Synthesis of attapulgite/graphene conductive composite and its application on waterborne coatings

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Abstract

Attapulgite/graphene conductive composite is modified by a silane coupling agent of *N*-(β -aminoethyl)- γ -aminopropyltrimethoxy-silane (KH-792) to make conductive attapulgite uniformly load on the surface of the graphene. The samples are characterized by X-ray diffraction, transmission electron microscopy and Fourier transform infrared spectroscopy. The results demonstrate that the conductive attapulgite is successfully grafted onto the surface of graphene. The characteristics of raw and modified absorbents are characterized by Fourier transform infrared spectroscopy, thermal analysis, scanning electron microscopy and transmission electron microscopy. The results show that the saturated mass fraction of the surface-adsorbed KH-792 silane coupling agent is about 3.0–5.0%. The electrical conductivity and mechanical properties of the conductive coating prepared from the modified conductive composite are investigated. The results show that the surface resistivity of the modified attapulgite/graphene conductive composite coating is smaller than that of the unmodified attapulgite/graphene conductive composite coating when the same amount of is added, and the mechanical properties are also greater than unmodified. As a comparison, when the composite material is 15% mass of the paint which can achieve a best performance.

Keywords Graphene · Conductive attapulgite · Silane coupling agent · Surface modification · Polyurethane waterborne coating

1 Introduction

Conductive coating is a special functional widely used for coating on the surface of non-conductive substrates, which has a certain of conduction current, eliminates static charge and corrosion resistance [1]. The composition of conductive coatings contains resin, pigment, fillers, curing agents, solvents and additives [2]. Volatile organic substance (VOC) is commonly used as solvents for traditional conductive coatings which will cause pollution in the operation room volatilizing during the film formation process and cause secondary pollution to the atmospheric environment. If humans and animals are exposed in high concentrations of VOC for a long time, it will increase the

likelihood of concurrent cancer [3]. Therefore, the traditional coatings industry needs to be upgraded and transformed. Now, water-based coatings have low VOC and even zero VOC emissions [4], which can improve production environment, reduce the cost of solvents. It reduces the production cost and makes the waterborne coatings more competitive. Therefore, it is inevitable that the waterborne coatings will gradually replace the solvent-based coatings [4, 5].

The ratio of filler to resin in conductive coatings is the decisive factor for its performance. Conductive fillers mainly include carbon system [6], metal system [7], metal oxide system [8] and so on. Tin oxide (SnO_2) is an n-type semiconductor with a wide bandgap, excellent

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mechanical properties, high visible light transparency and high stability. It has better conductivity after doping Sb in SnO_2 lattice [9]. Attapulgite clay, referred to as attapulgite, also known as palygorskite, is a one-dimensional nanostructured magnesium-rich silicate clay mineral natural crystalline material with rod-like or fibrous micro-morphology [10]. Graphene has excellent electrical conductivity, but it is prone to wrinkles and self-agglomeration. It reduces its excellent electrical conductivity in the coating system. Therefore, attapulgite is introduced to support the graphene sheet layer in the coating system, thereby reducing wrinkles and agglomeration of graphene. At the same time, because graphene is expensive, in order to reduce the production cost and reduce the amount of graphene, the surface of the attapulgite is coated with antimony doped tin oxide (ATO) to make it have conductive properties, and the conductive attapulgite, attapulgite is obtained. The stone itself does not have electrical conductivity. The antimony-doped tin oxide (ATO) is uniformly coated on the surface of the attapulgite, so that the attapulgite has electrical conductivity and reduces the amount of graphene. The conductive attapulgite and graphene are introduced into the waterborne coating system to achieve better application effects. The crystal has a diameter of 20–40 nm and a length of 500–5000 nm [11]. The basic structural unit consists of a siloxane tetrahedral double chain parallel to the c-axis. Each chain is connected by an oxygen atom to form nanorod structure with a special high aspect ratio [12]. The precursor is prepared by coating the ATO particles on the attapulgite by a coprecipitation method. The conductive attapulgite composite material is obtained by calcination. Graphene is a two-dimensional (2D) honeycomb lattice material formed by the close combination of planar single-layer carbon atoms [13]. It is only 0.3354 nm thick and is the world's thinnest two-dimensional material [14]. Graphene has a very high theoretical specific surface area ($2630 \text{ m}^2/\text{g}$) [15], which can be used to load various molecules including metals, metal oxides, biomolecules, fluorescent molecules and various drugs [16]. In addition, graphene has excellent mechanical properties (tensile strength up to 130 GPa is the highest of all known materials [17]), electrical conductivity and corrosion resistance. In order to make better use of the excellent properties of graphene, Meyer et al. [18] used it as a typical two-dimensional reinforcement phase, preparing the materials with different functions of graphene as the modified phase. And the conductive attapulgite/graphene is modified by surfactant to load on the surface of graphene sheet to form a three-dimensional network cross-linked structure, which reduces the folding

