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Synthesis of new Conjugated Schiff bases and their iron salts

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Abstract*:* Schiff base salt has the special property of absorbing electromagnetic wave, and has been used in the fields of national defense equipment stealth and electromagnetic protection. In this paper, a new conjugated Schiff base was synthesized by the condensation reaction of p-benzaldehyde, glyoxal and p-phenylenediamine, and a new kind of organic metal salt Schiff base was obtained by doping the Schiff base with Fe^{3+} salt and carbon nanotubes. The electrical conductivity of the sample was studied, and the structure and composition of the sample were characterized by IR, DSC and TG, and the electrical conductivity of schiff base with three different structures and their corresponding iron salts were measured, so as to discuss the main factors and mechanisms affecting the wave absorption performance of Fe-schiff base salt. The results show that the conductivity of the sample can be increased by 2-4 orders of magnitude when Fe ion and Schiff base form a mating bond after adding metal salt. The conductivity of carbon nanotubes can be improved by 7 to 8 orders of magnitude compared with simple Schiff base.

Keywords Conjugated Schiff Base; wave-absorbing materials; Conductive material; synthesis and characterization.

INTRODUCTION

With the wide use of communication equipment, such as telecommunications, LAN system, 5G technology, and radar system, as well as electrical appliances in the industrial field, industrial equipment and weapon equipment in the military field, the electrical application scale and scope continue to expand, resulting in a large number of electromagnetic waves entering the human space(Oyewopo, Olaniyi et al. 2017). Electromagnetic radiation leads to serious electromagnetic interference, which not only affects the operation of equipment, but also has a serious impact on human health. The economic loss caused by this is immeasurable. Therefore, how to effectively prevent electromagnetic radiation from harming human health and normal operation of equipment has become an important problem to be solved. In order to effectively solve the harm of electromagnetic radiation, it is one of the most effective and widely studied solutions to develop electromagnetic wave absorbing materials with different composition, structure and morphology (2017, Al-Qudsi and Al-Qahtani 2020).

In the field of national defense, the combat tends to be high-end technology, and the development demand of anti radar detection and anti detection technology is also higher and higher. As the core technology of "stealth" anti detection technology, the absorbing materials used in military equipment need to reduce the reflection or even non reflection as much as possible to achieve the purpose of "stealth", which puts forward further requirements for absorbing materials (Atay and Icin 2020). Stealth technology is actually a technology that weakens its detectability and makes itself hard to be found. This technology has greatly improved the defense performance of its core weapons, and every country attaches great importance to this technology (Liu, Ban et al. 2016, Kolanowska, Janas et al. 2018, Ahmad, Tariq et al. 2019, Chen, Ma et al. 2019, Fu, Du et al. 2019). Stealth technology includes radar stealth, infrared stealth, visible light stealth, acoustic stealth and magnetic stealth, among which radar stealth technology is particularly important. The core of radar stealth technology is a kind of stealth coating that can be coated on its own surface to absorb the electromagnetic wave of reconnaissance, attenuation or reflection signal, also known as absorbing material, which can absorb or reflect the electromagnetic wave emitted by radar (Ozdemir 2020). The working frequency band of radar is about 2-18 GHz. Different working frequency bands of radar correspond to different applications. See Table 1 for specific application scope(Fu, Yang et al. 2011).

Table 1 Application ranges of different radar frequency bands

Radar band abbreviation	Radar frequency band/GHz	Range of application
VHF	0.05 ~ 0.3	Ultra remote warning
UHF	0.3 ~ 1	Ultra remote warning
L	1 ~ 2	Long-range vigilance, air traffic control
S	2 ~ 4	Medium - range warning airport traffic control remote meteorological observation
C	4 ~ 8	Remote tracking, aviation meteorological observation
X	8 ~ 12	Short range tracking missile guided topographic survey maritime radar aerial interception
Ku	12 ~ 18	High resolution topographic mapping, satellite altitude
K	18 ~ 27	Use less
KA	27 ~ 40	High resolution terrain mapping, airport security
Millimeter wave	40 ~ 100	The experiment

