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Application of Nano-micronized SiO to Electrostatic Shielding Materials

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Nano-silica xz-g01, commonly known as gas-phase white carbon black, is a synthetic white amorphous powder, with a variety of specific surface areas and strict particle size distribution by volume. This product is a type of white, loose, amorphous, non-toxic, tasteless, odorless, pollution free and non-metallic oxide; whose primary particle size is between 7 ~ 80nm, and specific surface area is generally greater than 100 m^2 /g. Because of its nano-effect, it exhibits excellent performance in the following aspects: reinforcement, thickening, thixotropy, insulation, extinction, anti-sagging, etc.; and is widely used in rubber, plastic, coating, adhesive, sealant and other polymer industrial fields. This study focuses on the microstructure of silicon oxide nanoparticles, explores the physicochemical properties of this micronized silica, and finally applies it to electrostatic shielding materials so as to achieve a good shielding effect against static electricity.

1. Introduction

In the science and technology industry, the particles with a size of 1nm to 100nm are called nanoparticles, particles with a size of 0.1μm to 1μm are called submicron particles, and particles with a size greater than 1μm are called micro-particles. Nanoparticles have more superior properties than micro-particles, mainly due to the small size and large surface area of particles (Øien et al., 2013). Nanomaterials can produce a series of effects due to the large specific surface area: small size effect, surface effect, quantum size effect and macroscopic quantum tunnelling effect; and show many unique properties (Martin et al., 2009). When nanoparticles with special photoelectromagnetic properties are added to a polymer, they disperse in the polymer on the nanometer scale, the polymer-specific photoelectromagnetic properties make the polymer become a specific functional material in a good way, and will affect the research of polymer alloys and other new functional composites in the long run. Inorganic nanoparticles/polymer composites perfectly combine the rigidity, dimensional stability and thermal stability of inorganic materials with the toughness, processability and dielectric properties of polymers, as well as the properties of nanomaterials. Therefore, the use of nano-technology to modify the polymer has become one of the research hotspots in material science circle currently (Xie et al., 2017).
The essence of dielectric conductance lies in the movement of internal charge carriers. The intrinsic factor that affects the movement of charge carriers in the dielectric depends on the internal microstructure of the dielectric, which in turn determines the trap form inside the dielectric. When carriers move in the direction of the external electric field, these traps will likely trap part of the carriers, whereas different trap levels will be different for the carrier binding. The polarization of the medium is due to the constant trapping and delamination of carriers in these traps. From the microstructure point of view, pure polyethylene in the interface mainly by the amorphous and amorphous interface between the composition. With the addition of micro- or nano-particles, the interface in the composite increases the interface between the particles and the amorphous phase, making the composition of the interface that affects the charge-carrier transport properties complex in the composite. In order to study the influence of these interfaces on the electrical properties of the composite, the experimental research on the slow polarization of the macroscopic dielectric behavior at the interface of composite media is carried out. SEM scanning electron microscopy was used to understand the distribution and dispersion of nano-particles in polyethylene, to ensure the uniform dispersion of nano-silica in the composite medium, and with the test of mechanical properties, to understand the composite state of the

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additives and polyethylene bulk; to explore different The influence of external factors, such as temperature, electric field and additive concentration, on the slow polarization of the composites. The experimental results of the thermal stimulus current analyze the energy level distribution of interface traps in the composite media. In this paper, the slow polarization is studied not only by the time-domain method, but also by the comparison of the similarities and differences between the two methods by the measurement of wide-band dielectric spectra. The polarization phenomenon at higher frequencies than the time domain method is also studied. The effect of space charge on the slow polarization under the electric field under the electric field and the charge distribution inside the composite was investigated.

