Mechanical Properties of the Boron Nitride Analog of Graphyne: Scaling Laws and Failure Patterns**

By Matthew Becton, Xiaowei Zeng and Xianqiao Wang*

Recent years have witnessed the explosive growth of interest in novel two-dimensional materials beyond graphene, such as the boron nitride analogue BNyne. Here, the authors perform steered molecular dynamics (MD) simulations to probe the structure, mechanical properties, and failure of BNyne with a range of triple-single-bond linker numbers. The authors develop a set of general scaling laws for the cumulative effects of linkers based on MD, allowing extrapolation to extended BNynes. Results indicate that the number of linkers, and thus density, is a vital metric of material strength and stiffness. We find that BNyne is stronger in the armchair direction but stiffer in the zigzag direction. These findings are promising as the application of this strong, anisotropic 2D material becomes closer to reality.

1. Introduction

The past decade has seen an explosion of 2D material-related research, as these advancing edge materials have demonstrated tremendous promising applications in electronics, energy storage, composites, and biomedicine due to their outstanding physical properties which are unable to be seen in bulk materials.[1] Following graphene’s meteoric rise in popularity since its discovery, many other 2D materials have begun to be investigated. Of the many kinds of 2D materials currently drawing attention, boron nitride (BN) has become a major topic of research due to its structural equivalency to carbon allotropes and its outstanding mechanical,[2] thermodynamic,[3] chemical,[4] and electronic,[5,6] properties. Hexagonal boron nitride (h-BN) is an atomic lattice structure similar to graphene, but composed of the heterogeneous atoms boron and nitrogen in place of carbon.

The mechanical stability combined with h-BN’s natural sliding has enabled its fantastical applications in bulk lubrication for decades,[7] however, with the explosive growth of interest in many disparate 2D materials, focus has shifted toward the applicability of h-BN at the nano-scale, such as an insulator used as a foil to the conductor graphene,[8] a spin-filter for spintronic devices,[6,9] and a nanoscale filler as a strengthening component in ceramic composite materials.[10]

Following the discovery/invention of graphene, a type of materials called “graphynes” have been making an impact for their promising properties as well. Graphynes are a family of 2D materials composed entirely of carbon similar to graphene; but whereas all of the atoms in graphene are \(sp^2\)-hybridized with three neighbors apiece, graphynes all contain a percentage of \(sp^1\)-hybridized acetylenic triple-single-bond linkers, with the percentage and geometry of linkers defining the type of graphyne.[11,12] The inclusion of single and triple bonds and an enlarged lattice gives graphynes markedly different properties when compared with pristine graphene, opening new avenues and giving new alternatives to conventional energy storage,[13] electronics,[14] and filtration[15] technologies. Applying the expanded structure of graphyne to BN, a new class of 2D materials called “BNyne” has been theorized with boron and nitrogen in a graphyne-like sheet with analogous connecting triple-single-bond chains.[16] This fusion combines the heterogeneous atoms of BN and the heterogeneous bonding of graphynes to create a truly unique brand of nanostructured materials. Here, we focus on the regular linking of BN aromatic groups with identical and isotropic triple-single bond chains (see Figure 1), maintaining hexagonal symmetry and facilitating systematic comparison between systems and assessment of the
mechanical performance of BNynes. This class of materials is extremely novel, and as such is equally poorly understood. However, understanding the mechanical properties of these materials which are so full of potential will make it easier to characterize and manufacture them. Therefore, investigating the mechanical properties of BNynes and characterizing the results by the number of linkers in order to better understand the potential of this material will be the focus of this paper. In the following sections, we will discuss the computational methods for the tensile tests, explain the models, and characterize the results. In this manner, we hope to contribute to the development of BNynes.

2. Computational Model and Methods

First, an originally developed program is utilized to generate a lattice structure of BNynes with the specific number of acetylene-like, triple-single-bond, linkers of interest. In what follows, molecular dynamics simulations based on the open-source code LAMMPS\textsuperscript{[17]} are employed to accurately capture the behavior of BNynes, the Tersoff potential is utilized, which takes the following form:

\[
E = \frac{1}{2} \sum_{i,j} \sum_{\phi} f_C(r_{ij}) \left[ f_R(r_{ij}) + f_A(r_{ij}) \right]
\]

Here, \( f_R \) is a repulsive two-body term while \( f_A \) is an attractive three-body term managed by the \( b_{ij} \) bond function.

