VIBRATION AIDED VACUUM INFUSION OF BNNS MODIFIED CARBON FABRIC/EPOXY COMPOSITES

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ABSTRACT

Two-dimensional (2D) materials have aroused remarkable attention since the successful separation of graphene, atomic layers of carbon, has demonstrated novel electronic properties. Boron nitride (BN) is a structural analog of carbon. BN can be exfoliated to form unique 2D crystal structures called boron nitride nanosheets (BNNSs). BNNSs are believed to have potential to find applications in heat-releasing composite materials, since they are electrically insulating, besides being as thermally conductive and mechanically robust as graphene. In this study, a microfluidizer, high pressure fluid processor, was conducted for the first time to exfoliate few layer two dimensional (2D) boron nitride nanosheets (BNNSs) from micro-sized hexagonal boron nitride (h-BN) precursors of large flakes. The mixture of N,N-dimethyl formamide and chloroform was conducted as solvent. Secondary electron-scanning electron microscopy (SE-SEM) imaging, bright field-transmission electron microscopy (BF-TEM) imaging, energy filtering (EF) TEM-3 window elemental mapping, electron energy loss spectroscopy (EELS), high resolution (HR) TEM imaging and nano beam electron diffraction (NBED) techniques were carried out to characterize the sheets. Based on the findings obtained, the sheets were observed to have micrometer dimensions through in-plane, whereas nanometer dimensions through their thickness directions. Carbon fabric preforms containing 1 wt. % of BNNSs were then consolidated by dispersing the sheets in ethanol through sonication. The solution obtained was then used for through-the-thickness impregnation of carbon fabrics. The composites with BNNSs were then produced by membrane added vacuum infusion process (MAVIP) with application of mechanical vibrations at various different low frequencies, including 10, 25 and 60 Hz. For the sake of property comparison, identical static samples were also produced. A facile thermogravimetric analysis (TGA) based methodology was utilized for composite fiber volume fraction and void content measurements. Analysis was carried out on specimen-by-specimen basis, and the findings obtained were correlated with the interlaminar shear strength (ILSS) of the composites.

1 INTRODUCTION

Two-dimensional (2D) materials have garnered remarkable attention since the successful separation of graphene, atomic layers of carbon, demonstrates novel electronic properties [1–5]. Boron nitride (BN) is a structural analog of carbon, having cubic and layered structures [1,2]. BN exhibits high thermal stability, good mechanical strength and has been employed as a solid-state lubricant for years [2]. BN can be exfoliated to form unique 2D crystal structures called boron nitride nanosheets

(BNNSs) [3,4]. BNNSs have recently come under the spotlight due to their extraordinary properties [1–5]. In particular, BNNSs are believed to have potential to find applications in optoelectronic devices and heat-releasing composite materials, since they are electrically insulating, besides being as thermally conductive and mechanically robust as graphene [2–5]. However, compared to graphene, the novel physical properties of BNNSs have still remained unrealized, even though they possess superior advantages over graphene[3]. Actually, this is not owing to the fact that the properties of BNNSs are poor or underrated in comparison to the properties of graphene, rather this is mostly by reason of the lack of feasible approaches to producing very thin few or monolayer BN sheets in quantities large enough for practical use in industrial applications [6]. Warner et al. [4] utilized a simple technique based on 3 h sonication to prepare thin few layers of hexagonal BN with micro-sized dimensions using chemical exfoliation in the solvent of 1,2-dichloroethane. Zhi et al. [5] have prepared milligram quantities of BNNSs, conducting a simple two-step process that involves exfoliation of h-BN.

