



Silanization of boron nitride nanosheets (BNNs) through microfluidization and their use for producing thermally conductive and electrically insulating polymer nanocomposites



A. Tuğrul Seyhan^{a,b,*}, Yapıncak Göncü^a, Oya Durukan^a, Atakan Akay^a, Nuran Ay^a

^a Department of Materials Science and Engineering, Anadolu University (AU), İki Eylül Campus, 26550 Eskişehir, Turkey

^b Composite Materials Manufacturing Science Laboratory (CMMSL), Research and Application Center of Civil Aviation (RACCA), Anadolu University (AU), İki Eylül Campus, 26550 Eskişehir, Turkey

ARTICLE INFO

Keywords:

Microfluidization
Boron nitride nanosheets (BNNs)
Silane coupling agent
Polypropylene
Polymer nanocomposites
Thermal conductivity

ABSTRACT

Chemical exfoliation of boron nitride nanosheets (BNNs) from large flakes of specially synthesized micro-sized hexagonal boron nitride (h-BN) ceramics was carried out through microfluidization. The surface of BNNs obtained was then functionalized with vinyl-trimethoxy silane (VTS) coupling agent through microfluidization once again in an effort to make them compatible with organic materials, especially those including polymers. The morphology of BNNs with and without silane treatment was then systematically characterized by conducting various different analytical techniques, including Thermogravimetric analysis (TGA), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Bright field Transmission Electron Microscopy (BF-TEM), Contact angle analyzer (CAA), Particle size analyzer (PSA) and Fourier Transmission Infrared (FTIR) spectroscopy attached with attenuated total reflectance (ATR) module. As a result, the silane treatment was determined to be properly and successfully carried out and to give rise to the irregularity of large flakes of the BNNs by folding back their free edges upon themselves, which in turn assists in inducing further exfoliation of the few-layered nanosheets. To gain more insight into the effectiveness of the surface functionalization, thermal conductivity of polypropylene (PP) nanocomposites containing different amounts (1 wt% and 5 wt%) of BNNs with and without silane treatment was experimentally investigated. Regardless of the weight content, PP nanocomposites containing silanized BNNs were found to exhibit high thermal conductivity compared to PP nanocomposites containing BNNs without silane treatment. It was concluded that microfluidization possesses the robustness to provide a reliable product quality, whether in small or large quantities, in a very time effective manner, when it comes to first exfoliating two-dimensional inorganic materials into few layered sheets, and functionalizing the surface of these sheets afterwards to make it possible to utilize them as promising filler constituent in manufacturing thermally conductive and electrically insulating polymer nanocomposites that could be considered as whole or a part of a heat-releasing device.

1. Introduction

A surge of scientific attention has been recently directed to the exfoliation of single or very few layered graphene sheets from graphite to benefit from its excellent quantum transport and mechanical properties that are comparable or superior to one-dimensional carbon nanotubes [1–8]. More lately, this attention has shifted to the exfoliation of boron nitride nanosheets (BNNs) from hexagonal boron nitride (h-BN) ceramics, a structural analogue of graphite wherein alternating B and N atoms are substituted with C atoms [2–6]. In contrast to graphene, BNNs are electrically insulating materials, yet exhibit various graphitic-like plane (002) properties, such as high

thermal conductivity and extraordinary mechanical strength. BNNs have been therefore believed to have as much scientific potential as graphene sheets to find widespread use as promising filler in polymer nanocomposite-based heat-releasing devices [9–15]. For example, if a special engineering case was of concern where an electrically insulating device with high thermal conductivity is of fundamental importance, polymer nanocomposites with BNNs would certainly have superior advantages over polymer nanocomposites with graphene sheets. Nevertheless, the lack of a feasible and practical approach to synthesizing few layered BNNs or graphene sheets in quantities large enough to make an electronic device stands as an obstacle in the way of exploiting their use in polymer nanocomposites. [2–14]. Generally speaking, it is,

* Correspondence to: Anadolu University İki Eylül Campus Engineering & Architecture Faculty Materials Science & Engineering Department, 26480 Eskişehir, Turkey.
E-mail address: atseyhan@anadolu.edu.tr (A.T. Seyhan).

<http://dx.doi.org/10.1016/j.jssc.2017.02.020>

Received 5 October 2016; Received in revised form 28 January 2017; Accepted 19 February 2017

Available online 24 February 2017

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in fact, not only the case for BNNs and graphene sheets, but it is also a common challenge encountered during exfoliation of any types of 2D materials. Another point to take into account is that it is required that the surface of most inorganic materials, before blended with polymers, be chemically functionalized for the purpose of enhancing their compatibility during composite processing [15–23]. As is in our case, BNNs with their highly inert surface have a great difficulty, forming a homogeneous dispersion in polymers. More specifically, BNNs possess a great propensity to present in the form of coarse agglomerates in polymers along which the high interfacial thermal resistance takes place, which would reduce the thermal transport via phonon scattering, thus hampering the coherence of phonon propagation [24–31]. It is for this reason that the surface treatment of BNNs with functional organic molecules would sound highly promising, when it comes to benefitting from their high thermal conductivity and mechanical strength as promising filler in polymers [32–38]. However, easy and effective methods of modifying the surface of BNNs are still missing for large volume applications [22–28].