The ideal absorbing material needs to have the characteristics of thin thickness, light weight, absorbing frequency bandwidth and strong absorbing performance (Wang, Yan et al. 2016, Ghanbari, Dehaghi et al. 2020). In order to meet the needs of "thin, light, wide and strong" absorbing materials, many light structure absorbing materials, such as carbon nanotubes, graphene, MXene, nano diamond, conductive polymer and other light absorbing materials have been widely studied by many researchers. During the research, it is found that this kind of wave absorbing material can effectively improve the absorption intensity of electromagnetic wave, but it can not effectively meet the requirements of impedance matching, and its absorption bandwidth is greatly limited. In order to improve the characteristics of impedance matching difference, the most effective way is to add magnetic wave absorbing materials (Yang, Duan et al. 2020). As a kind of absorbing material, Schiff base has many advantages, such as adjustable electromagnetic content, light weight, high stability, good compatibility with resin and so on. According to Hugan Rubens approximation theory, high conductivity Schiff base absorbing materials may have some infrared stealth properties, and the higher the conductivity is, the lower the infrared emissivity is. In recent years, there have been some reports about low infrared emissivity Schiff base materials (Li, Liu et al. 2015). The synthesis and study of long chain Conjugated Poly Schiff bases and their metal salts are of great significance for the study of Schiff bases in the field of microwave absorbing materials.

MATERIALS AND METHODS

Materials

Test reagents: p-phenylenediamine, anhydrous ferric chloride, anhydrous ethanol, glyoxal, P-benzaldehyde, acetic acid, etc. are analytical pure

Experimental instruments: PerkinElmer-2000 infrared spectrometer, DF-101S digital display constant temperature oil bath, DSC-1 differential thermal scanning calorimeter, KQ-500E numerical control ultrasonic cleaner, VO-400 vacuum oven, RTS-9 four probe conductivity meter

Purification methods of some reagents:

Purification of anhydrous ethanol: put 200ml of anhydrous ethanol into a round bottom flask, add 3.5gcah2, put the round bottom flask into an oil bath pot for magnetic stirring, heat to boiling, condense and reflux for 20h, steam out, add a proper amount of 4A molecular sieve and seal for preservation.

Synthesis of p-phenylenediamine and p-benzaldehyde Poly Schiff base L1 and its iron salt C1

(1) Weigh 0.04 mol of p-phenylenediamine, fully dissolve the p-phenylenediamine in 80 ml of anhydrous ethanol, transfer it into a 250 ml three port flask, mix and dissolve 0.04 mol of P-benzaldehyde and anhydrous ethanol at the same time, stir until completely dissolved, and use a small amount of glacial acetic acid as catalyst. Under the protection of N2 atmosphere, drop the solution into three flasks by constant pressure titration, stir and reflux for 8 h, the reaction is over, and the sample is filtered by decompression for 2-3 times. Put the product into a vacuum drying oven, and use the vacuum drying oven to dry for 4 hours to obtain golden powder. The product was characterized by infrared spectrum and its conductivity was measured by four probe method.

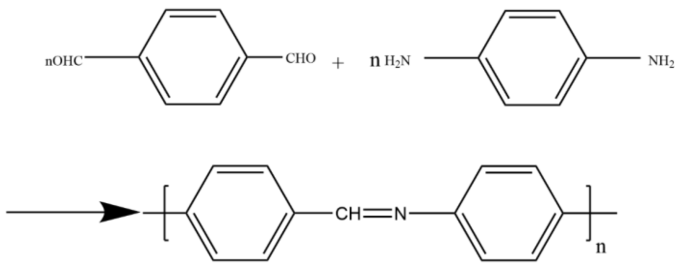


Fig.1．Schematic diagram of synthesis of Poly Schiff base of p-phenylenediamine and p-benzaldehyde

