO reusable, with good reusability and high application value.

Keywords: Graphene oxide, bio-based, epoxy resin, glutamic acid, cashew nut phenol.

1. Introduction

China in the "14th Five-Year Plan" pointed out the importance of environmental protection, to promote the construction of ecological civilization, reduce carbon emissions intensity, the State Council in October 2021 on "do a good job of carbon peak carbon neutral" work pointed out that: to save energy resources The State Council in October 2021 on "doing a good job of carbon peak carbon neutral" pointed out that: to put the conservation of energy and resources in the first place, the implementation of a comprehensive conservation strategy, and continuously reduce energy and resource consumption and carbon emissions per unit of output, to carry out iron and steel, building materials and other key areas of capacity. At present, with the importance of the marine economy highlighted, the main body of the marine economy: traditional metal materials as the main body of the production of major marine infrastructure and engineering equipment and the use of corrosion during the period will cause huge pollution of the environment. According to the results of research, over the past 50 years, the economic losses caused by corrosion have been equivalent to 3%-4% of each country's GDP, the global cost of etching is estimated to be 2.5 trillion dollars [1]. For the purpose of decreasing the losses which caused by corrosion, many ways to delay metal corrosion have been developed by human. For example, alloying, heat treatment, corrosion inhibitors coatings, etc [2]. Therefore, research on corrosion prevention of traditional metal materials is of great economic and environmental importance.

Among them, the organic coating is easy to attach to the surface of the metal material, and the anti-corrosion protection of the metal substrate are characterized by low cost, fast construction and excellent corrosion resistance [3, 4]. Epoxy resin coatings are widely used as organic coatings because they have good adhesion to metal surfaces and excellent chemical properties [5]. However, pure epoxy resin coatings are often used in combination with two-dimensional materials, such as graphene and its derivatives, molybdenum disulfide, and boron nitride, due to their high brittleness, low densification, and poor resistance to mechanical and thermal shocks.

Graphene is a new type of two-dimensional material consisting of carbon atoms in a monolayer lamellar structure with layers of sp2 hybridized carbon atoms. It also has a two-dimensional layer of semi-aromatic system formed by sp^2 hybridized carbon atoms in the form of hexagons. This carbonaceous compound has a number of features in its outermost layer, including different oxygen-containing groups such as -COOH and -OH. whereas graphene oxide (GO), a chemically oxidized derivative of graphene, also has a two-dimensional lamellar structure, in addition to an abundance of hydrophilic oxygen-containing functional groups on its surface. This makes GO different from traditional two-dimensional materials in addition to good barrier and shielding protection performance, but also has other more excellent performance. In particular, the carboxyl group of GO can easily combine with the carboxyl group on the side chain of aqueous polymers to form hydrogen bonds, which improves the dispersion ability in anticorrosive coatings. In addition, GO will esterify with the polymer molecular chain during the drying and curing process of polymer-based anticorrosive coatings, forming a crosslinked network structure, which effectively improves the stability and adhesion of anticorrosive coatings [6].

In view of the application of graphene oxide and its derivatives in composite anticorrosive coatings, the idea focuses on the study of graphene and epoxy resin coatings. At present, the review of the research on the application of bio-based modified graphene oxide in epoxy resin composite coatings is still limited to the study of two substances, cardanol and lignin, on epoxy resins, so the aim is to help readers quickly and clearly understand the characteristics of the bio-based modified graphene oxide epoxy resin coatings by synthesizing the latest progress of the relevant research.

2. Discussion

2.1. Cardanol

Cardanol is an oil derived from natural cashew nutshell oil from advanced technology The unsaturated alkylphenolic structure makes CO an important component in the preparation of polymer resins [7]. The unsaturated alkylphenolic structure makes CO Because of its volatility and low viscosity, it is a suitable choice for the preparation of reactive diluents for petroleum-based epoxy resins. On the one hand, because it has admirable compatibility with petroleum-based epoxy resins. The viscosity of the resin can be effectively decreased by adding the decent amount of cardanol, thereby reducing the consumption of organic solvents as well as petroleum-based epoxy resins. On the other hand, it can be concerned with the curing reaction and be conducive to form a compact three-dimensional cross-linked structure. A suitable cross-linking density can inhibit propagation and dispersal of corrosive materials, thus improving a number of the intrinsic properties of the epoxy resin layer, such as mechanical properties, water resistance and corrosion resistance [8, 9].

