PREPREG-LIKE, HIGH-NANOTUBE-CONTENT COMPOSITES FROM EPOXY-INFILTRATED BORON NITRIDE NANOTUBE BUCKYPAPERS

Jakubinek, M.B.[1]*, Ashrafi, B.[2], Martinez-Rubi, Y.[1], Laqua, K.[2], Park, D.[2], Octeau, M.A.[2], Simard, B.[1]

[1] Division of Emerging Technologies, National Research Council Canada, Ottawa, Canada
[2] Aerospace, National Research Council Canada, Montreal, Canada
* Corresponding author (michael.jakubinek@nrc-cnrc.gc.ca)

Keywords: *nanotubes, buckypaper, nanocomposites*

ABSTRACT

Production of nanocomposite materials containing a high fraction of nanotubes is crucial to better leverage the impressive properties of individual nanotubes for development of engineering composites. In the carbon nanotube (CNT) field, one of the most effective ways to achieve this has been through resin-infiltration of preformed nanotube sheets. The most common such sheets are nonwoven papers (often called buckypaper) formed either by vacuum filtration of dispersed nanotubes or by direct collection in the synthesis process. In this presentation we describe formation of similar composites based on boron nitride nanotubes (BNNTs), which offer complimentary properties to CNTs including similar mechanical properties and thermal conductivity but high electrical resistance and neutron absorption capability not obtained with CNTs. Considering the rheology and cure conditions, we develop a process to infiltrate BNNT buckypaper with a high-temperature epoxy resin and partially cure the composite forming B-staged, prepreg-like BNNT buckypaper-epoxy sheets with a degree of conversion of approximately 10%. These partially cured, resin-infiltrated BNNT buckypapers have improved handle-ability in comparison to dry buckypaper. Single or multiple composite sheets are subsequently cured in a vacuum bag setup, which is compatible with standard layup procedures, resulting in nearly fully converted composites, high BNNT content (over 25 weight percent), superior mechanical properties to the epoxy itself, and added multifunctional properties including 10 to 20 times higher thermal conductivity. This form of nanocomposite is being further explored and offers a promising approach to using nanotubes, specifically BNNTs, in advanced composites.

1 INTRODUCTION

Boron nitride nanotubes (BNNTs) have analogous structures and exhibit a range of properties that are as impressive as those of carbon nanotubes (CNTs), including comparable mechanical properties and density, but with different multifunctional advantages such as considerably higher thermal stability, polarizability, wide band gap, and high neutron absorption capability (Figure 1). These characteristics make BNNTs attractive for the fabrication of nano-enhanced composites complimentary to those based on CNTs; however, composites incorporating BNNTs, including polymer nanocomposites [1], have received only limited study. Increase in Young's modulus, in the range of 10 to 50% increased (with 1-3 wt% added BNNTs) [1-4], is the most common observation from dispersion of a low content of BNNTs. Tensile strength is often reported as minimally changed or decreased; however, significant strength improvements (~20-30 wt%) have been observed with functionalized BNNTs [2,3]. Other improvements, including in thermal conductivity and dielectric properties, have also been noted in composites containing dispersed BNNTs.

In the field of CNTs, one of the most promising ways to produce CNT-polymer composites is resin-infiltration of macroscopic assemblies of nanotubes such as buckypaper [5-7]. Unlike mixing approaches, this approach allows for high nanotube content and facilitates nanotube-orientation (random in plane or alignment). As such, the approach translates more of the CNT's potential to improve mechanical properties and functional features (e.g., higher electrical conductivity) to the composite. This approach has only recently been shown with BNNTs, where we reported production of BNNT composites through resin-impregnation of free-standing BNNT buckypaper sheets [8,9], analogous to approaches with CNT sheets. High BNNT-content nanocomposites have also been prepared by soaking supported BNNT mats in polymer solutions, achieving 18-37 wt% BNNT nanocomposites [10]. As described in our related work [8,11], BNNT paper wets easily with epoxy resins, allowing fabrication of composites. Here we describe these composites and more recent work showing production of partially-cured (B-stage) BNNT-epoxy fabrics and subsequent fabrication of BNNT epoxy composites. The B-staged composite will be a useful step to production of high-BNNT content composites and integration of BNNTs into composite structures.

