

Polymer Nanocomposites Incorporating Boron Nitride Nanotubes

M.B. Jakubinek*, Y. Martinez-Rubi*, B. Ashrafi**, J. Guan*, K.S. Kim*, K. O'Neill**,
C.T. Kingston*, and B. Simard****

*Security & Disruptive Technologies Portfolio, Division of Emerging Technologies
National Research Council Canada, Ottawa, Ontario, Canada

**Aerospace Portfolio, Division of Emerging Technologies,
National Research Council Canada, Montreal, Quebec, Canada

***Benoit.Simard@nrc-cnrc.gc.ca

ABSTRACT

Boron nitride nanotubes (BNNTs) are an attractive candidate for development of light-weight, multifunctional polymer nanocomposites. Such composites have received very limited attention in comparison to the more established carbon nanotubes as, over most of their history, only small quantities of BNNTs have been available for research. Here we highlight our recent work on fabrication of polymer nanocomposites, based on both dispersed BNNTs and free-standing BNNT sheets, enabled by recent advances in large-scale synthesis of BNNTs. The stiffness of a bulk epoxy composites increased with simple mixing of BNNTs into the resin at low loadings (up to 5 wt.%). High BNNT content nanocomposites were achieved by epoxy-impregnation of BNNT sheets (as high as > 30 wt.% BNNTs in epoxy) and by modification of BNNT sheets with polyurethane. Composites based on BNNT sheets in particular are subject to only a couple of related reports and production of the high-nanotube-content nanocomposites shown here is an important step in the direction of BNNT-based multi-functional composites.

Keywords: boron nitride nanotubes, pilot-scale synthesis, buckypaper, polymer nanocomposites

1 INTRODUCTION

Boron nitride nanotubes (BNNTs) are structurally analogous to carbon nanotubes (CNTs) and possess equally impressive mechanical properties along with a different set of multifunctional properties including higher thermal stability than CNTs, wide band gap, electrical insulation, polarizability, high neutron absorption cross-section, and transparency in the visible region. These characteristics make BNNTs attractive for the fabrication of enhanced composites with potential to impact a range of sectors including aerospace and defense; however, nanocomposites incorporating BNNTs have received only limited study. This is in contrast to CNT-polymer nanocomposites, which have been exploited in many studies and appear in an increasing number of commercial products [1]. A key reason for this discrepancy is that the methods available for synthesis of high-quality, small-diameter BNNTs were

previously limited to low production quantities and insufficient to support development of large-volume applications, including polymer nanocomposites [2]. Recent advances in BNNT production, including a pilot scale RF plasma process (~200 g/day) developed in our lab [3,4], a second plasma-torch-based approach enabling similarly impressive production rates [5], and the release of a high-quality, small-diameter BNNT material as a commercial product [6], have removed this obstacle leaving development of BNNT composites poised to accelerate quickly. Here we introduce the field of BNNT-polymer nanocomposites and, focusing on our recent works [3,4,7], highlight the new availability of large (composites-relevant) quantities of BNNT material and three resulting examples of polymer nanocomposites including: (a) bulk epoxy composites prepared by dispersion of BNNTs, (b) composite sheets prepared by epoxy-impregnation of BNNT buckypapers, and (c) BNNT sheets modified by integration of thermoplastic polyurethane.

2 BNNT COMPOSITES: LITERATURE

While the effect of incorporating BNNTs in various matrices has received limited attention, there are reports including polymer, metal and ceramic composites. Polymer nanocomposites are the most studied case and the status of the field was summarized in a recent, comprehensive review [2]. In terms of mechanical properties, increases in elastic modulus are most common (e.g., 10 to 50% with 1-3 wt% BNNTs [8-10]). Tensile strength is often reported as minimally changed or decreased; however, significant strength improvements (~20-30 wt%) have been observed with functionalized BNNTs [8,9]. Improvements in thermal conductivity and dielectric properties have also been noted in composites containing dispersed BNNTs, but have received only cursory study due to the early stage of BNNT composites research [2].