The parameters of the Tersoff potential utilized here for BN were documented by Matsunaga\textsuperscript{[18]} and are included in the Supplementary Materials Table S1. The BNyne types tested in this paper are labeled based on the number of triple-single-bond linkers between hexagons, from 0 to 6. For the purpose of convenience, boron nitride is labeled as 0-BNyne due to its lattice being identical to a case of there being 0 linkers. For the tensile tests, the simulated sample is a 20 × 20 nm\textsuperscript{2} square sheet under NVT ensemble using a Nose–Hoover thermostat to control the temperature. The standard velocity-Verlet time integration algorithm with a timestep of 1 fs is used to preserve a balance between accuracy and computational cost. In this work, the initial plane of the nanosheet is considered to be the \( x-y \) plane, the direction of tension is the \( x \) direction, and perpendicular to the nanosheet is the \( z \) direction. The lattice distance varies due to the expanded lattice for different numbers of linkers, and the lattice distance for each \( L \)-BNyne is labeled as \( a_L \), where \( L \) indicates the number of linkers. The boundaries are aperiodic so as to prevent self-interference in the sample, and a randomized initial velocity is applied to each atom in accordance with the sample temperature with sum zero linear and angular momenta. The sample then undergoes energy minimization following the Polak–Ribiere conjugate gradients method until the relative energy difference between successive steps is less than \( 10^{-20} \), and the finalized per-atom binding energy is listed in the Supplementary Materials Table S2.

Prior to applying tensile loading, the sample takes a long enough time to relax such that there is minimal prestress inside the sample. The tensile test process is as follows: the energy-minimized \( L \)-BNyne structure is kept at 1 K using Nosé–Hoover thermostating, so as to minimize the effects of the randomized temperature profile. In order to provide the tensile force to the sample, both ends of the sample are pulled via a virtual spring with a spring constant of 100 eV Å\textsuperscript{-1}. The pulling speed is set as 2.5 nm ns\textsuperscript{-1}, which is slow enough to have negligible velocity-dependent effects on the results as evidenced by Figure S1 of the Supplementary Materials.

3. Results and Discussion

3.1. Effect of Lattice Length on Mechanical Properties

The focus of this study is to investigate the mechanical behavior of several varieties of BNyne structures under tensile loading, and accordingly an important factor in the properties of the final structure is the composition of the initial sample. The integer of triple-single-bond linkers \( L \) between hexagonal cells in this study is varied from 1 to 6, with 0-BNyne being h-

Fig. 1. Bond-map comparison of BNyne structures. (a) BN, (b) 1-BNyne, (c) 3-BNyne, (d) 6-BNyne. In this image, the horizontal direction is “armchair,” and the vertical direction is “zigzag.” Blue atoms are nitrogen, yellow represents boron. The black lines depict the lattice length \( a_L \) for each BNyne (\( a_1 = a_2 = a_3 \)).
BN as shown in Figure 1. Each BNyne structure is a crystal lattice, the same as BN, and as such each structure has its own lattice length, defined here as $a_L$ for L-BNynes and $a_0$ for hexagonal boron nitride. As the lattice length of the unit cell in this 2D crystal structure grows larger, the atomic density of the BNyne decreases by the square of the lattice length. In order to characterize this structural uniqueness and provide the ease for the analysis, we define the scaled lattice length $\alpha_L$ and the scaled density $D_L$ as follows:

$$\alpha_L = \frac{a_L}{a_0}$$

$$D_L = \frac{\rho_L}{\rho_0}$$

Here, $\rho_L$ is the density of the L-BNyne and $\rho_0$ is the density of 0-BNyne, or pristine hexagonal boron nitride. Using the scaled lattice length makes it easier to see how the unit cell of the BNyne structure affects its mechanical properties; it has been shown for the structurally similar graphynes that many mechanical properties can be interpreted accurately as a function of the inverse lattice spacing.\(^{[12]}\) As BNynes have similar structures, the number of triple-single-bond linkers and the resulting lattice spacing may very well also play a similarly large effect on the properties of each sample; as such the mechanical properties of BNynes in this text are posed to show their relation to the lattice spacing $\alpha_L$.