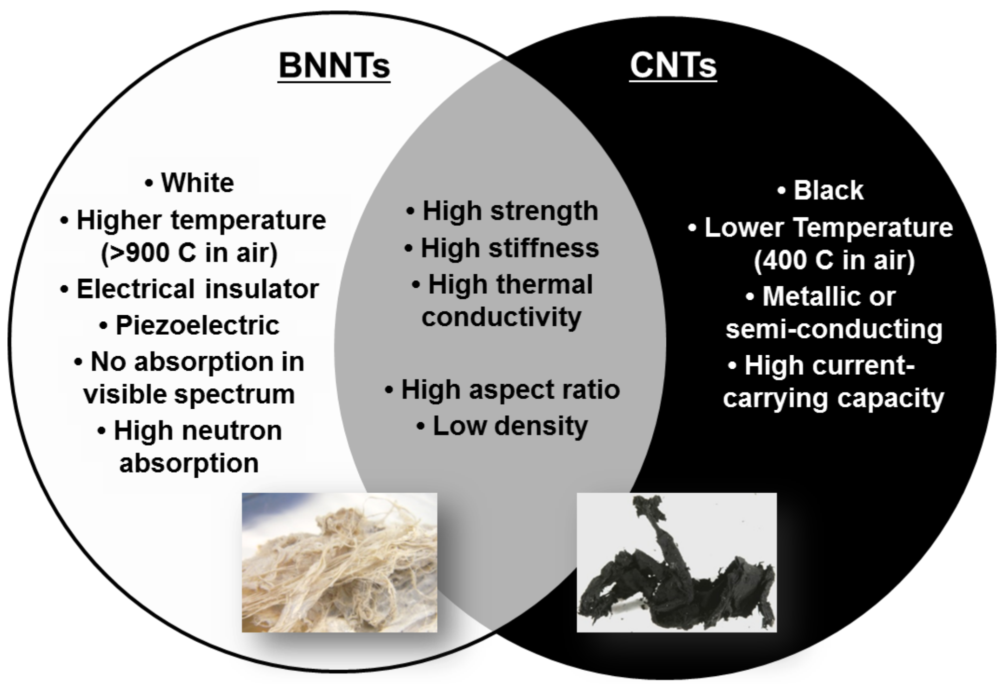

Figure 1. Venn diagram comparison of BNNT and CNT properties (insets show as-synthesized fibrous BNNT and CNT material). Image credit: National Research Council Canada.

2 METHODS AND RESULTS

2.1 BNNTs and BNNT Buckypaper Sheets

BNNTs were produced from an hBN feedstock using an RF induction thermal plasma system and the National Research Council's previously reported process for hydrogen-assisted BNNT synthesis, which produced highly crystalline, few-wall, small diameter (d_{avg} ~ 5 nm) BNNTs [12,13]. The raw, unpurified BNNTs are available commercially from Tekna Advanced Materials (Sherbrooke, QC, Canada) and Sigma Aldrich (product #802824). Prior to production of buckypaper, the raw BNNTs (~50 % BNNTs) were purified to remove the elemental boron impurity. Minimal effort was made to remove other hBN-related impurities and the partially purified BNNTs used for buckpaper and composites are estimated to be ~70% BNNTs.

Non-woven buckypapers were produced by dispersion of the purified BNNTs in ethanol followed by vacuum filtration [8,12]. To supply the size required for this work, a 30 cm x 30 cm sheet mold was employed. After filtration, the buckypaper was covered with parchment, sandwiched between layers of blotter paper, and dried under compression at room temperature prior to peeling from the filter membrane and further drying at 200 °C for 2 hours. Figure 2 shows as-synthesized BNNTs, purified BNNTs and the flexible, foldable BNNT buckypaper.