Multsiscale fiber-reinforced polymer-matrix composites (FRPCs) have aroused great attention in various industrial applications due to their high specific stiffness and strength. Conventional vacuum infusion process (CVIP) has been employed to manufacture large FRPCs [1]. In CVIP, the vacuum is used to draw resin in and air out to reduce the incidence of voids in resulting laminates. However, even despite additional attachments, such as bleeders and breathers, evacuated air cannot be effectively removed from the resin used in the process. On the other hand, a pressure gradient that develops during infusion causes a thickness gradient across the part, which adversely influences the fiber volume fraction, void content, and thus mechanical property variation across the part [1-6]. Therefore, when it comes to producing composites for aerospace applications, CVIP remains vastly lacking in terms of repeatability of the robustness. Therefore, vacuum bagging combined with autoclave is used instead. thermoplastic polyurethane (TPU), that permits uniform vacuum distribution during infusion. It is expected that the use of such membranes improve the consistency in the resin flow front and removes dry spots at no expense of reducing vacuum during the process [2]. More importantly, dry-spot removal during membrane added vacuum infusion process (MAVIP) is accomplished without optimized vent placement, as opposed to CVIP wherein it is inevitable. W Li et al. [2] studied the effect of a membrane layer on the composites properties. For this purpose, they produced E-glass reinforced epoxy composites through vacuum infusion with and without a membrane layer. They showed that composite parts produced by MAVIP exhibited a void content at a level comparable to autoclave process, and that more undeviating fiber volume fraction, and less void content accompanied with 77% reduction in overall thickness gradient were accomplished across the parts that were produced by MAVIP. In other words, voids are detrimental to particularly various matrix dominated mechanical properties of composites, including interlaminar shear, compressive, and flexural strengths [1-5]. It was also revealed that even if the same manufacturing process is used for production of the two identical composites, their own resulting mechanical properties would be different as a function of void content. Application of low frequency vibration during the processing of composites has been considered a promising approach to altering filling time, resin flow velocity, and the void content in final composites. Ghiorse and Jurta [5] subjected vacuum-bagged carbon fiber epoxy pre-preg to low frequency vibrations (50 Hz) during cure and compared the resulting void content, the number and size of the voids, and the density of the laminates produced with and without vibration. The void volume content of vibrated specimens was found to be decreased by more than 50%. (2.5 and 1.2% for the static and the vibrated samples, respectively). The major contribution of this study is to suggest using low frequency mechanical vibration to produce filler modified composites through MAVIP. To our best knowledge, this study is the first study in the literature that sheds a light on the mechanical vibration assistance in processing composites consolidated from preforms with fillers. Please note that we used (h-BNSs) as filler constituent because there are many promising studies in the literature that showed the improved mechanical and thermal properties of the polymers with h-BNSs addition [5].

2 EXPERIMENTAL PROCEDURE

2.1 Exfoliation of BNNSs

BNNSs were derived from exfoliation of specially synthesized h-BN micro-sized precursors of very thin large flakes. The proper combination of N,N-dimethylformamide (DMF) and chloroform (6–1 on weight basis) were prepared and conducted as solvent. Hexagonal boron nitride precursors (6 wt.%) were added to the prepared solvent (100 ml). To derive chemically exfoliated BNNSs, high pressure microfludization process was carried out with a commercially available microfluidizer (M-110P, Microfludics Corp.) at a constant intensifier pump pressure of 207 MPa (30,000 psi). Twenty (20) of circulation passes was applied on the dispersions. It takes about 0.6 min for 100 ml solution of h-BN precursors to complete one circulation pass. The yielding efficiency of 45% was observed to derive stable exfoliated sheets from precursor. The solution obtained was dropped on transmission electron microscope grid for examination. A field emission gun-scanning electron microscope (Zeiss Supra 50 VP) was used to characterize precursors of large flakes. The nanoscopic-scale characterization of BNNSs was performed using a field emission transmission electron microscope (Jeol 2100F), operating at 200 equipped with an energy filter (Gatan Inc., GIF Tridiem), parallel electron energy loss spectrometer (EELS), a high angle annular dark field scanning transmission electron microscope (HAADF-STEM) detector (Fishione), annular dark/bright field (ADF/BF) detectors (Gatan Inc., STEM Pack) and an energy dispersive X-ray (EDX) spectrometer (Jeol JED-2300T). In EELS and nano beam electron diffraction (NBED) analyses, an electron spot with 1–2 nm in diameter was used. The backgrounds in EELS and The backgrounds in EELS and energy filtering transmission electron microscopy (EFTEM) analyses were subtracted according to power-law. An approximate thickness of the BNNSs is determined based on the absolute log-ratio method. In EELS analysis, the convergence and collection semi-angles were used as 9.2 and 15.7 mrad, respectively.

