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ATOMISTIC SIMULATION TO STUDY DEFECTIVE NANOFILLERS

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Abstract - *Boron nitride (BN) is a 2-D Nano filler in which Boron (B) and Nitrogen (N) atoms are equal in number. h-BN has exceptional mechanical properties, exceptional thermal conductivity and a wide band gap (5-6eV), due to which it can be used in various applications. In this thesis, an atomistic model of h-BN is developed in molecular dynamics ensemble and its properties are investigated. Pristine form of h-BN is impossible to produce, so atomistic simulations are performed to study defective Nano fillers. Here STW types of defect are introduced in h-BN and their mechanical behaviour is discussed. It is found that varying the geometrical parameters, mechanical behaviour of h-BN is changed. Depending on number of defects, their nearest neighbour distances and orientation, various simulations is performed to find good results. Effect of STW defects on failure morphology is also discussed. Defects introduced in h-BN also changed failure morphology from brittle to mild ductile.*

***Key Words*: Boron nitride (BN), BN nanotubes (BNNTs), Chemical vapor deposition (CVD), chemical blowing, h-BN nanofillers.**

1. INTRODUCTION

Boron nitride (BN) is a binary compound consisting of an equal number of boron (B) and nitrogen (N) atoms. BN crystallizes either as a hexagonal layered structure or as a tetrahedral linked structure. Due to its white color and slippery properties hexagonal boron nitride (h-BN) is also known as white graphite or graphitic boron nitride. It was first synthesized as boron nitride nanotubes (BNNTs) in 1995. BN Nano fillers like BN nanotubes (BNNTs) and Nano sheets (BNNSs) have a hexagonal closed packed atomic configuration. BN Nano fillers (BNNT or BNNS) exist in the hexagonal form with alternatively placed boron (B) and nitrogen (N) atoms as shown in figure1.

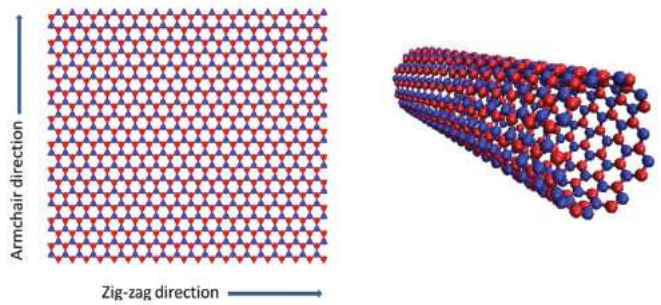

Fig -1: atomic configuration of single layer BNNSs and single walled BNNTs. Red and blue dotscorrespond to boron and nitrogen atoms respectively.

1.1 PRODUCTION METHODS

There are number of methods used for production of h-BN nanofillers.

- Exfoliated from bulk BN crystals either by mechanical cleavage/exfoliation or by a chemical solution derived method.
- Chemical vapor deposition (CVD)
- Sonication
- Ball milling
- High-energy electron beam irradiation
- Reaction of boric acid and urea
- A metalcatalyst free approach
- Chemical blowing (a mass production technique that relies on generating large bubbles of BNH or BNCH from a precursor ammonia borate compound)
- Using substitution reaction
- Via micro-fluidization
- Via laser ablation.

1.2 PROPERTIES AND APPLICATIONS OF h-BN

- These are good electric insulators as compared to carbon based nanofillers.
- Highly stable against oxidation at high temperatures and are chemically and structurally more stable as compared to carbon based nanofillers.
- Their thermal conductivity is in range of 1700-2000 W m^{-1} K^{-1}.
- They show deep ultraviolet photoemission and good amount of piezoelectricity.
- They have neutron absorption capacity
- They can adsorb hydrogen at ambient temperature.

Some applications of BN nanofillers are – Nano-sensors, bio-sensors, biomaterials, for corrosion resistant and thermally stable composites, to treat neurogenetic disorders, to treat cancer, in optoelectronics and tribology.

2. ATOMISTIC MODELING TECHNIQUES

2.1 Experimental techniques

Though experimental techniques are costly and time consuming, still these experiments are considered as a realistic tool for characterizing the behavior of materials. Some experimental techniques are-

- Transmission electron microscopy (TEM)
- Atomic force microscopy (AFM)

There are some limitations in estimating the localized mechanical or thermal behavior of these nanofillers at the atomistic level.

2.2 Modeling techniques (computational techniques)

Due to limitations of time and cost associated with experimental techniques, computational techniques are emerging as effective tools for predicting the mechanical as well as thermal behavior of these nanofillers. Atomistic simulations are not substituting experiments but are complementing them at the Nano scale.