Figure 2. Clockwise from top-left: ~20 g of as-synthesized BNNTs [8], purified/homogenized BNNT powder (fluff-like), BNNT buckypaper sheet, and a folded origami butterfly [12]. Reproduced from Jakubinek et al., TechConnect Briefs 2017 with permission (images originally from [8] and [12] are reproduced with permission of The American Chemical Society and The Royal Society of Chemistry, respectively.

2.2 Resin infiltration of BNNT Sheets

BNNT buckypapers were infiltrated with a low viscosity epoxy resins including Araldite MY0510, SC15 and Epon 862 used to produce high-BNNT content nanocomposites. Initial wetting was performed through the capillary forces and simple adding resin to the surface of the sheet. Favourable interaction (*i.e.*, wetting of BNNT buckypaper with resin) is indicated by the lower contact angle for an epoxy drop on the surface, where the initial contact angle of < 60° at room temperature was signfiicantly lower than the comparable case with a CNT buckypaper (Figure 3) [8,11]. For composites preparation, a hot-plate was used to heat the buckypaper to a suitable temperature to reduce viscosity of the particular resin (100 °C being the highest used for these resins). Excess resin on both surfaces of the buckypaper sheet was removed using lint-free absorbent wipes. The sheets, sanwiched between teflon plies for easy release, are then placed on an aluminum call plate and covered with a glass plate during oven curing.

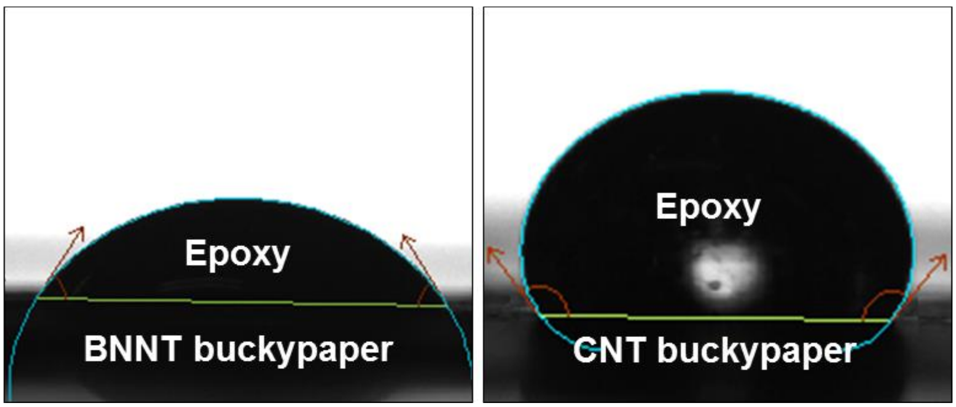

Figure 3. Wetting of BNNT and CNT buckypaper sheets with a drop of epoxy resin (T = 25 °C).

After epoxy-impregnation the void content was reduced from ~80% for dry buckypapers to ~5% and under based on estimates of the BNNT and composite density. This is also seen from SEM images before and after impregnation (Figure 4), which show reasonably uniform impregnation through the buckypaper thickness with the presence of small voids. Tensile tests performed using a micro-tensile test frame (Fullam Substage Test Frame) at a displacement rate of 0.5 mm/min, showed that the elastic modulus is greatly improved (>2x relative to the neat epoxy) and tensile strength also exceeds that of the epoxy (Table 1) [8,11]. A potential early application is in the area of thermally conductive electrical insulators, in particular for electronics substrates and packaging. Thermal conductivity was measured in the in-plane direction by the steady-state, parallel thermal conductance method indicating thermal conductivity of 10-20x typical polymers [9], while not altering the high electrical insulation of the epoxy (Table 1).

