



# Coating polyrhodanine onto boron nitride nanosheets for thermally conductive elastomer composites



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## ABSTRACT

Boron nitride nanosheets (BNNs) have captured much attention in the fabrication of thermally conductive and electrically insulating polymer-based composites. However, inert surface chemistry of BNNs largely hampers their applications in polymer composites. Herein, we report a facile approach for the fabrication of elastomer/BNNs composites with high thermal conductivity. BNNs were first wrapped by polyrhodanine in water to form the polyrhodanine@BNNs nanostructure (PRh-BNNs) and then compounded with styrene-butadiene rubber to form the elastomer composites. Due to the unique curing reactivity of polyrhodanine, strong interfaces were formed in the resulting elastomer composites. Accordingly, the SBR/PRh-BNNs composites exhibited unique combination of high mechanical properties and high thermal conductivity. Importantly, the orientation of BNNs in the elastomer led to further increase in thermal conductivity. Overall, the present work offers a new route for the design of thermally conductive elastomers through the combination of efficient interfacial modification and filler organization.

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## 1. Introduction

Hexagonal boron nitride nanosheets (BNNs), as a kind of iso-electric to graphene, have captured much attention for their extraordinary thermal conductivity and mechanical properties. Different from graphene, BNNs are electrically insulating due to their large band gap ( $\sim 5.5$  eV) [1]. Therefore, BNNs are especially promising in fabricating thermally conductive yet electrically insulating polymer composites. Generally, it is difficult to homogeneously disperse pristine BNNs into polymer matrices for their high surface energy. Consequently, a high interfacial thermal resistance usually results in these composites [2]. Thus, surface modification of BNNs is generally essential to ensure a quality dispersion and sufficient interfacial interaction of BNNs in a polymer matrix [3], which have been considered to be crucial for achieving high thermal conductivity [4]. The established functionalization approaches for BNNs may be categorized broadly into noncovalent, Lewis acid-base (ionic), and covalent ways [5]. Functional substances with conjugated structures or amphiphilic agents have been utilized to exfoliate or stabilize BNNs through  $\pi$ - $\pi$  or cation- $\pi$  interaction [3,6,7]. Alternatively, the electron-deficient boron atoms of BNNs act as Lewis acid and are susceptible to interact

with electron-rich Lewis bases such as octadecylamine (ODA) or amine-terminated polyethylene glycol (PEG) [8,9]. Though BNNs are thought to exhibit excellent chemical stability in strong acid and strong alkali [10], several reports have described the covalent functionalization of BNNs using oxygen [11] or nitrogen radical species [12] and dibromocarbene [13]. In addition, hydroxyl groups can be introduced or enriched on the surface of BNNs by the treatment with hydrogen peroxide [14], acid [2,15], alkali [16] and high temperature [17]. Silanes have been used to react with hydroxyl groups or amino groups on the edge surfaces of BNNs or h-BN [18,19]. Nevertheless, most of the reported methods require sophisticated control on the modification process or involved the utilization of hazardous or dangerous substances. In this regard, it is still highly desirable to develop a convenient and efficient strategy to functionalize BNNs.

Besides the surface modification of the fillers, the formation of the thermally conductive paths is another important issue for the improvement of thermal conductivity of a composite. Hybrid filler systems with different sizes, shapes or dimensionality have been introduced to fill the gaps among the fillers and allow the formation of effective thermal transfer pathways [20,21]. Owing to their significant anisotropy in thermal conductivity, the orientation of BNNs or h-BN in a composite may significantly enhance the thermal conductivity in aligned direction. Efforts have been contributed to fabricate aligned structure in the composites by

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magnetic field [22], electric field [23] and shear forces [24]. Among these methods, the orientation by two-roll milling is a promising way in practical production as it can be scaled up by easy operation and does not require complicated processing facilities.

Rhodanine is an organic substance derived from thiazolidine and has historically been used as an accelerator for rubber vulcanization [25]. Rhodanine tends to react rapidly with sulfur and transform into inactive crosslink precursor [26]. As a consequence, curing with rhodanine would result in scorching and long marching curing behavior. As a consequence, rhodanine was gradually replaced by a wide variety of alternative accelerators with much higher accelerating efficiency in the rubber industry [27]. Recently, several core-shell structure nanoparticles with polyrhodanine shell have been fabricated for various applications, such as antibacterial and adsorbent for heavy metal ions [28,29]. Typically, the oxidative polymerization of rhodanine proceeded preferentially on the surface of the core nanoparticles, where the initiator was located [25,28]. Inspired by the unique reactivity of rhodanine during rubber vulcanization, very recently, we have introduced polyrhodanine onto halloysite nanotubes to improve the interfacial properties in rubber/halloysite composites [30].