For this work, two sets of tensile tests are performed for each sample: along the “armchair” direction of the crystal lattice, and along the “zigzag” direction of the crystal lattice. For calculations of stress, the thickness of the BNyne sheet was taken to be 3.3 Å, as has been shown for layered graphite and BN structures.\(^{[19]}\)

First, uniaxial loading along the armchair direction in the BNynes was performed. Here, we introduce the per-atom stress tensor as follows:

$$S_{ab} = -[m\bar{v}_a\bar{v}_b] + \frac{1}{2} \sum_{n=1}^{N_f} (r_1 a F_{1b} + r_2 a F_{2b})$$

where $a$ and $b$ can take on values of $x, y,$ and $z$ to represent the six tensor values of $xx, xy, xz, yy, yz,$ and $zz$. The first term in the equation is the kinetic energy contribution to the per-atom stress, while the second term is a summation of all pairwise interactions in the simulation. All of the per-atom stresses are summed up and the result divided by the volume of the sample to get the stress in the direction of tension, which would be the $xx$ stress in this case. The resulting stress–strain curves for the BNynes in the armchair direction are depicted in Figure 2a. Judging from these curves, we can see that 1-BNyne has very similar ultimate strength as that of pristine BN, around 160 GPa, while for larger $L$ the strength rapidly decreases.\(^{[20]}\) There are two distinct phases before failure: i) up until just before 50% strain the stress rises gently as strain increases, and the curves are distinct according to the number of linkers the BNyne has; ii) at approximately 50% strain, however, each of the BNyne samples cease stretching and the stress builds up rapidly until failure with very little change in the strain. These two phases shall henceforth be referred to as the initial loading phase and the secondary loading phase. This particular phenomenon is due to the unique structure of BNynes, and is discussed in detail in the section on mechanical failure. It is worthwhile to note that after this build-up of stress, the number of linkers $L$ determines the stress upon failure, with a larger $L$, and thus a more sparse structure, the material becomes weaker and less elastic. This is most clear with small $L$, as the difference between the curves of 1-BNyne and 2-BNyne is very pronounced.

This trend is clearly seen in Figure 3, which is the fitted trend of the ultimate stress for each type of BNyne, plotted against the inverse of the scaled lattice length ($\alpha_i^{-1}$). It is clear that the ultimate stress increases in a linear fashion relative to $\alpha_i^{-1}$, such that a greater $L$ has a larger $\alpha_i$ and thus a smaller $\alpha_i^{-1}$. A linear trend is fitted to this data to represent the tensile strength (TS) of each L-BNyne as a function of the inverse of the scaled lattice length with the following equation:

$$TS_L = b \ast \alpha_i^{-1} + c$$

Fig. 2. Stress–strain curves for BNynes in the (a) armchair and (b) zigzag directions.
For armchair BNynes, $R^2 = 0.939$ and $b = 243.54$ and $c = 53.674$. BNynes display a similar trend in the stress–strain curves from tensile stress in the zigzag direction as in the armchair direction, shown in Figure 2b. It can be seen that around 50% strain, once again the BNynes of various $L$ cease their initial stretching phase and load up stress until failure. As Figure 3a demonstrates, the ultimate strengths of BNynes in the zigzag direction are inferior to those of the same BNyne in the armchair direction. This is due to the way stresses are aligned along linker chains, as will be shown in the following sections. However, the same linear dependence of ultimate strength on the lattice length can be seen in this relationship, although with parameters $b = 274.54$ and $c = -5.7362$. This results in an $R^2 = 0.979$, showing that this is a robust fit to this relationship. The steeper slope for this equation in the zigzag direction indicates that not only is the ultimate strength much less for all values of $L$, but that the strength decreases more sharply as $L$ increases and the lattice spacing gets larger. The direction of stresses along the linker chains is what causes this lowered strength, as the chains in zigzag formation do not support pure linear stressing, with the angled chains instead introducing shear stress into the structure, causing earlier failure. This phenomenon is shown clearly in the proceeding section on failure in BNynes.

