



Scalable fabrication of thermally conductive elastomer/boron nitride nanosheets composites by slurry compounding



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ARTICLE INFO

Article history:

Received 23 October 2015

Received in revised form

9 December 2015

Accepted 15 December 2015

Available online 20 December 2015

Keywords:

Boron nitride nanosheets

Slurry compounding

Silane

Thermal conductivity

Elastomer

ABSTRACT

So far, most of the preparation methods for polymer/boron nitride nanosheets (BNNs) composites are not suitable for mass production. Here, cost-effective and environmentally friendly water/ethanol were selected as the solvents to prepare BNNs slurry on large scale by liquid exfoliation/solvent exchange. The slurry was then compounded with styrene-butadiene rubber (SBR) to form the rubber/BNNs composites via conventional two-roll milling. The sulfide-containing silane was introduced to modify the interface between BNNs and the rubber. The silane modified BNNs (Si-BNNs) has been characterized by FTIR, XPS and TGA. It is found that, with *in situ* modification of the silane, the rubber/BNNs composites exhibited significantly improved thermal conductivity. With 10.5 vol% Si-BNNs incorporated, the thermal conductivity of the composites is increased by 253%, comparing to the neat SBR. Meanwhile, the mechanical properties of the composites are simultaneously largely enhanced. The scalable yet environmentally-friendly slurry approach paves the way for industrial-scale utilization of BNNs in thermally conductive polymer composites.

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1. Introduction

Two-dimensional nanoparticles have attracted great attention due to their extraordinary physical and mechanical properties and their structural similarities to graphene. The hexagonal boron nitride nanosheet (BNNs), an isoelectric analogous to graphene, possess outstanding properties such as high temperature stability, high resistance to oxidation (850 °C under air) [1], good chemical inertness [2], a wide band gap (~6 eV) [3], electrical-insulating properties, low dielectric constant, high hardness (15–24 kg mm⁻²), and large thermal conductivity (~6000 W m⁻¹K⁻¹) [4]. These outstanding properties make BNNs-based composite materials especially promising in the thermal management of energy systems such as solar cells, light emitting diodes, thermal interface materials [5]. Comparing to graphene, BNNs are especially attractive in fabricating thermally conductive yet electrically insulating polymer composites.

Broadly, BNNs can be obtained via bottom up or top down approaches. The bottom-up approaches usually involve the

synthesis of BNNs from boron and nitrogen precursors using CVD methods [6] or solid–state reactions [7]. These methods yield BNNs of large lateral sizes and low crystallinity. Alternatively, the top down techniques that mainly refer to the exfoliation of hexagonal boron nitride (h-BN) by different means, such as mechanical cleavage [8], liquid phase exfoliation [9], chemical functionalization [10]. BNNs from exfoliation methods are usually highly crystalline, limited in lateral sizes and monolayers fraction. Among the available approaches for BNNs production, liquid phase exfoliation seems to be promising as it is cheap, simple, versatile, and amenable for scale-up [11]. The best organic solvents for exfoliating h-BN are isopropanol (IPA) and N-methylpyrrolidone (NMP), which have similar surface energy to the BNNs. However these organic solvents are toxic, expensive and characterized by high boiling points. Generally speaking, water may be advantageous over organic solvents. Lin [12] directly exfoliated bulk h-BN powder into BNNs in water with a concentration of 0.05–0.1 mg/ml. The low concentration limited its large-scale applications in polymer composites. To overcome this drawback and further increase the concentration of aqueous BNNs dispersions, the h-BN particles could be treated with NaOH solution to attach the hydroxide functional groups on to the surface before sonication [13].

Regarding to the preparation of polymer/BNNs

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nanocomposites, most of the methods reported mainly are solution mixing [5,14] and *in situ* polymerization [15]. However, for real applications, it has significant importance to prepare polymer/BNNSs nanocomposites by mechanical milling or melt compounding. Xie [16] directly mixed the dried BNNSs powder with poly(ethylene-terephthalate) by melt-processing. Nevertheless, the BNNSs would inevitably restack and severely aggregate during the drying process. In the present study, we proposed a new slurry compounding method for the fabrication of rubber/BNNSs composites. Although similar slurry method have been utilized for the preparation of polymer/clay nanocomposites [17], to the best of our knowledge, the research on polymer/BNNSs composites by slurry method has not been reported. In the present work, h-BN was first exfoliated by sonication and suspended in water; this suspension was further solvent exchange with ethanol to form BNNSs-ethanol slurry. The slurry was then mixed with rubber to form rubber/BNNSs composites by two-roll milling. To further enhance the dispersion of BNNSs and strengthen the interface, a sulfide-containing silane was introduced during the preparation of slurry. Consequently, high performance rubber/BNNSs composites have been prepared by this method. The structures of the slurry and composites have been characterized and correlated to the observed the combination of high reinforcement and high thermal conductivity for the rubber/BNNSs composites.

2. Experimental

2.1. Raw materials

Hexagonal boron nitride (h-BN) (purity of 99.27%, average size 4 μm) was purchased from Yingkou Liaobin Fine Chemicals Co. Ltd. Emulsion-polymerized styrene-butadiene rubber (SBR, 1502, styrene content 23.5%) was obtained from Fujian Fuxiang Chemical Co. Ltd. Bis-(γ -triethoxysilylpropyl)-tetrasulfide (TESPT) was collected from Degussa, Germany. All the rubber ingredients were industrial grade and used as received.

