Study on conductive mechanism of graphene conductive and anticorrosive coatings on steel bar surface in concrete

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Abstract. When conductive and anticorrosive coatings are applied on the surface of reinforcing bars, electrochemical protection measures can be taken when the construction need secondary maintenance. Because graphene is a sp2 hybrid honeycomb structure, higher conductivity can be obtained by adding a small amount of graphene in the coating. In this paper, graphene-based conductive anticorrosive coatings were prepared with mixed conductive fillers (acetylene carbon black, conductive carbon black, graphite, graphene and zinc powder). The conductive mechanism was determined by studying the effects of conductive properties on the change of the content of different conductive fillers and analyzing the microstructural characteristics of conductive coatings with XRD, SEM, TEM and Raman spectroscopy tests. The results show that the conductivity of mixed fillers with different shapes in coatings is better than that of single filler in coatings when the filler content is the same. Because of the flexible structure and thin layer of graphene, the isolated fillers and conductive paths in different areas of the coatings can be connected with it and the conductive efficiency can be improved. The conductive paths are formed by the contact among conductive fillers in the coatings. Finally, the conductive mechanism model of graphene conductive and anticorrosive coatings was established.

1. Introduction

In engineering structures, in order to prevent steel from corrosion in reinforced concrete, coatings applied on concrete surface and on steel surface are commonly used as anticorrosion measures. At present, insulating coatings such as epoxy powder coatings are commonly used on the surface of reinforcing bars. If the surface coatings of reinforcing bars are damaged during construction or under environmental action, the corrosion of reinforcing bars may be accelerated. Because there is no electric connection between reinforcing bars coated with insulating coatings, the electrochemical cathodic protection can not be used in the maintenance of reinforced concrete structures, which makes the maintenance effect difficult to be guaranteed. If anti-corrosive coating with conductive property is applied on the surface of reinforcing steel bar, electrochemical protection measures can be adopted in the maintenance of reinforcing steel concrete.

Conductive coatings are a kind of functional coatings. According to the different conductive mechanism and preparation methods, they are generally divided into two types including intrinsic and composite coatings. The intrinsic conductive coatings can be either metal coatings (coating or plating) or conductive polymer coatings, which have conductivity themselves. The film-forming materials of the composite conductive polymer coatings are insulated. The conductive materials in the coating uniformly distribute in the coating to form a conductive path, which enables movement electrons to form current
through these conductive materials in the coating. The conductivity of the coating is related with the properties of conductive materials and their distribution in the coating. At present, the other conductive polymer is so difficult to be synthesized or manufactured that there is few intrinsic conductive polymer coatings except the conductive polyaniline coating [1,2]. Composite conductive coatings are widely used because of their wide selection of conductive filling materials, convenient preparation and low cost of coatings.

When pure zinc or aluminum coatings are coated or plated on the surface of steel bars, zinc or aluminum which are active metal and amphoteric metal will react to form insulating compounds in high alkaline environment of concrete and lose their conductive property gradually. At the same time, the volume expansion of corrosion products of zinc or aluminum may cause cracking of concrete. So pure active metal coatings are usually not used alone on the surface of steel bars. Non-active metal coatings on steel bars, such as copper coatings, can accelerate the corrosion of steel bars if the coatings are damaged during the operation of structures, so there are few engineering applications. Conductive filling materials in coatings include metal powder, metal-coated titanium dioxide, metal-coated mica powder and conductive carbon materials such as carbon black, graphite, carbon nanotubes, acetylene carbon black, graphene, etc. According to the previous statement of pure metal coating applied on steel bars, pure metal filling materials are also not suitable for conductive coatings coated on steel bar surface. Graphene which is obtained from the graphite is a sp2 hybrid honeycomb network structure. Graphene has been widely used in many fields due to its high carrier mobility, high thermal conductivity, flexibility, transparency, large specific surface area and high chemical and photoelectric sensitivity [3-5]. Therefore the conductive graphene may be added to coatings to form conductive and anti-corrosion coatings for steel bars in concrete.

In this paper, the effect of types and content of filling materials of coatings on the conductivity of coatings was discussed, and the conductive mechanism of coatings was studied through the morphology and electrical properties of coatings.