agglomeration of graphene sheets to achieve better conductivity and corrosion resistance.

2 Experiment

2.1 Experimental materials and chemicals

Conductive attapulgite: Changzhou Naou Technology Co., Ltd.; Graphene: laboratory-made; polyurethane resin: industrial grade, Kunshan Kelijia International Trade Co., Ltd.; defoamer BYK-110: analytical grade, BYK; silane coupling *N*-(β -aminoethyl)- γ -aminopropyltrimethoxysilane (KH-792): analytical grade, Aladdin; leveling agent EFKA3600N: analytical grade, BYK; cellulose, curing agent, ethanol, leveling agent: Analytical pure, Sinopharm Chemical Reagent Co., Ltd.

2.2 Conductive attapulgite/graphene surface treatment

Before the experiment, we took 40 g of conductive attapulgite/graphene powder with an electronic balance, added 400 g of ethanol at a mass ratio of 1:10, mixed them and dispersed them in a beaker which was transferred to a four-necked flask. The four-necked flask was heated in a water bath at 70°C . When the internal temperature of the four-necked flask was about 65°C , the pH was adjusted to 3–4 with 0.1 mol/L HCl solution. KH-792 [m(KH-792):m (Composite material) = 0.01, 0.02, 0.03, 0.05, 0.06] was added to the four-necked flask. The reaction mixture was stirred at 70°C for 3 h. The product was washed with deionized water until the filtrate was without Cl^- , subsequent to which the product was dried under vacuum at 80°C for 12 h. The powder was sieved to obtain a modified conductive attapulgite/graphene.

2.3 Composite mechanism

The attapulgite is coated with a layer of ATO conductive film to prepare the conductive attapulgite [19]. However, the surface hydroxyl groups of the conductive attapulgite are reduced after coating, which not only make it weaker in binding to graphene sheets but also affect the dispersion in the polyurethane aqueous coating. Therefore, the graphene/conductive attapulgite was modified by the surfactant *N*-(β -aminoethyl)- γ -aminopropyltrimethoxysilane to get favorable dispersibility and cross-linking with graphene sheets forming a three-dimensional network cross-linked structure [20]. It prevents the folding agglomeration of the graphene sheets to obtain the better property of conductivity and corrosion resistance in Fig. 1.

Fig. 1 The mechanism of graphene/conductive attapulgite composite **Table 1** The formulation of coating

Raw material	m/g
Polyurethane resin	20
Deionized water	50
graphene	1
Conductive attapulgite or conductive attapulgite/graphene	10–30
Defoamer	0.8
Cellulose	1
Leveling agent	1.2
Hardener	2

2.4 Complex treatment process

The polyurethane resin was weighed 60 g with an electronic balance, followed by the addition of 100 g of deionized water. The solution was put in the homogenizer and dispersed at high speed of 1500 r/min for 5 min. The graphene/conductive attapulgite powder and a small amount of antifoaming agent, leveling agent and curing agent are dispersed in the solution for 30 min to prepare the conductive paint. The formulation of coating is shown in Table 1.