Material	Density (g cm-3)	Elastic Modulus (GPa)	Tensile Strength (MPa)	Thermal Conductivity ($W\ m^{-1}\ K^{-1}$)	Electrical Resistivity (Ohm cm^{-1})
BNNT buckypaper	0.3	0.3 to 0.6	1.5 to 3	~ 1.5	-
Epoxy	1.2	~ 3	~70	~ 0.2	10^{15}
Buckypaper-epoxy	1.3 to 1.4	6 to 9	Up to 80	2 to 3	10^{15}

Table 1. Illustrative properties of buckypaper-epoxy composites using BNNTs and MY0510 epoxy [8,9,11]

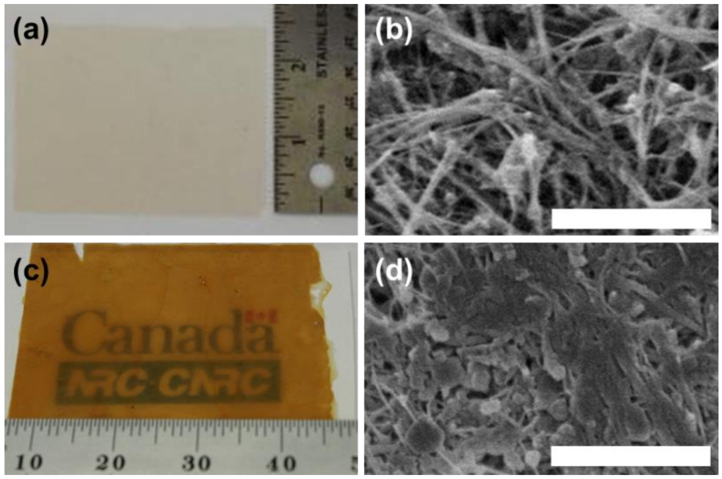

Figure 4. Photos and SEM images (scale bar = 1 micron) of BNNT buckypaper (a,b) and buckypaper-epoxy composites (c,d). Reproduced from [9] with permission.

We observed that compaction during the curing is helpful to remove excess resin and densify the sample. Sheets with only light compaction (to prevent warping) show a different colour and larger thickness than obtained for vacuum-bag-compacted samples due to an epoxy-rich surface layer less. To build composite thickness, resin-infiltrated sheets were also layered before compaction and curing. Figure 5 shows single layer composites with and without vacuum bagging, along with multilayer (3 and 12 layer) vacuum-compacted samples. After curing, the multilayer composites are equal to or slightly thinner than the equivalent number of single layers indicating that the compaction is effective in minimizing excess resin and forming dense samples even for the thicker composites.

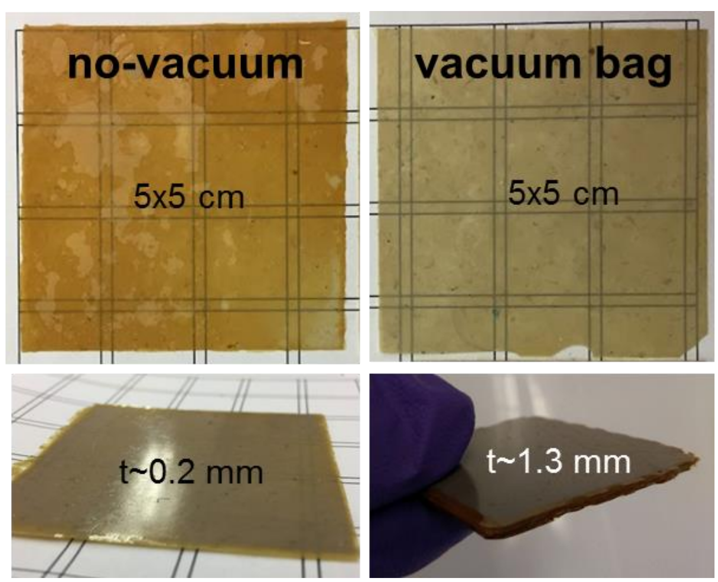

Figure 5. Single layer buckypaper-epoxy composites with and without vacuum bag compaction during infiltration/curing, along with multilayered, “thick” BNNT buckypaper-epoxy sheet composites.