2.2 Materials for composite production

Epoxy resin system (EPIKOTE Resin MGS® RIMR 135 and EPIKURE Curing Agent MGS® RIMH 1366) were purchased from Momentive. They were mixed together by a jiffy mixer at the specified weight ratio (100:30 w/w) for 5 min. The resin was degassed for a relatively short time (10 min) afterwards, as the use of the membrane layer was already shown to bring up a full vacuum gradient combined with a continued degassing across the part surface during infusion process [2]. T-300 carbon twill weave fabrics with an areal density of 200 g/m2 (balanced through weft and warp directions) were provided by TELATEKS Corp. Turkey. Hexagonal boron nitride sheets (h-BNSs) were obtained from BORTEK Corp, Turkey.

2.3 Preform consolidation

A method based on through-the-thickness impregnation of the fabrics was successfully conducted to consolidate the preforms with h-BNSs. Fig. 1 presents the schematic illustration of the process used for infiltrating the carbon fabric preforms with h-BNSs in this study. Ethanol solution containing h-BNSs (1 wt % of the total fabric weight)was subjected to sonication for 2 h in a stainless steel holder by employing a horn type sonicator (SONICS 750 VCF) at a frequency of 20 kHz, running in a pulse operation mode (on 10 s, off 30 s) with the power set at 750W. The fabric preforms composed of 20 individual plies with an initial thickness of (hi) were properly placed in the sonicated solution by hand. The upper press plate slowly squeezes the preform to the specified thickness (hf) at a pressure of 0.25 MPa for 5 min. After consolidation, ethanol containing preforms were placed in a vacuum oven at 80 _C until they become almost ethanol-free. This facile method is believed to be superior over in-plane impregnation of the preforms under vacuum wherein a solvent solution containing any filler is forced to wet the preforms.

