Preparation and properties of GO-SiO$_2$ anticorrosive coatings

X L Bai$^{1,2}$, B Wu$^1$, K Jiang$^1$, C J Liu$^1$, H Zhang$^1$, F Zhang$^1$, X Huang$^1$, M J Cai$^1$ and P F Wang$^1$

$^1$PLA Army Academy of Artillery and Air Defense, Hefei 230031, China

E-mail: xlbai@ustc.edu

Abstract. Epoxy resin is often used as raw material of anticorrosion, but in the curing process of resin, a large number of micropores are prepared in the solvent evaporation method, which reduces the performance of anticorrosion. In order to reduce internal defects and improve corrosion resistance, GO was compounded with SiO$_2$ modified by KH550 to prepare for GO-SiO$_2$. By means of mechanical stirring and ultrasonic dispersion, GO-SiO$_2$ was added to epoxy resin to prepare for the anticorrosive coating. SEM was used to observe the coating morphology, and the physical and electrochemical properties of the coatings with different mass fractions of GO-SiO$_2$ are tested for corrosion resistance. The results show that 3 wt% GO-SiO$_2$ coating shows the best performance, the coating hardness reaches H, the adhesion grade is II.

1. Introduction

Currently, corrosion costs are increasing, and preventive strategies have become an important industrial demand. Anticorrosive coatings on metal surface can play the role of shielding, passivation and electrochemical protection, which is of great significance to the research of metal corrosion and protection. Epoxy resin (EP) is a common anticorrosive coating with good chemical resistance, high temperature resistance, toughness and bonding ability. However, the outdoor weather resistance is poor, the brittleness of the coating film is high, and the volatilization during the curing process will cause many micro-holes inside the coating, which will reduce the corrosion resistance of the coating.

Graphene oxide (GO), a product of chemical stripping of graphite, has a two-dimensional lamellar structure and similar unique properties to graphene [1,2]. At the edge of GO, there are a large number of oxygen-containing functional groups such as epoxy groups, hydroxyl groups, ketones and carboxyl groups. These functional groups provide many active sites for the functionalization of GO, enabling it to be functionalized with organic and inorganic materials through chemical crosslinking to form stable chemical bonds [3,4]. Krishnamoorthy et al were prepared to have good antibacterial properties and prevent fouling heat resistance of graphene oxide modified alkyd resin coatings. The results show that the mechanical properties and corrosion resistance of graphene oxide coatings are improved, and the most important and anticorrosive properties are improved [5]. Jiang et al studied the influence of modified GO by active amino silane precursor on the corrosion resistance of epoxy coating and found that the modified GO by adding silane coupling agent could effectively promote the interface adhesion strength of coating and improve the corrosion resistance of coating [6].

Ramezanzadeh developed a sol-gel film on the basis of silane film, which is filled with GO nanosheets to improve corrosion resistance of EP coating and cathodic stripping performance on steel substrate [7].

Compared with GO, the coating with GO-SiO$_2$ has better mechanical properties, which may be due
to the fact that GO-SiO$_2$ can increase the crosslinking density between coatings, make the arrangement between particles in the coating more orderly, effectively improve the permeability resistance of the coating, and further improve the corrosion resistance of the coating [8-10]. Ma et al found that by adding nano SiO$_2$/graphene oxide compounds, epoxy resin coating anticorrosion performance compared to the pure epoxy resin coating as well as adding SiO$_2$ separately and GO nano filler of epoxy resin coatings, the anticorrosion performance improved significantly [11] Wang et al studied the self-healing and corrosion resistance of GO-mesoporous silicon layer nanostructure coating, and believed that there was a synergistic enhancement effect [12]. Compared with the pure EP coating, the hardness, adhesion and corrosion resistance of nano SiO$_2$-GO/EP are obviously enhanced [13]. The mutual barrier between GO and SiO$_2$ is used to inhibit the agglomeration of each other, and meanwhile, the synergistic modification effect of the two on EP is given full play, which is also reflected in other fields [14,15]. At present, many scientific mechanisms related to GO-SiO$_2$ anticorrosive coatings, such as dispersion problems, synergistic enhancement effects and interface problems have not been clarified.