- Continuum based finite element models
- Density functional theory
- Molecular dynamics based simulations

2.2.1 Molecular dynamics based approach

In this approach atoms are treated as classical particles. The atomic position and potential energy of the system help in computing the atomic forces that are further used in Newton's equation of motion. The relationship derived from the Newton's second law of motion is used for updating the position, velocity and acceleration of each atom in the system at an integrated time step.

$$m_\alpha a_\alpha = F_\alpha = -(\partial E/\partial r_\alpha)$$

α = 1, 2... N

N – Total number of atoms

m_α – mass of atoms

r – Position of atoms

F – Time dependent force acting on them

E – Potential energy

E' consists of an internal part (E^{int}) that accounts for the interaction between the atoms and an external part (E^{ext}) that accounts for external fields and constraints. E & F are functions of position and velocity vectors of atoms. position and velocity vectors are updated after each time step, usually by using any of the numerical integration algorithms. But the Velocity-Verlet algorithm (an extension of Verlet algorithm) is the most widely used integrating scheme in MD based simulations. The position vector 'r' at any time t and after an increment Δt, for any atom involved in the simulation can be expanded as a Taylor series expansion as given by equation

$$r(t+\Delta t) \approx r(t) + \dot{r}(t)\Delta t + \frac{\ddot{r}(t)\Delta t^2}{2} + \cdots$$

The updated velocity vector after time 't + Δt' can be easily obtained with the help of the Velocity-Verlet equation as:

$$v(t+\Delta t) = v(t) + \left(F(t+\Delta t) + \frac{F(t)}{2m}\right)\Delta t + \cdots$$

Success of any MD based simulation entirely depends on the interatomic potential employed for simulating the bonded as well as non bonded a interactions. Interatomic potentials are mathematical expressions for estimating the potential energy (E) of the system of atoms. Commonly used interatomic potentials are Tersoff, LJ, the embedded atom method (EAM), REBO and AIREBO. But tersoff type potentials are commonly used for simulating the mechanical and thermal behaviors of BN nanofillers.

The Tersoff potential can be expressed mathematically as given by equation

$$E = \sum_i E_i = \frac{1}{2}\sum_{i \neq j} V_{ij}$$

Where

$$V_{ij} = f_c(r_{ij})[a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})]$$

E – Total energy of system

E_i – site energy

V_{ij} – bond energy

R_{ij} – distance between atoms i and j

f_R & f_A – repulsive and attractive part of pair potentials

f_c and b_{ij} – cut off function and bond order function

f_R and f_A are expressed as

$$f_R(r_{ij}) = A \exp(-\lambda_1 r_{ij})$$

$$f_A(r_{ij}) = -B \exp(-\lambda_2 r_{ij})$$

These interatomic interactions are restricted within a cut-off distance with help of cut off function f_c and it avoids excessive computational cost. It is proposed in such a way that the energy of interaction between atoms as a function of distance will gradually reduce to zero. The mathematical expression of cut-off function proposed by Tersoff is:-

$$f_c = \begin{cases} 1, & r_{ij} < R_{ij} \\ \left(1/2\right) + \frac{1}{2}\cos\left(\frac{\pi(r_{ij} - R_{ij})}{R_{ij} - S_{ij}}\right), & R_{ij} < r_{ij} < S_{ij} \\ 0, & r_{ij} > S_{ij} \end{cases}$$

Cut-off distance (R_{ij}) is chosen in such a way that only first neighbor's shell is included

Terms which act to limit the range of interaction to the first neighbor's shell is included in b_{ij} (bond order) and can be expressed by as

$$b_{ij} = (1 + \beta^{n_i}\xi_{ij}^{n_i})^{-\frac{1}{2n_i}}$$

$$\xi_{ij} = \sum_{k \neq i\,j} f_c(r_{ik})g(\theta_{ijk})\exp[\lambda_3^3(r_{ij} - r_{ik})^3]$$

$$g(\theta_{ijk}) = 1 + \frac{{c_i}^2}{{d_i}^2} - \frac{{c_i}^2}{[{d_i}^2 + (h_i - \cos\theta_{ijk})^2]}$$

In addition, the interatomic force between atoms can be estimated by the expression given by equation.

$$F(r_{ij}) = -\frac{\partial V_{ij}}{\partial r_{ij}}$$

In this study, the cut-off function $fc(r_{ij})$ has been optimized in such a way that the lower cut-off distance defined by Rij has been made equal to higher value of cut-off distance Sij. and the cut-off function used in the range of R_{ij} and S_{ij} has been removed as expressed by equation.

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} < S_{ij} \\ 0, & r_{ij} > S_{ij} \end{cases}$$

This reduced cut-off function takes only a single value for cut-off distance.

To study tensile mechanical behaviour of BN nanofillers, simulations were performed in two phases.

i. In first phase, effect of cut-off function on potential energy and bond forces between a pair of boron and nitrogen atom is analyzed.
ii. In second phase mechanical behaviour in terms of fracture stress, strain and Young's modulus was studied with the help of optimized cut-off function.