(2) Weigh and take 0.04 mol of anhydrous $FeCl_3$ first, then add 60 ml of anhydrous ethanol to fully dissolve the anhydrous $FeCl_3$. After the above Schiff base solution is fully reacted, When the temperature is raised to 75 ℃, under the protection of N_2 atmosphere, the anhydrous $FeCl_3$ ethanol solution is slowly dripped into a three port flask by constant pressure titration, and the color of Schiff base solution in the system changes from golden yellow to black. After the completion of dropping, the reflux reaction was carried out by stirring condensation for 8 h. At the end of the reaction, when the temperature reaches room temperature, the sample is transferred to a suction flask for decompression and filtration, the filter cake is washed with anhydrous ethanol for 2-3 times, and then the product is transferred to a vacuum drying oven for 4 hours. The product is characterized by infrared spectroscopy, and its conductivity is measured by four probe method.

Synthesis of glyoxal p-phenylenediamine poly Schiff base L2 and its iron salt C2

(1) First, weigh 0.04 mol of p-phenylenediamine, dissolve it completely with 80 ml of absolute ethanol, and then transfer it into a 250 ml three port flask. At the same time, 0.04 mol of glyoxal was mixed with anhydrous ethanol, and then the temperature was raised to 75 ℃, under the protection of N_2 atmosphere, its solution was slowly dropped into a three port flask by constant pressure titration, and yellow precipitate was found in the solution, which was stirred, condensed and refluxed for 8 h. After the reaction, when the temperature reaches room temperature, transfer the sample to the suction flask for decompression and filtration, wash the filter cake with anhydrous ethanol for 2-3 times, and then transfer the product to the vacuum drying oven for 4 hours to obtain orange red powder. The product was characterized by infrared spectrum and its conductivity was measured by four probe method.

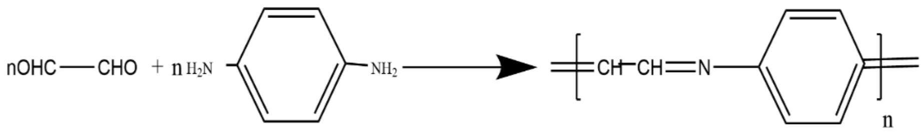


Fig.2. Synthesis mechanism of p-phenylenediamine polyschiff base synthesized by glyoxal

(2) Accurately weigh 0.04 mol absolute pure FeCl3, dissolve it fully with 60 ml absolute ethanol, after the reactant reacts fully, adjust the temperature to 75 ℃, under the protection of N2 atmosphere, use the constant pressure titration method to slowly drop it into the three mouth flask of reactant, the color in the system gradually changes from orange red to black. After dripping, the condensation reflux reaction was completed for 8 h. When the temperature is close to the room temperature, the product is moved into the vacuum suction flask for vacuum suction filtration. Before the sample is moved into the vacuum drying oven, the filter cake is washed with anhydrous ethanol for 2-3 times, and then dried in vacuum for four hours. Finally, the glyoxal condensed p-phenylenediamine poly Schiff base iron salt is obtained. The product was characterized by infrared spectrum and its conductivity was measured by four probe method.