GO-SiO$_2$ composite material is an ideal resin filler with excellent properties. SiO$_2$ particles are evenly distributed on graphene sheets, the two-dimensional structure of graphene is increased to three-dimensional structure. With such a special three-dimensional structure, it is not easy to overlap between graphene sheets and form a "stacked" structure coating. This method overcomes the disadvantage that GO and SiO$_2$ are easy to agglomerate and improves the dispersion performance significantly. The epoxy resin can be strengthened and toughened by adding the composite material to the resin matrix, and the corrosion resistance of the coating can be improved.

2. Experiment

2.1. Materials

Nano SiO$_2$ is provides by Shanghai Aladdin Biochemical Technology Co., LTD. Silane coupling agent, gamma-aminopropyl triethoxy silane (KH550), concentrated H$_2$SO$_4$, KMnO$_4$, NaNO$_3$, HCL, anhydrous ethanol, N, n-dimethyl formamide (DMF), acetone, NaCl are obtained from Sinopharm Chemical Reagent Co., LTD. All of the above are pure analysis. GO(>99 %) is provided by SuZhou TanFeng Graphene Technology Co., LTD..

2.2. Preparation of GO–SiO$_2$

SiO$_2$ was dried for 24 h in an electric thermostatic air drying oven at 100℃.10 g SiO$_2$ was added to 100ml anhydrous ethanol and deionized water mixture with a volume ratio of 3:1 for 30 min. Add 5 g KH550 to 50 ml anhydrous ethanol, adjust pH to 3 with acetic acid, stir magnetically for 1h, add to the above solution and stir in constant temperature water bath at 75℃ for 3h. Then wash repeatedly with anhydrous ethanol to remove the physically adsorbed silane coupling agent and reaction by-products on the surface, and dry in vacuum drying box at 60℃ for 12 h to obtain modified SiO$_2$.

0.1 g of modified nano SiO$_2$ was added to 200 ml of n, n-dimethyl formamide DMF, and ultrasonic dispersion was used for 30 min. 0.3 g of GO was added to the above solution, and ultrasonic dispersion was continued for 30 min. The mixed solution was put in an oil bath at 105℃ for about 4 h of magnetic stirring. After the reaction, the solution was filtered, washed with anhydrous ethanol for 3 times, and then dried in a vacuum drying box at 60℃ for 24 h for grinding.

2.3. Preparation of coatings

The mass percentage of GO–SiO$_2$ was 0 wt%, 1 wt% and 3 wt% of coating powder, and the samples were numbered as GS-0(EP), GS-1 and GS-3, respectively. The epoxy resin and GO were mixed evenly by dispersion-machine agitation, and the rotation speed was 1000 R/M for 20–30 minutes. Appropriate defoaming agent and curing agent are added in the state of mechanical agitation. Ultrasonic dispersion of the stirred slurry was conducted for 2 hours to obtain the GO-SiO$_2$ coated slurry. Planet ball mill (Nanjing NanDa Instrument Plant) is made of zirconia. After consulting
relevant literature, set the appropriate milling parameters, zircona ball of the ball diameter \( \Phi_5 \), respectively, \( \Phi_3 \), the ratio of its quality for \( \Phi_5 : \Phi_3 = 3:2 \). Ball material ratio of 2:1, ball mill speed of 220 R/M, ball grinding time of 4 h. Steel 616 (22SiMnTiB) is a low alloy high strength steel. The thickness of the plate used in this paper is 200 microns, and the alloy substrate is cut into 4 cm×4 cm block by the plate cutter. The glass rod is evenly coated on the treated steel sheet, and the hanging sheet is solidified for 3 days in an electric thermostatic air-drying oven at 60℃.