2. Experiments

2.1. Materials

Self-made graphene conductive and anticorrosive coating is mainly composed of water-borne epoxy resins, curing agents, conductive fillers and related additives. Conductive fillers are composed of graphene, conductive carbon black, acetylene carbon black, conductive graphite and conductive mica powder. Graphene materials which are labeled JG, SG and QG respectively come from products of three companies. The physical properties of conductive coatings in this paper are listed in Table 1.

| Items           | Results | Test Methods       |
|-----------------|---------|--------------------|
| Adhesive Force  | grade 1 | GB/T 9286-1998     |
| Impact Strength | 50 kg·cm| GB/T 1732-1993     |
| Flexibility     | 1 mm    | GB/T 1731-1993     |

2.2. Preparation of coatings

The component A of the composite coating is obtained according to following steps. They are added to the plastic cups in turn with stirring for some time at low speed, which are some of waterborne epoxy resin emulsion, toughening agent, leveling agent, defoaming agent, deionized water and so on. Then the remaining materials including filling materials will be added into the cup with stirring at medium speed to make it mix evenly. The component B of the coating is obtained by mixing epoxy curing agent with a small amount of water and corrosion inhibitors. According to the weight ratio of epoxy resin: curing agent = 4:1, a certain amount of component B is added to component A, and then it is statically cured for about 15 minutes after stirring evenly, then to coat. The test base material for coating is 120 mm × 50 mm × 0.28 mm steel plate or PTFE plastic plate. The film shall be dried in indoor environment for some time after coating.
2.3. Performance Testing and Characterization
The test of Electrical Conductivity of Coatings was done as following steps. The coating was coated on PTFE board, cured and torn off completely, and sheared into a square film of 2cm×2cm. Thickness of coating was measured by thickness gauge and surface square resistance R (Ω/□) was measured by M-3 digital four-probe tester.

The composition of graphene material was characterized by D8 ADVANCE X-ray diffractometer of AXS Company in Bruke, Germany. The copper target was excited by Kα ray. The working voltage and current were 40kV and 40mA, respectively. The scanning angle ranged from 5° to 80°. Graphene materials were characterized by laser Raman spectroscopy (Renishaw-Invia). The laser wavelength was 514 nm and the spectrum ranged from 100 cm⁻¹ to 4000 cm⁻¹. A small amount of graphene material was dispersed in absolute ethanol by ultrasonic disperser, and the supernatant was dried on copper mesh. The graphene materials were characterized by high resolution TEM (JEM2100). The field emission scanning electron microscopy (Zeiss Sigma 500) was used to study the character of filling materials and coatings.

3. Results and Discussions

3.1. Properties of different conductive fillers
3.1.1. SEM photos of different conductive fillers. SEM photos of flake graphite and two kinds of carbon black materials are showed in Figure 1. The results can be got from Figure 1 that conductive carbon black and acetylene carbon black are aggregated with spherical particles. The particle size of conductive carbon black is generally about 44 nm and that of acetylene carbon black varies about between 35nm and 65 nm. The aggregation density of acetylene carbon black is smaller than that of conductive carbon black, so the specific weight of acetylene carbon black is smaller than that of conductive carbon black. The size of flake graphite varies greatly and there are many smaller size graphite flakes attached on the larger size graphite flakes.
3.1.2. Characterization of Microstructure of Different Graphene. The XRD spectra of three graphene materials (JG, SG and QG) are showed in Figure 2(a). The results show that there is a sharp characteristic diffraction peak near the diffraction angle $2\theta=26.5^\circ$ for the three graphene materials, which corresponds to the graphene crystal plane (002). The interlayer spacing of graphene crystal plane is 0.335nm calculated from the Bragg equation $2dsin\theta=n\lambda$. It shows that the graphene materials are multilayer graphene with complete crystal structure and no oxidation peak. It also tells us that the structure of $\pi$ bond of these graphene materials is almost not destroyed by other groups, and the conductivity is maintained.

![Figure 2. Characteristics of graphene materials (JG, QG, SG).](image)

Raman spectra and characteristic peaks of graphene materials (JG, QG and SG) and flake graphite are shown in Figure 2(b) and Table 2. The peak G and peak 2D are the main characteristic peaks of graphene materials. Peak G is caused by in-plane vibration of sp2 carbon atoms. Peak 2D is a double phonon resonance peak. Peak G and peak 2D can reflect the number of graphene layers. With the increase of layers of graphene, the intensity of peak G increases, the position of peak 2D moves to the right, the half-peak width increases and the strength decreases. While the peak D generally reflects the defect degree of graphene, which is the disordered oscillation peak of graphene. The ratio of peak D to peak G indicates the sp3/sp2 hybrid ratio of graphene. For several graphene materials, the position of peak G and peak 2D are around 1580 cm$^{-1}$ and 2728 cm$^{-1}$ respectively and that of peak 2D moves to the right compared with the position of monolayer graphene 2700 cm$^{-1}$. The results that the peak 2D is not sharp and the ratio of peak G to peak 2D is more than 1.4 indicate that it is multi-layer graphene. Because the strength of peak D of JG is the weakest, it indicates that the structure integrity of JG is better. The results that the ratio of peak D to peak G of QG is 0.08, that of SG is 0.26 and that of flake graphite is 0.25 inform that QG and SG have some defects and the graphene SG has higher content of defect. The
reason may be that some carbon atoms form sp3 hybridization and destroy the structure of graphene layer.

