



Nanoreinforced Adhesives and Composite Laminates Incorporating BN Nanotubes

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ABSTRACT

Boron nitride nanotubes (BNNTs) offer complimentary properties to carbon nanotubes (CNTs) and interact more favorably with epoxies, which could make BNNTs a preferred option for reinforcing epoxy when electrical conductivity is not required, and particularly where transparency/color, neutron absorption or electrical insulation are advantages. Here we describe our recent work on the integration of BNNTs into epoxy resins and preparation of BNNT-reinforced adhesives joints and glass fiber reinforced polymer laminates with improved properties including joint strength and impact energy absorption [Jakubinek *et al.*, *Int. J. Adhesion Adhesives* (2018); Guan *et al.*, *Nanocomposites* (2018); Rahmat *et al.*, *ACS Appl Nano* (2018)]. The tensile properties of BNNT-epoxy nanocomposites are shown to be modified by BNNT incorporation with increases in at least some of stiffness, strength and toughness depending on the selection of loading and raw, purified or functionalized BNNTs. BNNTs functionalized with OH/NH₂ groups had a smaller effect on elastic modulus but, in contrast to raw-BNNTs, also increased tensile strength and toughness. Raw and purified BNNTs were also employed in the production of nanoreinforced adhesive joints, showing improved lap shear strength and nanotube pull-out during joint failure, and in multiscale laminates incorporating BNNTs as a matrix-reinforcement for glass fiber reinforced polymer laminates. The results emphasize the potential for BNNT-reinforced composites as a complimentary approach to carbon nanotube-reinforced composites and provide a basis for ongoing investigation and development of BNNT-epoxy nanocomposites.

KEYWORDS: boron nitride nanotubes, nanocomposites, adhesives, fiber reinforced polymer composites

1 INTRODUCTION[†]

Boron nitride nanotubes (BNNTs) are structurally analogous to carbon nanotubes (CNTs), with each carbon-carbon pair in a hexagonal sheet replaced by a boron-nitrogen pair and rolled into a cylinder of a given chirality as is commonly described for CNTs. However, while the bond strengths and the geometrical ball-and-stick models are close equivalents for both types of nanotube, the BN bond is partially ionic and BNNT show contrasting electron density distributions in comparison to CNTs. As a result, BNNTs possess equally impressive mechanical properties and low density, but offer a different set of multifunctional advantages including higher thermal stability, electrical insulation, high neutron absorption, piezoelectricity, and transparency in the visible region.

Due to their contrasting electronic structure, BNNTs have different chemistries that could include stronger interaction with polymers. Theoretical studies using density functional theory indicate much stronger interaction energy between BNNTs and selected polymers (PS, PT, PmPV) (Nasrabadi & Foroutan 2010). More recently, Chen *et al.* 2015 used single-nanotube pull-out experiments to demonstrate higher interfacial strength for BNNT-epoxy and BNNT-PMMA than for comparable CNT cases, which was supported by their molecular dynamics simulation. We also observed superior wetting and infiltration of BNNT buckypapers with epoxy (Kim *et al.* 2015). Such modeling and observations suggest BNNTs could be more favorable than CNTs for integration with polymers. In addition, Nigues *et al.* 2014 determined that inter-wall friction in BNNTs is much higher than for CNTs, which enables interwall load transfer that could make multi-walled BNNTs a more efficient filler than multi-walled CNTs.

Reviews by Meng *et al.* 2014, Kim *et al.* 2017, and Jakubinek *et al.* 2019 address recent advances in both manufacturing of BNNTs, which was previously a major limitation to BNNT composites research, and in BNNT composites research in more detail. In the present proceedings and presentation, we address our recent work in this area at the National Research Council Canada on the preparation of BNNT-epoxy composites and related nanoreinforced adhesive joints and composite laminates.

2 METHODS & RESULTS

2.1 BNNT-epoxy composites

BNNTs were produced by the National Research Council’s nanotube manufacturing facility. The unique synthesis, as described in detail by Kim *et al.* 2014, employs an RF induction thermal plasma process to synthesize BNNTs from hBN at high rate and produces highly crystalline, few-wall, small diameter ($d_{\text{avg}} \sim 5$ nm) BNNTs. BNNTs produced via this method are available commercially from Tekna Advanced Materials (Sherbrooke, QC, Canada). In the works discussed here, these BNNTs were used at: (1) as-synthesized purity (raw- or r-BNNTs) estimated to be ~50% BNNTs, (2) after purification to remove elemental boron impurities (purified- or p-BNNTs), and (3) after purification and chemical functionalization (functionalized- or f-BNNTs). The functionalization procedure, involving bromination and hydroxylation reactions, as described by Guan *et al.* 2018(a and b), offered OH and NH₂ groups expected to improve interaction with the epoxy.

