European Polymer Journal 100 (2018) 12–17

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Grafting rubber chains onto boron nitride nanosheets for highly flexible, thermally conductive composites

Xian Wu*, Wei Liu, Chun Zhang, Li Ren

College of Materials and Metallurgical Engineering, Guizhou Institute of Technology, Guiyang 550003, Guizhou, China

ARTICLE INFO

Keywords:
Boron nitride nanosheet
Rhodanine
Thermal conductivity
Rubber

ABSTRACT

An ultra-flexible, thermally conductive and electrically insulating composite paper based on BNNSs was fabricated by vacuum filtration. The paper was prepared via a facile two-step coating/grafting modification process. The surface of BNNSs was firstly wrapped by polyrhodanine and subsequently rubber chains were mechanochemically grafted onto the polyrhodanine coating. In addition, by controlling the content of grafted rubber chains, a flexible and electrically insulating composite paper with an in-plane thermal conductivity of up to 45.7 $Wm^{-1}K^{-1}$ has been achieved. This paper may have potential applications as high performance thermal-management materials in electronics.

1. Introduction

With the continuing miniaturization of smart electronics products and increasing level of dissipated power in portable devices, heat dissipation has become an extremely important issue as heat generation can increase the temperature of devices causing fatal damage and induce thermal fatigue that reduced operational efficiency and service life [1,2]. Current polymer composites used for conducting heat in electronics typically have a lower thermal conductivity, which hinders their practical applications [3,4]. Carbon-based nanofillers such as graphene and carbon nanotubes with excellent thermal conductivity are not suitable for applications in this filed due to their intrinsic electrically conductivity. In this regard, hexagonal boron nitride nanosheets (BNNSs), possessing very high thermal conductivity but electrical insulation, have demonstrated their advantages over carbon-based nanofillers in electronic industry [5]. Shtein et al. [6] found that boron nitride platelets can reduce the electrical conductivity and synergistically enhance the thermal conductivity of graphene/boron-nitride epoxy composites. These hybrid composites can effectively dissipate the heat from electronic devices. Zhou et al. [7] fabricated a boron nitride nanosheets/cellulose nanofiber bi-layer paper, this paper can be utilized in transparent and flexible substrates.

To achieve high thermal conductivity, intimate interface and well-designed orientation are generally required [8]. Good interface reduces the interfacial thermal resistance, while orientation provides pathways for phonon conduction [9]. Recently, several approaches have been developed for fabrication of BNNSs based papers [4,8,10]. Yao et al. [8] chose GO to reduce the interfacial thermal resistance between BNNSs. Poly(vinyl alcohol) [10] was also selected as matrix to link the BNNSs together. However, the failure strains of these papers are less than 5%, which greatly limits their applications. It is urgently needed to fabricate BNNSs papers with the combination of high flexibility and thermal conductivity.

Herein, we designed an ultra-flexible, thermally conductive and electrically insulating paper based on BNNSs by vacuum filtration. The paper was fabricated via a facile two-step coating/grafting modification process. The surface of BNNSs was firstly wrapped by polyrhodanine and subsequently rubber chains were mechanochemically grafted onto the polyrhodanine coating. The grafted rubber chains act as mortar to link the BNNSs bricks together, forming a highly oriented layer structure. In addition, by controlling the content of grafted rubber chains, a flexible and electrically insulating paper with an in-plane thermal conductivity of up to 45.7 $Wm^{-1}K^{-1}$ has been achieved, which is much higher than most of the reported BN-based composites or films. This novel strategy for constructing high thermally conductive papers opens a new avenue for design and fabrication of high performance materials.

2. Experimental section

Materials: Hexagonal boron nitride (h-BN) (purity of 99.27%, average size 4 μm) was purchased from Yingkou Liaobin Fine Chemicals Co. Ltd, China. Carboxylated nitrile rubber (XNBR) latex (44 wt% solid content, 26–28 wt% acrylonitrile content) was obtained from Hong Tai Rubber Co. Ltd. (Shijiazhuang, China). Rhodanine (99% pure) was purchased from Aladdin (Shanghai, China). Other chemicals were

* Corresponding author.
E-mail address: wuxian-scut@qq.com (X. Wu).

https://doi.org/10.1016/j.eurpolymj.2018.01.011
Received 30 October 2017; Received in revised form 8 January 2018; Accepted 10 January 2018
Available online 11 January 2018
0014-3057/