As demonstrated in the CNT literature, one of the most effective ways to produce nanotube-polymer composites is through resin-infiltration of macroscopic assemblies of nanotubes such as yarns, thin films or sheets [11-13]. High fractions of CNTs (up to ~40 wt%) have been achieved using nanotube sheets, but this approach is mostly unexplored for the case of BNNTs. The existing examples

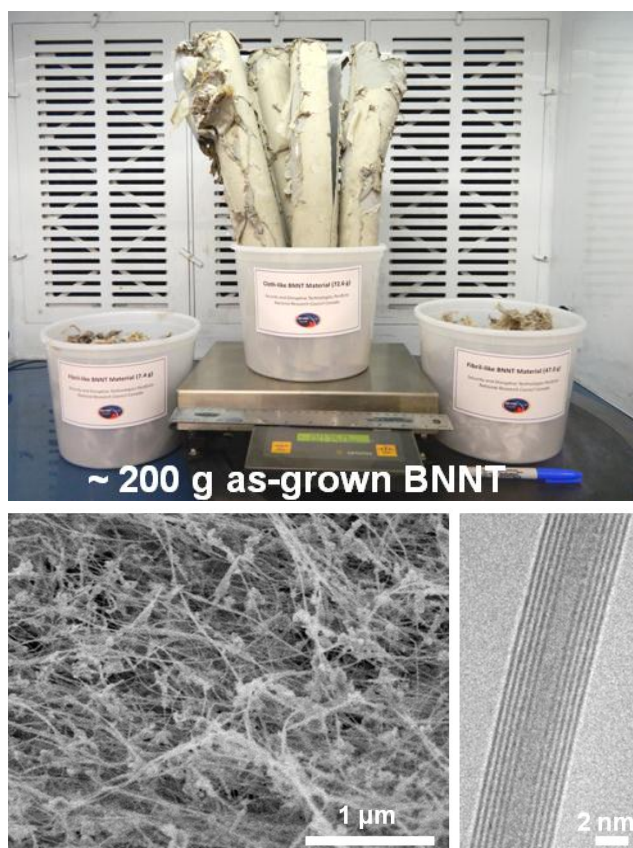


Figure 1: Images of as-produced BNNT material at various length scales. Reproduced from [4] with permission

include soaking of a supported BNNT mat in a polymer solution, which achieved a high wt% (18-37 wt%) nanocomposite, and two recent examples from our group. That work [7], adapted herein, reported high-BNNT-content nanocomposites fabricated by impregnation of free-standing BNNT buckypapers with epoxy, and by modification of BNNT buckypapers with polyurethane.

3 LARGE-SCALE BNNT PRODUCTION

The accessibility of multi-gram-scale and larger samples of high-quality, small-diameter BNNT reached a critical point over the last two years. As noted, two large-scale, continuous methods based on plasma torch technology were reported [4,5] and a commercial BNNT product was released [6].

Our approach at the National Research Council Canada (NRC) employs a radio frequency plasma torch to vaporize hexagonal boron nitride (hBN), although other sources of B and N can be used. The product from a single, continuous synthesis run is shown in Fig. 1. The features of the plasma, including high temperature ($\sim 10^4$ K), abundance of radicals, and high cooling rate allow for realization of a high yield of small diameter BNNTs, which had previously proved difficult. This new type of method, called the hydrogen-assisted BNNT synthesis (HABS) method, makes use of

hydrogen, to achieve high yield by impeding the otherwise easy re-formation of N_2 . In the HABS approach, the presence of hydrogen leads to formation of B-N-H containing intermediate species, which provide a source of available nitrogen for BNNT growth that is much more reactive than the direct $N_2 + B$ reaction, as explained in more detail elsewhere [4].

4 BULK COMPOSITES: BNNT-EPOXY

Bulk BNNT-epoxy composites using an Epon 828 epoxy matrix were prepared by planetary mixing and solvent dispersion methods. Fig. 2 compares the visual appearance of BNNT and CNT composite disks. While not completely transparent, the BNNT composites are semi-transparent and outperform a thin carbon nanotube-epoxy composite of similar loading, which is promising in terms of transparency given that no chemical means were employed to facilitate dispersion. In general, the viscosity also did not increase dramatically with the addition of BNNTs (up to 2 wt %) and was favourable for processing and composite preparation.

