State-of-the-art applied research on conductive composites

C Q Hu, Y M Huang, J S Yang, Q Yu and M Sun

1Guangzhou Panyu Cable Group Co., Ltd. Guangzhou, Guangdong 511442, China
2Guangdong University of Technology, Guangzhou, Guangdong 510006, China

Email: huchaoqiang@126.com

Abstract. The article introduces the types of conductive composites and analyzes several kinds of their conductive mechanisms based on the percolation theory, quantum tunneling effect, effective medium, and field emission theory. The current research progress concerning the effects of conductive materials’ matrix, conductive fillers, and doping on them is discussed in detail. Available preparation methods and applications of conductive composite materials are summarized. A future research direction on the refinement of conductive composites is outlined, which implies the development of new matrix systems and conductive fillers with higher and more stable electrical conductivity.

1. Introduction
Conductive composite materials emerged quite recently but their market share permanently grows. For example, composite polymer conductive materials are very instrumental in improving power transmission facilities. Intrinsic conducting polymers also play an important role in antistatic coatings and electromagnetic radiation protection. New conductive polymer composites have numerous advantages over conventional conductors, such as higher electrochemical corrosion resistance, acid and alkali resistance, water resistance, etc., which gives them a “must-have” status among advanced functional materials.

2. Conductive Composites
The conductive composite material is prepared either by using the polymer matrix and adding high-conductive metal powder, carbon fiber, or other types of conductive particles or fibers, or by doping the matrix to obtain a conductive composite. This technique is widely used in antistatic coatings, antistatic fabrics, power composite greases, conductive pastes, electrode materials, etc. [1-2].

2.1. Types of conductive composite materials
According to the electrical resistivity of the conductive polymer material, a volume resistivity of less than $10^{10} \Omega \cdot \text{cm}$ is called a polymer conductive material, $10^{10} \sim 10^{7} \Omega \cdot \text{cm}$ is a semiconductor, $10^{7} \sim 10^{4} \Omega \cdot \text{cm}$ is an antistatic material, and $10^{4} \sim 10^{0} \Omega \cdot \text{cm}$ is Conductive material, $10^{0} \sim 10^{-2} \Omega \cdot \text{cm}$ is superconducting material.

According to whether the matrix is conductive or not, the composite material can be subdivided into intrinsic and composite polymer conductive materials [3].

2.1.1. Intrinsic polymer conductive material. Common substrates of intrinsic polymer conductive materials include polyaniline, polypyrrole, and polyacetylene. The organic polymers contain a large...
number of conjugated double bonds, which is a kind of semiconductor material, and the conductivity is greatly improved after doping [4-5]. For example, after polyacetylene doping, the conductivity can be increased by 12 orders of magnitude. However, intrinsic conductive materials have poor stability, poor plasticity, and are hard to process, and are generally used in composite materials with other polymers.

2.1.2. Composite polymer conductive material. The composite polymer conductive material is based on mineral oil, synthetic lipid oil, silicone oil, epoxy resin, polyurethane, etc. [6-8], and conductive fillers such as copper powder, silver powder, graphite, nano carbon fiber, and the like are added. A uniformly soft paste or liquid which is dispersed and ground, and a conductive composite material which is directly prepared and formed.

3. Conductive mechanism
Studying the conductive mechanism of conductive polymer composites has important guiding significance for improving the performance of conductive composites. Since the middle of the 20th century, scholars at home and abroad have conducted in-depth research on the conductive mechanism of conductive polymer composites. The conductive mechanism of molecular composites mainly includes the theory of percolation, quantum tunneling, effective medium theory, and field emission theory [9].

3.1. Percolation theory
The percolation theory is to guide the conductive material in the paste to a certain level, and then the conductive paste has conductivity. When the content of the conductive filler in the polymer or organic matrix is too small, the conductivity is poor, close to that of insulators. However, when the conductive filler is gradually increased and the content reaches a certain content, the conductivity of the composite will be sharply improved. The researchers [10-11] reported that when the conductive filler content reached a certain concentration, the conductive particles formed a continuous conductive percolation network in the organic matrix. The critical volume fraction of the conductive filler is the percolation threshold of the material. The size of the percolation threshold is related to the type, shape, and dispersion of the conductive filler and the matrix [11].