2. Preparation for nano-micronization

Place a cavity conductor of any shape into the electrostatic field in order to realize electrostatic balance (Place a neutral conductor into the electric field, free electrons move in the direction of counterelectric field under the action of the electric field force to a certain extent, and stop when electrostatic balance is reached); and the electric field intensity in cavity is zero (Daniel et al., 2014). This phenomenon is called electrostatic shielding. Moreover, no matter if there exists an electric field in the cavity conductor or not, there still exists an electric field outside the conductor if the outer surface of the conductor is not grounded (Jenny, 2016). When the outer surface of the conductor is grounded, the induced charges on the outer surface are neutralized by grounding and exist within the conductor cavity, instead of acting outside the conductor, which is also known as the electrostatic shielding (Bandara et al., 2017).
According to the principle of electrostatic shielding, electrostatic-sensitive electronic products are required to be used in conductor materials to achieve the desired attenuation of the outside electric field, so as to completely shield the electrostatic field or electrostatic discharge generated by the electromagnetic pulse (Naeem et al., 2012). It is well known that the basic principle of electromagnetic shielding is mainly about making use of the reflection loss of electromagnetic wave in the shielding interface and the absorption loss inside the shield to attenuate the transmission energy; therefore, the higher the conductivity and permeability of the product material is, the greater the shielding performance is (Figure 1). The common international practice is to define a material with a surface resistivity of less than 1 x 104 Ω / □ as the electrostatic shielding material to shield the protective packaging. Through the aluminum coating surface resistance measurement control coating thickness, to set the resistance to stop the flame spraying. In order to prevent the oxidation and pollution of the aluminum coating, the conductive properties of the coating are affected. After the coating is sprayed on, the carbon fiber prepreg is cured and cured. After the curing is completed, the coating is completely transferred to the surface of the composite part. The appearance of the electrostatic shielding coating Layer transfer is complete, the surface is smooth, the shape is maintained well. Figure 1 shows a metallographic photograph of the composite surface with a transfer flame sprayed aluminum coating. As can be seen from Figure 1, the aluminum coating is continuously distributed. During the curing process of the composite material, the resin infiltrates the aluminum sprayed layer, and the aluminum coating and the composite material are solidified to form a whole, thereby increasing the reliability of the coating.

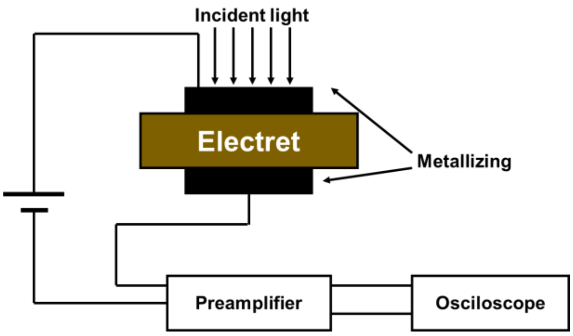

Figure 1: The sample with two metallizing electrodes

For the purpose of this paper, nano-SiOx/LDPE composites and micron SiO/LDPE composites are prepared through double-solution blending. The preparation process is shown in Fig. First, add nano-SiOx (or micron SiO) into chloroform (pure CHCl3 for analysis), and use KQ-250E ultrasonic cleaning device manufactured by Kunshan City Ultrasonic Instrument Co., Ltd. for ultrasonic dispersion, so that nanoSiOx (or micron SiO) particles can homogeneously dissolve in chloroform to prepare the nano Si Ox (or micron SiO) / chloroform solution. Then, prepare the LDPE / p-xylene solution by dissolving LDPE at 353 K using a DZF-6050 vacuum oven manufactured by a certain experimental equipment company. With p-xylene (chemically pure) being the solvent. Then, when the temperature reaches 353 K, slowly add the nanoSiOx (or micron SiO) / chloroform solution into the LDPE / p-xylene solution, and heat with a 85-2 type constant temperature magnetic stirrer at 2,000 rad / min for 2 hours to prepare the mixed solution containing nano-SiOx (or micron SiO). Finally, remove the solvent (102 Pa, 398 K) at a low pressure using a vacuum oven to obtain nano-SiOx/LDPE and micron SiO/LDPE composites of different concentrations.