The most significant change in mechanical properties was observed for the nanocomposites stiffness, which increased with the BNNT content for 1 wt% to 5 wt% composites (Fig. 2). The strength was not significantly changed, similar to other literature reports for BNNT-polymer nanocomposites. The elastic modulus increased up to 30% at 5 wt.% BNNT loading. Thermal conductivity also increased with BNNT loading, approaching a 20% increase at 5 wt% BNNTs.

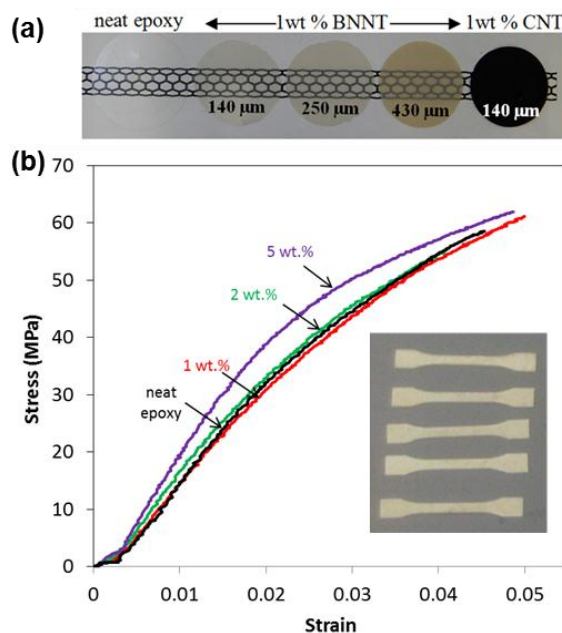


Figure 2: (a) 1 wt% BNNT-epoxy composite films of increasing thickness (compared to a 1 wt% CNT film) and (b) stress strain curves for BNNT-epoxy composites.

5 BNNT BUCKYPAPERS AND THEIR POLYMER NANOCOMPOSITES

Nonwoven sheets composed of nanotubes, often called *buckypaper* in the carbon nanotube literature, are commonly produced by filtration methods. We produced BNNT buckypapers using a solvent dispersion and vacuum filtration approach [4,7]. A 30 cm x 30 cm BNNT buckypaper made with purified BNNTs is shown in Fig. 3.

The fabricated BNNT buckypapers are flexible and foldable. These papers presently offer modest mechanical properties (strengths ~ 2 MPa, stiffness ~ 400 MPa). Carbon nanotube buckypaper is of interest for a range of multifunctional applications due to its electrical properties, such as electromagnetic interference shielding. BNNT buckypaper offers a different set of multifunctional properties and could prove the more useful nanotube paper for radiation shielding and flame resistance. Fig. 3, showing a BNNT paper airplane in a flame, illustrates both the foldability and high flame resistance of the buckypaper. TGA indicates purified BNNT material is stable to at least 900 °C [4] and BNNTs are expected to prove more suitable than CNTs for high-temperature applications.

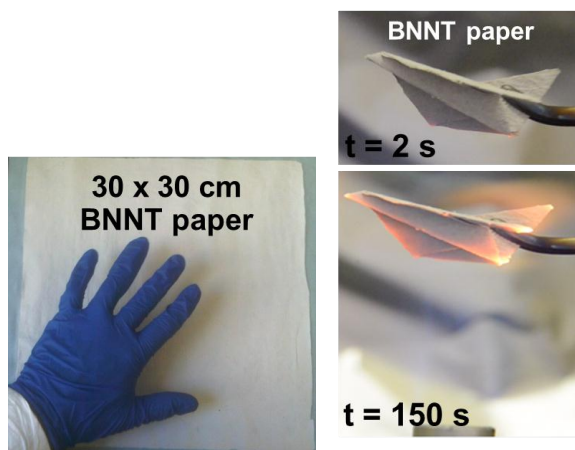


Figure 3: Large-size (30 cm x 30 cm) BNNT buckypaper and illustration of flame resistance of a BNNT paper airplane in a natural gas flame. Adapted from [7] with permission.

