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硕 士 学 位 论 文

聚苯胺复合防腐蚀助剂的制备 与环氧涂层性能研究

Preparation of PANI Composite Anti-corrosion Agents and Performance Study of Epoxy Coatings

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摘要

金属的腐蚀是自然界常见的现象,也会给人类的生产和生活带来极大的损失。故而采取有效的措施防护金属腐蚀十分必要。在各类金属腐蚀的保护措施中,对金属进行防腐蚀涂料的涂装是最直接、最有效的方法之一。在防腐涂料领域,添加了各种防腐蚀助剂的环氧(Epoxy)基涂料一直是最常用的种类,广泛应用于各种严重腐蚀环境中钢铁建筑物的防腐涂装中。随着技术的进步和产业的革新,防腐涂料经历了从含铅、锌类等重金属作为防锈组分,到采用偏硼酸钡等无机盐的无毒型品种,到目前引起国内外广泛关注的聚苯胺(Polyaniline, PANI)防腐蚀涂料品种三个阶段,并逐渐地向环保、功能化、高性能、低添加等方向迈进。由于 PANI 不溶、不熔,加工困难,成本较高且与环氧的相容性较差,因此不适用于直接进行添加。研究人员遂提出将 PANI 与其他有机、无机材料复合成 PANI 复合材料,作为 PANI 复合防腐蚀助剂进行添加,解决上述一系列问题。本文在前人工作的基础上,提出利用水热改性的有机蒙脱土(OMMT)、单分散聚甲基丙烯酸缩水甘油酯(PGMA)微球及石墨烯纳米微片(GNPs)分别与 PANI 进行复合得到三种 PANI 复合材料,再分别将三者与环氧涂料进行结合,制备 PANI-环氧复合防腐涂料。同时,实现 PANI 复合材料制备方法论的完善及 PANI 防腐涂料性能的提升。具体研究工作如下:

(1) 采用水热法改性 OMMT,利用二水合磺基水杨酸(SSA)分别与盐酸(HCl)和硫酸(H_2SO_4)按一定比例复配为混合酸作为苯胺(An)聚合的掺杂酸,制备出高电导率的剥离型 PANI/MMT 复合材料。在 160 °C 时所得改性蒙脱土层间距最大,为 4.88 nm; SSA/HCl 及 SSA/ H_2SO_4 混合酸中二者的摩尔比分别为 2.5:10 和 3.5:10 时,复合材料的电导率最大。

(2) 通过分散聚合和原位吸附-聚合法分别制备了 PGMA 微球及 PGMA@PANI 复合微球。通过控制聚乙烯基吡咯烷酮(PVP)添加量、GMA 浓度控制了 PGMA 微球的粒径和分散性。通过加入溶剂正戊醇、控制十六烷基三甲基溴化铵(CTAB)与 An 的质量比、An 与 PGMA 的质量比控制了 PGMA@PANI 复合微球的形貌。在 GMA 浓度为 0.10 g/mL, PVP 添加量为 GMA 的 10 wt%,

CTAB 添加量为 An 的 50 wt%、An 为 PGMA 的 30 wt% 并添加正戊醇的条件下，利用混合酸掺杂得到了电导率、产率综合最佳、表面致密均匀包覆 PANI 纳米线的 PGMA@PANI 复合微球。

(3) 加入 GNPs 与 PANI 形成复合材料可大幅提高 PANI 的电导率，且复合材料的电导率远高于本文所制备的其他两类复合材料。通过调控 GNPs 与 An 的质量比可控制 PANI/GNPs 复合材料的电导率和产率。在 SSA/HCl 混合酸掺杂体系中，GNPs 与 An 的质量比为 1:1 时为最优投料比，在 SSA/H₂SO₄ 混合酸掺杂体系中，GNPs 与 An 的质量比为 0.8:1 时为最优投料比。

(4) 将前述三种 PANI 复合防腐助剂及纯 PANI 分别与 XH 42801 复配制备测试涂层，讨论并总结了各种防腐助剂的最佳添加比。PANI-环氧涂层基本保持了原漆的机械性能，PANI/MMT-环氧、PGMA@PANI-环氧两类涂层的机械性能比原漆略有下降，PANI/GNPs 涂层机械性能最佳，硬度最高。四者的耐盐雾、盐水性能较原漆都有不同程度的提升，其中，划叉板/不划叉板的耐盐雾时间最长分别为 816 h (34 天) 和 312 h (13 天)，划叉板/不划叉板最长的耐盐水时间分别为 1680 h (70 天) 和 648 h (27 天)。