2.3 Partially converted BNNT-epoxy sheets

For the purposes of simplified handling, storage and layering to form thicker BNNT composite sheets, we recently prepared pre-preg-like buckypaper sheets, where in the epoxy resin was B-stage cured during the initial resin-infiltration step. Figure 6 shows steps involved in infiltrating, B-staging, and subsequent lay-up. Temperature and timing of the resin-infiltration and B-staging steps were selected based on rheology and cure kinetics measurements to minimize viscosity for infiltration yet avoid significant conversion during the infiltration step. Timing for the partial cure was estimated from differential scanning calorimetry scans on the epoxy resin, wherein the resin was partially cured, stored frozen, and then fully cured within the DSC (e.g., Figure 7). Following this approach, partially cured BNNT-epoxy composites were prepared with degree of conversion ranging from 5% to 50% estimated and stored for 1 month prior to final curing.

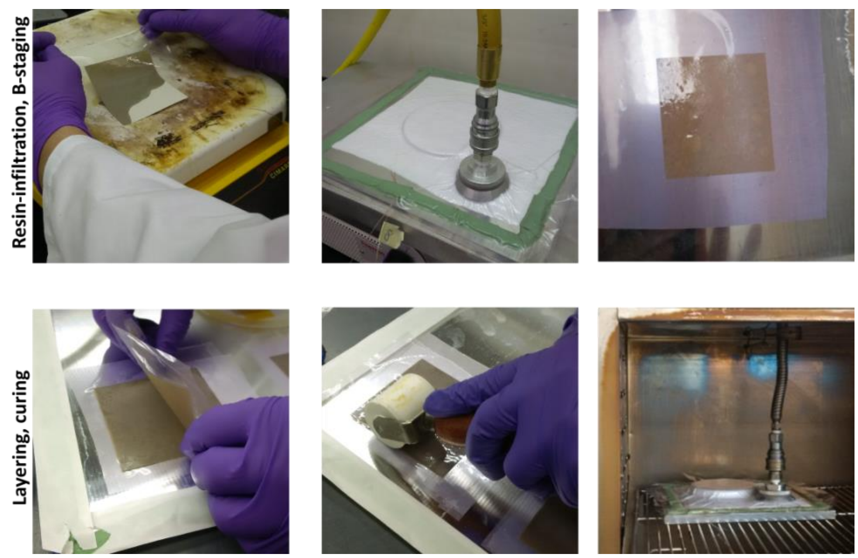

Figure 6. (Top) Epoxy infiltration and B-staging to form prepreg-like buckypaper sheets. (Bottom) Layup of multilayer composite sheets

3 CONCLUSIONS

In summary, composites with high nanotube content (> 25 wt.% BNNTs) were prepared based on epoxy infiltration of BNNT buckypaper. Stiffness, strength and thermal conductivity of the composites exceeded that of epoxy and dry buckypaper. Thermal conductivity and stiffness exceeded epoxy by factors of at least 10 to 20 and the approach offers fabrication advantages in terms of materials handling, consistency of the nanotube distribution, and ability to achieve high nanotube content, all of which are essential to translating the properties of BNNTs to applications.

4 ACKNOWLEDGEMENTS

The authors thank Mark Plunkett, Dean Ruth, Steven Walker and Dr. Keun Su Kim for their contributions to the production and purification of BNNTs. Characterization support from Hugo Laurin (DSC, rheology), and Gordon Chan (SEM) is also gratefully acknowledged. Funding was provided by the National Research Council Canada through the Security Materials Technology Program.