3 Results and discussion

3.1 XRD analysis of composites materials

Figure 2 shows the X-ray diffraction spectrum of graphene (a), conductive attapulgite/graphene (b) and conductive attapulgite (c). Comparing the three graphs (a), (b), and (c), we found that (b) the characteristic peaks of the

Fig. 2 XRD pattern of graphene (a), conductive attapulgite/graphene (b) and conductive attapulgite (c)

conductive attapulgite appear in the conductive attapulgite/graphene, and the characteristic peak of graphene also appears. It can be indirectly proved that the conductive attapulgite has stitching on the surface of graphene, the Fourier infrared and projection electron microscopy will further prove this composite mode.

3.2 Infrared spectrum analysis of composites materials

The infrared spectrum of the conductive attapulgite/graphene and the modified conductive attapulgite/graphene is shown in Fig. 3. The unmodified conductive attapulgite/graphene showed a Si–O–H anti-symmetric stretching

Fig. 3 FT-IR spectra of composite materials

peak bound to water at 3451 cm^{-1} and the bending vibration absorption peak of H–O–H appeared at 1631 cm^{-1} and 1030 cm^{-1} [21]. There is an absorption peak of C–O–C, which may be formed by the surface group of the conductive attapulgite and the surface group of graphene. After modification with a KH-792 silane coupling agent, the absorption peak intensity is also enhanced, indicating that the conductive attapulgite/graphene compound is more thorough, this also indicates the modification effect is good.

3.3 Thermal analysis of composites materials

Figure 4 shows the thermogravimetric analysis of unmodified conductive attapulgite/graphene and modified conductive attapulgite/graphene with different amounts of KH-792. When the temperature is below $200\text{ }^{\circ}\text{C}$, the weight loss rate of the conductive attapulgite/graphene is about 2.13%, which is caused by the removal of crystal water. When the temperature is between 200 and $600\text{ }^{\circ}\text{C}$, the weight loss rate of the conductive attapulgite/graphene is 3.74% because the crystal water on the surface of the material is completely removed caused the removal of structural water. After modification with KH-792 silane coupling agent, the weight loss rate will reach 6.28% and 6.60% when the coating ratio is 1% and 3%, respectively. It may be due to the burning of organic group on the surface of the modified conductive attapulgite/graphene. In the figure, the trend of the thermogravimetric curve is basically consistent when the amount of modifier is 5% and 3%, indicating that the surface of the composite has reached saturated adsorption. Thus, the optimum dosage

Fig. 4 TG curve of composites before and after modification a Composite material; b m(KH-792):m(Composite material)=0.01; c m(KH-792):m(Composite material)=0.03; d m(KH-792):m(Composite material)=0.05

of the modifier is 3–5%. The data shown in Table 2 is that of the mass change of samples in different temperature.

3.4 TEM and SEM analysis of composites materials

The TEM images of the conductive attapulgite and composite are shown in Fig. 5. It can be seen in Fig. 5a that the Sb-SnO₂ particles form a continuous and dense conductive layer on the surface of the attapulgite with a thickness about 20 nm. A very pronounced sheet structure of graphene can be seen in Fig. 5b. In Fig. 5c, which can be seen that a small amount of conductive attapulgite is presented on the graphene surface. It may be because the graphene sheet layer is curled and more conductive attapulgites are formed freely on the outside, which cannot form three-dimensional crosslinks with the graphene structure. Figure 5d shows the modified conductive attapulgite/graphene. We can clearly see that the conductive attapulgite appears on the surface of the graphene sheet to reduce the wrinkles of graphene.

Table 2 The mass change of samples in different temperature

Sample	0–200 °C weight loss/%	200–600 °C weight loss/%
Unmodified	2.13	3.74
1%KH-792	2.15	4.13
3%KH-792	2.15	4.47
5%KH-792	2.18	4.52

Fig. 5 TEM images of **a** conductive attapulgite, **b** graphene, **c** conductive attapulgite/graphene, **d** modified conductive attapulgite

The SEM image of the conductive attapulgite and the composite material are shown in Fig. 6. From Fig. 6a, it shows that the unmodified conductive attapulgite/graphene are not well combined and there are many conductive attapulgites in a free state. If it is used as a coating material, it will reduce the mechanical properties of the coating. However, it can be observed that the conductive attapulgite and graphene are cross-linked after modification by the silane coupling agent in Fig. 6b. The conductive attapulgite is arranged on the graphene sheet

to prevent the graphene sheet from wrinkling conductive properties of the conductive attapulgite can reduce the agglomeration of graphene sheets to achieve better performance.

