Original Research Article

Study on material of polymer-based electromagnetic shielding composites

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ABSTRACT

With the extensive application of electromagnetic resources in the information industry, electromagnetic interference has caused many hazards. Polymer-based electromagnetic shielding composite material as a new type of material has good shielding effect on the electromagnetic wave. This paper mainly introduces the types of polymer-based electromagnetic shielding composite materials and the performance evaluation method of shielding materials.

KEYWORDS: Benzoxazine; Dielectric properties; Copolymerization; Modification

1. Introduction

Macromolecule polymer materials had developed rapidly after 1970s because of its light weight, high strength, toughness, corrosion resistance and other good features. Macromolecule polymer material is gradually replacing metals in many fields especially it is extensively applied in the electronics, electrical industry. However, the electromagnetic radiation generated during the manufacturing of electronic equipment, causing the electromagnetic environment in human survival space getting worse, it is not only affect the production, and even directly harm human health. Electromagnetic pollution has become a new pollution source after air pollution, water pollution and noise pollution. While the macromolecule polymer is replacing metals and widely used in variety of electronic, electrical industry and most of the polymer material is almost completely transparent to electromagnetic waves and has no shielding effect on the electromagnetic waves. Therefore, the study of polymer-based electromagnetic shielding composite materials has attracted the attention of all countries in the world.

Early electromagnetic shielding technology mainly uses metal and its composite materials, although such materials have good shielding performance, but it is low elasticity, high density, easy to corrosion, expensive, difficult to adjust the shielding effectiveness, poor regeneration capacity. In recent years, polymer-based composites been widely used after its emergence and rapid development, and it has good potential in the field of shielding electromagnetic wave applications [1 ~ 3]. Electromagnetic shielding polymer materials are mainly divided into compound type and structure type [4]. Compound electromagnetic shielding polymer material is use insulating polymer as matrix, it is made by adding a certain amount of materials with excellent conductivity properties, the conductive process is depending on the free electron carriers provided by particles small particles of metal. Structural electromagnetic shielding polymer material refers to the polymer with molecule structure itself can be conductive or consists conductive function after doping such as polyacetylene, polypyrrole [5] and so on.

2. Electromagnetic shielding principle

The effect of electromagnetic shielding is to reduce the electromagnetic field effect in a certain area (not including these sources) generated by some radiation sources, and to effectively control the harm caused by electromagnetic radiation from one area to another. The principle of action is the use of low-resistance conductor material, because the conductor material has a reflection and guiding effect on electromagnetic energy flow and within the conductor material it create the current and magnetic polarization which is opposite with the source of electromagnetic field, thereby reduce the effect of radiation source in electromagnetic field, normally it represented by shielding effectiveness (SE) [6]. The shielding effectiveness refers to the ratio of the incident or reflection electromagnetic waves without to the reflection or transmission of electromagnetic wave under shielding at the same location, that is, shielding material to the attenuation value of electromagnetic signal, the unit is (dB).

According to Schelkunoff electromagnetic shielding theory, the electromagnetic shielding effect of metal material is the combination effects of the reflection loss of electromagnetic wave, the absorption loss of electromagnetic wave and the loss of electromagnetic wave in the process of reflection within the shield material. [7,8]. Silver, copper, aluminum and others are excellent electrical conductor, the relative conductivity αr is large, the electromagnetic shielding effect is mainly reflection loss; and iron and iron-nickel alloy is a high permeability material, the relative permeability μr is large, attenuation of electromagnetic shield is mainly based on absorption loss [9,10]. Under normal circumstances, the better the conductivity of the material, the better shielding effect is; with the frequency increases, electromagnetic wave penetration become stronger, and the shielding effect decreased.

When the electromagnetic wave propagates to the surface of the shielding material, it is usually attenuated by three different mechanisms: (1) reflection attenuation at the incident surface; (2) attenuation of the electromagnetic wave which is not reflected but absorbed by the shield material; (3) attenuation after multiple reflections inside the shield. The total shielding effect when electromagnetic wave pass through the shielding material can be calculated according to the following formula [11,12]

$$SE = A + R + B$$

$$A = 1.31t\ (f\mu r\alpha r)\ 1/2$$

$$R = 168\text{-}10\lg\ (\mu rf / \alpha r)$$

Where SE is the electromagnetic shielding effect; R is the surface single reflection attenuation; A is the absorption attenuation; B is the internal multiple reflection attenuation (only in the case of A <15dB significantly).

