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Full Length Article

Surface modification of silicon carbide with silane coupling agent and hexadecyl iodiele

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ABSTRACT

In this paper, two kinds of silane coupling agents, namely 3-aminopropyl triethoxysilane (KH550) and 3-mercaptopropyl trimethoxysilane (KH590), were adopted as preliminary modifiers to improve the hydrophobic surface properties of silicon carbide (SiC) powder for the first step. The factors that influence the modification effects were investigated by measuring the contact angle. The results showed that KH590 has a better effect than KH550 for the hydrophobic modification of SiC, and the contact angle improved most after SiC powder was reacted with 0.3 g KH590 at 75 °C in aqueous/alcohol solution for 4 h. On account of further enhancement of hydrophobicity, the study was focused on utilizing nucleophilic substitution between KH590 and hexadecyl iodiele to extend the length of alkyl chain. Compared with using KH590 alone, SiC powder modified by KH590 and hexadecyl iodiele showed better water resistance with an increase of contact angle from 106.8° to 127.5°. The Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectra (XPS) as well as X-ray diffraction (XRD) analysis results showed that KH550/KH590 and hexadecyl iodiele can be covalently bonded to the surface of SiC powder without altering its crystal configuration. This methodology may provide a new way of the modification of inorganic materials in further.

1. Introduction

In recent years, ceramic powders have become one of the most commonly applied materials in advanced ceramics, but their synthesis or processing is still considered problematic [1]. Inorganic particles [2] are very prone to agglomerate in media and show poor dispersion capacity in organic solvents or oil due to their high surface energy. Due to the bad consistent interfacial interaction, the combination of the inorganic particles with the polymer matrix is weak, and therefore the applications of inorganic particles are largely limited. Silicon carbide (SiC) particles are of great interest for various applications because of its high hardness and strength retention at elevated temperatures, good thermal stress resistance and excellent wear and oxidation resistances [3]. Recently, SiC has been demonstrated to be an effective multifunctional material, especially for the application as polymer reinforcements [4]. However, it has a strong tendency to agglomerate. To break down the particles agglomerates and improve the dispersibility of particles in polymer matrix, the technology of surface modification is in common use and effective [5].

Surface modification methods for inorganic particles can be loosely divided into two classes: chemical or physical. The selectable routs of physically modifying powder usually cannot meet the requirements of altering the nature permanently [6] or obtaining thick surfaces [7]. In the case of chemical modification, there are various surface modifiers. Among these surface modifiers, silane coupling agents have gained more attention because of their special structures. The general formula of trialkoxysilanes is $RSi(OX)_3$, where R is a functional group and OX is a hydrolysable group leading to a silanol group which can further condense with the silanols present at the particle surface [8]. In other words, silane coupling agents have two different functional groups, one that is attracted to the resin and the other that is attracted to the surface of the filler; thereby improve the performance of composite [9]. It has been reported that inorganic particles such as TiO_2, Al_2O_3, SiO_2, can be successfully modified with coupling agents to improve their dispersive capacity in organic solvents and polymer matrices. In the work of Li et al. [10], TiO_2 was modified by KH550 through silanization reaction and the modified particles are of both hydrophilicity and lipophilicity. Lan et al. [5] modified magnesium hydroxide (MH) with vinyltriethoxysilane (VTES) by dry process and found that

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the surface of MH powder was transformed from hydrophilic to hydrophobic and showed considerable improved dispersibility and compatibility of MH particles in the organic phase. According to the study of Zhang et al. [11], 3-methacryloxypropyltrmethoxysilane (KH570) was grafted to the silica surface by chemical bond and the physicochemical performance and surface chemistry structure of precipitated silica have been improved. Bonhomme et al. [8] systematically investigated the grafting of methylalkoxysilanes ($Me_xSi(OEt)_{4-x}$) on silica particles in water-rich medium and it was clearly evidenced the formation of covalent links between the organosilane entities and the silica surface. However, few papers have studied systemically the surface modification of SiC, let alone researches that further improve the hydrophobicity of SiC on the basis of the first modification with silane coupling agents. Therefore, it is most intensely desirable to devise an approach to increase hydrophobic property of SiC particles.