3. The main testing methods of electrostatic shielding performance of materials

The electrostatic shielding performance test is performed to evaluate the shielding capability of materials against electromagnetic pulse generated by electrostatic or electrostatic discharge. At present, the standard testing methods adopted in the field are specified in the following specifications and standards: *Specifications on Heat-sealable, Flexible, Anti-static Barrier Materials* (GJB 2605-96), MIL-STD-285, EIA-541 of American Electronics Industry Association, British standard of BS7506, etc.; which can be divided into the following categories: capacitance charge and discharge method and bipolar pulse discharge method. Inverse microemulsions (W/O) contain two different solvents that dissolve inorganic salts (or disperse inorganic nanoparticles) and organic precursors simultaneously. During the coating process, the precursors in the oil phase are hydrolyzed at the interface between oil and water to form a hydrophilic hydrolyzate into the water phase and form a coating in the water phase by dehydration and condensation. The use of reverse microemulsion method for silica coating is generally divided into two cases: the particles prepared in advance dispersed in reverse microemulsion coating; reverse microemulsion particle preparation and the original Bit coverage. In addition to inorganic pigments, organic pigments can also be coated with silica to enhance their weatherability and dispersibility. Yuan et al. employed silica coated on Pigment Yellow 109, which does not change the appearance of the pigment significantly, but the coating enhances the weatherability of the pigment. Nanomaterials have small particle size, large specific surface area and larger Gibbs free energy than the surface. Therefore, the melting point of metal nanoparticles is lower than the corresponding melting point of bulk metal, and is easily oxidized in the air. Silica, Can improve the coated particles of high temperature stability and oxidation resistance. At Fe, Co and Ni nanoparticles coated silica surface, can significantly improve the oxidation temperature of these particles

3.1 Capacitance charge and discharge method

The capacitance charge and discharge method is recommended by the American Electronics Industry Association in the EIA-541 (MIL-B-81705C used). Figure 1 shows the experimental diagram. Its principle is as follow: place the capacitive sensor probe in the packaging bag of the test material, then place them in the test device between the discharge electrode and ground electrode to charge the capacitor at a high voltage, use transfer switch to discharge the bag through discharge resistance, and finally the voltage signal induced on the capacitive sensor is introduced into the measuring instrument (including oscilloscope, plotter, etc.) for measurement and analysis. Based on the methods adopted by the measurement instrument, the capacitance charge and discharge method can be further divided into voltage measurement method and energy measurement method, as shown in Figure 2.

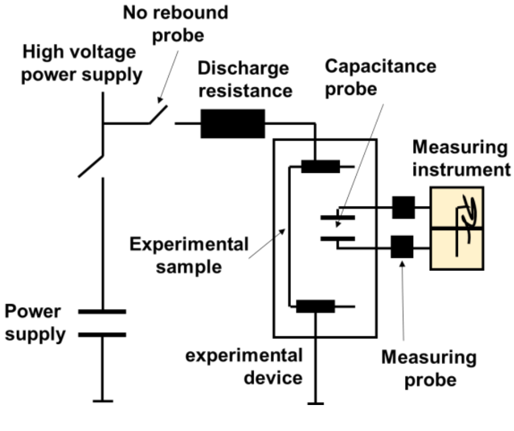

Figure 2: Capacitance charge and discharge method experimental schematic diagram

The separation membrane should meet the following requirements: uniform thickness, with a certain bonding force with the mold, flame spraying process cannot separate with the mold, resulting in bubbling, cocking, cracking, etc., to ensure that the metal coating intact; separation membrane and metal The coating has a certain combination of continuous flame sprayed metal coating on the separation membrane; after the composite component is hot-pressed and cured, the coating can be completely separated from the mold along with the composite part. In this experiment, a double-layer combination separation membrane was used. First, an organic volatile resin release agent was applied on the mold and the first layer of the composite separation membrane was formed after drying at room temperature. The thickness of this layer was only a few microns close to the mold, can fill the surface of the mold micropores and scratches, but the test showed that the separation membrane cannot form a stable continuous flame sprayed aluminium coating. Thus, a water-soluble polymer resin solution was coated on the first layer and dried at room temperature to form a second layer of the combined separation membrane. It should be pointed out that in the mold cannot be directly formed a stable continuous water-soluble polymer resin film, must rely on the first layer. The second layer thickness of the separation membrane tens of microns, flame spray test showed that the separation membrane and aluminium coating Good compatibility, the formation of aluminium coating continuous uniform.