3. WORKDONE

At first reduced size atomic system of BN is taken in which three bonded nitrogen atoms surround the boron atom as shown in fig. It ensures that bond angle remains constant.

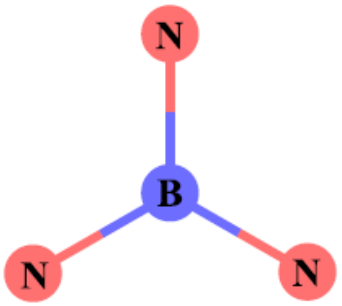

Fig -2: Reduced atomic system of BN.

In this study, tersoff potential parameters proposed by Sevik are used and simulations were performed to predict mechanical behaviour with optimised cut off function. MD simulations were carried out in large-scale atomic/molecular massively parallel simulator (LAMMPS) which is developed by Sandia National Laboratories. For performing simulation, a sheet of approximate size of 50×52 Å containing 960 atoms was created with a bond length of 1.45 Å.

Initially sheet was relaxed for 50ps at a constant simulation temperature of 300K. Integrations were performed with constant time step of 0.001ps. After relaxation uniaxial tension was applied at a strain rate of 10^{-9} s^{-1} in both armchair and zigzag directions at a temperature of 300 K.

Now simulations were carries out with different values of single cut-off distance using the optimised cut-off function assuming in plane orthotropic properties. Curves of stress and strain are shown in figure for both armchair and zigzag direction.

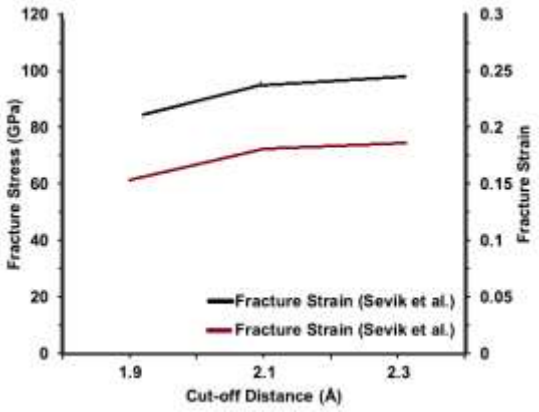

Fig -3: Fracture stress and strain in armchair direction

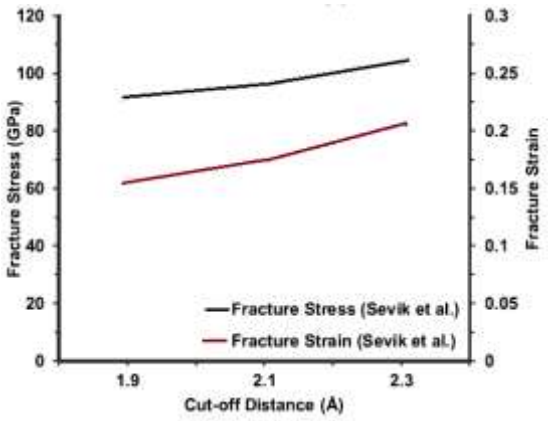

Fig -4: Fracture stress and strain in zigzag direction

It is seen that stress and strain are increasing with cut-off function and it is almost constant after a cut-off distance of 2.1 Å. For armchair direction fracture strain value is approximately 0.18 while for zigzag direction it is 0.2. Value of fracture stress for armchair direction is approximately 80GPa and for zigzag direction it is 90GPa.

These results are close enough to values estimated theoretically or using DFT techniques.

4. FUTURE WORKS PLAN

To simulate BN using various Tersoff potential parameters and comparing them with values estimated theoretically. As some defects are deliberately induced in nanofillers as they can enhance mechanical and thermal properties of nanofillers. But these defects are induced within a certain limit. So, defects will be induced in BN nanofillers and see the effects on various mechanical and thermal properties of BN.

REFERENCES

[1] Kumar R and Parashar A 2015 Atomistic modeling of BN nanofillers for mechanical and thermal properties: a review Nano scale 8 22–49.

[2] Tersoff J 1986 New empirical model for the structural properties of silicon Phys. Rev. Lett. 56 632.

[3] Tersoff J 1989 Modeling solid-state chemistry: interatomic potentials for multicomponent system Phys. Rev. B 39 5566.

[4] Kumar R, G rajasekaran ans avinash Parashar 2016 Optimised cut-off function for Tersoff-like potentials for a BN Nano sheet: a molecular dynamic study IOPScience nanotechnology 27(2016) 085706.

[5] Qi-lin X, Zhen-huan L and Xiao-geng T 2015 The defect induced fracture behaviors of hexagonal boron-nitride monolayer Nano sheets under uniaxial tension J. Phys. D: Appl. Phys. 48 375502.