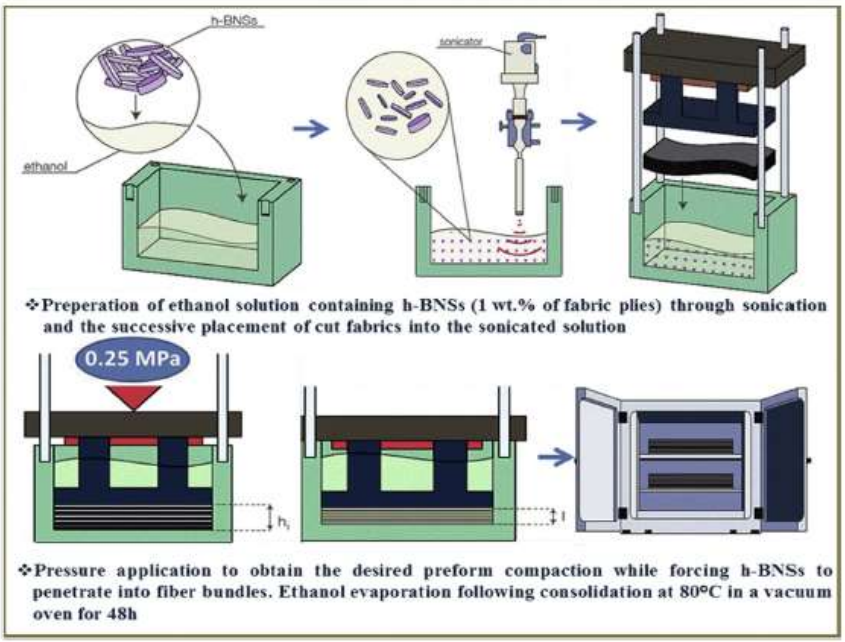

Figure 1 Schematic illustration of carbon fabric preform consolidation

2.4 Composite production

To produce composites with h-BNSs, fabric preforms were first placed on a flat surface of 10mm thick aluminum mold followed by their impregnation with the catalyzed resin under vacuum. Fig. 2 depicts the illustration of the experimental set up with the details of the processing constituents. Prior to each infusion, whether or not there was any vacuum leakage was checked by closing the valves and measuring the pressure increase inside the vacuum bag. A maximum increase of 0.05 kPa per minute was allowed. Once the infusion process was terminated, the inlet and outlet lines were left connected to the vacuum pump to ensure constant part thickness. A vibration engine (MVE 60/30 M) obtained from OLIVibrationstechnik was mounted on the bottom side in the middle of the aluminum tool. The rotational axis of the engine was adjusted perpendicular to the resin flow front direction. The whole system (mold and vibration engine) was supported by four coilsprings to eliminate damping as much as possible and to guarantee a defined oscillatory movement. The frequency of the engine is proportional to the frequency of the power supply and adjustment was accordingly made using a frequency converter (BLEMOER12). The vibration engine was mounted 10 mm away from the aluminum tool to get rid of the engine-generated waste heat through a cooling fan. Moreover, a thermocouple was placed in a point on the tool surface, very close to the engine body in order to monitor temperature rise, if any. Three different low mechanical frequencies, including 10, 25 and 60 Hz were applied during vacuum infusion until the parts were fully cured. At least two composite plates for each case were manufactured to accurately make the statistical assessment of the findings. After infusion, the composite parts were allowed to cure at room temperature followed by post curing at 80 _C for 12 h.

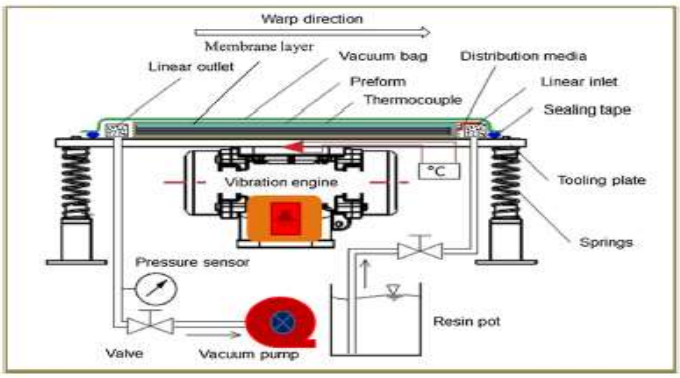

Figure 2. Composite production experimental set-up.

3. RESULTS AND DISCUSSION

In determination of to what extent the high pressure microfluidizer successfully exfoliated BNNSs from h-BN precursors of large flakes, quality and characteristics of h- BN precursors play a pivotal role. Structural characterization of the precursors is of importance in this respect. Fig. 3a–d image series acquired via secondary electron (SE)-SEM imaging, bright field (BF)-TEM imaging, EFTEM-3 window elemental mapping and EELS techniques, respectively, depict the general microstructural characteristics of specially synthesized h-BN precursors. Based on the observations in Fig. 3a and b, it is definitely certain that very thin large flakes with a thickness of around 100 nm constitute the majority of the corresponding micron-sized h-BN precursors. Moreover, the chemical detection of B-K (188 eV) and N-K (401) edges along the flakes evidently confirms that the precursor material is of h-BN (Fig. 3c and d).

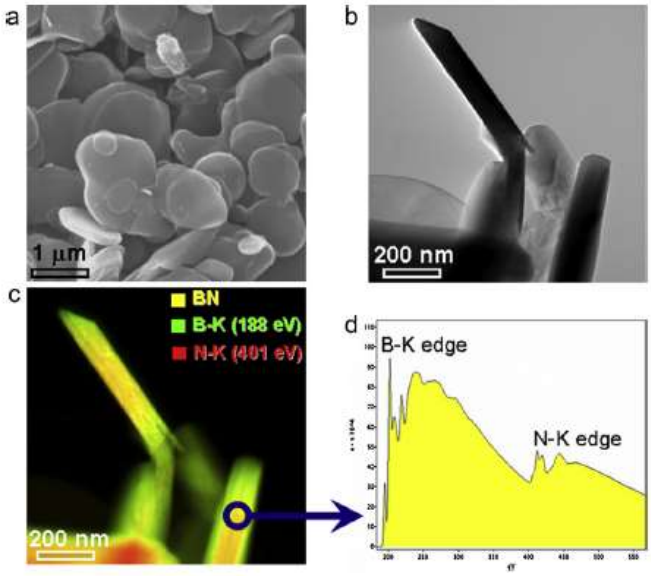

Figure 3. (a) Secondary electron (SE)-SEM image, (b) BF-TEM image, (c) Red-Green-Blue (RGB) EFTEM-3 window elemental mapping and (d) electron energy loss (EEL) spectrum of specially synthesized micro-sized h-BN precursors of very thin large flakes. Please also note that the circular point on the vertically positioned BN flake in (c) shows the corresponding locations from which EEL spectrum in (d) was taken. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Figure 4 shows the morphology of h-BNSs and their dispersion state in between the fiber bundles following preform consolidation. Figure 5 summarizes all the results obtained in this study. As seen in the figures, low mechanical vibration application works for the resulting composite properties in the way it is assumed at the very beginning.