In this work, a novel and facile strategy to improve hydrophobicity of SiC powder modified by silane coupling agent and hexadecyl iodiele was reported. In order to further study the effect of coupling agent on the composites interface and obtain hydrophobic SiC particles, 3-aminopropyl triethoxysilane ($NH_2CH_2CH_2CH_2Si(OC_2H_5)_3$, KH550) and 3-mercaptopropyl trimethoxysilane ($SHCH_2CH_2CH_2Si(OCH_3)_3$, KH590) were used as preliminary modifiers to control the surface properties of SiC. The modification effects of SiC powder under various conditions such as the amount of KH550/KH590, reaction temperature and reaction time were studied by focusing on the experimental parameter of the contact angle to establish their respective optimal reaction parameters, especially to compare their modification effects and lay foundation for a second modification. As is known to all, KH550 and KH590 have the advantage of reaction activity by the amine group and sulfhydryl group (nucleophilic) that facilitate alkylation reaction with haloalkane. On account of further enhancement of hydrophobicity, the study was focused on utilizing nucleophilic substitution between KH590 and hexadecyl iodiele to extend the length of alkyl chain. The bonding mechanism between modifiers and SiC was characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectra (XPS). The structural change of the modified SiC was studied by X-ray diffraction (XRD). The thermal stability was evaluated by thermogravimetric analysis (TGA). Contact angle measuring instrument and scanning electron microscopy (SEM) were also used in this experiment, and the relationship between surface morphology and contact angle was verified. Based on the results, the reaction mechanisms were discussed, simultaneously.

2. Materials and methods

2.1. Materials

Silicon carbide was provided by Hunan Jincheng New Material Technology Co. Ltd with average particle size of 5 μm. Potassium carbonate (99%), acetone (99.5%), ethanol (99.5%) and deionized water were all purchased from Jiangtian Chemical Reagents Co. Ltd. Two different kinds of silane coupling agents, namely 3-aminopropyl triethoxysilane (KH550) and 3-mercaptopropyl trimethoxysilane (KH590), were provided from Nanjing Capatue Chemical Co. Ltd and Nanjing Sheng Bicheng Chemical Technology Co. Ltd, respectively, while hexadecyl iodiele (98%, stab. with copper) employed in this study was obtained from Beijing inoke Technology Co. Ltd. All chemicals and materials were used without any further purification.

2.2. Synthesis of hydrophobic SiC-KH550/KH590 powder

A mixture of aqueous/alcohol solution (25 vol% deionized water:75 vol% ethanol) was transferred into a reactor equipped with a condensator. Then a certain amount of KH550/KH590 was added, and the mixture was agitated in the reactor for 30 min at a certain temperature. After the silane coupling agent was hydrolyzed absolutely, SiC powder was slowly added and the reaction was taken under stirring at a certain temperature for a given time. After the reaction, the mixture was filtrated by a sand-core funnels. In order to clean the unreacted silane coupling agent, the residue powders were ultrasonically washed by adequate ethanol for three times and 15mins for each time. Finally, the modified SiC powder (SiC-KH550/KH590) was separated by centrifuging and then dried at 90 °C for 12 h in a vacuum oven (with the pressure of 30KPa).

2.3. Synthesis of hydrophobic SiC-KH590-hexadecyl iodiele powder

Suspensions containing SiC-KH590 powder (2.0 g), acetone (40 mL), hexadecyl iodiele (0.5 g) and potassium carbonate (0.21 g) were prepared. The suspensions were blended thoroughly by a magnetic stirrer for 20 min at room temperature. Afterwards, the mixture was transferred into a reactor equipped with a condensator and the reaction was taken under stirring at 60 °C for 8 h in a water bath. The filtrated part of reaction production was thoroughly washed at least three times with acetone and three times with deionized water to remove the residual hexadecyl iodiele and other impurities, at last dried to constant weight in a vacuum oven (with the pressure of 30 KPa) at 80 °C.

2.4. Sample characterization

The degree of hydrophobicity was assessed from an optical water contact angle meter (DSA100; Kruss Company Ltd., Germany) with a computer-controlled liquid dispensing system. The powdery samples (0.6 g) were pressed into a small cylinder (in a 13 mm diameter) using a pressure of 8 MPa. Surface roughness of pressed cylinder was assessed using a non-contacting optical instrument and then the water droplet (5 μL) was placed onto the cylinder. The contact angle against water on a horizontal surface of a cylinder was obtained and three wetting experiments were done for each parameter.

Infrared spectra were collected using FTIR spectrometer (Nicolet 6700). The surface compositions were characterized by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha XPS spectrometer equipping 300 W Al Kradiations). The crystal structure of SiC was examined by the X-ray diffraction (XRD, Rigaku Dmax 2500) at a step size of 5°/min in the range of 10°–80°. The morphology was characterized using a field-emission scanning electron microscope (SEM, FEI Nanosem 430). The thermal behavior of the SiC powder before and after modification was evaluated with the NETZSCH STA 449C thermal analyzer at a constant heating rate of 5 °C/min.

3. Results and discussion

3.1. The influence of the reaction conditions on the modification of SiC powder by KH550/KH590

The contact angle characterization has been used very often as a relatively simple method for accessing the properties of surfaces as a result of their chemical or physical modification. The water contact angle (θ), $\theta < 90^\circ$ and $\theta > 90^\circ$ can indicate the surface is 'hydrophilicity' or 'hydrophobicity', respectively [12]. In order to