Shown by the tensile strength results, as the lattice length increases due to a larger number of linkers between BN hexagonal rings it creates a less mechanically robust structure; a claim which is further supported by the trend shown in Figure 3b. It can be seen from this figure that every $L$-BNyne is much less stiff than pristine BN, which has an elastic modulus on the order of 716–950 GPa.\cite{20} This is due once again to the qualitative difference between BN and BNyne, which is the inclusion of triple-single-bond linkers which act similarly to a spring with a different constant than that of the base hexagonal unit. Figure 3b shows the relationship between $a^{-1}/C_0 L$ and elastic modulus, which forms a trend similar to the one for ultimate stress. Elastic modulus here is defined as the change in stress over the change in strain, for small deformations ($e < 5\%$). A trendline is fitted to each data set in Figure 3b to represent the stiffness of each $L$-BNyne as a function of the inverse of the scaled lattice length with the following equation:

$$Y_L = b a^{-1} + c$$

For armchair BNynes, the fit is superb as $R^2 = 0.999$, with parameters $b = 439.71$ and $c = 24.475$. While the strength of BNynes in the zigzag direction is lessened due to the quirks of
geometry, the opposite is true for the stiffness. Figure 3c depicts the elastic modulus of BNynes in the zigzag direction as a function of scaled lattice length. By comparing these values with those in the armchair direction, it is clear that the stiffness of zigzag BNynes is higher for all values of L. The trendline fitted to this data has a good $R^2 = 0.988$ and parameters $b = 395.27$ and $c = 73.893$. The increased stiffness of BNynes in the zigzag direction is related to their geometry, as the same diagonal linkers which account for decreased strength also have the effect of increasing the elastic modulus during tension. Similarly, the density-scaled specific modulus (density being the same for zigzag and armchair alike), although it keeps a linear trend, is overall of a higher value for zigzag BNynes, as can be seen in Figure 3c. As the chains between rings become longer, there is an associated decrease in the stiffness of the material, which is likely due to the increased flexibility afforded by the sparseness of cross-links between load-bearing chains. The elastic modulus is directly relative to the areal density in each L-BNyne, and to show this we define the specific modulus $Y_s$, as the modulus of elasticity divided by the scaled density:

$$Y_s = \frac{Y_L}{D_L}$$

(7)

Here, $Y_L$ is the elastic modulus of each L-BNyne. The graph of specific modulus versus linker number is plotted in Figure 3c, where we can easily see that, when areal density is accounted for, the stiffness of each BNyne is approximately the same. This is due to accounting for the amount of area each “spring” covers of the total sample.

The toughness of a material is the amount of energy absorbed during fracture. Accordingly, the toughness of a material is a good metric of how useful it could be in high-impact or high-stress environments. Figure 3d displays the toughness of BNynes; from this figure, it can be seen that toughness decreases drastically for $L$ greater than 1 ($L = 1$ is the first data point). A trendline is fitted to each set of data to represent the toughness of each L-BNyne as a function of the inverse of the scaled lattice length with the following equation:

$$T_L = b + a_L^{-1} + c$$

(8)

Armchair BNynes show larger toughness values compared with their zigzag counterparts, with the fitted trendline having $R^2 = 0.937$ and parameters $b = 294.81$ and $c = -23.631$. For toughness, there follows a similar relationship as that displayed for strength, wherein the values for zigzag BNynes fall far behind those of armchair BNynes, demonstrating that these materials are strongly anisotropic. The relationship between toughness and scaled lattice length is shown in, where it is fitted with a trend having $R^2 = 0.949$ and parameters $b = 198.19$ and $c = -22.453$. These parameters demonstrate the reliance of the toughness of each BNyne as a function of the inverse of the scaled lattice length, and thus the number of triple-single-bond linkers. The fact that the slope of the line is far less than the equation for armchair BNynes demonstrates exactly how anisotropic this material is when it comes to toughness. It is easily seen from these figures that strength, stiffness, and toughness all sharply decline after 1-BNyne, while the properties are more similar for $L$ values of 4, 5, and 6. This is due to the great relative change each linker structure introduces in structure for L-BNynes from 0 to 1 and 1 to 2 when compared with the structural changes going from 4 to 5, 5 to 6, etc.

