Preparation and Properties of Graphene Anticorrosive Coatings for Transmission Towers

Liu Yang1,2,3, Li Xin1,2, He Zhen Yu1,2, Zhao Yue Ju1,3, Du Jing1,3, Wang Jinhui1,3, Zheng Yong Li1,3

1Nanrui Group (State Grid Electric Power Research Institute) Co., Ltd. 211106, Nanjing, Jiangsu
2Guodian Nanrui Technology Co., Ltd. 211106, Nanjing, Jiangsu
3Beijing Guodian Futong Technology Development Co., Ltd. 100070, Beijing

*Corresponding author e-mail: caser825@163.com

Abstract. The transmission tower is one of the largest equipment facilities in the transmission and distribution line network. It is mainly used to support the connection of overhead conductors to ensure the safe and stable transmission of power transmission lines. Due to the vast territory of China and the wide distribution of transmission towers, the operating environment faced by transmission towers is also extremely complex. In addition to the pulling force given by the transmission line, rain, snow, dust, salt spray, acid rain and other substances cause erosion and corrosion on the transmission tower. The use of anti-corrosion coatings is an effective way to avoid erosion and corrosion of transmission tower. Therefore, it is very important to prepare an anti-corrosion coating suitable for transmission towers for the safe operation of transmission towers. Graphene is a new type of functional nano-material that attracts attention. Its special layered structure can effectively shield the material, reduce the internal stress of the coating, and improve the adhesion, mechanical properties, anti-corrosion effect and other properties of the coating.

1. Introduction

The transmission tower is constructed of carbon steel [1] and will be hot-dip galvanized before leaving the factory. Although the surface of the hot-dip galvanizing treatment has a certain anti-corrosion effect, the thickness of the hot-dip galvanized surface is prone to uneven thickness [2]. In the South and coastal cities, acid gases and higher salinity and moisture content in the environment accelerate the consumption of galvanized layers [3-4]. Once the key parts of the transmission tower are corroded, the corrosion rate is extremely fast, which will have a very negative impact on the safe operation of the transmission line [5]. At present, the methods for improving the corrosion resistance of transmission towers mainly include increasing the thickness of hot-dip galvanized coatings and coating anti-corrosion coatings [6]. Compared with the method of increasing the thickness of hot-dip galvanizing, the process of coating anti-corrosion coating is simpler, and the re-coating technique is less difficult and the cost is relatively low [7].

Graphene is a two-dimensional nanosheet material [8], which itself is formed by the covalent bond of a single carbon atom. The thickness of a single layer of graphene is about 0.33 nm, although the graphene itself is very thin. However, it not only has good toughness but also can be bent to some extent. At the same time, graphene is one of the materials with the highest strength known [9].
Theoretically, the addition of graphene in anticorrosive coatings can improve the coating toughness and impact strength to some extent. In addition, due to the unique layered structure of graphene, after dispersing in the coating matrix, it can form a shielding effect, effectively infiltrate the penetration and diffusion of corrosive substances, reduce the corrosion rate, and achieve the effect of prolonging the corrosion life [10].

After functional modification, graphene is beneficial to improve the compatibility with the applied components and increase the dispersibility in the system [11-12]. Graphene is modified by silane coupling agent, which has better binding ability in epoxy phenolic coating system and is more conducive to its performance [13]. In this paper, the functionalization of graphene is modified to improve the compatibility with the epoxy resin matrix, greatly improving the adhesion, toughness and salt spray corrosion resistance, and preparing graphene suitable for the transmission tower. Anti-corrosion coating.

2. Graphene modification treatment and preparation of graphene anticorrosive coating

2.1 Graphene modification treatment
Modification step:
(1) 100 parts of graphene is added to 900 parts of xylene, and dispersed by an ultrasonic dispersing device to form a stable and uniform graphene slurry;
(2) Add 200 parts of absolute ethanol, 2 parts of ethylene triethoxysilane, 2 parts of nonylphenol ethoxylate, 2 parts of $\gamma$-glycidoxypropyltrimethoxysilane, 1 part of polyol, etc., using a planetary mixer to stir and disperse;
(3) After stirring for 5 minutes, continue to disperse in the ultrasonic dispersing device, wait until the solution is substantially uniform, add a small amount of deionized water, and adjust the PH value with 30% H2SO4 solution;
(4) The dispersion is washed with xylene under reduced pressure, and after washing, it is dried in a vacuum oven to obtain functionalized graphene;
(5) The modified graphene and xylene and n-butanol mixed solution (volume ratio of 7:3) were dispersed under ultrasonic conditions to obtain a modified graphene pulp dispersion system.

