

Research on the Application of Titanium Dioxide Nanotubes in Insulating Resins

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Abstract

The commonly used insulation paint for electric vehicle motors currently has poor flame retardancy, toughness, thermal stability, and wear resistance due to the use of polymer materials. In order to further improve the performance of insulation paint, it is necessary to doping inorganic materials. However, in order to achieve high performance, high doping is generally required, and high doping faces problems such as poor compatibility between doped particles and insulation paint. In order to further improve the flame retardancy, toughness, thermal stability, and wear resistance of insulation paint, researchers generally use the method of doping inorganic particle materials. Research has found that nano inorganic materials (such as nano titanium dioxide) can improve the flame retardancy of materials while also improving their thermal and mechanical properties. However, in order to achieve high performance, insulating paint generally requires high doping, and high doping will face problems such as poor compatibility between doped particles and insulating paint. On the one hand, due to the large size and uneven dispersion of doped particles, it is difficult to achieve a good composite effect; On the other hand, the incompatibility between thermal conductive materials and organic surface interfaces further limits the effectiveness of the material. Therefore, introducing titanium dioxide nanotube materials with smaller dimensions, better dispersibility, and surface hydrophobicity treatment into the insulation paint can improve the compounding effect and further enhance the resistance to ATF oil and flame retardancy of the insulation paint.

Keywords

Insulating Resins; Titanium Dioxide; Nanotubes.

1. Introduction

Titanium dioxide nanotubes have smaller dimensions and higher doping ratios, which can improve the flame retardancy of materials while also improving their thermal, corrosion resistance, and mechanical properties[1]. However, unmodified titanium dioxide nanotubes are not easily dispersed uniformly in the matrix due to their high surface energy. For this purpose, we use KH-550 coupling agent to modify the surface of hydrophilic nano titanium dioxide, improving the aggregation and dispersion of titanium dioxide nanotubes in the insulation paint matrix. Then, the modified titanium dioxide nanotubes are compounded with flame retardant insulation paint, and it is expected that the compounded flame retardant system can prepare flame retardant insulation paint with good comprehensive performance with low addition amount[2,3]. Therefore, this study aims to incorporate titanium dioxide into the insulation paint, which can be filled into the defects of polymers to improve the flame retardancy, toughness, thermal stability, corrosion resistance, and wear resistance of the insulation paint[4,5].

Patent "Preparation method for a flame retardant insulating paint resistant to ATF oil for electric vehicles (202010645829.2)", consisting of unsaturated polyester resin containing

halogen, diisocyanate, curing agent, initiator, benzoquinone, and diluent. Unsaturated polyester resin containing halogen is made by reaction of halogenated phthalic anhydride, polybasic acid, and polyol, and polybasic acid is composed of adipic acid and maleic anhydride, Polyols are composed of ethylene glycol and propylene glycol; The preparation method includes: mixing and polycondensation reaction of halogenated phthalic anhydride, adipic acid, maleic anhydride, ethylene glycol, and propylene glycol to produce an unsaturated polyester resin containing halogen; After adding the solvent, add diisocyanate dropwise, react, vacuum extract the solvent, add the remaining raw materials, mix, and make. The patent "Flame retardant insulating paint resistant to ATF oil for electric vehicles and its preparation method and application (201811318893.9)" includes polyester resin, curing agent, initiator, diluent, diisocyanate, unsaturated polyester resin containing halogens, unsaturated resin containing halogens is made by reacting halogenated phthalic anhydride, polybasic acid, and polyol, and polybasic acid is selected as adipic acid, phthalic acid At least two of maleic anhydride and glutaric anhydride, and at least two of polyols selected from propylene glycol, 1,4-butanediol, and ethylene glycol; Preparation method: Unsaturated polyester resin containing halogens is prepared from a formula amount of halogenated phthalic anhydride, polybasic acids, and polyols; Then react with diisocyanate in a solvent, and after the reaction is completed, separate the solvent and add the remaining raw materials[6,7].

2. Sample Preparation and Analysis:

Example 1: (Titanium dioxide nanotubes account for 3% of the total mass of the insulating paint material)

1. Prepare titanium dioxide nanotubes, add anatase phase titanium dioxide powder (with a particle size of about 50 nanometers) and a 10M concentration NaOH solution in a 1:5 mass ratio in a high-pressure reactor, seal, and react under hydrothermal conditions at 140 °C for 72 hours; After the reactor cools down, remove the white solid from the high-pressure reactor and wash it with 0.1M hydrochloric acid (HCl) solution, then rinse with a large amount of deionized water until the pH value of the effluent solution is neutral. Finally, dry the titanium dioxide nanotube product at 80 °C.

2. Add 10% -20% mass fraction of the reactant obtained from the previous reaction to a mixed solution of silane coupling agent (selected from one or more of KH570, KH550, and KH560) and anhydrous ethanol (volume ratio 1:10), and sonicate for 10 minutes; Subsequently, treat in an oil bath at 400 °C for 4 hours; After the oil bath is completed, the flocs obtained from the reaction are repeatedly washed with anhydrous ethanol and deionized water, filtered, and naturally dried at room temperature.

