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Preparation of boron nitride modified and thermally conductive polymer composites

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Abstract:

With the rapid development of electrical and electronic information technology, electronic components are becoming increasingly miniaturized and high-power, but heat dissipation issues are also becoming more prominent. The modification of boron nitride (BN) and the preparation of thermally conductive polymer materials have become hot topics in the field of materials science in recent years. On the basis of explaining the structural characteristics of BN, this article analyzes the ways to improve the anti-corrosion performance of BN modified polymer materials from the perspectives of covalent and non-covalent modification of BN. Finally, a summary of the surface modification and preparation of BN modified polymer thermal conductive composite materials is provided, and the future development direction of boron nitride modified and thermal conductive polymer materials is discussed in order to achieve efficient preparation of thermal conductive polymer materials. The combination of boron nitride modification and thermal conductive polymer compounds, as well as the creation of thermal conductive polymer materials, are the main topics of this article's review of the field's research developments.

Keywords: Boron nitride; Thermal conductive; polymer materials; Surface modification; antiseptic.

1. Introduction

In the process of modern industrial development, the annual waste of resources caused by metal corrosion is enormous, so the issue of metal corrosion prevention has always been a focus of people's attention. Among numerous anti-corrosion technologies, coating protection has become one of the most commonly used due to its economy and practicality. Coating protection is generally achieved through surface modification. There are currently two main modification methods, alkylamine modification and amino silane coupling agent modification. Because there are often more than one causes of corrosion in industrial production processes, anti-corrosion coatings often require the use of multiple materials in combination to achieve good anti-corrosion effects. Boron nitride (BN) has good electrical insulation, mechanical stability, thermal conductivity, and chemical inertness. It is widely used not only in chemical energy and

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electronics, but also in metal catalysis, corrosion prevention, demolding and other fields. After non-covalent modification, its potential applications in thermal conductive composite materials, lubricants and biomaterials are further released.

Wang Wei et al. modified BN with octadecyltrimethylammonium bromide as a surfactant and prepared a series of BN composite materials based on epoxy resin(EP). Experimental data shows that when the mass fraction of filler is 30%, the thermal conductivity of the composite material reaches 1.03 W/(m·K), which is 2.15 times higher than the unmodified BN/EP system (0.48 W/(m·K)[1]. This study clearly shows that surface modification is effective in lowering the thermal resistance at the interface of the filler matrix. Because the rubber matrix has low thermal conductivity, a significant amount of fillers must be incorporated to improve thermal conductivity. Yang et al. developed a new composite material by functionalizing boron nitride sheets with PCPA and then grafting them onto Si69[2]. Their findings revealed a substantial enhancement in thermal conductivity, with the samples exhibiting thermal conductivity 5.4 times greater than that of pure natural rubber, reaching 0.81 W/K when 30 wt% of BN-CPPA-Si69 was included. While the mechanical properties of polyurethane can be easily modified, its thermal conductivity remains inadequate. To improve thermal conductivity, polymer networks and fillers are utilized. Dibutyltin dilaurate lowers the activation energy for the reaction between NCO and OH by coordinating with tin atoms, which speeds up the formation of amino ester bonds. Its catalytic selectivity favors the gel reaction (NCO-OH) over the foaming reaction (NCO-H2O), thereby minimizing bubble defects and maintaining the integrity of the heat conduction network.

BN modification

Covalent modification

The current challenge in boron nitride modification is that the B-N bonds within the hexagonal boron nitride (h-BN) layer are strong covalent bonds, and the interlayer is bound by van der Waals forces and ionic bonds (“lip-lip” interactions), resulting in a lack of active functional groups on the surface and difficulty in forming chemical bonds with the substrate. Boron atoms can serve as Lewis acid sites due to their electron deficient properties (p-vacant orbitals), while lone pair electrons of nitrogen atoms can act as Lewis bases, providing theoretical entry points for covalent modification.

There are currently two main modification methods , alkylamine modification and aminosilane coupling agent modification. The lone pair electrons of the nitrogen atom in octadecylamine combine with the empty orbitals of the boron atom in h-BN[3, 4, 5]. Alkylamine modification involves mixing h-BN with alkylamine in a solvent, and achieving the reaction through ball milling or ultrasound assistance to improve its dispersibility in hydrophobic organisms such as EP.

The coupling agent modification of amino silane with γ - aminopropyltriethoxysilane can be carried out using a two-step process: first, the surface is hydroxylated by alkali treatment to generate - OH groups, and then reacted with the amino group of γ - aminopropyltriethoxysilane to form B-N coordination bonds. At the same time, the silane end can be connected to the polymer chain. It is widely used in improving neutron shielding performance of rubber composite materials. When DBN-L was ground into waterborne EP and the resulting composite coating (DBN-L/WEP) was applied to a steel substrate, the coating’s anti-corrosion properties were greatly enhanced [5]. The DBN-L/WEP coating showed the highest low-frequency impedance (| Z | 0.01=3.156 × 109 Ω cm2) after 35 days of soaking in a 3.5 weight percent NaCl solution. This was three orders of magnitude higher than the untreated WEP coating.