Zhang et al. prepared a epoxy coating rich in cardanol with high long-term anticorrosive properties. By using a cardanol up to a maximum weight fraction of 40 wt% and its modified graphene oxide nanomaterials, three factors determining the anticorrosive properties of the epoxy coatings (i.e., degree of cross-linking, filler barrier, and hydrophobicity) were synergistically optimized, and it was found that the cashew nut phenol-modified graphene oxide epoxy coatings possessed high densification, high barrier capacity, and high hydrophobicity, which resulted in superb durability against corrosion over time [10]. Two types of microcapsules containing either a cashew nutphenol-based resin or a cashew nutphenol-based curing agent were prepared by solvent evaporation method by Wu et al. Nano-sized epoxidized GO (E-GO)/cashew-nut phenol-based epoxy resin and aminated GO (A-GO)/cashew-nut phenol-based curing agent were encapsulated in two different sets of capsules to improve the barrier properties of the coatings after curing some of the scratches. The study revealed that the self-healing coating capability of the graphene oxide (GO)-modified capsules exhibited a remarkable enhancement of up to three orders of magnitude compared to the healing performance of the non-GO microcapsules, as measured by the low-frequency impedance modulus after being immersed in a 3.5 wt% NaCl solution for 60 days. In addition to the healing of the capsules modified with GO upon intrusion into the NaCl solution and air, demonstrating that the coatings are highly applicative and multifunctional [11].

2.2. Lignin

Lignin is an amorphous polymer consisting of phenylpropane units connected by carbon-carbon and ether bonds, and is the second largest reserve in the plant kingdom after cellulose. Biomass resources Lignin is produced annually by the paper and bioethanol industries, which produce nearly 100 million tons of lignin, most of which is used for combustion and electricity, despite the fact that less than 2% of the lignin material is employed as dispersants and additives [12]. And as a typical biomass material , lignin is not only one of the few renewable resources of aromatic compounds one of the few renewable resources, but it is also the only aromatic compound glutamate that is available in large quantities at relatively low cost (i.e., $50-750 per ton) [13]. Therefore, the application of lignin to the field of epoxy coating provides a good way to replace fossil resources and achieve the goal of renewable and sustainable development of resources.

Wang et al. prepared lignin-OH/graphene/WEP nanocomposites by a facile green pure water production route. Through electrochemical impedance spectroscopy, the results showed that the composite coatings exhibited excellent corrosion resistance compared to graphite/WEP and pure WEP at an addition of only 0.5% due to the good dispersion of lignin-OH/graphene in the matrix [14]. Xu et al. proposed a method that by modifying GO using lignin and pyridine derivatives, composite coatings with smart corrosion resistance were prepared in combination with epoxy vinyl ester resins. During the Tafel analysis, the findings revealed that ATGO-CM possessed minimal corrosion current density and substantial corrosion potential, attaining a coating protection efficacy of nearly 100%, which provided significant protection against galvanic corrosion [15].

2.3. Glutamic acid

L-Glu is a naturally occurring amino acid with hydrophobic properties that improve the separation of GO in water bodies [16]. Also, it is widely sourced and characterized by non-toxicity and green environmental protection. At the same time, L-Glu is also a green corrosion inhibitor, in which the amino and carboxyl groups can form complexes with iron ions, reduce the activity of iron ions, and play the role of corrosion inhibition on metals.

In anticorrosive applications, Ding et al. modified graphene oxide (GO) with L-glutamic acid (L-Glu) to improve the dispersibility of GO, and then doped the modified graphene oxide (L-GO) into epoxy resin (EP) as a filler to prepare L-GO/EP coatings. The morphology and surface properties of GO were analyzed by many experimental setup (XPD,FTIR and SEM)before and after the modification, and it was concluded that, compared with EP coatings, the GO-added coatings produced fewer corrosion products at scratches, whereas the L-GO-added coatings did not have any obvious corrosion products on the surface, which indicated that the L-GO-added coatings played an important role in the metal. GO coating has a better anti-corrosion effect on the metal. The electrochemical impedance test results revealed a substantial decline in the corrosion current density of the L-GO/EP coating when compared to the EP coating, following immersion in a 3.5% NaCl solution for 10 days. This underscores the excellent protective performance of the L-GO/EP coating against electrochemical corrosion on the mild steel surface [17] .

In the heavy metal adsorption application, Li et al. prepared GO by Hummers method and modified it with L-Glu to obtain L-Glu/GO.The experiments on static adsorption of Cu^{2+} by L-Glu/GO showed

DOI: 10.54254/2755-2721/89/20241049

that the adsorption of Cu^{2+} by L-Glu/GO could reach equilibrium only in 10 min, and the maximal adsorption amount of L-Glu/GO could be up to 292.460 mg/g in certain conditions. The maximum adsorption capacity of L-Glu/GO under certain conditions could reach 292.460 mg/g. The adsorption rate of L-Glu/GO on Cu^{2+} was determined after five repetitions. Cu^{2+} The adsorption rate of the L-Glu/GO made in this study was still above 92% after five repeated adsorption-desorption cycle tests, which indicates that the L-Glu/GO is reusable and has a high value of sustainable application [18] . Meanwhile, Li et al. further found the reaction between L-glutamic acid functionalized graphene oxide and its adsorption on U(VI) was a nucleophilic reaction of the amino group on L-glutamic acid attacking the epoxy group on GO, and also discovered that L-Glu/GO could be reused by desorbing the adsorbent with HCL solution, which further enhanced its economic and environmental value [19].