The BNNT-reinforced epoxy composites were prepared by mixing dry BNNTs into commercial epoxy resins by planetary mixing (Thinky ARE 310) followed by vacuum degassing. More recently, performing the integration using a vacuum planetary mixing was observed to be advantageous. Prior to mixing with epoxy resin, the BNNTs for a complete set of comparison samples were homogenized by mechanical grinding. The epoxy systems used in the work described here were Epon 828/Epikure 3223 obtained from Miller-Stephenson, and SC15 (part A and part B) provided by Applied Poleramic Inc/Kanenka Aerospace. After mixing of the BNNTs with the epoxy resin, the corresponding hardener

[†] Paragraphs 1 and 2 of the introduction are reproduced, with permission, from Jakubinek *et al.* 2019 (“BNNT composites and applications”), a recent review chapter by the authors.

was added by planetary mixing at ratios of 12 parts per hundred resin for Epikure 3223 in Epon 828 and 30 parts per hundred resin for SC15. Figure 1, which shows the color and transparency of 1 wt% BNNT-epoxy films in comparison to a clear, colorless epoxy and a similar nanocomposite prepared with CNTs, demonstrates that BNNTs can be employed to reinforce transparent or dye-able composites. Even with relatively simple integration, the samples with 1wt% purified BNNTs show promising transparency for applications requiring thin layers (*i.e.*, adhesives or coatings)

Tensile properties were evaluated using ISO 527-2, Type IBB dog-bone coupons die punched from thin films ($\sim 200\text{ }\mu\text{m}$ thick), which were prepared by curing the composites between two glass plates treated with a release agent. The results of tensile testing on a micro-tensile test frame (Fullam Substage Test Frame, displacement control, 0.5 mm/min) for Epon 828/Epikure 3223 epoxy nanocomposites are shown in Figure 2. As addressed in more detail in our recent works (Jakubinek *et al.* 2018, Guan *et al.* 2018a), r-BNNTs yielded the largest values for Elastic modulus, which increased progressively up to 5 wt% BNNTs. However, at an optimum loading of around 2 wt%, f-BNNTs were found to show a more exciting combination of tensile properties, with a smaller increase stiffness but with significant improvements in tensile strength, toughness, and ultimate strain in contrast to the trends for r-BNNTs.

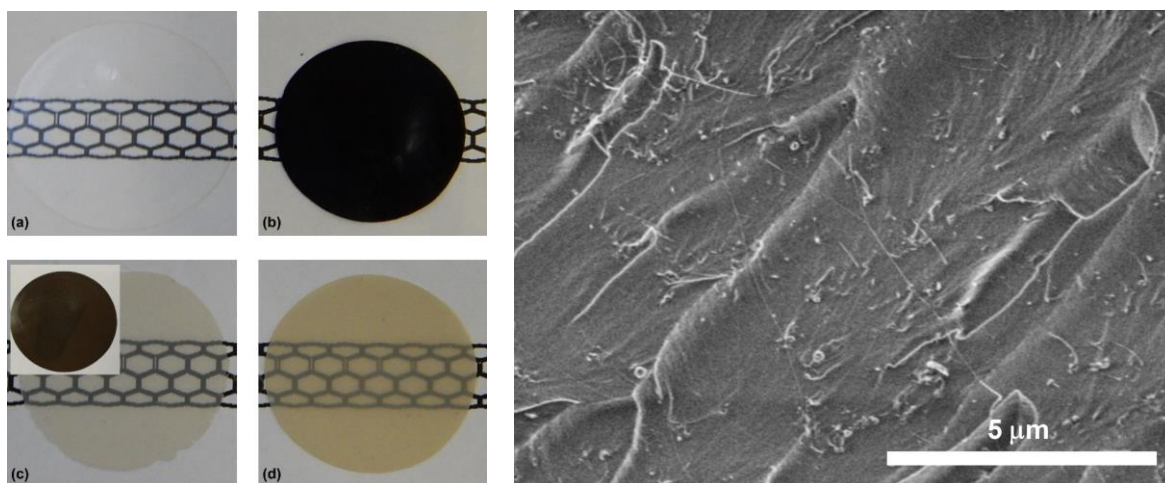


Figure 1. Photographs of (a) neat and (b-d) nanotube-modified epoxy films placed on top of an illustration of a nanotube structure. 1 wt% p-BNNT-epoxy composite films of (c) $250\text{ }\mu\text{m}$ and (d) $450\text{ }\mu\text{m}$ thickness provide good transparency while a thin ($125\text{ }\mu\text{m}$) CNT-epoxy film, (b), is opaque. The inset to (c) shows an equivalent composite with r-BNNTs where transparency is much lower and the background image is barely noticeable. Panel (e) shows an SEM image of the fracture surface of a 2 wt% BNNT composite. Source: Jakubinek *et al.* 2018 (Reproduced with permission).