3.2 Energy measurement method

In view of the problems and shortcomings of the above test method, the ANSI ESDS 11.31 of American National Standard and 61340-5-1 (2) of International Electro technical Commission (IEC) have raised new requirements on the electrostatic shielding performance of packaging materials. This measurement method is similar to that in Figure 3 and follows the test principle of IEC 61340-5-1 (2). The method does not require to measure the induced voltage value on the capacitive probe in the bag; but converts the induced voltage signal on the capacitive probe into the oscilloscope via current sensor; then performs energy calculation by means of software analysis to obtain the energy level penetrating into the bag during the test; at last determines the shielding effect of the bag according to the energy and total energy of electrostatic discharge (12CV2 determined, V is the discharge voltage). This method can be used to evaluate the shielding performance of materials, but cannot explain the shielding performance of materials under different pulse frequencies.

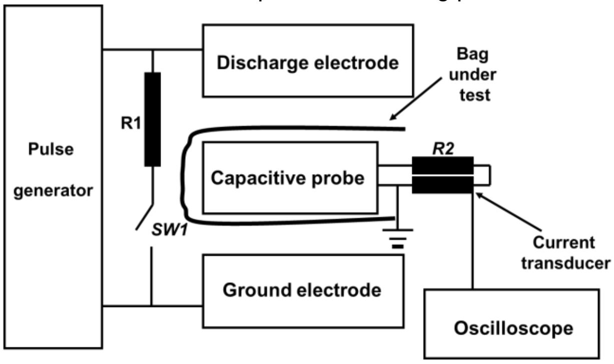

Figure 3: Electrostatic shielding tests principle in IEC 61340-5-1 (2) standard

The biggest advantage of this method is that it measures the signals through signal processing circuit, divides them into nine bands, and retains each band frequency of the sensor signals, making it easier to analyse the signal shielding performance of materials with different bands. With this method, we can measure the shielding performance of different materials with frequency, thus overcome the shortcomings of the capacitance charge and discharge method, which cannot determine the material shielding performance with frequency. This method employs the method of positive and negative pulse discharge, which is synchronous in terms of the amplitude and pulse waveform discharge. Its main purpose is to solve the unipolar discharge, since there are net charges on the sample layer; but not really detect the shielding properties of materials on different discharge polarities. The test sample adopted is a sample layer instead of a sample bag; thus, whether it can fully reflect the electrostatic shielding performance of the packaging bag in practical use is still under study. This method is relatively complex, thus, not many measurement instrument are available currently.

3.3 Bipolar high voltage pulse discharge method

This method is recommended by the British standard of BS 7506 on material shielding performance test method, as shown in Figure 4. A high-voltage electric field pulse having a symmetrical peak amplitude and a pulse waveform is discharged on a material with a predetermined width; the way of positive and negative pulse synchronous discharge (pulse rise time is ns stage and fall time is 0.1s) is adopted; and no sensor signal regarding residual static charge located on the other side of the measured sample is sent to the signal processing circuit for analysis. This method divides the observed signals into nine bands (from 10 Hz to 1 GHz, every 10 octaves for one band). The amplitude of each peak is retained in the peak detection and hold circuit and then sent to the microprocessor for analysis, display and data storage.

The biggest advantage of this method is that it can measure the signals through signal processing circuit, divide them into nine bands, and retain each band frequency of the sensor signals, making it easier to analyze the signal shielding performance of materials with different bands. With this method, we can measure the shielding performance of different materials with frequency, thus overcome the shortcomings of the capacitance charge and discharge method, which cannot determine the material shielding performance with frequency. This method employs the method of positive and negative pulse discharge, which is synchronous in terms of the amplitude and pulse waveform discharge. Its main purpose is to solve the unipolar discharge, since there are net charges on the sample layer; but not really detect the shielding properties of materials on different discharge polarities. The test sample adopted is a sample layer instead of a sample bag; thus, whether it can fully reflect the electrostatic shielding performance of the packaging bag in practical use is still under study. This method is relatively complex, thus, not many measurement instrument are available for currently.