Table 2. Raman spectrum eigenvalues of three graphene materials and graphite.

| Peak name | Peak position and strength ratio | JG | QG | SG | Graphite |
|-----------|---------------------------------|----|----|----|----------|
| D         | 1350                            | 1350| 1350| 1350|          |
| G         | 1582.955                        | 1582.102| 1579.545| 1578.693|          |
| 2D        | 2728.409                        | 2728.409| 2725| 2726.705|          |
| I(D)/I(G) | 0.004                           | 0.081| 0.26| 0.25|          |
| I(G)/I(2D)| 2.23                            | 2.77| 2.36| 2.70|          |

The transmission electron microscopy (TEM) photos of JG and QG graphene materials are shown in Figure 3.

![Figure 3. TEM photographs of graphene materials (a), (c), (e) QG & (b), (d), (f) JG.](image)

According to Figure 3, it can be seen that the thickness of the two graphene materials is thinner, the number of layers is more than 10 layers, and they all have larger lamellar size, and there is existence of folds and stacking of sheets. The lamellae of the QG are smoother. The JG has more serious agglomeration phenomenon and overlaps in some areas and shows opacity under the electron microscope. The results from Figure 3 and Table 2 show that the existence of a small number of defects will reduce the agglomeration degree of graphene and make graphene show better two-dimensional large lamellae structure.

3.2. Study on conductive mechanism of graphene conductive and anticorrosive coatings

There are three theories about conductive mechanism of composite conductive coatings: conductive channel theory, tunnel effect theory and field emission theory. The conductive channel theory holds that conductive filler particles directly contact each other in coatings, free electrons can transfer among adjacent conductive particles. When the content of conductive filler in coatings reaches a certain level, conductive particles contact each other in all areas of coatings. Thus, the coating conducts electricity as a whole. On the other hand, some conductive particles in the coating are separated by resin and not directly contacted, but free electrons can still transfer among them to cause the conduction of the coating. The reason may be that the current is generated by the transition of electrons. The tunneling effect theory is that tunneling current is formed by activating electrons under thermal vibration. The field emission theory is that the capacitance between conductive particles and the resin interface layer is formed under
the action of external voltage and the current is got by electrons migrating [6,7].

3.2.1. Microstructure of composite conductive coatings with different conductive fillers. For composite conductive coatings, the conductivity of coatings is closely related to the distribution of conductive fillers in coatings. In addition, the influence of conductive fillers of different shapes and sizes on the conductivity of coatings is different. Figure 4 is SEM (10k×) photographs of the fracture surface of the composite conductive coatings with different conductive fillers after brittle fracture in liquid nitrogen. Table 3 shows the resistance values of the composite conductive coatings from Figure 4.

Table 3. Coating resistance of different fillers in coatings.

| Fillers                        | Percentage of fillers relative to resin (wt%) | Surface Resistance of Coating (Ω/□) |
|-------------------------------|---------------------------------------------|-------------------------------------|
| Graphene                      | 4.0                                         | 20000                               |
| Carbon black                  | 10.0                                        | 7000                                |
| Graphite+Carbon black         | 2.0+8.0                                     | 5400                                |
| Graphene+Graphite+Carbon black| 4.0+60.0+12.5                               | 805                                 |
| Graphene+Graphite+Carbon black+Zinc | 4.0+20.0+10.0+100.0 | 5354                               |

From Figure 4, it can be seen that most of the carbon black directly forms the carbon black skeleton in the coating (Figure 4 (c) and area 2 in Figure 4 (d)). Free electrons can conduct along the path among the carbon black skeleton particles. Some carbon black particles do not form direct contact, but they are very close to each other (area 1 in Figure 4 (d)). Graphite can overlap with each other in the coating (area 3 in Figure 4 (e)) and form surface contact among carbon black particles and graphite or carbon black-resin-graphite (area 3 in Figure 4 (d)). Spherical zinc particles also become part of the conductive network by contacting with each other (area 3 in Figure 4 (f)). However, due to its larger specific gravity, the distribution density of spherical zinc particles in the coating is lower. Porosity exists around some block graphite and carbon black skeleton (area 2 in Figure 4 (e)). The graphene material in the coating can be completely embedded with resin (white circle area in Figure 4 (b)) and there is no obvious pore, but the distribution density in the coating is so small that the conductive network is difficult to be formed. The graphene can contact with carbon black and graphite to form conductive channels (area 1 in Figure 4 (e)). The graphene material can be extended among resins and fillers (area 1 and area 2 in Figure 4 (f)) to connect conductive fillers in different regions and to increase the electronic conduction paths in conductive network because of its large flexible layer structure. It can be seen that conductive network can be obtained through contact with each other of conductive fillers in the coating.

