2004年上海大学博士学位论文 ⑳

纳米复合绝缘材料设计、制备及耐变频性研究

作　者：马寒冰
专　业：材料学
导　师：沈嘉年
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Shanghai University Doctoral Dissertation (2004)

Design, Preparation and Property of High-frequency Resistant Nanocomposite Insulation Materials

Candidate: Ma Hanbing
Major: Materials Science
Supervisors: Prof. Shen Jianian
Prof. Shi Liyi

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本论文经答辩委员会全体委员审查，确认符合上海大学博士学位论文质量要求。

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答辩委员会对论文的评语

马寒冰同学的博士学位论文《纳米复合绝缘材料设计、制备及耐变频性研究》研究开发了一种添加纳米 TiO_2 的耐变频复合绝缘材料，对该材料的设计、制备及耐变频性能进行了大量较深入的研究。主要研究内容有：

(1) 根据对变频电机用电磁线绝缘材料失效机理的分析，经过筛选实验，确定了纳米级金红石型 TiO_2 是最佳添加物，并且制备了纳米 TiO_2/聚酰胺酰亚胺(PAI)复合绝缘材料。

(2) 以 $TiCl_4$ 与 NaOH 为原料，采用液相反应法，在最佳工艺条件下制得理想的高纯金红石型相结构纳米 TiO_2 颗粒。

(3) 研究了砂磨和超声工艺对纳米 TiO_2 颗粒分散性的影响，建立了数学模型，探讨了分散机理，研究了两者联用对纳米 TiO_2 分散效果的影响。

(4) 研究了化学表面修饰对纳米 TiO_2 分散性的影响，提出了无机/有机物复合表面修饰的机理和方法。

(5) 利用自制的纳米 TiO_2/PAI 复合绝缘材料，分析了耐变频性能和机理，研究了制备工艺对复合材料耐变频性能的影响。

论文内容涉及多个学科，有一定的学术意义和重要的应用价值，研究工作量大，内容充实，工作深入、系统，有所创新，实验数据真实可靠，文笔通畅，已达到博士学位论文水平。答辩时能正确回答问题，表明作者具有扎实的基础理论知识和较强的科研工作能力。

答辩委员会表决结果

经答辩委员会表决，全票同意通过马寒冰同学的博士学位论文答辩，建议授予工学博士学位。

答辩委员会主席：周邦新

2004 年 2 月 20 日

摘　要

根据对变频电机用电磁线绝缘材料破坏过程的分析，及对纳米 TiO_2、SiO_2、Al_2O_3、ZnO、MgO、Fe_2O_3、ZrO_2 和 $BaTiO_3$ 等无机材料作为耐变频绝缘漆改性材料的筛选实验研究，提出了添加纳米 TiO_2 的变频绝缘漆的设计. 采用液相反应法制备上述纳米颗粒，并在有机绝缘树脂聚酰胺酰亚胺中均匀分散制备纳米无机/有机复合绝缘材料. 通过 XRD 和 TEM 等测试手段研究纳米颗粒形态和结构特征，用耐高频脉冲电压实验测定纳米复合材料耐变频特性. 结果表明，纳米 TiO_2、SiO_2、Al_2O_3、ZnO、MgO、ZrO_2 和 $BaTiO_3$ 改性聚酰胺酰亚胺复合绝缘材料均能够提高电磁线的耐变频寿命，其中纳米级金红石型 TiO_2 由于具有较好的介电性能、热传导性能、紫外光吸收性能和适宜的导电性能而大幅度提高绝缘材料耐变频寿命，制备的新型电磁线常规性能达到国家标准 GB/T6109.11-1990 的要求，耐高频脉冲电压实验下的老化寿命较普通电磁线提高了 7.45 倍，适合于变频电机使用. 新型纳米耐变频复合绝缘材料经企业试用后反映良好，新型耐变频纳米复合绝缘材料将具有良好的应用前景.

以 $TiCl_4$ 和 NaOH 为原料，通过控制工艺条件制备不同粒径金红石型纳米 TiO_2，通过 XRD、TEM 等手段对纳米 TiO_2 颗粒形态结构进行表征. 结果表明，当 NaOH 浓度在 5.5~13.75 $mol \cdot L^{-1}$、反应温度高于 82℃、陈化时间大于 2.0 h 时，可以直接制备金红石型纳米 TiO_2. 纳米 TiO_2 粒子生长表观活化能在 1 023K 分两段，其中温度为 873~1 023 K 时表观活化能为 0.3

$kJ \cdot mol^{-1}$，1 023~1 273 K 时表观活化能为 1.4 $kJ \cdot mol^{-1}$，随着煅烧温度升高和煅烧时间的延长，纳米 TiO_2 晶格畸变值减小. 实验制备 TiO_2 颗粒中 TiO_2 含量高达 99.7 %，粒径为 25~250 nm，呈纯金红石相结构.