3.2. Quantum tunneling effect
The quantum tunneling theory holds that microscopic particles have the ability to penetrate the barrier. If a thin layer of insulator is sandwiched between metal conductors to form an electron tunnel junction, electrons can pass through the insulating layer under the action of an electric field. This phenomenon is called the tunneling effect. This theory clarifies the fact that when the conductive filler content in the conductive paste is small, the conductive particles in the matrix do not form a network, but there is still a phenomenon of current passing [12].

3.3. Effective medium theories
The effective medium theory is an effective method for dealing with the electron transport behavior in a binary random symmetry system. When dealing with the conductive mechanism of the conductive paste, it is considered that the conductive particles of each size are uniformly dispersed in the mixed system, and both are insulated. Being separated, the conductive particles do not touch each other. The conductivity of the mixed system is calculated by the following formula [12]:

$$\sigma_m = \sigma_h \left(1 - \frac{3}{2}f \right)$$  \hspace{1cm} (1)

The resistivity is calculated as follows:

$$\rho_m = \rho_h (1-3\varphi)$$  \hspace{1cm} (2)
Here $\sigma_m$ and $\sigma_h$ are the total and high-conductive phase conductivities, respectively; $f$ is the volume fraction of the low-conductive phase; $\rho_m$ and $\rho_h$ are the total resistivity and that of the low-conductive phase, respectively; $\phi$ is the volume fraction of the high-conductive phase [12].

3.4. The field emission theory

The field emission theory envisages that when conductive particles in the composite are located less than 10 nm apart from each other, their electric field induces the electron emission, thereby generating an electric current [12].

4. Research Status of Conductive Composites

Foreign studies on conductive composites were earlier. In 1974, Shirakawa et al. discovered that doped polyacetylenes had a high conductivity similar to metals [13], which dismissed a prior prejudice that polymers are insulators. However, intrinsic conductive polymerization has the characteristics of poor solubility. Scientists mainly modify their monomers, access hydrophilic groups, or carry out graft modification, blend modification, etc. Polyaniline and polyacetylene are mature polymers that are widely used in antistatic coatings, electromagnetic interference shielding coatings, etc. [14].

In the research of composite polymer conductive materials, Du et al., as well as Li et al., have developed such products as epoxy resin conductive paste, which could replace tin-lead solder [10, 15] in low-temperature, environmental protection, and other applications. There is also a conductive paste for high-voltage power transmission and metal fittings for temperatures up to 230 °C. The use of conductive paste can effectively protect the metal contact surface of the cable joint, prevent electrochemical corrosion, arc corrosion, and reduce heat generation [11].

4.1. Research progress of conductive paste

With a rapid economic development, the consumption of electricity permanently increases. The lack of gold fitting connections in the power transmission and transformation has become an urgent problem. There are many works on processing and preparation of alternative fitting materials. Thus, a patent applied by State Grid Co., Ltd. in May 2018 [16] introduced a kind of silicone oil as the matrix, with modified copper powder, modified silver powder and modified graphite as conductive. The conductive paste of the filler is stirred at a high temperature and then vacuumed to remove low-boiling substances, thereby obtaining a novel conductive paste with high dropping point, strong adhesion and long service life [16].

The use of conductive paste can prolong the service life of connecting fittings. Zhou [17] studied the application of conductive paste in aluminum alloy connectors and found that the connector using conductive paste is less than the conductive paste. The connector has a resistance close to 40% of the unused conductive paste connector at multiple temperatures, and the time to failure is by 126% longer than that of the connector without the conductive paste [17].

Yan [18] used polyethylene oxide polypropylene oxide monobutyl ether as the base oil, using polytetrafluoroethylene as a thickener, vapor-grown carbon fiber, copper powder, silver powder, etc. as conductive filler, tested conductive paste The dropping point reaches above 230°C, and the performance is the same as that of foreign advanced products. The conductive paste prepared in the 110KV substation is used to reduce the resistance at the joint.