The ultimate strength and toughness of zigzag-oriented BNynes are inferior to those of armchair BNynes of the same number of linkers, but the Young’s Modulus is superior, indicating that these materials are uniquely anisotropic. For BNynes, the zigzag orientation is shown to be notably stiffer yet weaker (in terms of both strength and toughness) than the armchair orientation. However, in both cases 1-BNyne is much superior to the other BNynes, with much less differentiation among higher $L$ values. However, to uncover more clues as to the behavior of BNynes under tensile failure, further investigation is needed. Thus, after characterizing the basic mechanical properties of BNynes, it would be beneficial to get a firm grasp of the mode of failure observed in BNynes along the two principle directions by taking a close look at the failure process.

3.2. Failure Mechanism of BNyne

To further understand the reasons for the mechanical properties displayed by BNynes along either direction, it is
highly beneficial to take a close-up look at how deformation and failure occurs in BNynes. For each failure, it was noticed that the bonds to break are those in the hexagonal rings, specifically those bonds which do not run parallel to the direction of tension. This causes the structure to degenerate into individual strands of boron–nitrogen chains; this process we will refer to as “unraveling.” To better observe this phenomenon, Figure 4 displays the entire process of failure from the beginning of loading until full unraveling. The failure of 4-BNyne is displayed as a representative of the failure of BNynes in the armchair direction in Figure 4. The stages of pre-failure are shown in Figure 4a and b. These two images are indicative of the initial and secondary loading phases displayed in Figure 2. For the initial loading phase, the sample stretches noticeably while the force increases. After the critical strain, the sample drastically reduces the rate of stretching while stress builds up until failure, such that strain increases imperceptibly until a ring linker fails and the failure cascades rapidly. In Figure 4c, the initial sudden failure is displayed, a close-up of which is shown in Figure 5. It can be seen that a single layer of linkers snap before any further damage is done, and as Figure 4d and e illustrate, the material begins to unravel until a mere one or two single chains are connected. These images allow one to see clearly that the linear chains which run across the sample in the x direction support the majority of the stress, with very little stress supported by the cross-linkers which connect hexagonal rings oblique to the x direction. Figure 6 details an extreme close-up of the bond structure at failure, making it obvious that failure occurs from the breaking of the hexagonal boron–nitrogen rings, while, as can be seen from Figure 4e, the linear BN chains are the last part of the structure to break. The two-atom, \( sp \)-hybridized bonds in the triple-single-bond linkers and resultant BN chains are quite strong along the line of force, with failure stemming from \( sp^2 \)-hybridized bonds which are not parallel with the tensile force. This specific mode of failure is due to the contribution of two factors: that the bonds in the chains are at least as strong as the bonds in the rings, and that the cross-links induce a shear component to the stress on the hexagonal rings, as can be seen from Supplementary Materials Figure S3. For the first factor, the bonds of the linear chains can

![Figure 5](image5.png)

*Fig. 5. Close-up of sudden onset failure in armchair 4-BNyne. Shown is a stress-map of 4-BNyne (a) before and (b) after the sudden failure onset.*

![Figure 6](image6.png)