2.2 Adhesive Joints

Informed by tensile characterization of r-BNNT/epoxy composites, adhesive joints were prepared using up to 5 wt% r-BNNTs in Epon 828/Epikure 3223 and evaluated based on ASTM D1002 single-lap-shear tests with aluminium substrates as described in more detail in our recent report (Jakubinek *et al.* 2018). The aluminium surfaces were prepared for bonding by grit blasting and a sol-gel treatment, and the joint panels were cured at room temperature under compression followed by a $120\text{ }^{\circ}\text{C}$ post-cure prior to coupon cutting. As shown in Figure 3, the single-lap-shear strength is increased by addition of 1 and 2 wt% r-BNNTs but decreased with the 5 wt% r-BNNT adhesive, which is likely explained by more difficulty preparing the higher loading nanocomposite adhesive joint due to higher viscosity of that adhesive. In addition to offering better transparency (Figure 1), a comparison case using 1 wt% p-BNNTs resulted in a 15% improvement in joint strength and proved to be the most efficient of the BNNT-reinforcement cases evaluated here.

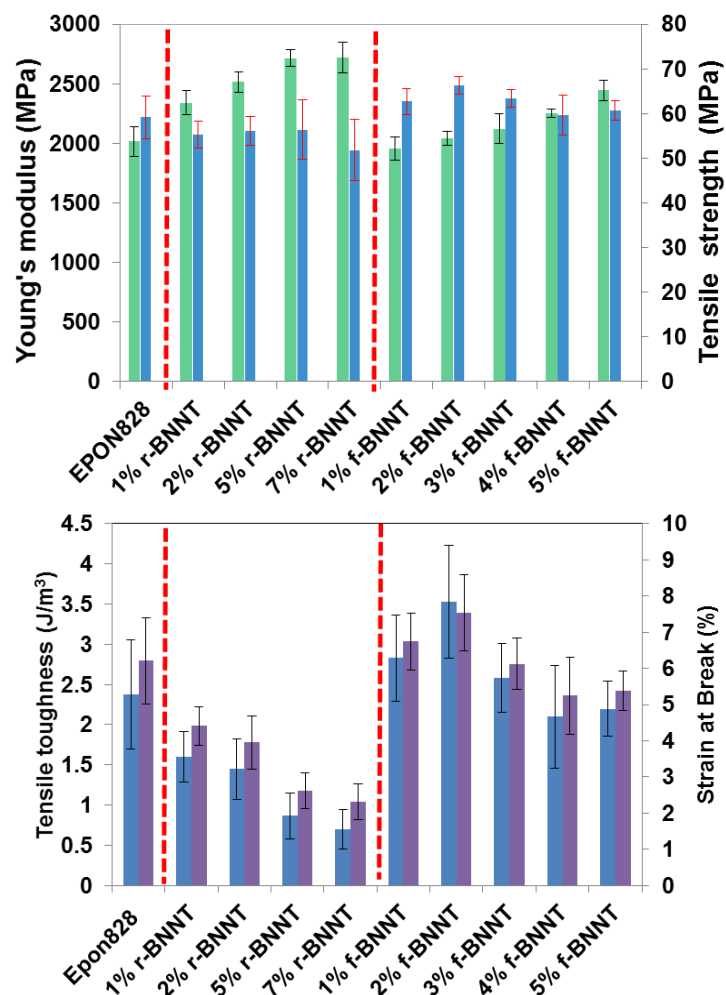


Figure 2. Tensile properties of BNNT-epoxy nanocomposites produced from r-BNNTs or f-BNNTs in a matrix of Epon 828/Epikure 3223. Source: Guan *et al.* 2018a. Reproduced with permission.