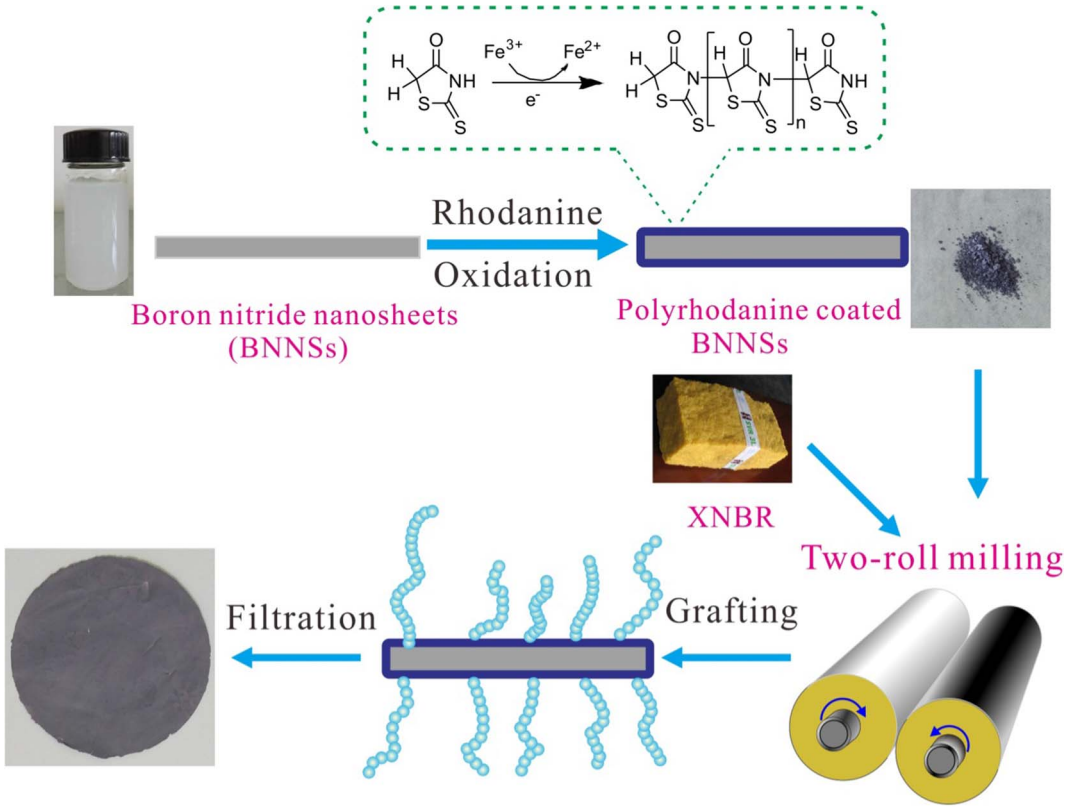

Fig. 1. Schematic illustration of proposed fabrication procedure of BNNS-XNBR papers.

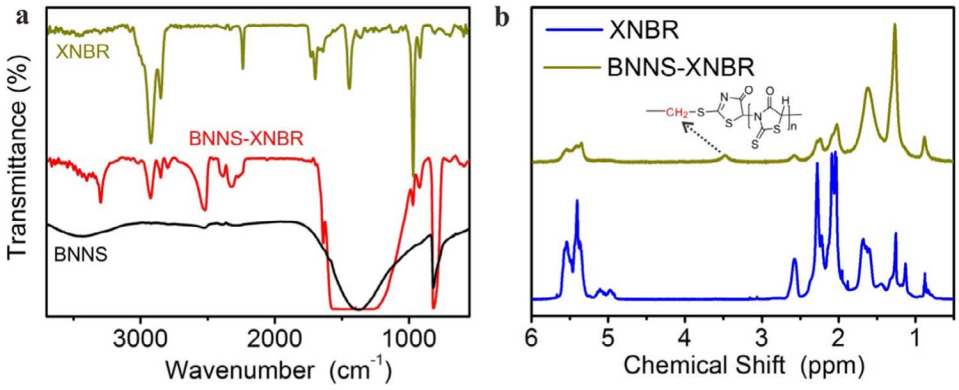

Fig. 2. (a) FTIR spectra of BNNS, XNBR and BNNS-XNBR. (b) ^{1}H NMR spectra of XNBR and BNNS-XNBR.

analytically pure and used as received.

Preparation of XNBR-graft-BNNSs (BNNS-XNBR)*:* The BNNS-XNBR was prepared by a two-step surface modification procedure. Firstly, polyrhodanine coated BNNSs (PRh-BNNSs) were prepared according to our previous work [11]. Briefly, rhodanine (variable) was added into Fe (III) impregnated BNNSs, and stirred at 90 °C for 12 h. And then polyrhodanine coated BNNSs were obtained after filtering. Secondly, PRh-BNNSs and dried XNBR (1:10 by weight) were subjected to shearing compounding in a two-roll mill for 15 min, where mechanochemical grafting occurs. The resulting mixture was dispersed and washed by tetrahydrofuran (TFH) completely to remove any non-grafted XNBR chains.

Fabrication of BNNS-XNBR papers: The composite papers were prepared by filtering BNNS-XNBR TFH suspension (~2 mg/ml, 20 ml) through a 0.22 μm nylon membrane under vacuum assistance. After the solution filtration, the dried papers were immersed into formic acid solution to remove the nylon membrane. And then the free-standing papers were rinsed with deionized water three times and dried in a vacuum oven at 35 °C for 24 h before further analysis.

Characterization: ^{1}H NMR (400 MHz) spectra were recorded by Bruker AVANCE III HD 400 spectrometer using $CDCl_3$ as the solvent. TEM images were obtained by a JEM-2100F (JEOL, Japan) electron microscope. FTIR spectra were collected under the attenuated total reflectance mode (Bruker Vertex 33). Atomic force microscopy (AFM) was characterized by Nanoscope 3a operated in a tapping mode. The morphology and the microstructures of the samples were examined by a FE-SEM (Hitachi S-4800, Japan). Thermal gravimetric analysis (TGA) was performed on a TGA Q500 instrument (TA, USA) under nitrogen purging at a heating rate of 10 °C/min. The mechanical properties of the samples was conducted on a DMA Q800 instrument. The papers were cut with a razor into rectangular strips (3–6 mm wide) for mechanical test and were gripped using a film tension clamp.

The in-plane thermal conductivities of the papers were calculated using Eq. (1):

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

where λ, α, ρ and C_p represent thermal conductivity, thermal diffusivity, density and specific heat capacity of the samples, respectively.