Synthesis of poly Schiff base L3 doped with carbon nanotubes

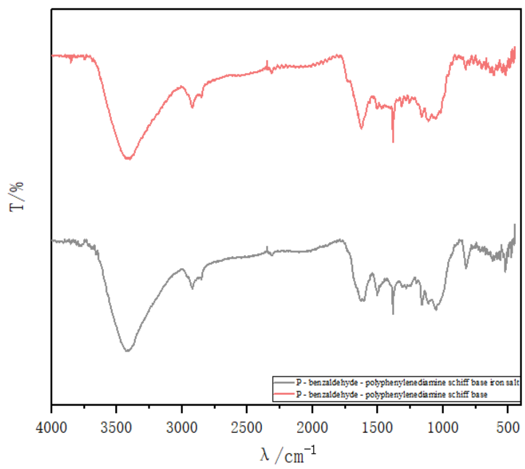
Weigh 0.04 mol of p-phenylenediamine, dissolve it fully with 100 ml of absolute ethanol, weigh 2.0 g of carbon nanotubes, add 250 ml of three beakers respectively, and fix the three beakers on the magnetic oscillator to stir and dissolve it fully. Disperse for half an hour, and then disperse the ultrasonic wave in three flasks for half an hour. Adjust the temperature to 75 ℃, and fully dissolve 0.04 mol of p-benzaldehyde and 40 ml of ethanol at the same time. Under the protection of N2 atmosphere, slowly drop the solution into three flasks by constant pressure titration. After the completion of the dropping, the stirring condensation reflux reaction was carried out for 8 h. When the temperature is close to the room temperature, Transfer the product into the vacuum suction bottle for the vacuum suction filtration operation, wash the filter cake with anhydrous ethanol for two to three times, transfer the sample into the vacuum drying oven, and dry for 4 h continuously, then obtain the dark green block sample, characterize the product with infrared spectroscopy, and determine its conductivity with four probe method.

Synthesis of poly Schiff base L4 with p-phenylenediamine and glyoxal doped by carbon nanotubes

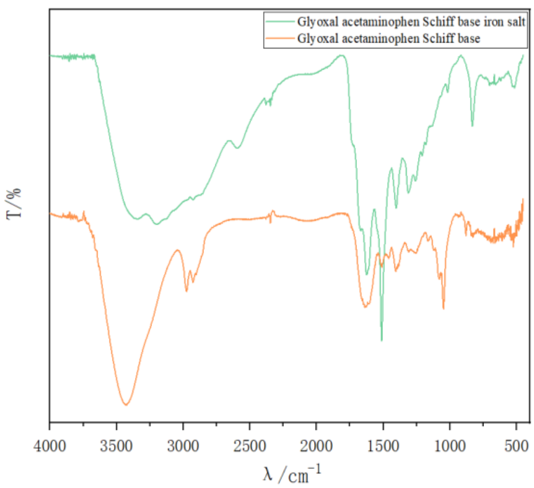
Weigh 0.04 mol of p-phenylenediamine and 100 ml of anhydrous ethanol to mix evenly, weigh 2.0 g of carbon nanotubes, fix the three port flask in the digital display constant temperature oil bath, transfer the p-phenylenediamine, anhydrous ethanol and carbon nanotubes into the three port flask, stir and dissolve quickly. After half an hour, move the three flasks to the ultrasonic oscillator, and the ultrasonic is dispersed for half an hour. Fully mix 0.04 mol glyoxal with 40 ml ethanol, and raise the temperature to 75 ℃, under the protection of N_2 atmosphere, slowly add the solution to three flasks by constant pressure titration. Wait for 8 h for condensation reflux reaction after dripping. After the reaction is completed completely, and the solution is cooled to room temperature, the filter cake is filtered under reduced pressure. For the final filter cake, it needs to be washed two or three times with anhydrous ethanol, and then the filter cake is transferred to a vacuum drying oven. After vacuum drying, the brown bulk sample is obtained, and the product is characterized by infrared spectroscopy. Then the conductivity of the filter cake is measured by four probe method.