2.4. Characterization
Scanning electron microscope (SEM, jeol-jsm-6700f) was used to observe the surface morphology and interface morphology of the coating. The corrosion resistance of salt spray coating is characterized by salt spray test. The coated steel 616 sheet was put into the salt spray test chamber, and the temperature of the salt spray test chamber was controlled at 35℃. The relative humidity of the salt spray test chamber was > 95%. 5% NaCl solution was sprayed with steam through the action of air compressor, and the ph of the atomized NaCl solution remained neutral. The steam volume flow rate is sprayed at the speed of 1.2 ~ 2.0 mL.h⁻¹ per 80 cm². Water resistance was tested according to GB/T11733-1993, acid/alkali resistance according to GB/T9274-1988. Mechanical properties test coating flexibility test according to GB/T1731-1993, pencil hardness test according to GB/T1731-2006, adhesion test according to GB/T 9286-1998.

3. Results and discussion
3.1. Morphology of GO–SiO₂ coating
SEM was used to observe the surface and cross-sectional morphology of the coating, and to compare the differences of the microstructural morphology of GS-0 samples (EP). GS-1 GS-3 was used to investigate the effect of GO-SiO₂ on the microstructural morphology of the coating. It can be seen from figure 1 that after mixing with the ball mill, the coating materials are evenly distributed, and the mixing effect is good. No particles of large size appeared on the coating surface. Particle size was refined by ball grinding to achieve satisfactory results. No agglomeration of go was observed on the surfaces of the doped GO coatings (samples GS-1 and GS-3), suggesting that GO was well mixed with the coating slurry and dispersed in the coating slurry after mechanical agitation and ultrasonic dispersion. It can be seen from the SEM photos of the surface morphologies of samples GS-0, GS-1 and GS-3 that the coating surface is relatively flat, indicating that the coating prepared by coating method has a good surface state. As shown in figure 1(c), cracks 5 to 10 microns wide appeared on the surface of sample GS-1. The cracks on the coating surface are caused by the volume shrinkage of SiO₂ based coating paste during solidification and sintering, which makes it easy to produce relatively large internal stress in the coating, and the internal stress will be concentrated in local areas. When the concentrated stress is greater than the bonding strength inside the coating, the crack will occur. In figures 1(b), 1(d) and 1(f) it can be seen that pore structures of different sizes appear on the surfaces of samples GS-0, GS-1 and GS-3.Compared with sample GS-1, the aperture of pore structure on the surface of sample GS-3 is smaller, and the size and quantity of pore structure on the coating surface of sample GS-3 are smaller than that of sample GS-0. This means that the doped go expands in the coating. Other coating components attach to the surface of GO.

Compared with samples GS-0 and GS-1, the pore structure on the surface of sample GS-3 is smaller in diameter, and the pore structure size of the coating surface of sample GS-3 is smaller than that of sample GS-0, and the number is less, and the flake increases. It indicates that GO-SiO₂ expands in the coating, and the coating is connected into a whole, and the coating organization is more compact.
3.2. Morphology of coating

![Figure 1](image1.png)

**Figure 1.** SEM photos of coating surface morphology. (a) (b) sample GS-0; (c) (d) sample GS-1; (e) (f) samples GS-3.

![Figure 2](image2.png)

**Figure 2.** SEM photos of cross-section morphology. (a) (b) sample GS-0; (c) (d) sample GS-1; (e) (f) samples GS-3.

Figure 2 shows SEM photos of section morphologies of the coatings doped with GO (samples GS-0,
GS-1, and GS-3). The thickness of each coating can be roughly estimated from the SEM photos in figures 2(a), 2(c) and 2(e). The thickness of sample GS-0 is 67 microns, the thickness of sample GS-1 is 43 microns and the thickness of sample GS-3 is 56 microns. It can be seen from the figure that the coating is tightly bound to the substrate without gaps, and there is a clear interface between them, indicating that the coating prepared by brush coating method can be well bound to the substrate. As shown in figures 2(d) and 2(f), the flake structure appears in the coating doped with GO, and the more doped GO content in the coating, the flake structure becomes more and more obvious. However, no similar flake structure appears in the undoped go coating. The sheet structures introduced by doped GO form a large number of interfaces and barrier layers in the coating.