As shown in Fig. 1, the graphene slurry after dispersion can be observed to have uniform dispersion of graphene in a solvent, and it is proved that the modified graphene has good dispersibility in xylene. At the same time, the functionalized graphene was analyzed by SEM. It can be seen in Fig. 2 that the functionalized graphene still has a distinct multi-layered sheet structure, indicating that the modification has little effect on the apparent state of graphene.

![Figure 1. Dispersion state of modified graphene in xylene](image1)

![Figure 2. SEM results of modified graphene](image2)

2.2 Preparation of Functionalized Graphene Thermal Conductive and Anticorrosive Coatings
The functionalized graphene thermal conductive anticorrosive coating is composed of the coating component A and the curing agent component B, and is designed to be a room temperature curing method. The resin in component A is an epoxy phenolic system, and the component B is a SY-115 polyamide normal temperature curing agent.
Component A is dispersed by F51 epoxy phenolic resin, epoxy toughener, BYK 066N defoamer, BYK-104S wetting and dispersing agent, silane coupling agent and a small amount of xylene and n-butanol diluent. The time is around 10 minutes. After the dispersion is uniform, the modified graphene slurry, 500 mesh zinc powder, S190 iron oxide ash, GA-4 wet mica powder, 1500 mesh talc powder, 958 bentonite, color paste and the like are sequentially added. The material is dispersed and ground under the action of a sand mill, and the grinding and dispersing time is not less than 40 min. After using a squeegee fineness meter to measure, after the fineness is not more than 50 μm, BYK Chemical 1958 thixotropic agent, BYK Chemical 1790 defoaming agent and diluent are added, and the material is uniformly dispersed to obtain a coating component A.

The curing agent firstly heats the SY-115 polyamide curing agent to about 90 °C and has fluidity, which facilitates processing. The preheated SY-115 polyamide is mixed with the diluent, and after mixing, the adhesion enhancer is added and stirred uniformly. Component B.

3. Performance test of graphene anticorrosive coating

The performance indicators of anti-corrosion coatings are relatively large, and the corresponding national standards are also more. In combination with the provisions of the power industry standard DL/T1453-2015 “Transmission line tower anti-corrosion protection coating”, the salt spray corrosion resistance and adhesion of the coating were investigated. This is because the salt spray and adhesion requirements are the highest in the actual use of the transmission tower anti-corrosion coating, and it is also an effective method to verify the performance and life of the transmission tower anti-corrosion coating.

3.1 salt spray corrosion test

The functionalized graphene thermal and anticorrosive coatings were comprehensively investigated for their corrosion resistance and compared with ordinary zinc-rich anticorrosive coatings. The test procedure was carried out in accordance with the requirements of Standard GB/T 1771-2007 "Determination of Neutral Salt Spray for Paints and Varnishes". The experiment uses the YW/R-150 salt spray corrosion test box produced by Tianjin Surui Technology Development Co., Ltd., and the temperature inside the box is always maintained at 35 °C. The sample was a carbon steel sheet of Sa2.5 grade after sand blasting, and the size was 150 mm×70 mm×1.5 mm. After the coating was dried, the surface was cross-knife. The modified graphene thermal anti-corrosion coating was compared with the traditional anti-corrosion coating after the 1500 h salt spray test. There is no obvious corrosion phenomenon on the scratch surface of the graphene anticorrosive paint sample, but the surface of the ordinary zinc-rich anticorrosive paint has a large area of corrosion. This indicates that the graphene anticorrosive coating has excellent salt spray resistance. The test results are shown in Fig. 3.

Figure 3. Comparison of salt spray test between ordinary zinc-rich anticorrosive coating (left) and modified graphene thermal anticorrosive coating (right)

The salt spray corrosion resistance of graphene anticorrosive coatings is better than ordinary anticorrosion mainly because graphene as a two-dimensional nanomaterial has a special layered structure, which has excellent electrical conductivity, mechanical properties and shielding properties against water molecules and air. The use of graphene super strong conductivity and ultra-high strength combined with the cathodic protection of zinc powder, applied in anti-corrosion coatings, showing superior corrosion resistance and versatility than the original zinc-rich anti-corrosion coating.
Moreover, the layered structure of graphene hinders the formation of corrosion paths, greatly slows down the corrosion rate, and exhibits excellent salt spray corrosion resistance.