RESULTS AND ANALYSIS

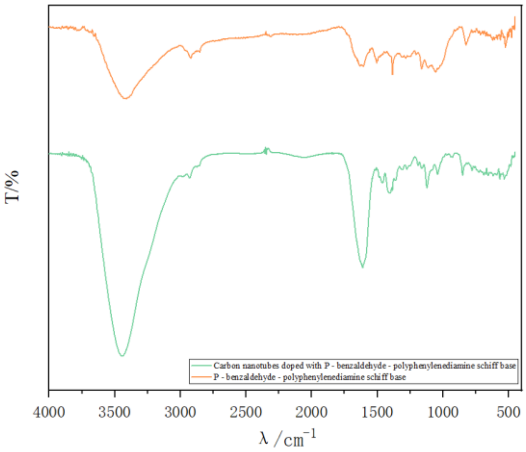
Infrared spectrum analysis



(a)



(b)



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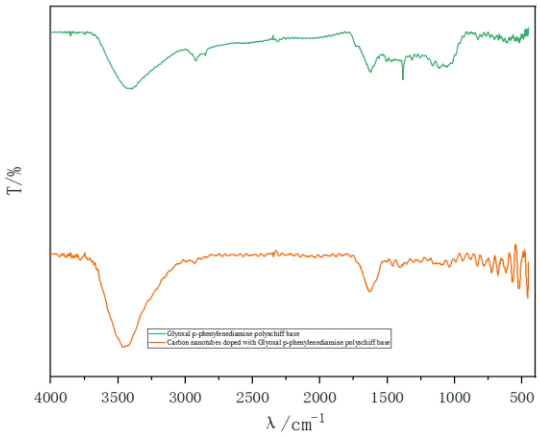
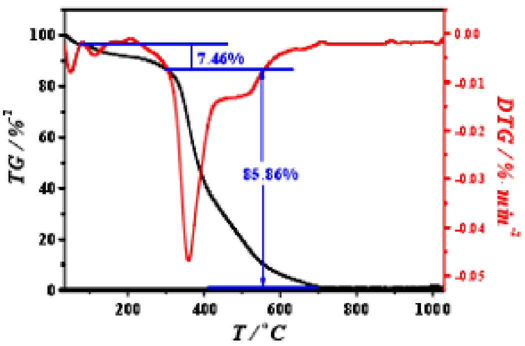


(d)

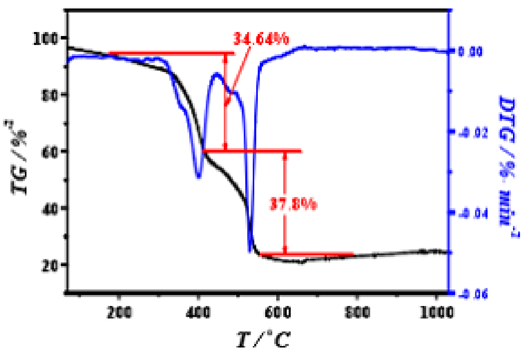
Fig.3 p-phenylenediamine and p-benzaldehyde Poly Schiff base（a）L1 and its iron salts C1、Glyoxal p-phenylenediamine polyschiff base （b）L2and its iron salts C2、Carbon nanotubes doped with glyoxal p-phenylenediamine Schiff base （c）L3、Carbon nanotubes doped with glyoxal p-phenylenediamine Schiff base（d） L4 Infrared image

According to the analysis of the characteristic peaks of the above infrared spectra, the infrared spectra of the two Schiff base salts are different, but due to the similarity of the main functional groups, there are characteristic peaks of C=N, which range from 1590 to 1690cm^{-1}. At 1550m^{-1}, 1450m^{-1} and 1400cm^{-1}, the characteristic peaks of stretching vibration of benzene ring skeleton are found in the above figure. From Fig. 2.2 (a) (b) (c) (d) infrared spectrum, the characteristic peak of imine group can be clearly seen, and 3600cm^{-1} is the N-H characteristic stretching vibration absorption peak. In Fig. 2.2 (a) (b), there are characteristic peaks of Fe^{3+} and Schiff base forming coordination bonds at 540cm^{-1}, indicating that Schiff base has been formed and complexes with iron salt have been formed.