采用砂磨和超声振荡对纳米 TiO_2 颗粒进行分散，并通过沉降性分析、粒度分布分析和颗粒重新团聚实验研究砂磨和超声工艺对纳米 TiO_2 颗粒分散性的影响. 运用基于支持向量机算法的模式识别方法建立新的砂磨分散和超声分散数学模型，并对 Pisch 数学模型进行了修正. 建立了评价工艺条件对超声波分散效果影响的数学模型. 结果表明，纳米粒子经超声波分散后，颗粒的重新团聚情况分为 3 个阶段. 通过砂磨/超声分散联用，将纳米 TiO_2 颗粒在水中的初始体积平均粒径控制在 150 nm 以下，重新团聚到 2 μ m 的时间 DIS 值从 32 min 提高到 164 min，纳米 TiO_2 在 PAI 中的团聚体大小从 30 μm 减小到 50 nm 以下，纳米颗粒的分散性明显提高.

采用均匀沉淀法对纳米 TiO_2 进行无机表面改性，及溶液吸附法对纳米 TiO_2 进行有机表面改性，并用 XPS、XRF 和 TG 等测试手段表征纳米 TiO_2 颗粒的形态结构；用 ζ 电位仪、激光粒度仪等分析纳米 TiO_2 粒径分布和表面带电特性，并通过纳米 TiO_2 颗粒重新团聚实验来分析纳米颗粒在有机溶剂 2-甲基吡咯烷酮 (NMP)中的分散. 结果表明，纳米 TiO_2 表面沉淀 Al_2O_3 为成膜包覆，并形成新的化学键，能提高纳米 TiO_2 颗粒在 NMP 中的 ζ 电位和粒子重团聚性能 DIS. 纳米 TiO_2 表面包覆钛酸丁脂偶联剂和高分子聚乙烯吡咯烷酮后，颗粒表面 ζ 电位绝对值降低，但其在 NMP 中的重团聚性能提高，DIS 值增大；纳米 TiO_2 表面吸附阴离子表面活性剂月桂酸钠后，颗粒表面 ζ 电位绝对值增加，在

NMP 中的重团聚性能提高，DIS 值增大；十二烷基硫酸钠、钛酸丁脂偶联剂和高分子 PVP 均能改善纳米 TiO_2 颗粒在 NMP 中的重团聚性能 DIS. 经过无机/有机复合表面修饰，纳米 TiO_2 在 NMP 中的 DIS 值从包覆前的 166 min 提高到 438 min，分散性显著提高. 用颗粒重团聚实验得到的DIS值能准确地反映纳米颗粒的分散情况.

采用耐高频脉冲电压实验研究纳米 TiO_2 粒径、含量、无机表面修饰、有机表面修饰、机械分散手段以及涂布条件对纳米 TiO_2/PAI 复合材料耐变频性的影响，并用高阻计、UV-VIS、热传导率仪等手段分析纳米 TiO_2 颗粒和 TiO_2/PAI 复合材料的导电率、导热率和紫外光吸收率等，以推测纳米 TiO_2/PAI 复合电磁线耐变频机理. 结果表明，纳米 TiO_2 形态结构、含量及其在复合材料中的分散性对材料耐变频性有较大的影响，纳米 TiO_2 在电晕放电下能形成较致密的纳米 TiO_2 无机保护层，快速传导热量和累计的空间电荷，有效阻挡带电粒子和紫外光对内层有机绝缘材料的破坏，从而大幅度提高电磁线绝缘材料在高频脉冲电压下的使用寿命.

关键词　变频电机，绝缘材料，纳米二氧化钛，分散性，表面改性

Abstract

Based on the analysis to the premature failure processes of insulation material in the inverter-fed motor and the selective experiment for the modification additives of TiO_2, SiO_2, Al_2O_3, ZnO, MgO, Fe_2O_3, ZrO_2, $BaTiO_3$, a design for the material with nano TiO_2 modification was proposed. The morphologies of the nano particles were observed by XRD and TEM. The nano particles were dispersed into polyamideimide(PAI) evenly and thus inorganic/organic nanocomposite insulation materials were prepared. The high-frequency resistant properties of the relative nanocomposite insulation materials were investigated by the high-frequency resistant experiments. Experimental results indicated that the high-frequency resistant property of PAI could be improved by adding nanoTiO_2, SiO_2, Al_2O_3, ZnO, MgO, ZrO_2, $BaTiO_3$. Among the particles, the nano rutile TiO_2 was the best material to improve the high-frequency resistant property of PAI. The regular properties of the new electro-magnet wire prepared with nanocomposite TiO_2/PAI insulation material were met to the requests of Chinese National Standard GB/T6109.11-1990, which permitted the new electro-magnet wire to be used in reality. More important, for the rutile nano TiO_2 prepared was a good dielectric material with good properties such as dielectric property, thermal conductivity, ultraviolet radiation absorbing ability and electric conductivity, the

service life under high-frequency pulse voltage of the new composite electro-magnet wire could be raised to 7.45 times. After probation use in relative manufacturing enterprises, the new nanocomposite material obtained good appraise and showed good application prospect.