China's transmission towers have a wide operating range and complex operating environment. Excellent salt spray corrosion resistance is beneficial to the use of coatings in coastal and southern rainy and humid areas, reducing the corrosion of iron towers caused by large salt and high humidity, and improving the safety of transmission tower operation. At the same time, its excellent salt spray resistance makes it universally adaptable in different regions and can be used in many regions.

3.2 adhesion test
The test method for coating adhesion is divided into two methods: the pull-open method and the cross-cut method. The pull-off method is for the sample with a coating thickness greater than 200 μm, and the cross-cut rule is for the sample with a coating thickness of less than 200 μm. Adhesion test samples of a film thickness of 200 μm or less and a film thickness of 200 μm or more were respectively prepared according to the preparation method of the standard sample. To distinguish the samples, a graphene anticorrosive paint containing different color pastes was used.

The test results of the hundred-grid method show that the adhesion of the gray graphene anti-corrosion coating (138μm) has reached the level 0 standard specified in GB/T 9286-1998 "The cross-cut experiment of paint and varnish paint film", that is, the cutting edge Completely smooth without the requirement of a single drop(see Fig. 4).

The yellow graphene anticorrosive coating (280μm) is tested according to GB/T 5210-2006 "Painting and varnish pull-off adhesion test". The experimental results are shown in the Fig.5. The results of the pull-open test are shown as adhesives. The cementation in the test column is destroyed, and the surface of the coating is not damaged. The final results of the pull-opening method were 13.0 MPa, 12.5 MPa, 11.1 MPa, and the average value was 12.2 MPa.

Both tests have shown that graphene anti-corrosion coatings have excellent adhesion and can accommodate a variety of thick and thin coating thickness requirements. This is due to the excellent electrical conductivity of the graphene and the large specific surface area, which can greatly reduce the amount of zinc powder in the primer, which is more conducive to improving the adhesion, mechanical properties and compactness of the primer coating.

For transmission towers, the excellent adhesion of anti-corrosion coatings is an important guarantee for safe operation. During the inspection, maintenance and operation, the tower faces the pedaling during the overhaul and the friction and impact of foreign objects. If the adhesion of the anti-corrosion coating is poor, the effective running time of the anti-corrosion coating on the transmission tower will be greatly shortened, corrosion will occur, and the workload and maintenance cost of the transmission tower maintenance and maintenance will be increased.

3.3 actual environment coupon test
In order to investigate the actual use effect of the coating, in July 2018, the hanging film operation test was carried out on the offshore wind power platform of China Southern Power Grid. Samples of graphene anticorrosive coatings were tested and hung on the base tower No. 25 of the offshore wind
turbines near the Sanjiashan Island in Zhuhai City (see Fig.6). The unit has been completed when the film is hanged, and it will be connected to the grid during the commissioning phase.

The marine environment is much more corrosive to the material than the land area. The corrosive industry divides the marine corrosion area into four areas: the atmospheric zone, the splash zone, the tidal zone and the underwater zone. Among them, the wave splash zone has the most serious corrosion due to environmental factors such as impact, water vapor and atmosphere. After the sample is fixed in a safe position in the splash zone (Fig. 7), the corrosion of the sample is observed from time to time. As of April 2019, the surface of the sample is shown in Figure 8. It can be seen that the surface of the sample has not corroded, and no peeling, wrinkling, blistering or falling off occurs(see Fig. 8). This graphene anticorrosive coating has excellent corrosion resistance, especially in areas with high humidity, high salt content and strong ultraviolet rays. The sample test environment on offshore wind turbines is far worse than the operating environment of land transmission towers. The operating conditions of offshore wind turbines are very similar to those of terrestrial transmission towers. The good test-hanging effect of offshore wind turbines indicates that the use of graphene anticorrosive coatings is an excellent anti-corrosion measure for power transmission towers. Provide a certain guarantee for the safe and stable operation of the transmission tower.

Figure 6. Triangle Wind Turbine No. 25 Offshore Wind Turbine

Figure 7. Sample Suspension Position

Figure 8. Test suspension sample suspension in early April 2019

4. Conclusion
The safe and stable operation of the transmission tower and the maintenance cycle depend on the effect of anti-corrosion measures. Excellent anti-corrosion measures will effectively reduce the corrosion of the transmission tower, prolong the maintenance cycle and reduce maintenance costs. Compared with the hot-dip galvanizing process, the anti-corrosion coating has the advantages of low cost, relatively uniform coating thickness, and simple construction and coating. However, the anticorrosive coatings currently on the market have problems such as short delay time and general adhesion. In view of the special requirements for salt spray corrosion resistance and adhesion of power transmission towers, graphene anticorrosive coatings for transmission towers were developed.