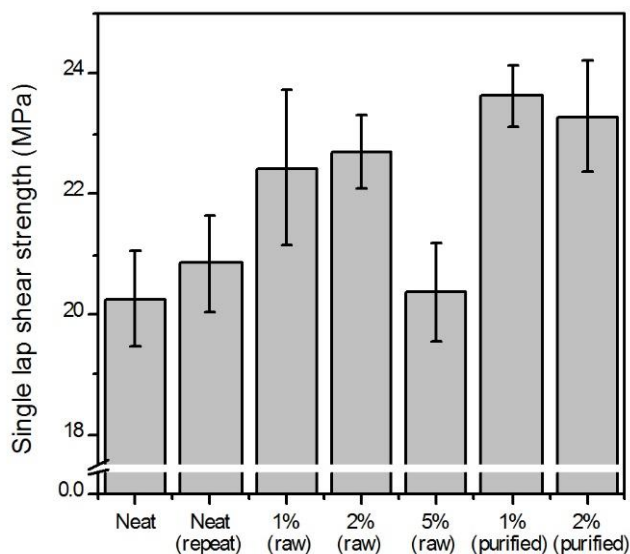


Figure 3. Lap-shear strength of Epon 828/Epikure 3223 and related BNNT composite adhesive joints using r-BNNTs and p-BNNTs. Source: Jakubinek *et al.* 2018 (Reproduced with permission).

Observation of the failure surfaces revealed that the fracture surface, which followed the adhesive-adherend interfaces, switched between the two adherend surfaces near the center of the bondline. This was similar to previous observations for single-lap-shear joints reinforced with functionalized carbon nanotubes by Sydlík *et al.* 2013, who attributed increased joint strength to crack deflection by nanotubes where the fracture path travels through the adhesive layer. As shown in SEM images along this failure path (Figure 4), many BNNTs are observed protruding from the adhesive and aligned in the test direction for joints with lower BNNT-content and improved lap-shear strength. Combined with imaging of a higher BNNT-content adhesive joint (5 wt%), which exhibited lower joint strength and less pull-out and alignment of BNNTs, this supports the role of BNNTs in reinforcement of the joint despite initial observations of primarily adhesive failure along the adhesive-adherend interface.

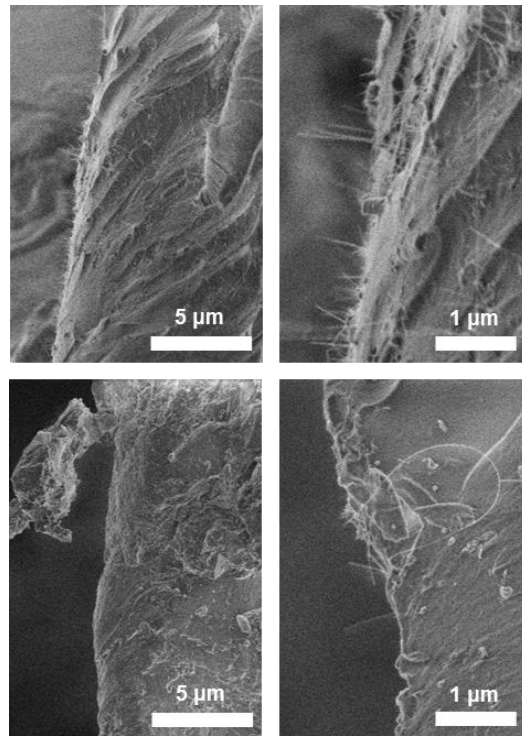


Figure 4. SEM image of tilted (34°) lap-shear failure surfaces along the line where the failure surface transitioned from one adherend to the other. The 2 wt% r-BNNT-epoxy adhesive joint (Top) shows substantially higher alignment of the pulled out BNNTs along the failure direction than for the higher nanotube content joint (5 wt% r-BNNT; Bottom). Source: Jakubinek *et al.* 2018 (Reproduced with permission).

2.3 Glass fiber laminates

Glass fiber reinforced polymer laminates were prepared using BNNT-reinforced SC15 epoxy and plain weave S2-glass fabric (ACP Composites). Both hand lay-up and vacuum-assisted resin transfer molding (VARTM) techniques were employed and the resulting laminates were characterized by shear punch (ASTM D732), short beam shear (ASTM D2344), and modified Charpy impact tests (ISO 179, type 1) as described in more detail in our recent work (Rahmat *et al.* 2018). Each laminate consisted of 21 layers of glass fiber fabric ($17\text{ cm} \times 34\text{ cm}$). The completed panels had thicknesses of $2.4 \pm 0.2\text{ mm}$, corresponding to glass fiber volume fractions of $40 \pm 5\%$. Laminates produced by hand lay-up using r-BNNTs, p-BNNTs and the neat epoxy are shown in Figure 5. The addition of BNNTs did not cause noticeable changes in the thickness or fiber content; however, VARTM-produced specimens were thicker and had a correspondingly higher resin content.