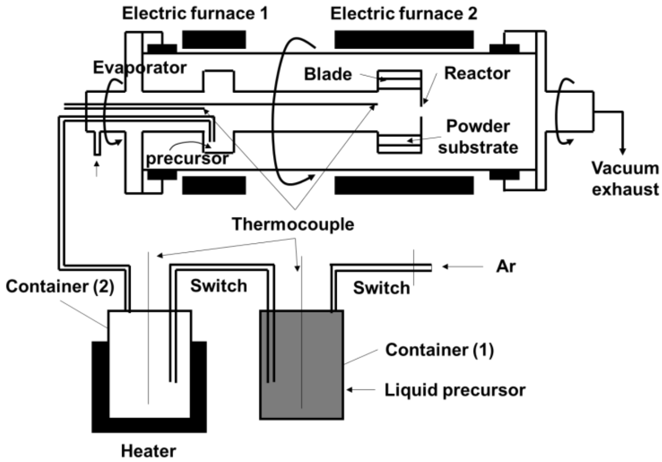

Figure 4: Schematic diagram of rotary chemical vapor deposition apparatus for precipitation of SiO2 on cBN powder

The binding force between the coating and the composite matrix should be a matter of concern; however no test standard on the strength of the flame coating in the composite coating is available. In this test, the test piece for tensile strength is a 25 mm × 25 mm × 2 mm composite matrix, the aluminum coating is prepared by transfer method on one side of the test piece, and the E-7 adhesive is used. Meanwhile, the test piece for shear strength is a 60 mm × 25 mm × 2 mm composite matrix, and the adhesive area of aluminum coating on one end of the sample prepared by transfer method is 20 mm × 25 mm. The conventional spraying method is adopted for comparison which is as follow: spray the electrostatic shielding coating, and then carry out the shear test of the coating on the surface; finally, apply the adhesive to permeate the coating. The coating has a thickness of 0.16 to 0.17 mm, and also uses the E-7 adhesive, as shown in Table 1.

Table 1: Coating resistance and coating thickness of the measured results.

Measuring point	1	2	3	4	5
Resistance/mΩ	3.465	2.568	1.564	0.587	0.589
Thickness/mm	0.465	0.258	0.145	0.123	0.156
Measuring point	6	7	8	9	10
Resistance/mΩ	0.486	0.345	0.256	0.245	0.25
Thickness/mm	0.178	0.256	0.236	0.412	0.315

4. Discussion and conclusions

This paper describes the preparing methods of the silica-coated core-shell materials in detail, including the principle, characteristics and shortcomings. Through the entire process of the coating method, it can be discovered that the method is gradually transitioning from the initial complex multi-step method to a simple "one-pot" method; it is getting more mature; and almost all the micro-nanoparticles can pass the method for silica coating. In addition, the sources of silicon are diversified from the initial orthosilicate and sodium silicate to the elemental silicon and nano-silica particles subsequently; and the formation mechanism of the coating layer also changes for different silicon sources and coating methods The Silica-coated micro-nanoparticles also enjoy very popular applications, since two or more nanoparticle composite structure often exhibits excellent performance.

There is still a very large development space regarding from the perspective of overall performance in a particular area. So far, remarkable results have been made in the research of silica-coated micro-nanoparticles after nearly 30 years of development; however, problems still exist in the preparation and application, requiring further study and improvement of the coating mechanism of particles. Besides, the preparing method of the core-shell particles with uniform morphology at a large-scale is yet to be developed, so as to conduct industrial production. With the deepening and refinement of the research, it will become easier and faster to prepare the silicon oxide-coated core-shell micro-nano materials; the research will be more deeply; and the materials will be gradually used in real life. The electromagnetic shielding materials are essential for the development of protection materials in modern electronics industry; and they are not only related to human health, but also related to information security. Relevant research and development of such materials are strengthened both at home and abroad, producing a certain K research results. The research in this area in China is started late; thus, we should strengthen the research and development of the electromagnetic shielding materials, produce diversified materials and improve the electromagnetic shielding performance; so as to enhance the competitiveness substantially. Meanwhile, with the socio-economic development, the electromagnetic shielding materials, as protective materials, will have a good application prospects and realize huge economic benefits in the future.

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