According to the size of the SE, the value of the electromagnetic shielding material can be divided into the following categories: 0-10dB for the basic non-electromagnetic shielding material; 10 - 30dB for the low electromagnetic shielding material; 30-60dB for the electromagnetic shielding material can be used for general industrial or commercial use of electronic products; 60 -90dB for high electromagnetic shielding materials, can be used for aerospace and military equipment shielding; 90dB or more for the best electromagnetic shielding material for high precision, high sensitivity requirements of the product. It is generally believed that the material used as electromagnetic shielding for conventional electronic equipment has an effective shielding effect in the frequency range of 30 ~ 1000MHz and its SE value reaches 35dB with the effect of electromagnetic shielding.

3. Types of polymer-based electromagnetic shielding composites [13]

3.1. Structural Polymer-based Electromagnetic Shielding Composites

Conductive mechanism of structural conductive polymer: The electronically conductive polymer molecule contains a linear conjugated π electron system, which is conductive by the free migration of carriers in the polymer. The ion conductive polymer is electroconductivity by directional migration of positive and negative ions in the system under the action of electric field.

Structural type (ie, intrinsic) conductive polymer (ICP) is formed by some polymer with a conjugate π bond formed by chemical or electrochemical doping, the conductivity can be extended from the insulator to the conductor range of a class of polymer material. Polyacetylene is the earliest discovered ICP, the method is doped with iodine or arsenic in polyacetylene, the results of polyacetylene conductivity increased by 12 orders of magnitude or more, so that the conductivity is close to the metal copper, with good shielding effect. Polyaniline (PAN), polypyrrole (PPy) and polythiophene (PTH) were found late, because of its environmental stability, its development is relatively rapid, has become one of the three major varieties of ICP.

Compared with other intrinsic electromagnetic shielding polymers, polyaniline has many advantages, such as simple synthesis, excellent electrical conductivity, and is widely studied as electromagnetic shielding materials. Koul [14] studied the effect of composite materials on the shielding effect of the electromagnetic wave in the PAN / ABS composites doped with heteropoly acid. With the increase of the content of PAN, the effect of the composite on the electromagnetic wave was gradually enhanced. At the frequency of 1OGHz, shielding effectiveness (SE) can up to 70dB.

3.2. Composite polymer-based electromagnetic shielding composite materials

Conductive mechanism of composite conductive polymer: With the increase of the concentration of conductive filler, the conductivity of the polymer increases slowly. When the concentration reaches a certain value, the conductivity increases sharply, the polymer becomes a conductor, and the filler concentration continues to increase but electroconductivity has not changed much. The conductivity filler concentration at which the conductivity changed abruptly is called the 'diafiltration threshold'. So its conductive mechanism has two main theories: one is the conductive channel theory; the other is the tunnel effect theory. The conductive channel mechanism plays a major role in the high concentration of conductive filler, which means that when the content of the conductive filler reaches the 'diafiltration threshold', the conductive particles contact each other to form an infinite network. The formation of conductive channels, carriers can freely move within the system. Thereby making the composite conductive. The tunneling effect plays a major role in the low packing concentration, which means that there is a certain spacing between the conductive particles. Electrons in the thermal vibration under the action of migration, thus forming a conductive network. So that the composite polymer conductive.