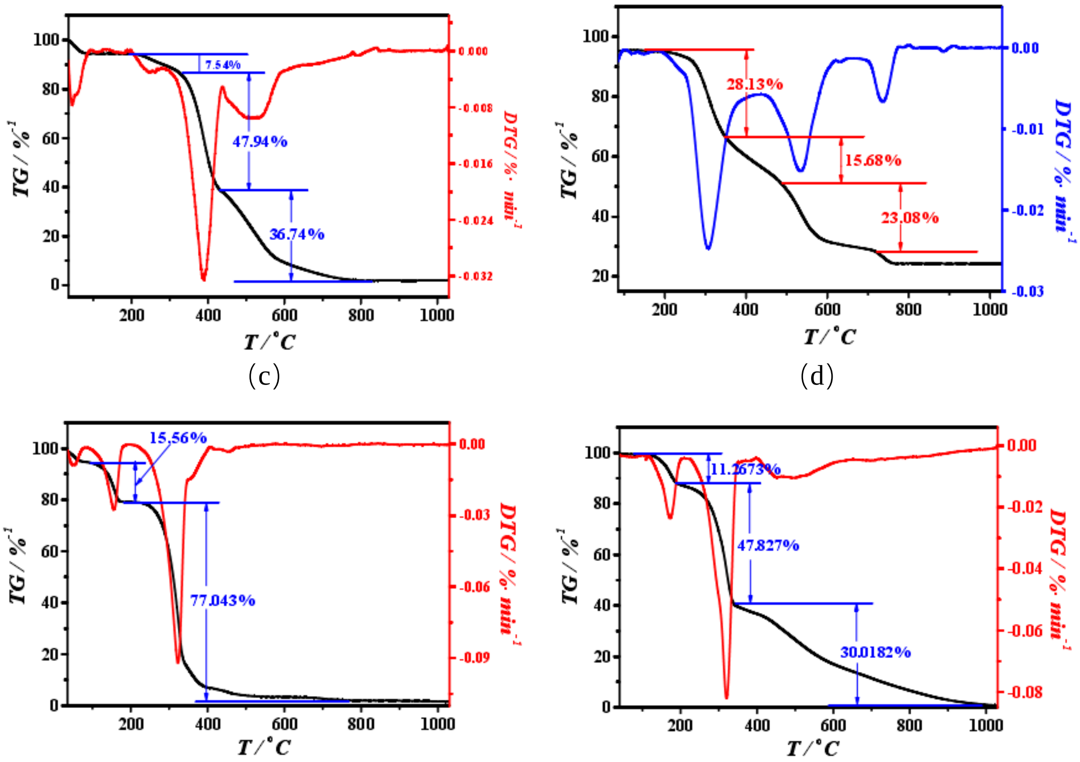
2.2 TG / DTG ANALYSIS



(a)



(b)



(c) (d) (e) (f)

Fig.4 p-phenylenediamine and p-benzaldehyde Poly Schiff base（a）L1 and its iron salts (b) C1、Glyoxal p-phenylenediamine poly schiff base（c）L2and its iron salts(d) C2、Carbon nanotubes doped with p-phenylenediamine and p-benzaldehyde Poly Schiff base（e）L3、Carbon nanotubes doped with glyoxal p-phenylenediamine Schiff base（f） L4 TG、DTG image

TG / DTG analysis of L1 (a) and C1 (b): L1 Schiff base decomposes slowly before 290 ℃. The decomposition trend is about a platform, and the weight loss is about 7.46%. The decomposition of L1 is accelerated at 290-766 ℃. During this period, the skeleton of L1 Schiff base decomposes, and the weight loss rate is stable after 766 ℃, and the residue rate is about 0; The decomposition rate of C1 before 321 ℃ is relatively small, and the weight loss rate is 34.64%. When the temperature reaches 795 ℃, the weight loss rate is about 72%, and the residual rate is about 28%. The residual may be Fe3 + salt and carbon deposition.

