



Surface functionalization of hexagonal boron nitride and its effect on the structure and performance of composites

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ABSTRACT

A new organized hexagonal boron nitride (OhBN) with significantly increased amount of amine groups was synthesized, and characterized by Fourier Transform Infrared (FTIR), X-ray Photoelectron Spectroscopy (XPS), Thermogravimetric (TG) analysis, UV–vis Transmittance Spectra, Transmission Electron Microscope (TEM) and the potentiometric titration. The content of amine groups for OhBN is about 5 times of that for original hexagonal boron nitride (hBN). Based on the preparation of OhBN, new composites consisting of OhBN and bismaleimide (BD) resin were developed, which show greatly improved integrated performance (including dynamic mechanical, dielectric and thermal properties) compared with BD resin and the hBN/BD composites. In the case of the OhBN/BD composite with 15 wt% OhBN, its storage modulus, dielectric loss, thermal conductivity and coefficient of thermal expansion are about 1.2, 0.56, 1.11 and 0.92 times of the corresponding values of hBN/BD composite, respectively; moreover, the glass transition temperature of the former is 15 °C higher than that of the latter. These interesting results suggest that the integrated performance of the composites is closely related to the surface nature of the fillers because the change in the surface nature not only varies the chemical structure, free volume and crosslinking density of the composite, but also determines the interfacial nature between inorganic fillers and the resin matrix. This investigation demonstrates that the method proposed herein provides a new approach to prepare organized inorganic fillers as well as corresponding composites with controlled structure and expected performances for cutting-edge industries.

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1. Introduction

High performance polymeric composites with high thermal conductivity and low dielectric loss have attracted great attentions worldwide owing to their great importance in many cutting-fields industries [1–3]. A simple and effective method for preparing thermally conductive materials is adding thermally conductive inorganic particles into a polymer [4,5]. Many kinds of inorganic fillers possess high thermal conductivity, but few of them simultaneously own desirably low dielectric loss. Recently, we prepared a composite based on hexagonal boron nitride (hBN) and bismaleimide (BMI) resin [6], and found that the thermal conductivity and dielectric loss of the hBN/BMI composite are much better than those of other composites. However, the concentration of amine groups on the surface of hBN is so small (about 0.113 wt%) that the composite cannot get desirable interfacial adhesion, and thus does not show desirable integrated performance, especially the glass transition temperature (T_g) and dielectric loss need to be further

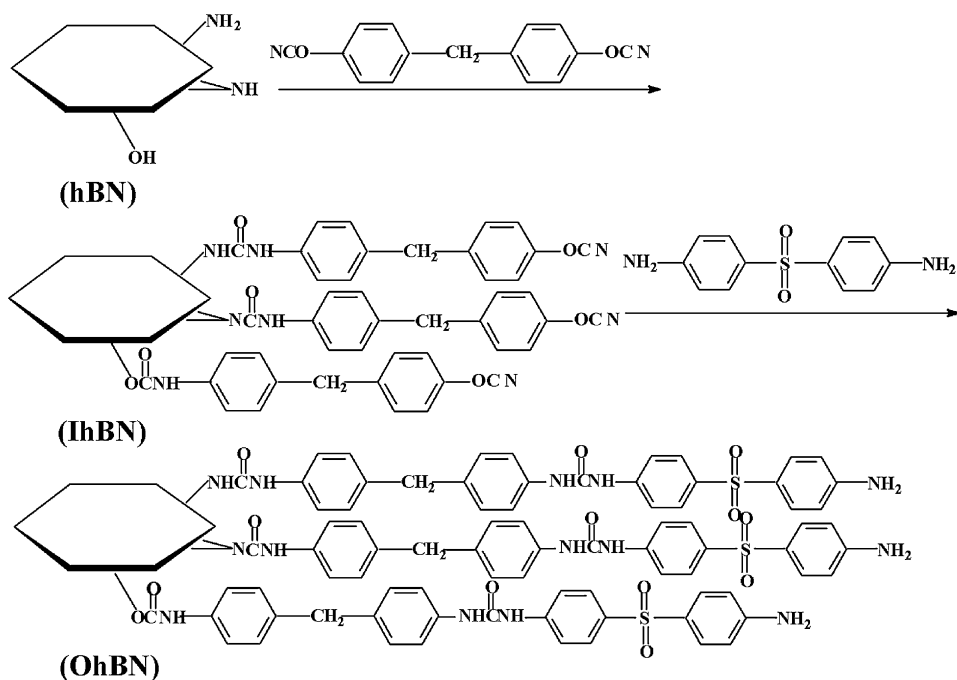
improved. Therefore, it is of great interest to synthesize modified hBN with more active groups, and developing composites with significantly improved integrated performance.