These BNNT buckypapers were used as a starting point for high-BNNT content nanocomposites. Our first example is an epoxy-impregnated BNNT buckypaper composite made by infusing a low viscosity, aerospace-grade epoxy resin into a BNNT buckypaper [7]. Fig. 4 shows a photo of an epoxy-impregnated BNNT buckypaper composite containing > 30 wt.% BNNTs. A good interaction (i.e., wetting of BNNT buckypaper with resin) is indicated by the contact angle for an epoxy drop on the surface. The initial contact angle of $< 60^\circ$ shown in Fig. 4 is significantly lower than the comparable case with a CNT buckypaper ($> 100^\circ$). After impregnation, the void content decreased from 80% to less than 5%, suggesting that nearly full impregnation of

the BNNT buckypaper was achieved. SEM imaging also supports effective impregnation and show evidence of pull-out of BNNT ropes at fracture surfaces.



Figure 4: A BNNT-buckypaper-epoxy composite (> 30 wt.% BNNTs, ~ 60 μm thick) and contact angle image showing the initial contact angle for the epoxy with BNNT buckypaper at room temperature. Adapted from [7] with permission.

After epoxy-impregnation, the elastic modulus is improved by almost 20 fold (to 7.7 GPa, see Fig. 5) as compared to the pristine BNNT buckypaper and by a factor of 2 in comparison to the neat epoxy (not shown). The ultimate tensile strength of the composite (42 MPa) is 20x higher than the pristine BNNT buckypaper; however, this value is still only about 60 % that of the neat epoxy (~ 70 MPa). Measured strain at failure of 0.6% indicates the brittleness of the composite. Improvements in BNNT purity and the impregnation method, as well as stronger interaction between BNNTs and epoxy (e.g., via BNNT functionalization) should further improve the mechanical properties and, along with multifunctional properties, this a subject of current research.

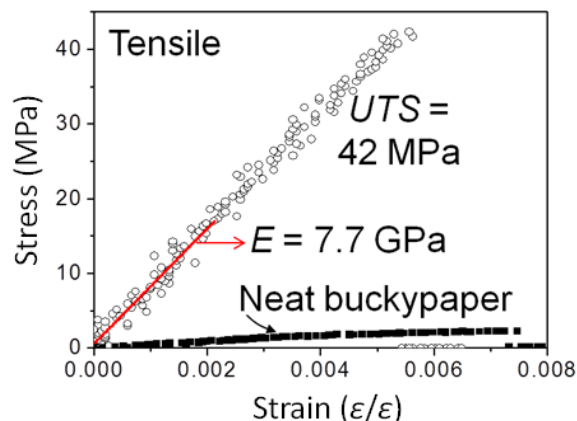


Figure 5: Example stress-strain curves for BNNT buckypaper and epoxy-impregnated BNNT buckypaper. Reproduced from [7] with permission.

In a second example based on BNNT buckypaper, nanocomposites were prepared by using thermoplastic polyurethane (TPU) to modify the buckypaper properties [7]. The TPU-modified BNNT buckypaper composites shown here were prepared by a one-step filtration method, wherein solvent dispersions of BNNT containing TPU were filtered in a single step and the ratio of BNNTs to polyurethane could be controlled using combination of good and bad solvents for TPU.

Nanocomposites with higher BNNT:TPU ratios (93:7 and 75:25 by weight) are more flexible and mechanically robust than pristine BNNT buckypaper and, in contrast to epoxy-impregnated composites, retain the porous morphology of buckypaper and a low density ($\sim 0.5 \text{ g/cm}^3$). At low TPU-content the polymer improves the buckypaper properties (stiffness, yield strength, ultimate strength and failure strain) but the behaviour is still buckypaper-like showing higher stiffness and brittle failure. The highest mechanical properties were observed for a 75:25 ratio composite as shown in Fig. 6. Conversely, at high TPU-content the properties are qualitatively different and more resemble the TPU polymer, i.e., lower stiffness, higher density, and much higher strain at failure (~ 2000 times higher than the BNNT buckypaper and approaching that of the neat TPU) but with higher yield strength and stiffness than TPU. The method appears to be effective for the fabrication of light-weight, high-BNNT-content nanocomposites with tailor-able mechanical properties. Due to its porous character, TPU-modified BNNT buckypaper could also serve as an intermediate to preparation of other high-BNNT content polymer nanocomposites.