3.2.1 Metal composite type shielding material

Metal powder or fiber and other good conductor are mixed with polymer can obtained the polymer / metal composite material, when the metal particles reach a certain content, in the polymer matrix to form a micro-conductive network, in order to achieve the shielding properties of composite materials. Among the metal, silver is the best conductor, the volume resistivity is up to 10-10-5Ω cm, with excellent shielding performance, because the price of silver is expensive, it generally only applied to special areas. Nickel is affordable, has good electrical conductivity and permeability, it is the ideal shielding material. In addition, there are copper, iron, stainless steel and other metal powder or fiber can be used as shielding material. Wu Meng et al. [15] studied the electromagnetic shielding effect of polyaniline and metal nickel powder composite conductive filler. It was found that the higher the volume fraction of nickel powder, the higher the electromagnetic shielding effect of the material under the condition of constant volume fraction of polyaniline. Under the condition of the volume fraction of nickel powder, the shielding effect of the material was not the same as the volume fraction of polyaniline The best value is with the volume fraction of nickel powder and the different types of polyaniline and change, and its shielding effectiveness of 70dB or more. Xie Na et al [16] studied the performance of LDPE / stainless steel fiber electromagnetic shielding materials and found that the addition of stainless steel fiber, the electromagnetic shielding properties of the material increases with the increase in stainless steel fiber, and stainless steel fiber diameter ratio is proportional.

Surface-type conductive materials, composite conductive coating is also a common form of composite shielding materials. The formation of surface conductive film usually requires special construction equipment, such as metal plating which is used to arc melt the metal zinc, with high-speed air flow to blow the zinc and fine particles to the plastic shell, so that the plastic surface to form a layer of thin metal, the thickness is about 70um, volume resistivity is below 10-2Ω cm, SE value is up to 40dB or above. Electroplating or electroless plating method to plating metal Ni or Cu / Ni to ABS and other plastic surface, the obtained metal coating conductivity is good, bonding is firm. The coating thickness is 50 μm, the SE value is about 60 dB. In the composite conductive coating, Ruan Shipeng and Zhu Guohui et al. [17] studied the effect of different metal fillers on the shielding effectiveness of electromagnetic shielding coatings. It was found that the coatings prepared with different morphologies of metal powder showed some differences in microstructure. The extent of the impact of the shielding effect of the material. In the metal powder, the silver powder and the silver-plated copper powder are flake in the material preparation process, and the overlapping of the metal sheets effectively reduces the voids so as to improve the high-frequency shielding performance while the nickel powder is spherical and has a high Hardness, so there are more hollow in the microstructure, so as the electromagnetic wave frequency increases, the electromagnetic wave on the coating penetration capacity increases, resulting in reduced electromagnetic shielding performance.

In addition, the conductivity of a single metal can be improved through a variety of metal composite method. Mao Qianjin et al [18] using electroless plating to coat surface of copper powder with silver, and it obtained the Cu / Ag composite electromagnetic shielding agent with excellent conductivity, after the material is made by using this agent, the electromagnetic shielding effect of Cu / Ag composite coating is 80dB in the range of 101kHz -1.5GHz, which greatly improves the shielding performance of copper shielding agent.

3.2.2 Metal oxide based polymer matrix electromagnetic shielding composite material

Metal oxide conductive filler mainly are tin oxide, zinc oxide, titanium oxide, ferrite and so on. Metal oxide used as a conductive filler, because of its small density, good stability in the air and can be used in preparing transparent plastic and other advantages and these advantages are widely used in the field of shielding. Zhu Jiahua et al [19] studied the polyurethane-filled Fe @ SiO2 nanoparticles composite material can improve its electromagnetic shielding effectiveness. Polyurethane filled with Fe @ SiO2 nanoparticles can have a higher reflection loss (RL <-20dB) and a high absorption band width. Cheng Guo et al. [20] used sodium dodecylbenzene sulfonate as emulsifier and dispersant in the presence of Fe304 nanocrystal particles, by regulate the acidity using HCL, to synthesize the conductive and magnetically Fe304 polyaniline nanocomposites, the composite has good conductivity and permeability.

3.2.3 Carbon-based polymer-based electromagnetic shielding composite materials

Carbon mainly are graphite, carbon black or carbon fiber-based, there are two type of it which are powder and fiber. Such materials have the advantages of low price, low density, easy settlement, strong corrosion resistance and so on. The disadvantage is that the surface contains a large number of polar substances, difficult to disperse. LiNing et al. [21] studied the electromagnetic shielding properties of single layer carbon nanotubes epoxy resin composites. It was found that the SWNT-epoxy resin composites filled with 15wt% SWNTs, had an electromagnetic shielding efficiency of 49dB at 10MHz and an electromagnetic shielding efficiency of 15dB-20dB at 500MHz-1.5GHz. This composite material could be used as low electromagnetic shielding material.