3. Weigh each raw material according to the formula, mix the weighed halogenated phthalic anhydride, polybasic acid, titanium dioxide nanotube powder, and polyol, and undergo a condensation reaction at 190 200 °C until the acid value is $\leq 50\text{mg KOH/g}$ to obtain the unsaturated polyester resin containing halogen; Cool down to 100 120 °C, add solvent, continue to cool down to 50 70 °C, add diisocyanate dropwise, react at a temperature less than 100 °C, continue insulation reaction after dropwise addition, separate the solvent, add remaining raw materials, and mix to obtain the flame retardant insulation paint for electric vehicles, with titanium dioxide nanotubes accounting for 3% of the total mass of the insulation paint material.

Example 2: (Titanium dioxide nanotubes account for 5% of the total mass of the insulating paint material)

The preparation method and steps of Example 2 are basically consistent with Example 1. Among them, titanium dioxide nanotubes account for 5% of the total mass of the insulating paint material.

Example 3: (Titanium dioxide nanotubes account for 7% of the total mass of the insulating paint material)

The preparation method and steps of Example 3 are basically consistent with Example 1. Among them, titanium dioxide nanotubes account for 7% of the total mass of the insulating paint material.

Example 4: (Titanium dioxide nanotubes account for 9% of the total mass of the insulating paint material)

The preparation method and steps of Example 4 are basically consistent with Example 1. Among them, titanium dioxide nanotubes account for 9% of the total mass of the insulating paint material.

Ratio 1: (undoped titanium dioxide nanotubes)

The preparation method and steps for proportion 1 are basically consistent with Example 1. Titanium dioxide nanotubes were not added.

Ratio 2: (Titanium dioxide nanotubes account for 7% of the total mass of the insulating paint material, without hydrophobic treatment)

The preparation method and steps for proportion 2 are basically consistent with Example 1. Without the use of step 2 silane coupling agent in the treatment process, titanium dioxide nanotubes account for 7% of the total mass of the insulating paint material.

Ratio 3: (Using titanium dioxide particles instead of titanium dioxide nanotubes)

The preparation method and steps for proportion 3 are basically consistent with Example 1. Using step 2 silane coupling agent treatment process, add anatase phase titanium dioxide powder (with a particle size of about 100 nanometers) to account for 7% of the total mass of the insulation paint material.

Ratio 4: (Directly mix titanium dioxide nanotubes into the insulation paint)

The preparation method and steps for proportion 4 are basically consistent with Example 1. Step 3 is changed to: weigh each raw material according to the formula, mix the weighed halogenated phthalic anhydride, polybasic acids, and polyols, and undergo a condensation reaction at 190 200 °C until the acid value is $\leq 50\text{mg KOH/g}$, to prepare the unsaturated polyester resin containing halogen; Cool down to 100 120 °C, add solvent, continue to cool down to 50 70 °C, add diisocyanate dropwise, react at a temperature less than 100 °C, continue the insulation reaction after dropwise addition, separate the solvent, add remaining raw materials and titanium dioxide nanotube powder, and mix to obtain the flame retardant insulation paint for electric vehicles, with titanium dioxide nanotubes accounting for 3% of the total mass of the insulation paint material.

Table 1. Performance Comparison

	Example 1	Example 2	Example 3	Example 4	Pair ratio 1	Pair ratio 2	Pair ratio 3	Pair ratio 4
Curing temperature (°C)	121	123	112	123	111	112	112	112
Bond strength (wire harness method) (N)	863	874	823	812	814	823	831	832
Dielectric constant (50Hz)	4.1	4.2	3.8	3.6	2.7	3.9	3.6	4.0
Breakdown strength (KV/mm)	32	33	35	28	24	32	33	24

3. Summary

Nano TiO₂ is the most widely used inorganic material in the 21st century. One of them. Nowadays, its preparation technology is also approaching maturity, but free regulation of the size, crystal form, color, and morphology of TiO₂ particles. Currently, in order to expand the application range of nano TiO₂, inorganic or organic and other methods are used to modify its surface and combine it with various environmentally friendly methods compounding toxic polymers to prepare multifunctional new composite materials, widely used in pollution control, UV resistance, biomedicine, etc domain. However, the current problem is how to integrate nanometers TiO₂ composite with polymer matrix and maintain its excellent performance with polymer performance. Therefore, future research directions mainly focus on the following aspects: (1) The surface modification technology of nano TiO₂ is still not perfect. There are shortcomings in all modification methods, and further optimization of the modification process is needed technological conditions: Exploring the optimal temperature, time, pH for the modification process and reaction mechanism, etc., to improve the performance of modified nano TiO₂ in solvents redispersibility; (2) Nanocomposite materials are still one of the recent research hotspots. Therefore, it is necessary to choose appropriate modifiers that can enhance the performance of nano TiO₂ Its photocatalytic and optoelectronic properties can also be combined with various polymers. The matrix has good compatibility, which endows the polymer with certain advantages excellent performance, expanding its application fields; (3) Optimizing the preparation method of nano TiO₂/polymer composites law and process are also new directions for future research. Currently, most Several studies were conducted by means of blending, sol gel and in-situ polymerization, but the products obtained all have different defects, and in order to avoid agglomeration can only add a lower content of nano TiO₂;

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