In view of the potential interaction between BNNs and polyrhodanine and the illustrated curing activity of polyrhodanine [26,30], in the present work, we attempted to introduce polyrhodanine onto BNNs to form polyrhodanine@BNNs, aiming at lowering the interfacial thermal resistance. Previously, the oxidative polymerization of rhodanine has been conducted in organic solvents. In this work, we performed the *in situ* oxidative polymerization of rhodanine in presence of ferric chloride-impregnated BNNs in water, enabling a green modification process. Styrene-butadiene rubber (SBR) was selected as matrix because it is a general-purpose synthetic rubber and widely employed in the tire industry and for other rubber items. Further the orientation of BNNs in rubber matrix was achieved by two-roll milling. Consequently, the elastomer composites with the combination of high thermal conductivity and high mechanical properties have been fabricated.

## 2. Experimental

### 2.1. Raw materials

Hexagonal boron nitride (h-BN) (purity of 99.27%, average size 4  $\mu\text{m}$ ) was purchased from Yingkou Liaobin Fine Chemicals Co. Ltd, China. Emulsion-polymerized styrene-butadiene rubber (SBR, 1502, styrene content 23.5%) was obtained from Fujian Fuxiang Chemical Co. Ltd, China. Rhodanine was purchased from Aladdin (Shanghai, China). Other chemicals were analytically pure and used as received. All the rubber ingredients were industrial grade and used as received.

### 2.2. Fabrication of polyrhodanine coated BNNs

The h-BN particles were suspended in a 5 M sodium hydroxide (NaOH) solution at 120 °C for 24 h to introduce the hydroxide functional groups onto the surface [16,31]. Then, the treated h-BN particles were sonicated in deionized water using a bath sonicator (KQ-400GKDV) for 8 h to obtain BNNs according to our previous work [32]. The SEM images of BNNs are depicted in Fig. S1. To prepare Fe(III) impregnated BNNs, 1 g of ferric chloride ( $\text{FeCl}_3$ ) was added into a 4 L well-suspended BNNs aqueous dispersion (0.25 mg/mL), followed by vigorous stirring at room temperature for 12 h. The obtained impregnated BNNs (BNNs-Fe(III)) displayed a yellow color. Rhodanine (1 g) was dissolved in 50 mL hot water under vigorous stirring and then introduced into the

BNNs-Fe(III) complexes. Vigorous stirring was continued and the temperature was maintained at 90 °C during the whole polymerization process. After 12 h, polyrhodanine coated BNNs (PRh-BNNs) were obtained by filtration and rinsed with ethanol twice (each 100 mL).

### 2.3. Preparation of SBR/PRh-BNNs composites

Various contents of PRh-BNNs were dispersed in tetrahydrofuran (THF) to generate a homogenous dispersion after sonication for 1 h. Then SBR was added into the mixture and stirred until the rubber was completely dissolved in THF at room temperature. The SBR/PRh-BNNs compounds were obtained by completely removing the solvent in vacuum oven at 30 °C. Then the compounds were mixed with rubber ingredients with two-roll mill and subjected to compression at 150 °C for 30 min (this time has been verified to be sufficient for full curing without reversion). The formulation of the composite is as follows: SBR 100, sulfur 1.5, zinc oxide 5, stearic acid 1, N-cyclohexyl-2-benzothiazole 1.5 and 2, 2'-dibenzothiazole disulfide 0.5 (all in weight).

### 2.4. Characterizations

Transmission electron microscopy (TEM) images were obtained with a JEM-2100F (JEOL, Japan) at an acceleration voltage of 200 kV. 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. A Zeta-Sizer (Malvern, Nano ZS90) was used to measure the  $\zeta$ -potential of the dispersions. The element composition of BNNs and PRh-BNNs was determined by X-ray photoelectron spectroscopy (XPS, Escalab 250XI). Diffuse reflectance Infrared Fourier transform (DRIFT) spectra were collected on a Bruker Vertex 33 spectrometer. Ultraviolet-visible (UV-Vis) spectra were acquired using a TU-1810 (Persee, China) spectrometer. Thermogravimetric analysis (TGA) was attained using a Q500 (TA, USA) instrument under nitrogen purging at a heating rate of 10 °C/min. 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 °C/min. The frequency and strain were set as 3 Hz and 1% respectively.

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. The rubber-filler interaction was evaluated by equilibrium swelling [33], freezing point depression and aggregation/interaction energies calculations based on the contact angles. The freezing point depression of cyclohexane in vulcanizate was carried out on a differential scanning calorimeter (DSC, 204F1, Netzsch) [34]. Static contact angles were measured using the Micro OCA40 drop shape analysis system (Dataphysics, Germany).

Thermal conductivity of the composites at 30 °C was calculated using Eq. (1).

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

where  $\lambda$ ,  $\alpha$ ,  $\rho$  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. Specific heat capacity ( $C_p$ ) of the samples was measured by differential scanning calorimetry (DSC, 204F1, Netzsch). The preparation of random and oriented samples for the thermal diffusivity test was illustrated in Supporting information.

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