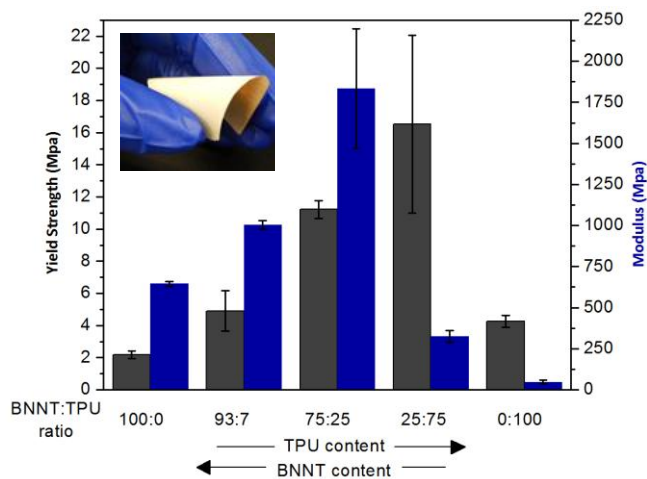


Figure 6: Comparison of yield strength and elastic modulus for TPU-modified BNNT buckypapers, pristine BNNT buckypaper and TPU.

6 CONCLUSIONS

In summary, enabled by relatively new advances in large-scale production of BNNTs, polymer nanocomposites were prepared based both on dispersed BNNTs and on

BNNT buckypapers. The production of high-BNNT-content nanocomposites, shown here by epoxy impregnation of BNNT buckypapers and by incorporation of thermoplastic polyurethane in a porous BNNT-TPU sheet, is an important step for realization of BNNT-enhanced composites

REFERENCES

- [1] M.F.L De Volder, S.H. Tawfick, R.H. Baughman, A.J. Hart, *Science* 339, 535, 2013.
- [2] W. Meng, Y. Huang, Y. Fu, Z. Want, C. Zhi, *J Mater Chem C* 2, 10049, 2014.
- [3] K.S. Kim, C.T. Kingston, B. Simard, WO 2014/169382 A1, 2014.
- [4] K.S. Kim, C.T. Kingston, A. Hrdina, M.B. Jakubinek, J. Guan, M. Plunkett, B. Simard, *ACS Nano* 8, 6211, 2014.
- [5] A. Fathalizadeh, T. Pham, W. Mickelson, A. Zettl, *Nano Lett* 14, 4881, 2014.
- [6] BNNT, LLC press release: www.bnnt.com/news/24-better-nanotubes
- [7] K.S. Kim, M.B. Jakubinek, Y. Martinez-Rubi, B. Ashrafi, J. Guan, K. O'Neill, M. Plunkett, A. Hrdina, S. Lin, S. Denomme, C. Kingston, B. Simard, submitted to *RSC Advances*, 2015.
- [8] C. Zhi, Y. Bando, C. Tang, S. Honda, H. Kuwahara, D. Golberg, *J Mater Res* 21, 2794, 2006
- [9] S.-J. Zhou, C.-Y. Ma, Y.-Y. Meng, H.-F. Su, Z. Zhu, S.-L. Deng, S.-Y. Xie, *Nanotechnol.* 23, 055708, 2012.
- [10] L. Li, Y. Chen, Z.H. Stachurski, *Prog. Nat. Sci.: Mater. Int.* 23, 170, 2013.
- [11] Z. Wang, Z. Liang, B. Wang, C. Zhang, L. Kramer, *Compos. A* 35, 1225, 2004.
- [12] S. Wang, Z. Liang, G. Pham, Y.-B. Park, B. Wang, C. Zhang, L. Kramer, P. Funchess, *Nanotechnol.* 18, 095708, 2007.
- [13] B. Ashrafi, J. Guan, V. Mirjalili, P. Hubert, B. Simard and A. Johnston, *Compos. A* 41, 1184, 2010.