Carbon-based conductive filler belongs to the semiconductor, the resulting composite material conductivity is much smaller than the metal filler. In the graphite, carbon fiber and other materials coated with a layer of metal film or other conductive materials, improve the conductivity of graphite, carbon fiber, etc., and obtained good shielding effect. Yin qin and Zhong Liang et al. [22] studied the preparation of electromagnetic shielding materias by carbon fiber chemical composite plating. It is found that the surface of carbon fiber is copper-plated and then nickel-plated, as the electromagnetic shielding material filler, its conductivity is improved obviously, it is an ideal electromagnetic shielding and conductive filler of absorption material.

Carbon nanotubes are the finest 'molecular wires', and their unique tubular and helical structures make them excellent in electrical conductivity. Carbon nanotubes used for electromagnetic shielding materials in recent year in the field of electromagnetic shielding research. Jean-Michel Thomassin et al. [23] studied the multilayer carbon nanotubes / polyethylene nanocomposites with excellent electromagnetic shielding properties.

4. Evaluation method of shielding performance of polymer-based electromagnetic shielding composite materials

4.1. Far field test method

The distance field is the distance between the shield and the electromagnetic radiation source $r \geq \lambda / 2\pi$, λ is the wavelength of the radiation electromagnetic wave, the far electric field and the magnetic field are perpendicular to each other, the phase is the same, the energy of any point of E and H is shared half, it attenuated with the increase of r, so SEE = SEH. In the far field test method, the most used at home and abroad is the coaxial test method.

Coaxial test method [25,26] is a method used in testing the effectiveness of material shielding recommended by the United States National Bureau of Standards (NBS), in 1995, the method was issued in China about the electronics industry military standard SJ20524-1995. Coaxial test method test diagram was shown in Figure 1, the method consists of test fixture and network analyzer and other equipment to form a test system to measure the fixture no-load electromagnetic wave power P0 (dB) and the sample after the transmission of electromagnetic power P1 (dB). The material shielding efficiency is calculated by the formula SE (dB) = P0-P1. The key device of the test system is coaxial flange fixture. At present, most of our country adopts coaxial test fixture developed by Southeast University Electromagnetic Compatibility Research Laboratory.

The coaxial method is simple and fast. The test device is cheap and does not require an expensive shielded room. The dynamic range is wide and the thickness of the material can be extended to 10 mm. But the test results were affected by the contact impedance between test material and the fixture. The test results are less reproducible: the cutoff frequency of the method is limited by the inner diameter of the outer conductor of the fixture: $Fc = C0 / (\pi (b / 2.3 + b)) = 1.62GHz$ [27], therefore, the shielding performance is usually in the range of 100kHz- 1.5GHz frequency

4.2. Near field test method

The near field is the area where the distance from the shield to the electromagnetic radiation source $r < \lambda / 2$. Λ is the wavelength of the radiated electromagnetic wave, the phase difference between E and H in the near field is 90 degrees, and E are attenuated by 1 / r2 or 1 / r3 with the increase of r. In the near field, the electromagnetic energy flows back and forth between the source and the field, so SEE $\neq$ SEH.

1 double box method

In the near field test method, the double box method [28] is widely used, the test device is shown in Figure 3.

The method system comprises of a double-box device and a signal generator, a signal receiver and the others. The transmission antenna is used to measure the transmission power P0 (dB) of the double-box no-load electromagnetic wave and the transmission power P1 (dB) of the electromagnetic wave after the sample is added. (DB) = P0-P1 used to calculate the shielding effectiveness of the material. The double box method is quick and easy to measure and does not require expensive shielded room. But the frequency of the dual chamber cavity will resonate with the physical size of the cavity, the test results are unstable. Repeatedly affected by the state of the spring support piece. The applicable frequency range of 1-30MHz, sample thickness ≤ 4 mm, the dynamic range of 5OdB.

