Effect of ITO Content on Properties of Functional Graphene Coating on Cotton Fabric

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Abstract. In order to investigate the effect of indium tin oxide (ITO) on the performance of graphene functional coating on cotton fabric, different contents of ITO were added to the graphene coating system, and the effects of ITO content and curing time on various properties of graphene coating were studied. The results showed that the ITO particles adsorbed on the graphene sheets and filled the gaps between the graphene sheets, forming a dense conductive network, which could further improve the conductive performance of the functional coatings. When ITO content was 1.2%, the resistivity of the coating reached the lowest 1.8 Ω·cm, and the overall ultraviolet transmittance and reflectance were the lowest. With the increase of ITO content, the infrared reflectance will first decrease and then slowly increase, but the infrared reflectance is all below 0.5%. When the curing time reached 90 s, the resistivity and UV transmittance of cotton fabric coating decreased. With the extension of curing time, the coating on infrared reflectivity gradually increased, but the infrared reflectivity of the overall < 1%.

1. Introduction
Graphene is a material with a two-dimensional honeycomb structure composed of a single layer of carbon atoms. It not only has a unique two-dimensional nanostructure, excellent electrical conductivity, thermal conductivity, high carrier mobility, larger specific surface area, high transparency, good mechanical properties, thermodynamic stability, chemical stability and easy functionalization, etc., but also has good microwave absorption properties. It has a wide range of application prospects in the coating field, it can prepare conductive coating, thermal conductive and high-strength coatings[1-6]. Fabric-based special coating materials have better flexibility than conventional conductive materials, and have broad application prospects in wearable clothing, flexible sensors and other fields[7,8]. ITO material has good conductivity, light color, compatible with multi-band stealth, and conductivity of cotton fabric can be enhanced by mixed ITO[9-11].

In this paper, ITO and graphene were applied in the coating system, blended to prepare ITO/graphene functional coating, and coated on the surface of cotton fabric. The influence of ITO content on the optical and electrical properties of graphene functional coatings were studied by measuring the reflectance of visible light, infrared emissivity, electrical conductivity, ultraviolet transmittance and infrared
reflectance and other properties. It is hope that the coatings can be applied to textiles to prepare special functional textiles with good conductivity and reflectivity.

2. Experimental

2.1. Materials
Pure cotton fabric (the warp and weft density is 520 pieces/10 cm×400 pieces/10 cm, the weight is 126 g/m²); ITO (Xiya reagent), graphene paste (Deyang Carbon Technology Co., Ltd.), Thickener PFL (Shanghai Yuhui Chemical Co., Ltd.), aqueous polyurethane (Jining Baiyi Chemical Co., Ltd.), polyvinylpyrrolidone K-30 (PVP, Sinopharm Chemical Co., Ltd.).

2.2. Equipments
T18 digital ULTRA-TURRAX homogenizer (Guangzhou Yike Laboratory Technology Co., Ltd.), R-3 baking machine (Taiwan RUBI Dyeing Testing Machine Co., Ltd.), SZT-2A four-probe measuring instrument (Suzhou Tongchuang Electronics Co., Ltd.), TM3030 scanning electron microscope (Hitachi High-Tech Co., Ltd.).

2.3. Experimental method

2.3.1. Preparation of ITO/graphene coating. ITO powder with the content of 0.5%、1.0%、1.2%、1.4%、1.6%、1.8%、2.0% were added into the graphene (0.8%) slurry, and add deionized water and dispersant PVP (the relative dosage ratio of ITO is 1:1), and was stirred at a speed of 9000 rpm for 30 min by homogenizer to make the graphene and ITO more uniformly dispersed in the coating system. Then aqueous polyurethane with the mass ratio of 10% was added, and the mixture was evenly mixed and placed in a vacuum oven. The air bubbles in the paint were removed under -0.1 MPa, and an ITO/graphene functional paint was prepared.

2.3.2. Preparation of functional coating on cotton fabric. The prepared functional coating is coated on the cotton fabric by a wire bar coater. After the coating is completed, use a baking machine to bake at 150 °C. Then the coating is based by a baking machine at 150 °C, and after baking, it can be coated again. Coatings with different coating times (thickness) are prepared on the cotton fabric and their performance is tested.

3. Results and discussion
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Figure 1. ITO/graphene coating

The morphology of the ITO/graphene is shown in Figure 1, in which the content of ITO and graphene is 1.2% and 0.8% in the ITO/graphene coating, respectively. It can be observed that the ITO particles
are attached to the surface of the graphene sheet, and the graphene sheet have large number of folds. It may be that the ITO particles adsorbed on the surface hinder the contact between the graphene sheets, resulting in the graphene sheets flatness. But the existence of ITO particles also fills the voids and gaps between graphene sheets. The carrier density of the ITO/graphene coating would be increased due to a continuous and stable conductive network is formed, and the conductivity is improved.