Figure 7 is the SEM image of the addition of conductive attapulgite/graphene and modified conductive attapulgite/graphene coating. As shown in Fig. 7(a), (b), obvious cocoon-like agglomeration and large voids appear in the coating when conductive attapulgite/graphene is added, which failed to form a complete conductive network,

Fig. 6 SEM image of **a** conductive attapulgite/graphene, **b** modified conductive attapulgite/graphene

Fig. 7 SEM images of **a, b** electro-attapulgitite/graphene coating; **c, d** modified conductive attapulgitite/graphene coating

indicating that the graphene was unevenly dispersed in the coating resulting in the appearance of the coating. because of that the coating fails to form a complete conductive network, indicating graphene is unevenly dispersed in the coating and agglomerated in the coating, causing voids in the coating and affecting its electrical conductivity and affecting its electrical conductivity. From Fig. 7(c), (d), the modified conductive attapulgitite/graphene coating are uniformly dispersed in the resin without agglomeration. The middle fillers are bridged with each other to form a complete conductive path making the prepared coating with an excellent electrical conductivity, which is consistent with the results of surface resistance value.

3.5 Surface resistance and AC impedance curve and salt spray test analysis

The amount of conductive filler added is measured as a percentage of the total coating system. The surface resistance of the composite coating is shown in Fig. 8. As shown in the figure, the surface resistance of the coating decreases with the increase of the conductive filler increases and Surface resistance refers to the coating formed after the coating is applied to a non-conductive plastic sheet, and the resistance of the surface of the

Fig. 8 Effect of modifier on surface resistance of coating

coating is measured by four probes. According to seepage threshold theory, as the content of conductive filler increases, the probability of formation of conductive network becomes larger and larger and the gap between particles becomes smaller and smaller. When the content of conductive filler reaches a critical value, the particles originally dispersed in the coating system will contact each other to form a complete conductive path, which

is macroscopically manifested in a rapid decrease in the resistance of the composite coating. When the conductive network is completely formed, the resistance will tend to be stable and the addition of conductive filler will have little effect on the resistance [22, 23]. In addition, the surface resistance of the modified conductive coating is significantly smaller than that the unmodified coating at the same conductive filler content because the modified conductive filler has better dispersibility in an aqueous solvent at low contents. Meanwhile, a complete conductive path has also been formed.

Figure 9 is the AC impedance curve of conductive attapulgite, graphene, conductive attapulgite/graphene and modified conductive attapulgite/graphene in the coating. We can get the components in the coating from the slope of the curve in the figure. The covers show that the coatings have conductivity and corrosion resistance. We

Fig. 9 AC impedance curves of different material coatings

Fig. 10 Picture of the coating sample before and after the 120 h salt spray test

can then find that the performance of modified conductive attapulgite/graphene > conductive attapulgite/graphene > conductive attapulgite. Therefore, the accuracy of the surface resistance curve value of the coating can be proved. It is also shown that the modifier does contribute to the recombination of the conductive attapulgite/graphene.

Figure 10 is a photograph of a carbon steel sample coated with a conductive attapulgite coating and a modified conductive attapulgite/graphene coating after a 120 h salt spray test. Figure 10(a) is a conductive attapulgite coating and Fig. 10(c) is the modified conductive attapulgite/graphene coating before the salt spray test. After the salt spray test, it is found that the conductive attapulgite is unevenly dispersed in the aqueous polyurethane paint, we can see there is a large area of corrosion occurring in carbon steel sheet. However, in the comparison of (b) and (d), the carbon steel sheet with the modified conductive attapulgite/graphene coating (d) is substantially free of corrosion, and on the carbon steel sheet, we find the corrosion occurring on the surface of the carbon steel where no coating was applied., this also indicates that the addition of graphene played a role in slowing down corrosion.