3.3. Mechanical properties and corrosion resistance
The mechanical properties of GS-0, GS-1 and GS-3 coatings prepared were tested, and the results are shown in table 1. With the increase of the amount of GO-SiO$_2$, coating flexibility are all meet the national standard (3 mm or less), coating adhesion increased, when the dosage of 3% reach level II coating adhesion. This is because the oxygen-containing functional groups such as the hydroxyl group on the surface of GO react with the epoxy resin, and the epoxy group can also chemically react with the hydroxyl group on the surface of the steel plate, thus increasing the adhesion of the film. The increase of GO also increased the hardness, flexibility and viscosity of the film.

| Table 1. Mechanical properties of coating. |
|-----------------------------------------|
|                                | GS-0 | GS-1 | GS-3 |
| Adhesive grade                   | III  | III  | II   |
| Pencil hardness                  | H    | H    | H    |
| Viscosity/mPa · s                | 2510 | 2519 | 2531 |

Three coatings were tested for corrosion resistance, as shown in table 2. It was found that adding GS-3 coating had better corrosion resistance. This may be due to O$_2$, some corrosive medium, such as water and ions can be generated by EP surface of microchannel reach the surface of the metal substrate, corrosion reactions, with metal layers GO with special favour winding path on the surface of the electrolyte to enter the body, the surface load of the SiO$_2$ can fill the coating porosity, slowing the rate of electrolyte to metal substrate, reduce the corrosion of the metal substrate. The combination of GO and SiO$_2$ can reduce the agglomeration of SiO$_2$ and improve the compatibility between the material and EP, thus protecting the metal substrate. Figure 3 shows the photos of 20 days soaked in 20% HCL solution.

| Table 2. Main technical indexes and test results of three coatings. |
|---------------------------------------------------------------|
|                                | GS-0(EP) | GS-1 | GS-3 |
| Water resistance                | 20d, no significant change | 30d, no significant change | 30d, no significant change | 23±2℃ |
| Acid resistance                 | 20d, scattered vesicles | 20d, no significant change; 30d, scattered vesicles | 20d, no significant change; 30d, scattered vesicles | 20%HCL |
| alkali resistance               | 20d, scattered vesicles | 20d, no significant change; 30d, scattered vesicles | 20d, no significant change; 30d, scattered vesicles | NaOH saturated solution |
| salt water resistance           | 20d, scattered vesicles | 20d, scattered vesicles | 20d, no significant change; 30d, scattered vesicles | NaCl saturated solution |
Both nano SiO$_2$ and GO have large specific surface areas. After modification by silane coupling agent surface, nano SiO$_2$ can easily interact with EP to form a dense grid structure. The lamellar GO surface contains many oxygen-containing organic functional groups, which can form excellent compatibility and combination structure with EP and enhance the mechanical properties of EP coating. Since the coating hardness is also related to the dispersion uniformity of nanomaterials in the coating, fully mixed GO-SiO$_2$ can reduce the agglomeration of SiO$_2$ particles, and evenly dispersed GO-SiO$_2$ can fill the gap between EP molecular chains, making the coating close to the metal matrix and improving the permeability.

4. Conclusions
GO was compounded with SiO$_2$ modified by KH550. GO-SiO$_2$ was added to epoxy resin to prepare the anti-corrosion coating. The GO-SiO$_2$ coating was prepared on steel 616 sample. The anti-corrosion performance of GO-SiO$_2$ coating was tested, and its anti-corrosion mechanism was preliminarily discussed. The results show that the coating hardness reaches H, the adhesion grade is III, and 3 wt% GO-SiO$_2$ coating shows the best performance. In addition, lamp-structured composite materials like GO-SiO$_2$ may open up a new anti-corrosion strategy and have a positive application prospect in the field of nano-thin films of anti-corrosion coatings.