2 MIL-STD-285 near field method

The MIL-STD-285 method was established in 1956 by the US Department of Defense and used to measure the shielding performance of high-impedance fields and low-impedance fields in near-field and near-field plane waves. MIL-STD-285 test device is an improved near-field test device, as shown in Figure 4.

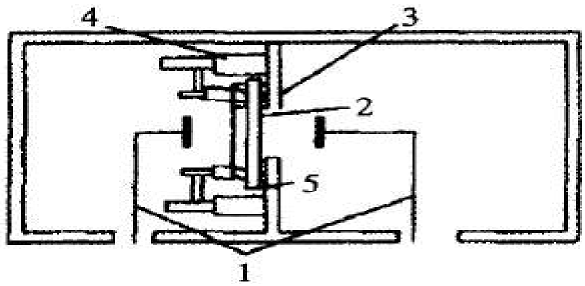

Figure 1. improved MIL-STD-285 test device

The test principle is similar to the double box method, but the test environment from the double box into the shielding room, the emission and receiver equipment is basically the same. The device introduces into a shielded room environment and increases the cost of the device and requires more stringent in electric contact between the specimen and at the edge of the hole, but the method can be used to produce better test results.

3 shielding room method

The shielded chamber method was introduced by the American Society of Electrical and Electronics Engineers in 1969 and was amended in 1991 and 1997 twice. Introduced the standard IEEE STD299-1997 in shielding room to test material shielding performance. It is undoubtedly the best to use the shielded chamber method to test the shielding performance of the material when the material is between the far field and the near field and in the wider frequency range. Its scientific research also has a certain application [29], test schematic diagram shown in Figure 5.

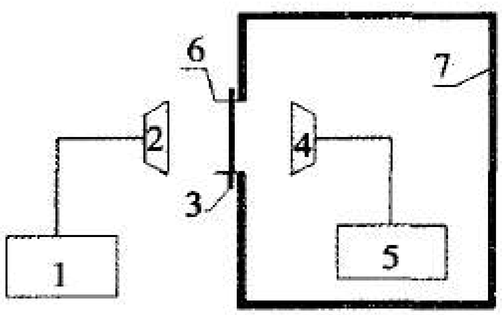

Figure 2. shielded room test method schematic

Shielded room is a large hexahedron that made of metal net or metal plate, the metal materials has excellent shielding performance, and can ensure that the test process is not affected by external electromagnetic environment. The shielding chamber test method uses the receiving and transmitting antenna which inside and outside the shielded room to test the attenuation of the transmitted wave after the electromagnetic wave passes through the material and calculate the shielding effectiveness. The shield chamber is equivalent to a rectangular waveguide resonator. In a certain frequency to produce resonance, shielding room screen effect greatly reduced, resulting in a large test error, and the shield room is expensive. But the frequency range of shielding chamber method is wide, the frequency range from 9kHz up to 18GHz (can be expanded to 50Hz - 100GHz) can be measured using this method: in the condition of no resonance, the shielding chamber method results are more accurate than other methods.

5. Conclusion

(1) With the continuous development and application of electronic products, electromagnetic radiation is becoming increasingly serious, in the application has different purposes and requirements which often need to take into account of other aspects of integrated design, so the development of comprehensive performance is good, convenient, applicable and low cost. Electromagnetic shielding materials have important social and economic benefits. Therefore, the polymer-based electromagnetic shielding composite material as a new type of shielding material should be developed toward aspects of the shielding effectiveness, shielding bandwidth, comprehensive performance and other more excellent aspects.

(2) The electromagnetic shielding performance of the material is related to the physical and chemical properties of the material, the frequency (or wavelength) of the electromagnetic wave, the physical size of the test specimen, the size of the test space, the distance of the radiation source and the test environment. In the specific selection of test methods, we should fully consider these factors, especially the characteristics of the sample, the characteristics of the radiation source and the adaptability of the selected test method, or the results obtained by the test cannot objectively and truly evaluate the electromagnetic properties of the material.

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