Wu [19] used polyether, polyalphaolefin and mineral oil, metal (Ag, Cu) and ionic liquid additives 1-butyl-3-methylimidazolium tetrafluoroborate (LB104) and 1-hexyl-3- Methylimidazolium tetrafluoroborate (LB106) is used as a conductive additive, and polytetrafluoroethylene is used as a thickening agent to prepare a conductive paste. Studies have shown that polyether is the base oil, and the antifriction effect of silver powder is better than that of copper powder. When the dosage is less than 20%, the ionic liquid can replace the metal powder. LB104 performs better than LB106 at low concentrations.
Feng et al. [20] used a reducing agent to reduce silver ions on carbon nanomaterials to obtain Ag-C composite nanomaterials, which were prepared with 60 wt% Ag-C composite nanomaterials and 11 wt% epoxy resin and 29 wt% organic solvent. The conductive paste had good electrical conductivity.

Li et al. [21] used the alcohol heating method, where the AgNO₃ solution was added dropwise to a three-necked flask containing PVP solution under vigorous stirring, and heated to 210°C to prepare nano-scale silver wire, using nano silver sheets as In the control group, the effect of the filler content on the electrical resistivity and shear strength of the conductive paste was investigated. The results show that when the filler content is less than 50% by weight, the conductive paste using nano-silver wire has a lower resistivity than the conductive paste using the nano-silver sheet and has higher shear strength.

Fan [22] used polyethylene glycol (PEG) as the base oil, LiBF₄, LiPF₆, LiNTf₂ three kinds of lithium salts as conductive ions, prepared anti-wear conductive grease, characterized by three-dimensional confocal surface topography. It was found that these three lithium ions greatly improved the lubricating properties of the grease. The use of XPS to characterize the metal surface of the grease used, the results show that the reactive ions in the grease react chemically with the metal to produce an anti-wear material. It is thus found that the physical adsorption and chemical reaction of the conductive grease improves the surface abrasion resistance and electrical conductivity of the joined metal.

Yim et al. [23] studied conductive adhesives used for soldering electronic components and compared copper powders with aliphatic coupling agents and aromatic coupling agents, with epoxy resins and curing agents. The conductive adhesive was prepared by catalyst and compared with the conductive paste of gold-plated polymer microspheres and gold-plated nickel microspheres as conductive fillers. Experiments showed that the conductive paste treated with the copper powder as the conductive filler was more than the other two. The conductive paste has a lower resistivity (7.5 × 10⁻⁴ Ωcm) and resistance to moist heat.

4.2. Research progress on conductive fibers
Li et al. [24] synthesized conductive nanofiber yarns using carbon nanotubes and thermoplastic polyurethane (TPU) nanofiber yarns. The experiment used an electrospinning device to prepare a continuous TPU elastic nanofiber yarn. In order to impart conductivity to the nanofiber yarn, the fiber obtained by ultrasonic adsorption, and then the unmodified single-walled carbon nanotubes (SWNTs) adsorbed. Two carbon nanotubes can be produced between the substrate and the two carbon tubes to produce a continuous and highly conductive elastic nanofiber yarn. The elastic yarn has higher electrical conductivity than the fiber yarn prepared by separately adsorbing MWNTs and SWNTs. The yarn has high elasticity, high electrical conductivity, stretchability, linear braidability, etc., and has great potential applications in wearable electronic devices, and has bright future in the fields of electromagnetic shielding, antistatic, sensors, and flexible energy devices. Application prospects.

Li et al. [25], first used carboxylation modification of multi-walled carbon nanotubes. The reaction of carboxyl groups with amine groups, pyrrole was polymerized on the surface of carbon nanotubes, and the amount of pyrrole was different to obtain composite carbon nanotubes with different thickness. Then, it was mixed with polyurethane to obtain a poly(pyrrole)carbon nanotube/polyurethane conductive composite material, which could be applied to a sensor. Polypyrrole is rigid and difficult to process. If polypyrrole is added to the polymer alone, the amount of addition needs to be large to form a conductive network. However, the researchers have effectively combined polypyrrole with long-fiber carbon nanotubes, polypyrrole/carbon nano. The conductivity of the tube is greater than the conductivity of the polypyrrole alone.