In Table 3, the order of resistance of the composite coatings with different fillers is: graphene > carbon black > (graphite+carbon black) > (graphite+zinc+graphene+carbon black) > (graphite+graphene +carbon black). According to Table 3 and Figure 4, it can be found that the more complex the conductive network in the coatings is, the smaller the surface resistance of the coatings is.

(a) no filler  
(b) graphene
3.2.2. Influence of content of conductive fillers on electrical conductivity. The surface resistances of coatings containing different contents of carbon black fillers are listed in Table 4. The information in Table 4 shows that when the content of acetylene carbon black is adjusted by single factor, the resistance decreases from 7000Ω/□ to 1380Ω/□ with the content of acetylene black increasing from 10.0% to 20.0%. The result that the resistance decreases sharply when the content of acetylene black increases from 10.0% to 11.0% indicates that the circuit of acetylene carbon black particles conducts instantaneously. The rule of subsequent change of resistance is close to linear relationship, with the slope of -146Ω/□. When the content of conductive carbon black is adjusted by single factor, the variation rule of resistance with the content is close to linear relationship, and the slope is about -69Ω/□. According to the results above, the contribution of acetylene carbon black per 1.0% to the reduction of resistance value is greater than that of conductive carbon black. The result 1055Ω/□ of measured resistance value of 10.0%YT+40.0%DT is almost the same as the resistance values 1078Ω/□ (284Ω/□ is set as the value of 10.0%YT) of the shunt resistance of the two fillers, and it indicates that the more contacts among particles in the same region there is, the smaller the resistance value is.

The content of acetylene carbon black or conductive carbon black is fixed and the content of graphene is adjusted during test. The resistance value varied slightly with the content of graphene increasing from 1.0% to 5.0%. The result shows that the circuit is completely turned on after the 1.0% graphene is added into the coating. The change of resistance value shows a linear relationship with the content variation of graphene from 0 to 1.0%, the slope with 10.0% acetylene carbon black is -5512Ω/□, and the slope with 40.0% conductive carbon black is -947Ω/□. It can be concluded that the contribution of graphene to the decrease of resistance value in conductive carbon black with lower resistance value is lower than that in acetylene carbon black with higher resistance value. It also can be considered that the bridging characteristic of graphene is more suitable for coatings with higher resistance value.

The resistance of 15.0%YT is almost the same as that of 10.0%YT+1.0%JG. The resistance of 50.0%DT is almost the same as that of 40.0%DT+1.0%JG. It shows that the effect of 1.0% graphene on the conductivity of coatings is greater than that of 1.0%YT or 1.0%DT. The reason may be that the large layer structure of graphene overlaps carbon black in the conductive network, which reduces the required
carbon black content for forming conductive channels.

Table 4. Resistance value of composite conductive coatings with different contents of carbon black.

| Filler           | Content /% | Resistance /Ω/□ | Content  | Content of JG | Resistance /Ω/□ |
|------------------|------------|------------------|----------|---------------|-----------------|
| Acetylene black  | 10.0       | 7000             | 0        |               | 7000            |
| (YT)             | 11.0       | 2696             |          |               | 5100            |
|                  | 15.0       | 1480             | 0.5%     | 10.0%YT       | 1488            |
|                  | 20.0       | 1380             | 1.0%     |               | 420             |
|                  | 40.0       | 1737             | 5.0%     |               | 1737            |
| Carbon black     | 45.0       | 1256             | 0        |               | 1491            |
| (DT)             | 50.0       | 787              |          | 40.0%DT       | 790             |
|                  | 55.0       | 699              | 0.5%     |               | 761             |
| 10.0%YT+40.0%DT  | 1055       | 5.0%             |          |               | 761             |

Table 5. Resistance value of conductive coatings with different contents of graphite.

| Graphite (GI)/% | Resistance /kΩ/□ | Graphene (GP)/% | Resistance /kΩ/□ | GI+YT       | Resistance /kΩ/□ |
|-----------------|-------------------|-----------------|-------------------|-------------|-----------------|
| 20.0            | 16.0              | 0.5             | 1000              | 8.0%GI+2.0%YT | >1000           |
| 60.0            | 9.0               | 2.0             | >1000             | 5.0%GI+5.0%YT | 20.0           |
| 85.0            | 3.9               | 4.0             | 280.0             | 2.0%GI+8.0%YT | 5.4            |