Adding ITO to the graphene paint will have a certain degree of influence on the conductivity of the coating. Adding different contents of ITO to the graphene paint (the content of graphene is 0.8%), and coating 6 layers paint on the surface of cotton fabric using four probes. The needle measuring instrument the conductivity of coatings containing different ITO contents were measures by the four-probe measuring instrument. The result is shown in Figure 2.

![Figure 2. Effect of ITO content on the conductivity of the coating](image)

Compared with the graphene paint coating, the resistivity of the coating is reduced when the graphene paint added the ITO powder. The results indicate that graphene and ITO has a synergistic effect in terms of excellent conductivity. The ITO particles are in close contact with the graphene and filling the gaps between the graphene particles, forming a dense conductive network, and making the conductive coating structure on the cotton fabric more complete. The carrier of ITO and the free electron movement in graphene are less hindered which together improve the conductivity of the coating. However, the
addition of ITO does not greatly improve the conductivity, and as the ITO content increase, the conductivity of the coating decreases first. After reaching the lowest value when the ITO content is 1.2%, the resistivity slowly increases trend. The possible reason is that the addition of the dispersant PVP has a certain influence on the conductivity of the coating. Moreover, as the ITO content continues to increase, the number of ITO particles adsorbed on the graphene sheets increases, which will hinder the effective contact between the graphene sheets, thereby reducing the conductivity of the coating.

In order to study the effect of the addition of ITO on the UV protection performance of the coating, the UV transmittance of the coating with different ITO content was measured, and the measurement results are shown in Figure 3.

The UV permeability of the coating has a great influence after adding ITO to the graphene paint (Figure 3). Compared to the graphene coating without ITO, the UV transmittance of the coating of the graphene paint added ITO will be further reduced, and the transmittance in most of the UV bands is almost zero. When the ITO content is 1.2% or 2.0%, the overall UV permeability is the lowest, and the UV protection performance is the best, the effect is the best. This may be the absorption of ultraviolet rays by ITO is mainly manifested as intrinsic absorption, and the intrinsic absorption line $\lambda_0$ is determined by the following formula (1).

$$\lambda_0 = \frac{1.24}{E_g(eV)} (\mu m)$$

In the formula, $E_g$ is the forbidden band width. The band gap of ITO is between 2.60~3.75 eV, and its corresponding intrinsic absorption wavelength is between 331~477 nm, so ITO has a certain absorption effect on ultraviolet rays. ITO and graphene work together to reduce the transmittance of the coating to ultraviolet rays and enhance the ultraviolet protection performance of the coating.

In order to study the influence of the addition of ITO on the reflectance of visible light reflectivity of coatings, the visible light reflectivity of coatings with different contents of ITO was measured, and the measurement results are shown in Figure 4.

![Figure 4. Influence of ITO content on visible light reflectance](image)

It can be seen from Figure 4 that, compared with the coating without ITO, the addition of ITO can further reduce the reflectance of visible light of the coating from 7.4% to about 6.4%; and with the increase of ITO content increase, the visible light reflectivity shows a trend of first decreasing and then increasing. When the content reaches 1.2%, the reflectivity of the coating is the lowest. If the content of ITO continues to increase, the visible light reflectivity is mainly because the ITO particles attached to the surface of the graphene sheet make the graphene surface rough and reduce the specular reflectivity of the coating surface to visible light. With the increase of the ITO content, the ITO particles as the scatter increase, the diffuse reflection of the coating to visible light is enhanced, and the reflectivity of the coating to the visible light is enhanced.
Because ITO has special properties in the infrared region, the addition of ITO in graphene paint will affect the infrared reflection performance of the coating. The infrared reflectance of coatings was measured when added with different ITO content.

![Graph showing influence of ITO content on infrared reflectance](image)

Figure 5. Influence of ITO content on infrared reflectance

It can be seen from Figure 5 that, compared with the coating without ITO, the reflectivity of the coating containing ITO to the infrared band is further reduced. And as the content of ITO increases, the infrared reflectance is below 0.5%. Because with the increase of ITO content, the reflection start wavelength of the coating obviously decreases, the number of scatters in the coating increases, and density of carriers in the coating. The plasmon resonance wavelength was shift to the shortwave direction, increasing the absorption of infrared. These two factors work together to reduce the infrared reflectivity of the coating.

The conductivity of the ITO/graphene coating is affected by the degree of drying and curing, and the curing degree is greatly affected by the curing time. The resistivity of the coatings was measured for different curing times as shown in Figure 6.