After the salt spray test, we also make a comparison of the quality changes of the samples. The quality change of the sample can also reflect the degree of corrosion in another aspect. The data shown in Table 3 is that of the mass change of the pre-coated and post-coated carbon steel samples. It can be seen from the data that the modified conductive attapulgite/graphene coating has the least mass loss, and the carbon steel surface has the least degree of corrosion, which confirms the salt spray test results to be right.

Table 3 Mass change and surface change of coated carbon steel after salt spray test

Sample	Pre-test quality (m/g)	Post-experiment quality (m/g)	Quality loss (m/g)	Surface condition
Carbon steel	15.3325	15.2038	0.1287	A lot of rust
Conductive attapulgite coating	16.5387	16.3628	0.1759	Partially rusty
Modified conductive attapulgite/graphene coating	16.5517	16.4928	0.0589	Basically not rusting

Table 4 Effect of different filler loadings on other properties of conductive attapulgite/graphene coating

Add amount	Hardness	Adhesion	Flexibility (mm)	Impact resistance (cm)
5 (wt%)	5B	2	1	35
7.5 (wt%)	5B	2	1	35
10 (wt%)	4B	2	1	40
12.5 (wt%)	3B	1	1	45
15 (wt%)	3B	1	1	45
17.5 (wt%)	3B	2	1	45

Table 5 Effect of different filler contents after modification on other properties of conductive attapulgite/graphene coating

Add amount	Hardness	Adhesion	Flexibility (mm)	Impact resistance (cm)
5 (wt%)	3B	2	1	40
7.5 (wt%)	3B	1	1	40
10 (wt%)	3B	1	1	45
12.5 (wt%)	2B	1	1	45
15 (wt%)	B	1	1	50
17.5 (wt%)	B	2	1	45

3.6 Other performance characterization of the coating

The mechanical properties of the composite conductive attapulgite/graphene coating and the modified composite conductive attapulgite/graphene coating are shown in Tables 4 and 5. It can be seen that as the filler content increases, the hardness and impact resistance of the modified composite conductive attapulgite/graphene coating increase: the hardness increases from 3B to B, and the impact resistance increases from 45 to 50 cm. At the same time, the flexibility of the coating remains unchanged. When the modified composite conductive attapulgite/graphene coating is added in an amount of more than 15%, the filler cannot be completely wrapped by the resin to form a gap, and too much filler makes the coating too viscous. Which cause the mechanical properties performance of the coating correspondingly degradation.

4 Conclusion

In this paper, the composite conductive attapulgite/graphene material was modified by KH-792 silane coupling agent, we can verify the silane coupling agent was successfully grafted into the conductive attapulgite composite by XRD, TEM and FT-IR. The surface of the powder is applied to the modified conductive composite. The results show that the KH-792 silane coupling agent helps the conductive attapulgite/graphene surface to bond by chemical bonds, and they are cross-linked to form a three-dimensional network structure. The modifier changes the properties of the conductive attapulgite/graphene surface so that they are evenly combined. The results show that the modified conductive attapulgite/graphene composite powder has better dispersibility and anti-corrosion performance in polyurethane water-based paint, the surface resistance of the modified powder is also better than the unmodified conductive attapulgite/graphene when the same amount is added. We can measure the lowest surface resistance is $1.0 \times 10^4 \Omega/\text{sq}$. It also shows better adhesion, flexibility and impact resistance. The modified conductive composite powder achieves the best performance when the amount is 15%, the hardness is B, the adhesion is 1, the flexibility is 1 mm, and the impact resistance is 50 cm.

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Compliance with ethical standards

Conflict of interest They have no conflict of interest.