关键词：聚苯胺；复合材料；防腐助剂；防腐涂料

Abstract

The corrosion of metals is a common phenomenon in nature, which can bring huge losses to production and life of human beings, so it is necessary to take effective measures to metal corrosion protection. Spraying anti-corrosive coatings is one of the most direct and effective way in all kinds of metal anti-corrosion methods. In the field of anti-corrosion coating, epoxy coatings adding various anti-corrosion agents had always been the most commonly used, which are widely used in all kinds of severely corrosive environment. With the progress of technology and industrial innovation, anti-corrosive coatings had experienced variety three stages from containing heavy metals such as Pb, Zn as antirust components, to use the inorganic salts such as BBO, to arose widespread attention at home and abroad of the polyaniline anti-corrosive coatings, and gradually to the environmental protected, functional, high performance and low adding direction. Due to insoluble, cannot be melted, high costing and difficult to be processed, polyaniline is difficult to compatible with epoxy and not suitable for directly adding. The researchers suggest to prepare the polyaniline composites with polyaniline and other organic or inorganic materials which served as anti-corrosive agent and can solve those problems. On the basis of previous work, this paper puts forward three kinds of polyaniline composites which prepared by hydrothermal modified organic montmorillonite, PGMA monodisperse microspheres and graphene nanosheets, respectively. And then adding these three polyaniline composites into polyaniline-epoxy mixture to prepare the final anti-corrosion coatings. In the same time, realizing the perfection of polyaniline composite material preparation methodology and upgrading the performance of polyaniline anti-corrosive coatings. The main achievements of this paper are shown as follows.

(1) Organic montmorillonite was modified by hydrothermal method. SSA, HCl and H₂SO₄ in different formulations as mix acid can be added with aniline to prepare exfoliated PANI/modified MMT composites with high conductivity. At 160 °C the

maximum inter-layer space of hydrothermal modified montmorillonite (4.88 nm) was obtained. The composites with the highest conductivity were obtained by the mole ratio of SSA/HCl and SSA/H₂SO₄ were 2.5:10 and 3.5:10, respectively.

(2) PGMA microspheres and PGMA@PANI composite microspheres were prepared by dispersion polymerization and in-situ adsorption polymerization, respectively. Particle size and dispersion of PGMA microspheres were controlled by the PVP content and concentration of GMA. The morphology of PGMA@PANI composite microspheres can be controlled by adding n-pentanol and changing the proportion of An/PGMA as well as CTAB/An. PGMA @ PANI composite microspheres coated with PANI nanowires were obtained under the condition as follows: 0.10 g/mL GMA, 10 wt% PVP, 50 wt% CTAB and 30wt% An.

(3) PANI/GNPs composites, which prepared by adding GNPs, can significantly improve the conductivity of PANI, and its conductivity is much higher than the other two composites mentioned above. The conductivity and yield of PANI/GNPs composites can be controlled by regulating the mass ratio of GNPs/An. To preparing the best PANI/GNPs composites, in the SSA/HCl mix acid doping system, the best weight ratio is 1:1, while in the SSA/H₂SO₄ mix acid doping system, the mass ratio is 0.8:1.

Testing coatings were prepared by compositeing PANI composite anti-corrosion agents with epoxy coating (XH 42801), the best content of those agents was discussed and summarized. The mechanical performance of PANI/MMT-epoxy coatings and PGMA@PANI-epoxy coatings is slightly lower than epoxy coating, the PANI/GNPs-epoxy coatings show the best mechanical performance among those mentioned above. In terms of the anti-corrosion performance, the longest salt spray resistance time of cross testing plates/no cross testing plates is 312 h (13 days) and 816 h (34 days), respectively. The longest salt water resistance time of cross testing plates/no cross testing plates is 1680 h (70 days) and 768 h (32 days), respectively.

Keywords: polyaniline; composite; anti-corrosion agents; anti-corrosion coating

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