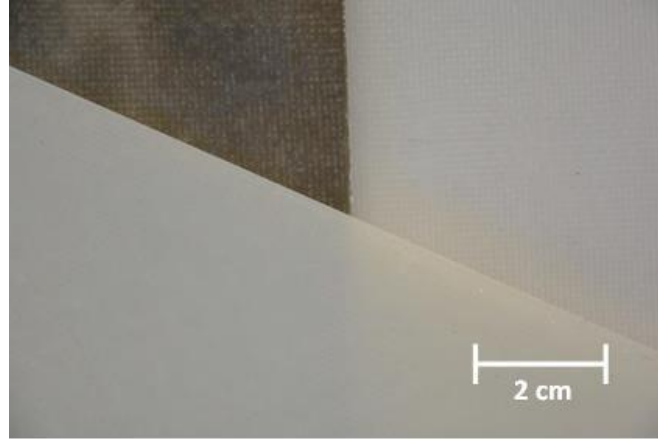


Figure 5. Glass fibre – epoxy laminates incorporating r-BNNT (top left), p-BNNT purified (top right), and neat resin (bottom). Source: Rahmat *et al.* 2018 (Reproduced with permission).

Performance of the GFRP laminates was found to be maintained or increased by the addition of 1 wt% BNNTs in all test cases, including average increases of: 8% for specific shear punch strength, 15% for specific short beam shear strength, and 22% for specific fracture energy per area in modified Charpy tests (Rahmat *et al.* 2018). BNNT addition had a relatively small effect where the loading is closer to pure shear (shear punch tests), a larger effect in short beam shear, and the largest effect for modified Charpy (Figure 6) where the contributions of normal stress (bending loads) are progressively larger. Laminates produced by VARTM exhibited non-uniform color consistent with filtration of the BNNT filler material, which is likely a factor in the discrepancy between wet lay-up and VARTM specimens.

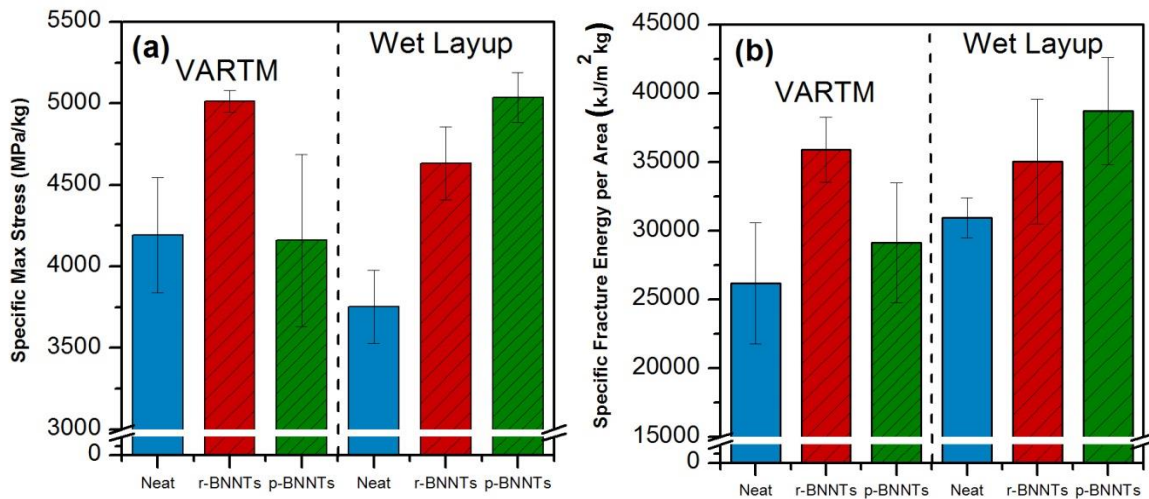


Figure 6. (a) Specific maximum stress, and (b) specific fracture energy per area obtained from modified Charpy tests. Source: Rahmat *et al.* 2018 (Reproduced with permission).

3 CONCLUSION

BNNTs, which offer complimentary functional properties to CNTs and are potentially advantageous for mechanical reinforcement of polymers, are increasingly being explored in nanocomposites R&D. Here we introduced the potential of BNNTs for polymer nanocomposites and specifically highlighted our recent works on the topic of BNNT-reinforced epoxy. Addition of 1-2 wt% raw, purified or functionalized BNNTs was found to be favorable for tensile properties. Structural

performances of BNNT-reinforced adhesive joints and fiber reinforced polymer laminates, recently reported for the first time, were significantly improved in single-lap-shear joint tests and modified Charpy impact tests, respectively. This emphasizes the potential and accessibility of BNNTs as a complimentary approach to carbon nanotube-reinforced composites and provide a basis for ongoing investigation and development of BNNT-epoxy nanocomposites.

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