Having focused on the scientific essence of the aforementioned issues, two important challenges seem to require being resolved before talking about BNN modified polymer nanocomposites with high thermal conductivity that would be employed for the development of new microelectronic devices. The former is to get some ways of robustly and repeatedly exfoliating very few layered nanosheets in large quantities, while the latter is to come up with an efficient methodology to chemically functionalize their surface to make them compatible with polymers. As for the first challenge, mechanical exfoliation by Scotch tape has emerged to be the first method conducted to prepare free-standing or very few layered graphene sheets [7]. Herein, the pulling force during the mechanical cleavage disrupts the weak van der Waals interactions between graphene layers, thereby leaving the sp^2 bonded in-plane structure intact. This method was shown to work on other layered materials, too, such as h-BNs and molybdenum disulfide (MoS_2). However, since a large number of high-quality nanosheets are to be harvested for advanced engineering applications, mechanical exfoliation by Scotch tape with extremely low yield turned out to be impractical for production of nanosheets in large quantities. As a result, ball milling has been further deemed an impending prospect for thickness reduction of 2D layered materials [6–9]. However, although powerful, ball milling treatments have been reported to be uncontrollable in some cases during which shear force coupled with compression might be detrimental to the in-plane crystal structure, thus causing a great number of structural flaws to occur on the milled particles, even though the large number of relatively small steel balls was proposed to be used during milling in an attempt to alleviate this drawback. As a consequence, a planetary mill was proposed as a more promising machinery tool to control the rolling balls in such a manner that it applies only shear force on the milled particles [7–9]. The use of lubricants was also suggested in planetary milling to avoid the damage to the structures while also eliminating the welding effect. Apart from those methods mentioned above, chemical methods have also come under spotlights for the same purpose to take advantage of the exfoliation capability provided by the polar solvent, despite being claimed to cause high defects in crystal structures compared to pure mechanical exfoliation. Zhi et al. [10] prepared milligram quantities of BNNs, conducting a simple two-step process that involves exfoliating h-BN powders into nanosheets in dimethylformamide (DMF) through sonication, followed by separation of the exfoliated BNNs by centrifugation. They concluded that the BNNs obtained by centrifugation at 8000 rpm and 5000 rpm were of 3 nm and 7 nm thick, respectively. Many other similar studies can be found in the literature that utilized various different chemical solvents to prepare very thin few layered BNNs by applying sonication at different periods of time and energy consumption levels [9–14]. However, although beneficial to preparing BNNs in milligram levels, sonication has not been found good enough for large scale production of BNNs. For this reason, it is required that

more scalable and sophisticated methods be utilized to unveil the extraordinary physical properties of very few layered BNNs for innovative engineering applications. In our former studies [20,21], we revealed that microfluidizer is highly capable of high throughput exfoliation of very few thin layered sheets and of dispersion of carbon nanotubes with a relatively short dwell time in an epoxy resin, at the same energy consumption level as in sonication.

As for the second challenge, surface functionalization is expected to induce a significant effect on the degree of dispersion of nano-sized materials in organic materials [23–27]. From this perspective, the covalent functionalization of BNNs with organic molecules to alter the surface chemistry and to enhance the interfacial interactions would be highly reasonable. In other words, it should be therefore of interest to graft organic functional molecules of choice to exfoliated BNNs in a controllable manner. Although BN allotropes are known to exhibit excellent chemical stability, whether in strongly acidic or basic conditions, several reports have described the covalent functionalization of boron nitride nanotubes (BNTs) and BNNs by using oxygen and nitrogen radical species [22]. Parallel to this, the generation of a highly reactive nitrene species was utilized for covalently functionalization of the BNNs [22]. Moreover, Lewis bases, such as amine molecules with long lipophilic or hydrophilic chains, were also used to form complexes or adducts with the electron-deficient boron atoms on BNNs. It was reported [23] that the complexation of a Lewis base with BNNs facilitated the further exfoliation of the layered structure of the bulk material, resulting in thin planar BNNs that are readily dispersible or soluble in organic solvents. On the other hand, alternatively, the boron sites in the BN lattice could be theoretically activated by oxidation in concentrated acid solutions, which is expected to result in yielding hydroxyl groups at the BN surfaces. Subsequently, the hydroxylated BN could be further modified by grafting with surface coupling agent for better adhesion and dispersion of BN particles in polymers. From this point of view, silane coupling agents, widely used as the surfactant to modify or functionalize the surfaces of inorganic particles, might prove to offer promise. It was already reported that epoxy composites containing 30 wt% of silane treated h-BNs exhibited 6.14 times higher thermal conductivity than neat epoxy at no expense of mechanical and thermal rigidity.

In this study, we present a systematic route to the covalent functionalization of the surface of the exfoliated BNNs utilizing a silane coupling agent through microfluidization in order to render their surfaces more hydrophobic and compatible with common organics, including polymers. BNNs obtained from the exfoliation of the micro-sized h-BNs through microfluidization were then subjected to silanization through microfluidization once again. To our best knowledge, this study is the first study in the literature that utilizes a microfluidizer both to exfoliate and to chemically functionalize the surfaces of 2D inorganic materials in sequence. Whether the surface of BNNs was properly functionalized or whether the BNNs were morphologically altered was monitored and verified by systematically employing various analytical techniques, including Thermogravimetric analysis (TGA), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Bright field Transmission Electron Microscopy (BF-TEM), Contact angle analyzer (CAA), Particle size analyzer (PSA) and Fourier Transmission Infrared (FTIR) spectroscopy attached with attenuated total reflectance (ATR) module. To evaluate the performance of the silanized BNNs when used for materials engineering applications, they were blended with polypropylene (PP) through melt compounding followed by hot pressing. The findings obtained were discussed in a concise manner with emphasis being placed on the silane-induced morphology alteration of the BNNs and its effects on the thermal conductivity of the resulting PP nanocomposites.

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