The graphene anticorrosive coating prepared herein has excellent salt spray corrosion resistance and adhesion. A method of functionalizing a graphene by a silane coupling agent, and a method of
dispersing a graphene to prepare a graphene paste suitable for combination with an epoxy resin. Compared with ordinary graphene, its dispersibility and bonding strength in epoxy resin are improved, and the final product graphene anticorrosive coating has excellent adhesion. Due to the unique sheet-like barrier structure of graphene, the corrosion resistance of the anticorrosive coating is improved, and the salt spray resistance is improved compared with the conventional anticorrosive coating.

The improvement of adhesion and salt spray corrosion resistance makes the graphene anticorrosive coating more suitable for the application of transmission towers, which provides an important guarantee for the safe and stable operation of transmission towers and reduces maintenance costs.

References
[1] Wu Bao Yong, Design and Research of Transmission Tower of Xijiang Great Crossing, Guang Xi Water Resources & Hydropower Engineering. 6,13(2018) 51-53.
[2] Cui Jian Nan, Cheng Chang, Analysis and Improvements of Anti-corrosion Technique for Mast of TV Tower, Steel Construction. 1,33(2018) 109-111.
[3] Li Xiao Guang, Li Sheng Long, Design points of transmission tower foundation in saline soil area, Electrotechnical. 3(2109) 108-109.
[4] Liu Feng, Song Hong Qing, Huang Zheng Ran, Fan Ya Zhou, Lin Yue Ling, Long Zi Jun, Xu Li Kun, Anti-corrosion Properties of Protective Coatings for Transmission Line Iron Tower in Coastal Area, Equipment Environmental Engineering. 12,4(2015) 76-81.88.
[5] Chen Yun, Qiang Chun Mei, Wang Guo Gang, Miao Wen Hua, Corrosion and Protection of Transmission Towers, Electric Power Construction. 31,8(2010) 55-58.
[6] Chen Yao Cai, An Zhen Ji, Corrosion Analysis and Protection Design of Organic Coatings about Transmission Tower, Modern Pint and Finishing. 13,10(2010) 23-27.
[7] Tian Zhen Yu, Li Zhi Gang, Zhai Yan, Application of Zinc/Graphene Composite Heavy-Duty Anticorrosive Coatings, Coatings Technology & Abstracts. 36,9(2015) 30-34.
[8] Tapas Kuila, Ssswata Bose, Ananta Kumar Mishra, Partha Khanra, Nam Hoon Kim, Joong Hee Lee, Chemical functionalization of graphene and its applications, Progress in Materials Science. 57(2012) 1061-1105.
[9] R.K.Singh Raman, P.Chakraborty Banerjee, Derrek E.Lobo, Hemtej Gullapalli, Madusha Sumandasa, Ashwin Kumar, Lokesh Choudhary, Rachel Tkacz, Pulickel M.Ajayan, Mainak Majumder, Protecting copper from electrochemical degradation by graphene coating, Carbon. 50 ,11(2012) 4040-4045.
[10] Chi-Huo Chang, Tsao-Cheng Huanga Chih-Wei Peng, Tzu-Chun Yeh, Hsin-Ilu, Wei-IHung, Chang-Jian Weng, Ta-Yang, Jui-Ming Yeh, Novel anticorrosion coatings prepared from polyaniline/graphene composites, Carbon. 50,14(2012) 5044-5051.
[11] Kung-Chin Chang, Min-Hsiang Hsu, Hsin-I Lu, Mei-Chun Lai, Pei-Ju Liu, Chien-Hu Hsu, Wei-Fu Ji, Tsao-Li Chuang, Yen Wei, Room-temperature cured hydrophobic epoxy/graphene composites as corrosion inhibitor for cold-rolled steel, Carbon. 66(2014) 144-153.
[12] Li Si Yi, Dong Yu Hua, Zhou Qiong, Liu Qing-qing, Corrosion Performance of Graphene and Graphene/Epoxy Composite Coating, Corrosion & Protection. 36,8(2015) 748-753.
[13] Li Min Feng, Li Jun Xia, A Brief Talk on the Lower Surface Treatment Coatings, Modern Paint & Finishing. 9(2010) 11.