Resistance value of conductive coatings with different contents of graphite filler is shown in Table 5. It can be seen from Table 5, when the content of flake graphite is less than 20.0%, the surface resistance of the coating is very high. When the content of flake graphite is 60.0%, the resistance of the coating is 16.0 kΩ/□. When the content of graphite continues to increase, the relationship between the decrease of the resistance of the coating and the increase of content of the graphite is linear. The slope is -185Ω/□, which is lower than the absolute value of slope of acetylene carbon black or conductive carbon black (see Table 4). Flake graphite has larger size, thicker flake shape, smaller specific surface area and smaller probability of contact with each other, so the graphite has poor ability of forming effective conductive paths in coatings.

When the content of graphene is less than 1.0%, the resistance of the coating is so high that the conductivity of coating is almost not observed. When the content of graphene increases from 2.0% to 4.0%, the resistance of the coating decreases from 280.0 kΩ/□ to 20.0 kΩ/□. However, when the content of graphene is further increased, it is difficult to form a coating because the solid content of graphene slurry are so low that the solid content of the coating is also very small.

Graphite and acetylene carbon black are mixed into the coating with the total content of fillers at 10.0%. The surface resistance of the coating decreases with the increase of the content of acetylene carbon black. It shows that the resistance of the coating is mainly controlled by the content of acetylene carbon black. Acetylene carbon black is a nano-sized spherical particle with large specific surface area. The resistance value of the coating will decrease with the increase of the content of conductive filler, and the obstacle of electronic transmission between conductive filler and resin will gradually decrease, and that is exactly the conductive mechanism of conductive electrostatic coating.

3.2.3. Conductive model of graphene-based composite conductive coatings. According to the experimental phenomena and results above, it can be seen that conductive fillers with small specific surface area need a higher adding amount to contact effectively. But sheet materials have overlapping function and can form conductive paths more quickly than spherical particles at the same specific surface area. The contact surface among spherical particles is small, and more content of spherical particles are needed to form conductive paths. Therefore, sheet conductive materials must be mixed with spherical particles to form conductive paths and to reduce resistance value (parallel resistance of particle accumulation) effectively. Because the graphene has these properties with flexibility, light weight and high specific surface area, it is possible to replace more spherical materials with a smaller amount of
graphene, which not only reduces the pigment/binder ratio and but also improves the performance of coatings. Therefore, the role of graphene is very important in conductive coating.

![Graphene, Flakes Graphite, Spherical Conductive Material](image)

Figure 5. Conductive model and equivalent circuit diagram of graphene conductive coatings.

According to the above test results, different resistances are formed among conductive fillers, which are connected with series or parallel resistance. Figure 5 is a model of conductive fillers in coatings. The forms of conductive fillers are spherical (such as acetylene carbon black, conductive carbon black), flake (such as graphite) and thin film (such as graphene), which randomly form conductive paths. The lower part of Figure 5 is an equivalent circuit diagram converted from the model. Once the circuit is broken, the conductive channel is cut off, but it can still form a conductive electrostatic channel. Electrons can be transmitted between conductive fillers and resins. Therefore, the conductive properties of conductive coatings are closely related to the types and content of conductive fillers, the connection properties of resins, the coating methods and the environment conditions.

4. Conclusions

One or more of these conductive fillers which includes graphene, conductive carbon black, acetylene carbon black, graphite and zinc powder were mixed with epoxy resin to form conductive coatings. The shape of fillers and the characteristics of filler particles in the coatings were characterized by TEM, SEM, Raman spectroscopy and XRD diffraction spectroscopy. The effects of different content of conductive fillers on conductivity and conductive mechanism were studied. The conductive model of graphene conductive coatings was established. The results show that: (1) fillers with large specific surface area contribute more to conductivity, thin flake graphene contributes most, spherical acetylene carbon black and conductive carbon black contribute moderate, and flake graphite contributes least; (2) Several conductive fillers mixed contribute more to conductivity than single filler; (3) conductive channels of coatings are formed by stacking and contacting among fillers. The series and parallel resistance are formed by stacking of fillers and constitute the resistance of the conductive coating. The resistance of the coating decreases with the increase of the filler content, which almost follows the linear relationship between the resistance and the filler content before or after the inflection point. 4) The conductive model of the coating clearly shows the bridging characteristics of graphene, the conductive channel formed by the contact among fillers and the characteristics of series and parallel resistance.
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