In the development of anti-electromagnetic radiation materials, Gao et al. [26] used dopamine to modify the polypropylene non-woven fabric, and then used hydrazine hydrate to reduce silver trifluoroacetate on the modified non-woven fabric, on the surface of the non-woven fabric. A layer of silver is obtained, and then immersed in perfluorododecanethiol to obtain a final product with a conductivity of 4000 S/m and an EMI shielding effectiveness of up to 49 dB in the range of 12.5-18
GHz. The non-woven fabric exhibits super-hydrophobic properties, and the acid-base salt solution remains substantially unchanged after being ground and bent.

5. Preparation method of conductive composite material

5.1. Preparation method of conductive paste
Most of the conductive paste is prepared by physically mixing the substrate with the conductive filler. In order to make the prepared conductive paste uniform in texture and stability, it is important in the preparation process to maximize the fineness and dispersibility of the conductive filler. Many scholars have studied how to prepare conductive particles of nano- or micro-orders of magnitude. For example, Zhang et al. [27] used ascorbic acid as a reducing agent to reduce copper hydroxide to nano-copper particles in an alcohol solution, and the particle size distribution was about 390 nm. The nano copper powder is dispersed in an ethanol solution, and silver nitrate is added for replacement to obtain a Cu-Ag nanosheet in which a part of the atoms are replaced by silver. PVP is used as a dispersing agent and a structure directing agent to grow Ag on a plane, and finally obtained. The product is in the form of a sheet rather than a sphere. 80 wt% of the metal particles are separated from the epoxy resin, the curing agent, and the like under high-speed stirring to obtain a conductive paste, and the volume resistivity after curing is $4 \times 10^{-5} \ \Omega \cdot \text{cm}$.

5.2. Preparation method of conductive fiber material
Since the pure intrinsic conductive polymer has poor solubility and high rigidity, it is not suitable for direct processing, such as polyaniline, polypyrrole, polythiophene, etc., and needs to be combined with a thermoplastic polymer matrix. Common methods are physical blending, in-situ polymerization, and copolymerization.

The physical blending method is simple, mainly using a dispersing agent and mechanically dispersing the conductive polymer in the matrix. The conductive composite prepared by this method has a great relationship between the conductivity and the mixing ratio. The copolymerization method is to add a monomer with a functional branch in the reaction monomer to improve the plasticity of the polymer, but the copolymerization law tends to lower the conductivity of the polymer. The in-situ polymerization method is to carry out polymerization of monomers on the surface of other materials to form a coated composite material. The product obtained by the total preparation method has good stability and the conductivity is maintained or even improved.

Pan [28] used in-situ polymerization of caprolactam monomer and initiator in expanded graphite to obtain nylon 6/graphite nanocomposites. The relationship between the volumetric conductivity of the composite and the graphite volume fraction was measured. The conductive percolation thresholds of the composites obtained by using the untreated graphite were 0.75 and 2.1 vol%, respectively. The resulting composite material by in-situ intercalation polymerization has better electrical conductivity.

6. Summary
Conductive composite materials are increasingly used in power transmission and distribution, electronic component packaging, antistatic coatings, and flexible wearable devices. The rapid development of China's economy has rapidly increased the demand for electricity, and the miniaturization and integration of electronic products have provided a broad space for the development of conductive and conductive composite materials.

At present, there are few studies on conductive composite materials in China, especially conductive pastes that can be used in the field of high voltage transmission and distribution. The development of conductive paste in the future may start from the following aspects:

1) Develop new conductive fillers. There are currently a limited number of conductive fillers on the market. Silver powder, gold powder and other conductive properties are expensive and pure silver powder will migrate in a humid environment, which is not suitable for practical applications. Graphite conductive fillers are cheaper, but the use of carbon-based fillers causes the conductive paste to be black,
and the electrical conductivity is generally limited, which limits the range of use of the conductive paste to some extent. At present, there are copper powders for modification at home and abroad, such as electroless silver plating of copper powder and silane coupling agent treatment on the surface of copper powder. Both of them have good anti-oxidation and excellent electrical conductivity. In the future, the types and dosages of silane coupling agents may be used. The relationship between the amount of silver coating and the dispersion and conductivity of copper powder was investigated.