Non-covalent modification

BN non-covalent modification, through weak interactions such as π - π stacking, hydrogen bonding, and electrostatic adsorption, effectively solves the problems of poor compatibility and easy aggregation with EP while retaining its inherent properties such as excellent mechanical properties, thermal stability, chemical stability, and impermeability. For example, polyvinylpyrrolidone can be used to treat boron nitride nanosheets with, as a non-covalent surface modification method.

In EP paint coatings, the diffusion path of corrosive media can be extended, cross-linking density can be increased, coating integrity can be improved, micropores and voids can be reduced, and the diffusion of ions and water to the coating/metal interface can be reduced. After non-covalent modification, its potential for application in thermal conductive composite materials, lubricants, and biomaterials can be further released.

Preparation of Thermal Conductive Polymer Composites

Thermal Conductive Resin

Wang Wei et al modified BN with octadecyltrimethylammonium bromide as surfactant, and prepared a series of BN/EP composites based on EP [6]. The experimental findings indicate that at a filler mass fraction of 30%, the thermal conductivity of the composite attains a value of 1.03 W/(MK). This represents a 2.15-fold increase compared to the thermal conductivity of the unmodified BN/EP system, which measures 0.48 W/(MK). This significant enhancement underscores the efficacy of surface modification in diminishing the thermal resistance at the filler-matrix interface.

Thermal Conductive Rubber

Natural rubber (NR), as a nonpolar matrix material, is widely used in medical, architectural, aerospace and other fields. Adding a high proportion of filler to enhance the thermal conductivity, so as to solve the short board with low thermal conductivity of rubber matrix itself. Hexagonal boron nitride (h-BN) is easy to form a heat conduction network under low load, and has a high thermal conductivity. Many methods have been invented or discovered to increase the interfacial interaction between the filler and matrix of thermal conductive polymer composites. For example, some researchers have modified the surface of BN layered crystals through covalent modification methods. Yang et al. prepared a new composite material, which was functionalized boron nitride sheet with PCPA and then grafted onto Si69. It was found that the thermal conductivity of the prepared samples was greatly improved, and the thermal conductivity of the samples was 5.4 times that of pure NR, and the thermal conductivity reached 0.81W/K when 30wt% BN-CPPA-Si69 was added[2].

Thermal Conductive Polyurethane

Polyurethane, which can adjust the physical and chemical stability, is widely used in many fields. It is known as the “fifth largest plastic” and is a new multifunctional polymer material. The application fields of this product include aerospace, mechanical engineering, electronic information engineering technology, architecture, automobile manufacturing, packaging engineering, military industry, navigation and so on. Polyurethane has high corrosion resistance, radiation resistance and plasticity, and its thermal conductivity can be enhanced by constructing polymer network and adding fillers. The mechanical properties of polyurethane are highly adjustable, but its thermal conductivity is poor. Enhance thermal conductivity through polymer networks and adding fillers. Dibutyltin dilaurate reduces the activation energy of the reaction between NCO and OH through the coordination of tin atoms, accelerating the formation of amino ester bonds [7]. Its catalytic selectivity preferentially promotes gel reaction (NCO-OH) rather than foaming reaction (NCO-H_2O), thus reducing bubble defects and ensuring the continuity of heat conduction network.

Dibutyltin dilaurate is a core additive for constructing low interfacial thermal resistance thermal conductive polyurethane through precise catalysis of NCO-OH reaction. Its application requires matching filler modification processes (such as BN Lewis base modification) and graded curing strategies to attain low defects and high thermal conductivity (> 1.5 W/m·K)and low defect comprehensive performance. The future direction focuses on the development of low toxicity alternative catalysts and biomimetic orientation structure design, breaking through the processing bottleneck under high filling.

Conclusion

The solid pairing of electrons through Lewis acid site provides a theoretical breakthrough point for covalent modification. By using the modification method in this paper, the corrosion resistance of the coating is obviously improved. In epoxy paint coating, the corrosion medium diffusion path can be prolonged, the crosslinking density can be increased, the coating integrity can be improved, micropores and voids can be reduced, and the diffusion amount of ions and water to the coating/metal interface can be reduced. After noncovalent modification, its application potential in the fields of thermal conductive composites, lubricants and biomaterials can be further released. The thermal conductivity of boron nitride was effectively improved by treating EP with BNMB stent and surface treatment with 18 alkyl trimethyl ammonium bromide. The thermal conduction network formed by hexagonal boron nitride under low load was combined with natural rubber by covalent modification to produce thermal conduction rubber with thermal conductivity 5.4 times that of natural rubber. By adjusting the amount of dibutyltin dilaurate (usually 0.1-0.3 wt%), the settlement or agglomeration of filler caused by too fast reaction can be avoided, the curing rate can be controlled, and the integrity of heat conduction path can be guaranteed. Dibutyltin dilaurate is the core additive for building thermal conductive polyurethane with low interfacial thermal resistance by accurately catalyzing NCO-OH reaction. Its application needs to match the filler modification process (such as BN Lewis base modification) and grading curing strategy to attain low defects and high thermal conductivity (> 1.5 W/m·K). In the future, we will focus on the development of low-toxic alternative catalysts and the design of bionic orientation structure to break through the processing bottleneck under high packing.

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