3. Conclusion

The study illustrates that the application of bio-based modified graphene oxide epoxy composite coatings was discussed in depth and it was concluded that this kind of coating is to functionally modify graphene oxide (GO), introduce specific groups to improve its dispersion and compatibility in the resin, and then add the modified GO (such as ATGO) as a filler to the epoxy vinyl ester resin. Under heating conditions, the free radical polymerization reaction of double bonds is initiated, so as to prepare composite coatings. At the same time, compared with the traditional solvent-based heavy anti-corrosion epoxy coating, the epoxy composite coating of bio-based modified graphene oxide is more environmentally friendly and solvent-free, avoiding environmental pollution and the risk of solvent retention during coating. Through the review and summary of the latest related research, it is found that it has the following characteristics: 1. Cardanol, lignin and glutamic acid and other materials have a wide range of sources, green environmental protection, and wide application prospects, which are in line with the theme of sustainable economic development today. 2. The anti-corrosion performance of bio-based modified graphene oxide epoxy composite coating is better than that of unmodified composite coating, which not only has a good protective effect against salt spray corrosion, but also has a very good barrier and inhibition effect on metal electrochemical corrosion. 3. Cardanol-modified graphene oxide epoxy coating not only has good coating healing ability, but also has high density, high barrier ability and high hydrophobicity under GO modification. 4. Glutamate-modified graphene oxide epoxy coating can be deactivated and adsorbed by using HCL solution, so that L-Glu/GO can be reused, with good reusability and high application value.

References

[1] Nazari, M.H., et al., Nanocomposite organic coatings for corrosion protection of metals: a review of recent advances. progress in Organic Coatings,. 2022. 162: p. 106573.
[2] Wang, S., et al., Co-modification of nano-silica and lysine on graphene oxide nanosheets to enhance the corrosion resistance of waterborne epoxy coatings in 3.5% NaCl solution. polymer, 2021. 222: p. 123665.
[3] Cheng, L., et al., Polydopamine modified ultrathin hydroxyapatite nanosheets for anti-corrosion reinforcement in polymeric coatings. corrosion Science, 2021. 178: p. 109064.
[4] Sun, J., et al., Silane functionalized plasma-treated boron nitride nanosheets for anticorrosive reinforcement of waterborne epoxy coatings. Progress in Organic Coatings, 2022. 167: p. 106831.
[5] Liu, T., et al., Smart protective coatings with self-sensing and active corrosion protection dual functionality from pH-sensitive calcium carbonate microcontainers. Corrosion Science, 2022. 200: p. 110254.
[6] Cheng, Qiu. , Advances in the study of polymer-based graphene anticorrosive materials. 2024.
[7] Wang, H., Making alkyd greener: modified cardanol as bio-based reactive diluents for alkyd coating. progress in organic coatings, 2019. 135: p. 281-290.

DOI: 10.54254/2755-2721/89/20241049

[8] Zhong, F., et al., Graphene/V2O5@ polyaniline ternary composites enable waterborne epoxy coating with robust corrosion resistance. reactive and Functional Polymers, 2020. 151: p. 104567.

[9] Zhang, F., et al., Application of polyether amine intercalated graphene oxide as filler for enhancing hydrophobicity, thermal stability, mechanical and anti-corrosion properties of waterborne polyurethane. Diamond and Related Materials, 2020. 109: p. 108077.

[10] Zhang, Y., et al., Synergistically enhancing the performance of cardanol-rich epoxy anticorrosive coatings using cardanol-based reactive diluent and its functionalized graphene oxide. Progress in Organic Coatings, 2022. 171: p. 107060.

[11] Wu, W., et al., Fabrication of graphene oxide-modified self-healing microcapsules for Cardanol-based epoxy anti-corrosion coatings. progress in Organic Coatings, 2023. 183: p. 107777.

[12] Zhang, X., et al., Lab-scale structural insulated panels with lignin-incorporated rigid polyurethane foams as core. industrial crops and products,. 2019. 132: p. 292-300.

[13] Ľudmila, H., et al., Lignin, potential products and their market value. Wood Res, 2015. 60(6): p. 973-986.

[14] Wang, S., et al., Green synthesis of graphene with the assistance of modified lignin and its application in anticorrosive waterborne epoxy coatings. Applied Surface Science, 2019. 484: p. 759-770.

[15] Xu, C.-A., et al., Mimosa inspired intelligent anti-corrosive composite coating by incorporating lignin and pyridine derivatives grafted graphene oxide. Chemical Engineering Journal, 2024: p. 149316.

[16] Zhou, W., et al., Surface functionalization of graphene oxide by amino acids for Thermomyces lanuginosus lipase adsorption. journal of colloid and interface science, 2019. 546: p. 211-220.

[17] Ding W., Preparation and anticorrosive properties of L-glutamic acid modified graphene oxide composite epoxy resin coating. 2024.

[18] Li Shiyou, et al., Adsorption of Cu~(2+) by L-glutamic acid modified graphene oxide. Chemical Environmental Protection, 2020. 40(04): p. 418-424.

[19] Li, Shiyou, et al., Preparation of L-glutamic acid functionalized graphene oxide and its adsorption study on uranium. Journal of Safety and Environment, 2019. 19(01): p. 231-238.