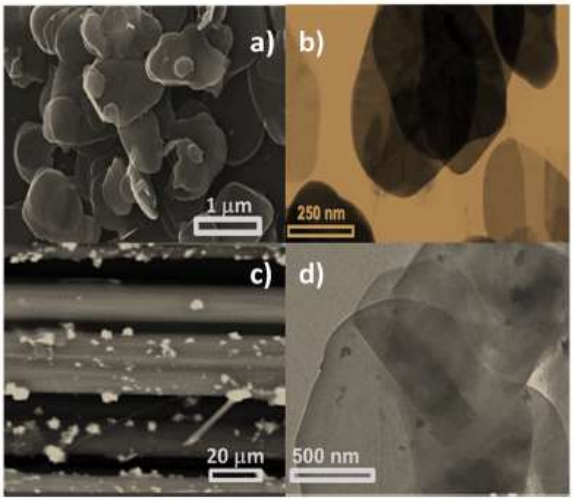

Figure 4. Morphology of h-BNSs a) SEM image b) TEM image c) In between carbon fiber bundles after the through thickness impregnation d) TEM image at a higher magnification.

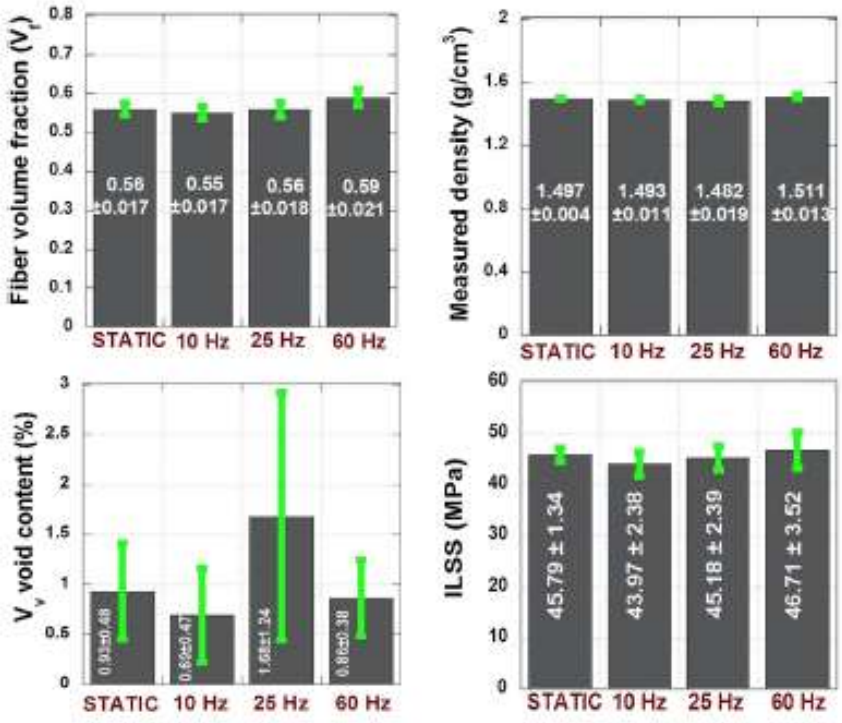

Figure 5. Fiber volume fractions, (from the TGA based methodology), void contents (according to ASTM D2734), and experimentally determined density of the composites (according to ASTM D-792) produced with and without mechanical vibration, and the resulting ILSS of the composites.

4 CONCLUSIONS

Utilization of low frequency mechanical vibration was proposed to produce filler modified composites. Carbon fabric preforms were impregnated through the thickness with h-BNSs. Composites with h-BNSs were produced through MAVIP at three different mechanical frequencies

including 10, 25 and 60 Hz. The highest fiber volume fraction, density, and ILSS values were obtained From the composites produced at 60 Hz. In fact, establishing a mathematical expression or any simple linear relationship between the frequency level and the final composite properties was found more complicated when they are consolidated from preforms modified with fillers.

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