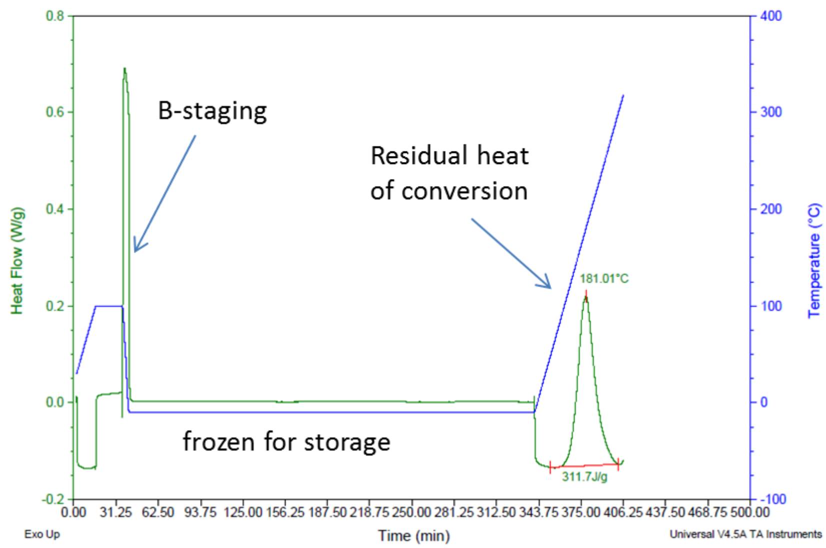

Figure 7. DSC of neat epoxy for determination of suitable B-staging conditions. Residual heat of conversion was determined after partial-cure and freezing steps and compared to the heat of conversion of the as-received epoxy.

5 REFERENCES

[1] W. Meng, Y. Huang, Y. Fu, Z. Want, C. Zhi. *J. Mater. Chem. C* 2, 10049, 2014.
[2] C. Zhi, Y. Bando, C. Tang, S. Honda, H. Kuwahara, D. Golberg. *J. Mater. Res.* 21, 2794, 2006
[3] S.-J. Zhou, C.-Y. Ma, Y.-Y. Meng, H.-F. Su, Z. Zhu, S.-L. Deng, S.-Y. Xie, *Nanotechnol*. 23, 055708, 2012.
[4] L. Li, Y. Chen, Z.H. Stachurski, *Prog. Nat. Sci.: Mater. Int.* 23, 170, 2013.
[5] Z. Wang, Z. Liang, B. Wang, C. Zhang, L. Kramer. *Compos. A* 35, 1225, 2004.
[6] S. Wang, Z. Liang, G. Pham, Y.-B. Park, B. Wang, C. Zhang, L. Kramer, P. Funchess. *Nanotechnol.* 18, 095708, 2007.
[7] B. Ashrafi, J. Guan, V. Mirjalili, P. Hubert, B. Simard, A. Johnston. *Compos. A* 41, 1184, 2010.
[8] K.S. Kim, M.B. Jakubinek, Y. Martinez-Rubi, B. Ashrafi, J. Guan, K. O'Neill, M. Plunkett, A. Hrdina, S. Lin, S. Denommee, C. Kingston, B. Simard. *RSC Adv.* 5, 41186 (2015).
[9] M.B. Jakubinek, J.F. Niven, M.B. Johnson, B. Ashrafi, K.S. Kim, B. Simard, M.A. White. *Phys Stat Sol A* 213, 2237 (2016).
[10] C. Y. Zhi, Y. Bando, T. Terao, C. Tang, H. Kuwahara and D. Golberg, Adv. Funct. Mater., 2009, 19, 1857-1862.
[11] B. Ashrafi, M.B. Jakubinek *et al.*. Submitted 2017.
[12] K.S. Kim, C.T. Kingston, A. Hrdina, M.B. Jakubinek, J. Guan, M. Plunkett, B. Simard. *ACS Nano* 8, 6211, 2014.
[13] K.S. Kim, M.J. Kim, C. Park, C.C. Fay, S.-H. Chu, C.T. Kingston, B. Simard. *Semiconductor Sci Technol* 32, 013003 (2017).