*Fig. 6. Detailed flat close-up of sudden onset failure in armchair 4-BNyne. Shown is a bond-map of 4-BNyne (a) before and (b) after the sudden failure onset. Blue atoms are nitrogen, yellow represents boron.*
be approximated as having at least the tensile strength of the bonds in the hexagonal units if we consider them analogous to the single-chain form of carbon, carbyne, which has been shown to have similar strength to that of the hexagonal structure, graphene.\[^{[21]}\] It has been shown by ab initio calculations that B–N monochains are at least as stable energetically as C–C monochains.\[^{[22]}\] For the second factor can be seen in the stress map in Figure 5, the cross-linker chains contribute a compressive force (in blue) to the sides of the hexagonal units. This compressive force, coupled with the tension from the chains along the direction of tension, leads to a shear stress (see Supplementary Materials Figure S3) which causes the hexagonal unit to first distort, as the bond angles change but not bond length. This distortion more easily allows the hexagonal unit to fail in such a way that the cross-linking chains become an “extension” of sorts for the chains already under tension (as is depicted in Figure 6), temporarily relieving stress in the linear chains while also distorting the entire structure, leading to further failure. This diagonal failure process is similar to the “shear bands” seen in the failure of ductile or quasi-brittle nanomaterials.\[^{[23]}\] Since the entire structure is held together by the hexagonal rings, BNynes with larger \(L\) values have fewer rings to support the tensile load, and thus fail at a lower load, as evidenced in Figure 3. For BNynes in the zigzag direction, we will show that, while there are similarities with ring failure and unraveling phenomena, the deformation of the sample up to failure is a markedly different process.

BNynes under the zigzag loading direction unravel in a similar manner when compared with the armchair direction; however, even for larger values of \(L\) there is no orderly initial row of broken linkers as is seen for the armchair direction for BNynes. This is due to the different way stress accumulates for the zigzag mode samples, which in turn leads to a different mode of destruction upon failure. The deformation, failure, and subsequent unraveling phenomenon are shown in Figure 7. As the material is stretched along the \(x\) direction, it undergoes a far larger decrease along the \(y\) direction (perpendicular to tension direction) than occurs for BNynes in the armchair direction. The linear chains which support the majority of the stress for the armchair BNynes are now along the \(y\) direction, and during the tensile process they support no stress, instead bulging out of plane as the tension causes the oblique cross-links to be stretched along the \(x\) direction, as is shown with a close-up view in Figure 8. This figure is colored based on the absolute value of \(z\) for each atom, with the initial plane of the sample set as \(|z| = 0\). The stress-map in Figure 7 demonstrates that most of the tensile stress is concentrated in the hexagonal units, while the bulging out-of-plane cross-linkers are subject to compressive stress due to the squeezing effect in the \(y\) direction. Similar to the behavior in the armchair direction, the material fails at the hexagonal units, as the oblique chains are pulled apart from one another by the strong force in the \(x\) direction caused by the tensile process, as can be seen by the close-up bond stress map in Figure 9. The similarity of the failure of the
zigzag BNyne to the process shown in Figure 4 demonstrates that, although zigzag-oriented BNynes is stiffer and weaker than armchair-oriented, they still undergo similar modes of deformation and failure, with the breaking of cross-linkers causing an unraveling phenomenon in each case, although the directionality of the remaining chains creates a very clear difference in strength, toughness, and stiffness, as shown in the previous sections. This breaking of the cross-linkers is shown in detail in Figure 9a and b, and one can also clearly see the bulging-out-of-plane phenomenon occurring for the linear chains along the y direction which are highlighted in Figure 8. Carefully observing the failure process allows for better expectation and design when using this strong new material in future applications.

4. Conclusions

Due to the recent meteoric rise in interest of hexagonal BN materials, it is therefore important to characterize the properties of its allotrope, BNynes, in order to better understand how to utilize them in the nanodevices. Here, molecular dynamics simulations are performed to investigate the mechanical properties and failure patterns of various BNynes under the tensile loading. Simulation results indicate that BNynes in both the armchair and zigzag directions undergo two distinct phases of deformation leading up to failure, and experience similar unraveling behavior after failure. It is shown that 1-BNyne is consistently much stiffer, stronger, and tougher than BNynes with higher numbers of triple-single-bond linkers, while less distinction is made among other L. However, BNyne shows strong anisotropy for the same number of acetylene-like linkers, stiffer yet weaker in the zigzag direction than the armchair direction. Linear theoretical analyses are developed to relate the strength, stiffness, and toughness of the BNyne to its scaled lattice spacing, enabling us to develop simple scaling laws for L-BNynes of any size. With these intriguing findings in mind, it can be envisioned that BNynes can be considered a light but tough multi-responsive material in the nanodevices.