However, note that it is difficult to modify the surface of hBN due to its special structure. In detail, hBN has molecularly smooth basal planes without functional groups for chemical bonding and/or interaction [7]. Some researchers used silane-based coupling agent to modify the surface of hBN [8–11], however, the method did not achieve success because the method is extensively applicable to the inorganic fillers with rich hydroxyl groups, unfortunately, the condition does not fit the situation of hBN. Kochetov's group studied the mechanism of modifying the surface of hBN by using silane-based coupling agent, and concluded that silane coupling agent can react with the boron oxide (B_2O_3) layer covering the hBN particles and create covalent bonds [12]. But the volume of B_2O_3 is greatly depended on the processing procedure, and usually is so small that only a very small grafting amount of silane coupling agent can be grafted on the surface of hBN. Obviously, this does not guarantee the good dispersion of modified hBN in polymer matrix, and thus the desirable integrated performance of prepared composites.

Note that compared with the modification of hBN by using silane coupling agent, no better method has been set up up-to-date. The

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Scheme 1. The surface treatment of hBN.

aim of our present work is synthesizing a new organized hBN that has significantly enlarged amount of active groups.

As is well known that the surface treatment of inorganic fillers is to gain a good interface between the inorganic fillers and organic matrix, hence the surface modification must consider the chemical structure of the resin. BMI resin is known to be the representative of thermally resistant thermosetting resins, and has great applications in many cutting-edge fields owing to its outstanding integrated performance [13,14], so BMI resin is chosen as the matrix for our present research.

In the structure of BMI monomer, the C=C double bond of imide ring is active due to the strong electron-withdrawing effect of two adjacent carbonyl groups [15]. According to this feature, a new method is built to organize hBN, its mechanism is transforming secondary amine and hydroxyl groups at the edge of the hBN layer into primary amine groups; moreover, introducing molecular chains which also have many active groups. The detail synthesis of organized hBN is described herein; in addition, new high performance composites based on BMI resin and organized hBN are developed, and the effect of the organization of hBN on the structure and performance of the composites is systematically investigated.

2. Experimental

2.1. Materials

hBN with a purity of 99.3% was supplied by Zibo Jonye Ceramic Technologies Co., Ltd (China), and its purity was 99.3%. 4,4'-Bismaleimidodiphenyl methane (BDM) was obtained from Northwestern Chemical Engineering Institute (China), o,o'-diallylbisphenol A (DBA) was provided by Soochow University (China), N,N-dimethylformamide (DMF) and 4,4'-methylenebis(phenyl isocyanate) (MDI) were purchased from Aladdin-reagent Co., Ltd. (China), and diamine diphenyl sulfone (DDS) was bought from Zhejiang Dinglong Chemical Co., Ltd. (China).

2.2. Synthesis of organized hBN

The mechanism of synthesizing organized hBN is shown in Scheme 1, which consists of two steps, the first one is introducing reactive groups (isocyanate) on the surface of hBN, and the second step is attaching the amine groups through the $-\text{NCO}$ groups. The detail procedure is described as follows. hBN was dispersed in DMF with an ultrasonical agitation under a nitrogen atmosphere to form a mixture, and then an excess amount of MDI was added into the mixture with stirring followed by heating to 70°C and maintaining at the temperature for 30 min. After that the particles were quickly vacuum-filtered to completely remove free MDI to get a crude product, which was then washed using DMF for 5 times, and dried, successively. The resultant intermediate product was coded as IhBN.

The IhBN particles were blended with DMF to form a slurry, and then an excess amount of DDS was slowly added to the slurry, followed by heating with stirring to 50°C and maintaining at that temperature for 12 h. After that the crude product was filtered, washed and dried, successively, and the resultant product was the organized hBN, coded as OhBN.

2.3. Preparation of BMI/DBA prepolymer and cured resin

Appropriate quantities of BDM and DBA with a molar ratio of 1:0.86 were placed in a beaker with a mechanical stirrer and a thermometer. The mixture was heated to $130\text{--}135^\circ\text{C}$ and maintained within that temperature range with stirring until a clear and brown liquid was obtained. The liquid was maintained at that temperature for an additional 30 min to obtain a transparent prepolymer, which was BD prepolymer.

BD prepolymer was poured into a preheated glass mold for degassing under vacuum at 130°C for 30 min. After that, the mold was put into an oven for curing and postcuring via the procedures of $150^\circ\text{C}/2\text{ h} + 180^\circ\text{C}/2\text{ h} + 200^\circ\text{C}/2\text{ h} + 220^\circ\text{C}/2\text{ h}$, and $230^\circ\text{C}/4\text{ h}$, respectively. The resultant product was cured BD resin.

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