![Graph showing effect of curing time on resistivity](image)

Figure 6. Effect of curing time on resistivity

It can be seen from Figure 6 that the resistivity of the cotton fabric coating gradually decreases with the increase of the curing time, and the lowest value is 12.8 Ω·cm. When the curing time reaches 90s...
seconds, the resistivity of coating decreases slowly and then remains basically unchanged. This result is mainly due to the evaporation of the solvent in the coating film. The curing process of the coating is the process of solvent volatilization, polyurethane resin shrinkage brings the pigment and filler particles close to each other and contact each other in the process. The conductivity of the cotton fabric coating is mainly the conductive filler ions contact with each other to form a chain and form a conductive network. Before the paint is dry and solidified, the resin and the fill are filled among the conductive filler particles, the value and the conductive fill are in an independent state, mutual contact is insufficient, and the conductivity is relatively poor. Therefore, when the coating is naturally air-dried, the surface resistivity of the coating is 20.3 Ω·cm. This is because the solvent volatile resin and the filler ions are mixed, cured and interwoven together, and the conductive filler ions are contacted and connected with each other to form a conductive network, so the coating has conductive performance. With the extension of curing time, the coating dried and cured, and the resistivity of the coating decreased. When the curing time reaches 90s, the solvent evaporates completely, and the conductive network between the conductive ions of the layer continues to increase, and the resistivity of the coating decreases no longer significantly.

Figure 7. Effect of curing time on UV transmittance of coating

Figure 8. Effect of curing time on visible light reflectance
In order to study the effect of curing time on the UV transmittance of the coating, the transmittance of the coating at different curing times was measured and the results are shown in Figure 7. The result indicated that the transmission of the cotton fabric with coating to the ultraviolet ray is all low. In addition, as the curing time increases, the UV transmittance of the coating will decrease, and the UV transmittance of curing for 90s is very low; when curing for 120s, the UV can hardly pass through the coating, and the UV protection effect is excellent. The reason is probably that, as the curing time increases, the moisture in the coating evaporates faster, and the resin polymers form bonds with each other to form a three-dimensional coating network. Tightly wrap graphene particles together, the particles are in close contact with each other, changing from a disordered state to an ordered state. Effectively reduce the gap of the coating, thereby reducing the transmittance of ultraviolet rays. Moreover, the longer the curing time, the denser the coating was formed by contact between the particles, and the lower the UV transmittance.

The reflectivity of the coating was measured at different curing times for studying the effect of curing time on the coating reflectivity in the visible light, and the results are shown in Figure 8. The results shows that the reflectivity of the coating to visible light gradually increases when the increase of the curing time of the coating, but the increase is small, and the overall stability is between 6.4% and 6.8%. The reason probably is the content of the pigment and filler particles in the coating is unchanged, and thus the visible light absorptivity of the coating does not change much. As the curing time increases, the solvent evaporates rapidly, and the resin and the pigment and filler particles are close to each other and the probability of contact increases. The graphene particles and ITO particles will become tighter as the resin molecules form bonds, and the coating particles will change from a “wet” disorderly state to “dry” orderly state. The surface of the coating would become more smoothly. Compared with a non-smooth and rough surface, a smooth surface is conductive to the reflection of visible light by the coating, thereby increasing the reflectivity of visible light.

The curing time can affect the distribution of filler particles on the surface of the cotton fabric, and then affect the infrared reflectance of the coating. The infrared reflectance of the coating with different curing times are measured and shown in Figure 9.

The results shown that the reflectivity of the coating to infrared rays gradually increases when the curing time increases, but the over reflectivity of infrared rays is less than 1%, and there is no selective reflection of infrared rays, and only the far infrared has a slight increase. The main reason is that the solvent between the filler and the resin on the coating is volatilized more fully and completely with the curing time increases, and the resin polymer chains are interconnected to form a three-dimensional network structure. The pigment and filler particles were encapsulated and the distance between the
graphene and the ITO particles becomes smaller, the distribution is closer, and the contact is more complete. The transparency to infrared is reduced with the stacking of graphene sheets increases, and the reflectivity is increased; the carrier density of ITO particles increases, which promotes the ion resonance wavelength to move to the shortwave direction, and the ITO scatterers increase greatly at the same time. The two factors are common the effect is to gradually increase the infrared reflectivity of the coating.

4. Conclusion
In this paper, the conductivity and reflection properties of cotton fabric with graphene coating was studied by adding the different content of ITO powder and the different the curing time. The results show that ITO particles added into graphene paint and would be adsorbed on the surface of the graphene sheet after forming a coating of cotton fabric. And the conductivity of the coating is further improved with the increase of ITO content. When the content of ITO reaches 1.2%, the conductivity of the coating is the best, and the resistivity is only 18 Ω·cm. And the reflectivity of the coating is also lowest, the infrared reflectivity of the coating would slowly decrease. In addition, it is found that the conductivity of the coating will increase when the curing time increases. However, when the curing time reaches 90s, the conductivity of the coating will not change much if the curing time continues to increase. The minimum conductivity value of the coating is only 12.8 Ω·cm. The resistivity of the coating was measured before and after washing. It was found that the resistivity before and after washing did not change much, indicating that the coating was better.

Acknowledgments
This work was supported by the Natural Science Foundation of Jiangsu Province Special Equipment Safety Supervision Inspection Institute (KJ(Y)2020036).

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