Rutile TiO_2 particles with different sizes were synthesized with $TiCl_4$ and NaOH, and were prepared by controlling processing parameters. Experimental results indicated that as the concentration of NaOH was in range of 5.5 $mol\cdot L^{-1}$ to 13.75 $mol\cdot L^{-1}$, and the reactive temperature was higher than 82℃, the stay time in reactor was longer than 2 hours, the nano rutile TiO_2 could be obtained directly. The apparent activation energy of grain growth of nano TiO_2 could be splitted into two sections at the point of 1 023 K, and the apparent growth activation energy was 0.3 $kJ\cdot mol^{-1}$ as the calcining temperature was in range of 873 K to 1 023 K, and it was elevated to 1.4 $kJ\cdot mol^{-1}$ as the calcining temperature was elevated. The crystal lattice aberration of nano TiO_2 was decreased as the calcining temperature was increased and the calcining time was increased. The purity of the TiO_2 particles prepared was 99.7wt%, and the particle size was in the range of 25 nm to 250 nm, and the crystal structure was rutile.

The nano TiO_2 particles prepared were dispersed by sand milling and ultrasonic fragmentation, and the effects of relative processing parameters on the dispersing results were investigated with settlementation analysis, granularity analysis and re-agglomeration experiments. New mathematic models of sand milling and ultrasonic fragmentation were established with the Support Vector Machine Pattern Recognition, and the Pisch model was be modified. The new mathematic model indicated that with ultrasonic fragmentation, the re-agglomeration process of the nano TiO_2 particles was shown three steps. With combination of sand milling and ultrasonic fragmentation dispersing method, dispersing effect of nano TiO_2 was raised greatly. Initial average volume particle size of the nano TiO_2 in water was dominated to below 150 nm, DIS value of nano TiO_2 in water was raised from 32 min to 164 min, and the diameter of nano TiO_2 agglomeration in PAI was decreased from 30 μm to 50 nm with the combination dispersing method.

The surface of the nano TiO_2 particles synthesized was treated with inorganic oxides and organic materials, and the morphologies and structures of the nano TiO_2 particles were characterized by XPS, XRF and TGA. The size distribution and surface charges were measured with the ζ electric potential analyzer and the laser granularity analyzer. The dispersing results of the nano TiO_2 particles in solvent N-methyl-pyrrolidone (NMP) were measured with re-agglomeration experiments. Experimental results indicated that when the surface of the nano TiO_2 particles were treated with Al_2O_3, the Al_2O_3 could covered the TiO_2 as form of thin film, and new chemical bonds were observed and which could elevated the ζ electric potential and DIS value of the nano TiO_2 in NMP solvent. And the ζ electric potential of TiO_2 was decreased when the surface of TiO_2 particles was treated with the tetra-n-butyl titanate or polyvinylpyrrolidone, but the DIS value was increased. The ζ electric potential and DIS value of TiO_2 was increased after the surface of TiO_2 particles was treated with anion surfactant sodium laurate. The DIS value of nano TiO_2 in NMP was raised from 166 min to 438 min with combination of inorganic surface treatment and organic surface treatment, and the dispersing effect of nano TiO_2 in NMP was raised greatly. Experimental results also indicated that the DIS value could characterize the disperse ability of nano TiO_2 particles more accurately.

With the high-frequency resistant experiments, critical factors about high-frequency resistant property of nanocomposite insulation material TiO_2/PAI such as the particle size, concentration, surface treatment method, mechanical dispersing parameters of the nano TiO_2 particles and coating parameters of TiO_2/PAI were investigated. The electric conductivity, the thermal conductivity and the ultraviolet light absorbing ability of the nano TiO_2 particles and nanocomposite TiO_2/PAI material were measured with Megger, UV-VIS Spectrograph and Thermal Conductivity Meter. The mechanism of TiO_2 improving the high-frequency resistant ability of PAI was deduced here. Experimental results indicated that the high-frequency resistant property of TiO_2/PAI would be affected greatly by the morphology, concentration and dispersing effect of the nano TiO_2 particles, and the nano TiO_2 particles were formed a compact inorganic protective insulation layer under the Partial Discharge (Corona) conditions, and the heats and the space charges could be conducted quickly, and the organic insulation layer were

protected from harms of charged particles and ultraviolet light, thus the service-life of the magnet wire under high-frequency pulse voltage was increased greatly.

Key words inverter-fed motor, insulation material, nano titanium dioxide, disperse, surface treatment

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