References

- Du XS, Jiao HY (2009) Research progress of conductive coatings. *China Coat* 24(2):19–22
- Swarup S, Simpson DA, Luchansky MS et al (2018) Curable film-forming compositions containing acid functional curing agents and multilayer composite coatings: U.S. Patent Application 15/296,548. 2018-4-19

3. Liu GJ (2010) New technology of modern coating technology. China Light Industry Press, Beijing, pp 72–75
4. Ho J, Mudraboyina B, Spence-Elder C et al (2018) Water-borne coatings that share the mechanism of action of oil-based coatings. *Green Chem* 20(8):1899–1905
5. Haase MF, Grigoriev DO, Möhwald H et al (2012) Development of nanoparticle stabilized polymer nanocontainers with high content of the encapsulated active agent and their application in water-borne anticorrosive coatings. *Adv Mater* 24(18):2429–2435
6. Athawale VD, Nimbalkar RV (2011) Waterborne coatings based on renewable oil resources: an overview. *J Am Oil Chem Soc* 88(2):159–185
7. Azim SS, Satheesh A, Ramu KK, Ramu S, Venkatachari G (2006) Studies on graphite based conductive paint coatings. *Prog Org Coat* 55(1):1–4
8. Wu S (2007) Preparation of ultra-fine copper powder and its lead-free conductive thick film. *Mater Lett* 61(16):3526–3530
9. Daoli Z, Zhibing D, Jianbing Z, Liangyan C et al (2006) Micro-structure and electrical properties of antimony-doped tin oxide thin film deposited by sol–gel process. *Mater Chem Phys* 98(2/3):353–357
10. Shuo WU, Zhao Q, Miao D et al (2010) Synthesis and characterization of Sb-doped SnO_2 –(CeO_2 – TiO_2) composite thin films deposited on glass substrates for antistatic electricity and UV-shielding. *J Rare Earths* 28(s1):189–193
11. Zhu Z, Fan W, Liu Z et al (2018) Construction of an attapulgite intercalated mesoporous g-C₃N₄ with enhanced photocatalytic activity for antibiotic degradation. *J Photochem Photobiol A* 359:102–110
12. Wang AQ, Wang WB, Zheng YA et al (2014) Crystallization of attapulgite rods and their nano-functional composites. Science Press, Beijing
13. Molle A, Goldberger J, Houssa M et al (2017) Buckled two-dimensional xene sheets. *Nat Mater* 16(2):163
14. Chen TH (2003) Nanoscale mineralogy and geochemistry of suspension attapulgite clay. Hefei University of Technology, Hefei
15. Novoselov KS, Ueim AK, Morozov SV et al (2004) Electric field effect in atomically thin carbon films. *Science* 306(5696):666–669
16. Liu J, Cui L, Losic D (2013) Graphene and graphene oxide as new nanocarriers for drug delivery applications. *Acta Biomater* 9(12):9243–9257
17. Zhang YB, Tang TT, Girit C et al (2009) Direct observation of a widely tunable bandgap in bilayer grapheme. *Nature* 469(7248):820–823
18. Meyer JC, Geim AK, Katsnelson MI et al (2007) The structure of suspended graphene sheets. *Nature* 446(7131):60–63
19. Kim KS, Zhao Y, Jang H et al (2010) Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Natur* 457(7230):706–710
20. Tkalya EE, Ghislandi M, de With G et al (2012) The use of surfactants for dispersing carbon nanotubes and graphene to make conductive nanocomposites. *Curr Opin Colloid Interface Sci* 17(4):225–232
21. Hu P, Yang H (2010) Controlled coating of antimony-doped tin oxide nanoparticles on kaolinite particles. *Appl Clay Sci* 48(3):368–374
22. Bilotti E, Zhang H, Deng H, Zhang R, Fu Q, Peijs T (2013) Controlling the dynamic percolation of carbon nanotube based conductive polymer composites by addition of secondary nanofillers: the effect on electrical conductivity and tuneable sensing behaviour. *Compos Sci Technol* 74:85–90
23. Shang Q, Hao S, Wang W, Fu D, Ma T (2013) Preparation and characterization of antistatic coatings with modified BaTiO₃ powders as conductive fillers. *J Adhes Sci Technol* 27(24):2642–2652

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