2.2. Preparation of BNNSs slurry and Si-BNNSs slurry

The h-BN particles were suspended in a 5 M sodium hydroxide (NaOH) solution at 120 $^{\circ}\text{C}$ for 24 h to introduce the hydroxide functional groups on to the surface [13]. After the treatment with the base solution, the particles were rinsed with deionized (DI) water and centrifuged several times until the pH value was neutral. To exfoliate the h-BN, the treated h-BN particles were sonicated in deionized water using a bath sonicator (KQ-400GKDV) for 8 h [12]. The mixture was then centrifuged at 1000 rpm for 10 min to remove the unexfoliated large particles and the supernatant was decanted immediately. The concentration of the obtained “milky” BNNSs suspension was 1–3 mg/ml. The yield of exfoliated BN after sonication is about 13.3%. However, the yield may be effect by many facts, such as initial concentration, sonication time and power, centrifugal speed and time, etc.

The BNNSs slurry was prepared by a solvent exchange method reported by our group [18]. Typically, the BNNSs suspension was first centrifuged at 14000 rpm for 30 min, and then the wet BNNSs sediment was re-dispersed in ethanol. Repeated the cycles of centrifugation and washing with ethanol 3 times, the water was replaced by ethanol. Finally, the BNNSs sediment was mixed with a small amount of ethanol and sonicated until forming uniform slurry. The concentration of the slurry was about 50–60 mg/ml. To prepare TESPT-modified BNNSs slurry, 2 wt% TESPT (relative to rubber) was added into the slurry and sonicated for 3 h to get uniform dispersion.

In order to reveal the reaction between TESPT and BNNSs, model

compound was prepared. TESPT (10 times weight relative to BNNSs) was added into ethanol suspension of BNNSs with a concentration of 1 mg/ml and stirred at 70 $^{\circ}\text{C}$ for 24 h. The reaction product was washed and centrifuged three times with ethanol to remove unreacted TESPT and then dried in an oven at 50 $^{\circ}\text{C}$ for 12 h. The obtained model compound was used for the characterizations of Si-BNNSs.

2.3. Preparation of SBR/BNNSs composites and SBR/Si-BNNSs composites

The SBR/BNNSs composites were prepared by a slurry compounding method on a conventional two-roll mill. The BNNSs slurry was added in the SBR during milling. The compounds were kept at room temperature for 24 h to volatilize the residual ethanol. Then the compounds were mixed with rubber ingredients with two-roll mill and subjected to compression at 150 $^{\circ}\text{C}$ for the optimum curing time determined by the U-CAN UR-2030 vulcameter. The formulation of the composite is as follows: SBR 100, sulfur 1.5, ZnO 5, stearic acid 1, N-cyclohexyl-2-benzothiazole (CZ) 1.5 and 2, 2'-dibenzothiazole disulfide (DM) 0.5 (all in weight). For comparison, SBR/BN composites were prepared by directly mixed on a two-roll mill. For simplicity, the SBR/BN composites are abbreviated as **Bx**, the SBR/BNNSs composites prepared by a slurry compounding method are abbreviated as **Sx** and those modified with TESPT are abbreviated as **Six**, where x denotes the filler content (vol%) in the composites.

2.4. Characterizations

The morphology of BN particles and the tensile fractured surfaces of the composites were observed by using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800). Before SEM observations, these samples were sputter coated with a thin gold film. The element composition of the modified BNNSs was determined by X-Ray photoelectron spectroscopy (XPS, Escalab 250XI). The thickness of the BNNSs was measured by atomic force microscopy (AFM, Nanoscope 3a) in a tapping mode. Fourier transform infrared spectra (FTIR) of BNNSs before and after treatment with TESPT were collected on the Bruker Vertex 70 FTIR spectrometer. Thermal gravimetric analysis (TGA) was conducted to evaluate the grafting content on BNNSs by using a TA Q500 instrument (USA) under nitrogen purging at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. X-ray diffraction (XRD) analysis was performed using an X'pert Pro diffractometer (Panalytical, Netherlands). The measurements of the mechanical properties of the rubber composites were conducted on a universal testing machine (GOTECH AI-7000S, Taiwan) at room temperature with a cross-head speed of 500 mm/min following ISO 37–2005 protocol. Dynamic mechanical properties were determined by a dynamic mechanical analyzer Q800 (TA Instrument, Inc., USA). The tests were carried out under tensile mode at heating rate of 3 $^{\circ}\text{C}/\text{min}$. The frequency and strain were set as 3 Hz and 1% respectively.

Thermal conductivity of the composites at 30 $^{\circ}\text{C}$ was calculated using the following equation:

$$\lambda = \alpha \times \rho \times C_p \quad (1)$$

where λ , α , ρ and C_p represent thermal conductivity, thermal diffusivity, density and specific heat capacity of the composites, respectively. The thermal diffusivity of composites was measured by a non-contact laser flash method (LFA-447, Netzsch) according to ASTM E1461. The samples for the test were 12.7 mm in diameter and about 2 mm in thickness, spray-coated with a thin layer of graphite powder at both sides. The thermal conduction direction

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