TG / DTG analysis of L2 (c) and C2 (d): the weight loss of L2 before 223 ℃ is relatively small and the Plateau state is maintained, indicating that the temperature of this stage is not to the melting point of poly Schiff base. When the temperature reached 830 ℃, the weight loss rate reached 92.22%, and the residue rate was close to 0, which indicated that the poly Schiff base chain had been basically decomposed; C2 is a platform before 262 ℃, and the platform period is longer than L2, which means that the poly Schiff base iron salt C2 is more stable. When the temperature reaches 765 ℃, the weight loss rate reaches 66.89%, and the residual rate is 33.11%, which is due to the carbon deposition effect of Fe3 + inorganic salt.

TG / DTG thermogravimetric analysis of L3 (E) and C3 (f): L3 has always been a platform before 125 ℃, indicating that it has not started to decompose before that: when the temperature reaches 176 ℃, the weight loss rate is 15.56%, which is the first stage. When the temperature reached 762 ℃, the weight loss rate reached 92.60%, and the residue rate was close to 0, indicating that the process of poly Schiff base decomposition had been basically completed; C3 is slightly weightless at the beginning, which is the first stage. When the temperature reaches 1000 ℃, the cumulative weight loss rate reaches 90%, which is related to the carbon deposition.

Conductivity test

As can be seen from the above table 3:

Table 3 Conductivity of Schiff base and its composite system

Schiff bases	conductivity/S .cm^{-1}
Poly Schiff base of p-phenylenediamine and p-benzaldehyde	4.022×10^{-11}
Poly Schiff base of p-phenylenediamine and p-benzaldehyde iron salts	$4.232*10^{-9}$
P-phenylenediamine glyoxal poly schiff base	4.332×10^{-9}
P-phenylenediamine glyoxal poly schiff base iron salts	3.091×10^{-7}
Carbon nanotubes doped with poly schiff base of p-phenylenediamine and p-benzaldehyde	1.82×10^{-4}
Carbon nanotubes doped with p-phenylenediamine glyoxal poly schiff base	2.30×10^{-2}

(1) Compared with pure Schiff base, Schiff base composite iron salt has excellent performance. For example, the conductivity of p-phenylenediamine-p-schiff base is 4.332 × 10-9 s.cm-1, while that of glyoxal-p-phenylenediamine-p-schiff base iron salt is 3.091 × 10-7 s.cm-1. This is mainly because F3 + forms a coordination bond with N atom in the main chain, N atom loses electrons, and can share electron pairs with Fe3 + on the polymer chain, and can move along the polymer chain, so the conductivity of Schiff base can be improved.

(2) Compared with pure Schiff base and its iron salt, the conductivity of carbon nanotube doped Schiff base is increased by four to five orders of magnitude, for example, the conductivity of Carbon nanotubes doped with p-phenylenediamine glyoxal poly schiff base is 2.30 × 10-2 Carbon nanotubes doped with p-phenylenediamine glyoxal poly schiff base is 1.82 × 10-4. This is mainly due to the fact that the carbon nanotubes are on the surface of the composite system, which improves the conductivity. Thus, the infrared emissivity can be reduced.

CONCLUSION

(1) In the iron salt of Schiff base, the formation of N-Fe3 + coordination bond makes the thermal stability of the iron salt of Schiff base higher than that of the single Schiff base; Because of the formation of N-Fe3 + coordination bond, the conductivity of Schiff base iron salt is higher, the conjugation effect is increased, the introduction of iron salt can increase the magnetic effect, accordingly, the infrared emissivity will be reduced.

(2) The conductivity of Schiff base can be improved by selecting ligands and increasing conjugated structure, or by increasing magnetic effect, the Schiff base with lower infrared emissivity can be obtained.

(3) Schiff base absorbing materials, as dielectric loss absorbers, can reduce infrared emissivity on the basis of increasing conductivity, so doped carbon nanotubes can achieve remarkable results, in order to make a breakthrough in national defense stealth technology.

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