Acknowledgment
This work is supported by the Self-Topic Fund of PLA Army Academy of Artillery and Air Defense.

References
[1] Nanda S S, Papaefthymiou G C and Dong K Y 2015 Functionalization of graphene oxide and its biomedical applications Rev. Solid State Sci. 40 291-315
[2] Jiang F W, Zhao W J, Wu Y M, Dong J D, Zhou K H, Lu G M and Pu J B 2019 Anti-corrosion behaviors of epoxy composite coatings enhanced via graphene oxide with different aspect ratios Prog. Org. Coat. 127 70-9
[3] Ye Y W, Zhang D W, Li J Y, Liu T, Pu J B, Zhao H C and Wang L P 2019 One-step synthesis of superhydrophobic polyhedral oligomeric silsesquioxane-grapheneoxide and its application in anti-corrosion and anti-wear fields Corros. Sci. 147 9-21
[4] Ramezanzadeh B, Niroumandrad S, Ahmadi A, et al 2016 Enhancement of barrier and corrosion protection performance of an epoxy coating through wet transfer of amino functionalized graphene oxide Corros. Sci. 103 283-304
[5] Krishamoorthy K, Jeyasubramanian K, Premanathan M, Subbuah G, Shin S H and Kim S J 2014 Graphene oxide nanopaint Carbon 72 328-37
[6] Jiang M Y, Wu L K, Hu J M et al 2015 Silane-incorporated epoxy coatings on aluminum alloy (AA2024), Part 2: Mechanistic investigations Corros. Sci. 92 127-35
[7] Ramezanzadeh B, Ahmadi A and Mahdavian M 2016 Enhancement of the corrosion protection performance and cathodic delamination resistance of epoxy coating through treatment of
steel substrate by a novel nanometric sol-gel based silane composite film filled with functionalized graphene oxide nanosheets Corros. Sci. 109 182-205

[8] Haeri S Z, Ramezanzadeh B and Asghari M 2017 A novel fabrication of a high performance SiO2-graphene oxide nanohybrids: Characterization of thermal properties of epoxy nanocomposites filled with SiO2-GO nanohybrids J. Colloid Interf. Sci. 493 111-22

[9] Guo L et al 2018 Enhanced dispersion of graphene in epoxy-acrylic waterborne anticorrosion coating: Bifunctional ligands linking graphene to SiO2 Int. J. Electrochem. Sci. 13 11867-81

[10] Ramezanzadeh B, Haeri Z and Ramezanzadeh M 2016 A facile route of making silica nanoparticles-covered graphene oxide nanohybrids (SiO2-GO); fabrication of SiO2-GO/epoxy composite coating with superior barrier and corrosion protection performance Chem. Eng. J. 303 511-28

[11] Ma Y et al 2016 Fabrication of silica-decorated graphene oxide nanohybrids and the properties of composite epoxy coatings research Appl. Surf. Sci. 360 936-45

[12] Wang W et al 2019 Self-healing performance and corrosion resistance of graphene oxide-mesoporous silicon layer-nanosphere structure coating under marine alternating hydrostatic pressure Chem. Eng. J. 361 792-804

[13] Sui L L et al 2018 Preparation and corrosion resistance of nano SiO2-graphene oxide/epoxy composite coating Acta Materiae Compositae Sinica 35 1716-24

[14] Hossein H, Mohsen M, Ehsan S and Amin R B 2017 Microstructure, deposition mechanism and corrosion behavior of nanostructured cerium oxide conversion coating modified with chitosan on AA2024 aluminum alloy J. Alloy. Compd. 725 968-75

[15] Li Y, Wu F, Zhao W J, Li H, Jin G, Wu X D and Xue Q 2015 Tribological performance of acrylic resin coatings modified by micro/nano SiO2 particles Lubrication Eng. 40 11-22