2) Develop conductive paste for use in curable power lines. Conventional conductive pastes can cause matrix loss when used for a long time and in high temperature and rain. If the curable epoxy resin can be applied to high-voltage transmission and distribution and transformer equipment, and solve the problem of brittleness of epoxy resin at low temperature, it is believed that the curing system will have broad application prospects in the field of high-voltage transmission and distribution.

3) Research on intrinsic conductive composite system. Intrinsic conductive polymers have broad application prospects, but most of the polymers have unstable doping properties [28-30], and the weavability is poor. Future research should focus on finding more stable dopants, as well as suitable attachment or hybrid substrates.

Acknowledgments

This study was financially supported by the Project of 2017 Guangzhou Panyu District Innovation Leading Team - The R&D and Industrialization of the Intelligent Power Grid Transmission and Distribution Line Connection Products (2017-R01-7)

References

[1] Jing J, Xie J, Chen G Y, et al. 2015 J. Exp. Nanosci. 10(17) 1347-56.
[2] Kai Y, Zhou K, Wu B, et al. 2019 Exp. Sci. Technol. 17(05) 108-11.
[3] Zhang W. 2011 Wuhan University of Technology (Wuhan, China).
[4] Wang S. Meng L 1991 Acta Chim Sinica (01) 26-31.
[5] Wang S 2014 Southwest University.
[6] Shu Z 2015 North China Electric Power University.
[7] Ge X, Xia Y, Feng X et al. 2015 Chin. J. Mech. Eng. 51(15) 61-6.
[8] Chen Y, Han Y, Pan Y et al. 2016 CN10523799A.
[9] Lu J, Wu D, Chen G et al. 2004 Plastics (05) 43-7.
[10] Du L, Zhou Z, Lin X, et al. 2010 Adhesion 31(08) 38-41.
[11] Chao Z 2016 North China Electric Power University (Beijing, China).
[12] Liu Z 2018 Synthetic Mater Aging Appl. 47(3) 100-4.
[13] Song G, Chen Z, Chen Y 2013 New Chem Mater, 41(11) 152-4.
[14] Zhang B, Su X, Deng X et al. 2004 Petrochemical Technology & Application (06) 461-6.
[15] Li Z 2016 Guangdong University of Technology (Guangdong, China).
[16] Liu Y, Liu J, Zhang J et al. 2018 J. FUNCT. MATER 49(11) 11096-101.
[17] Zhou Y, Lan F, Kong Z, et al. 2016 PHM IEEE.
[18] Yan J 2017 North China Electric Power University (Beijing, China).
[19] Wu L 2013 North China Electric Power University (Beijing, China).
[20] Feng B, Gu X, Zhao X, et al. 2017 J. Mater. Sci.: Mater. Electron. 28(11) 7686-91.
[21] Li X, Xiang X, Wang L 2018 Rare Met. 37(3) 191-5.
[22] Fan X, Xia Y, Wang L 2014 Friction 2 (4) 343-53.
[23] Yim M J, Li Y, Moon K S, et al. 2007 Electr. Eng., 82-8.
[24] Guo Z, Li Y, Bing Z, et al. 2017 J. Mater. Chem. C, 6(9) 10-1039.
[25] Li S, Hao X, Jia J et al. 2017 Acta Polym Sin. (03) 524-33.
[26] Gao J, Luo J, Wang L, et al. 2019 Chem. Eng. J. 364 493-502.
[27] Zhang Y, Zhu P, Li G, et al. 2019 Acis Appl. Mater. Interfaces 11(8) 8382-90.
[28] Pan Y, Yu Z, Ou Y et al. 2001, Acta Polym Sin. (01) 42-7.
[29] Bai L, Shen Y, Zhang H et al. 2011, Shanghai Textile Science Technology 39(08) 1-5.
[30] Liu Z 2018 *Synthetic Mater Aging Appl*, **47**(3) 100-4.