CARBON NANOTUBE SOFT BODY ARMOR

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(TUBEY AND THE NANOS)

Department of Materials Science and Engineering · Capstone · ENMA490 · 2014

MOTIVATION

- Hard body armor is made from heavy ceramic plates, and is used to stop higher caliber rounds. [1]
- Soft body armor is made from 20-50 layers of Kevlar. [1]
- The average soldier already carries over 100 lbs in gear, bulky armor only makes this load more unwieldy. [2]
- A stronger material will allow for a lighter, less bulky vest. This will allow service men and women more flexibility and ease of movement.
- Stronger, lighter body armor has the potential to save lives.

Image taken from postgradproblems.com

Image taken from parade.condenast.com

MATERIALS SCIENCE ASPECTS

- **This project relies heavily on the mechanics of materials. Strong and lightweight CNTs used in conjunction with Kevlar fibers can create a very strong composite material.**
- **Characterization of mechanical properties through tensile testing required**
- **Knowledge of nanosized materials for applications and safe use of CNTs. PBA is used to strongly adhere CNTs to prevent aerolization.**
- **Many macro and nanoscale characterization techniques used:**
    - Macro: Optical microscopy, tensile testing, TGA
    - Nano: AFM, SEM
- **Fundamentals of macroprocessing used to scale up small samples into efficient vest manufacture.**

PREVIOUS WORK AND INTELLECTUAL MERIT

Previous Work

●Kevlar vests have been around since 1971. Various weave patterns and orientations have been used to increase impact resistance and energy dissipation.

●The use of shear thickening fluid in body armor is currently being investigated to reduce vest size.

●Dupont is currently working with CNT fabrics for body armor.

●Amendment II has a commercially available CNT body armor.

Intellectual Merit

●Our project is based off the research of Liu et. al. and their modification of cotton with PBA modified CNTs and the research of O'Connor et. al. who used NMP-CNT solution to increase mean strength of Kevlar from 4 to 5 GPa with 1wt% of unmodified CNTs. [3][4]

●Dr. Morgan Trexler at JH APL is doing research similar to O'Connor and has seen ~35% improvement [4]

●Our process was modified to fit Kevlar based on advice provided by Dr. Zhihong Nie.

ETHICS CONSIDERATION

Benefits

- **Strength increase of Kevlar bulletproof vests to potentially save lives of service men and women**

Concerns

- **Aerolization of CNTs upon vest impact is poorly understood; prolonged exposure to airborne CNTs is toxic**

- **Chemical process scale-up could produce large amounts of CNT containing waste fluids that must be disposed properly**

SAMPLE CHARACTERIZATION

- **Optical Microscopy**
  - Examined Kevlar 29 fibers at a magnification of 200x at each phase of the process
  - Determined success of etching step and coverage of fibers with CNTs

- Atomic Force Microscopy
  - Method failed; potentially due to the low stiffness of Kevlar fabric

- Scanning Electron Microscopy
  - Method failed due to sample charging
  - Future attempt would minimize charging through:
    - Finding E2 energy level
    - Using copper tape to ground the sample

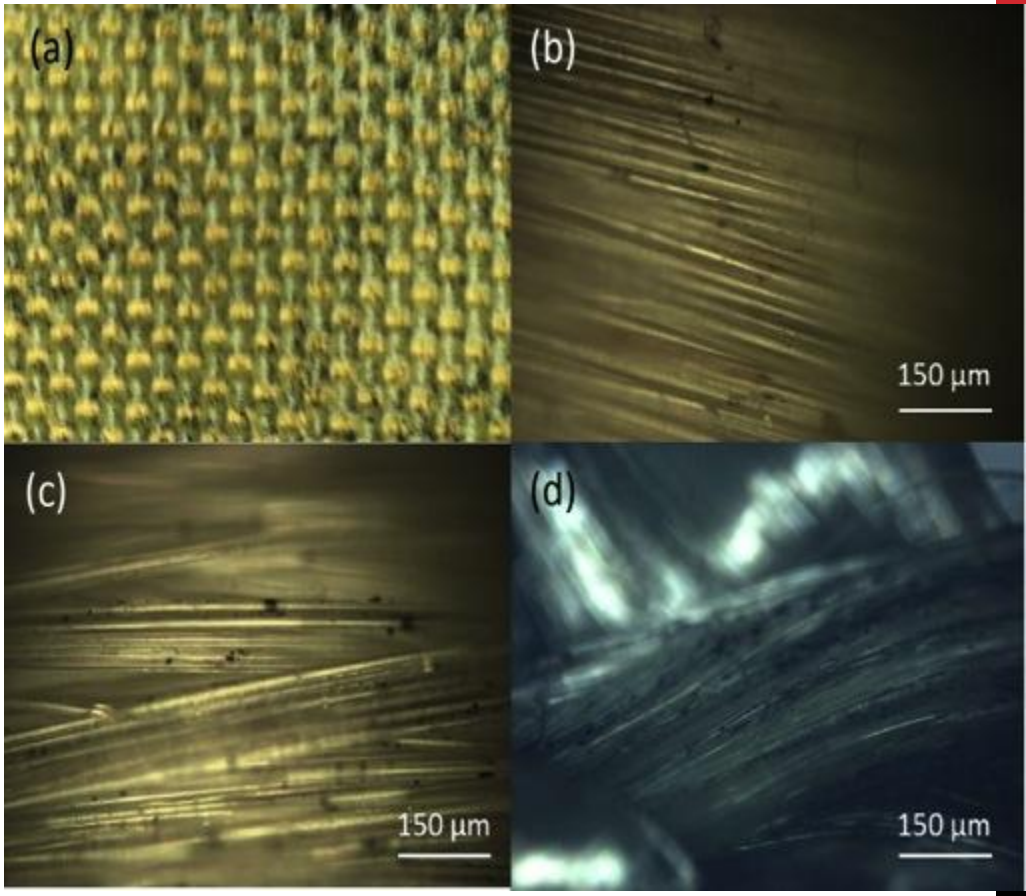


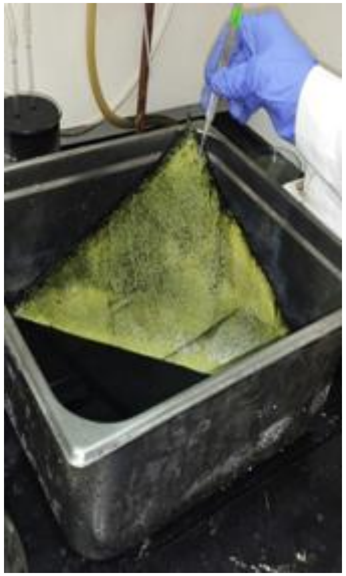
Figure 4. (a) Digital image of modified Kevlar 29.

Optical microscope images at a magnification of 200X of Kevlar 29 (b) before treatment, (c) after HCl etching, and (d) after full CNT treatment.

CHEMICAL PROCESSING

- Process modified from research done by Liu et. al.
- Sample Preparation: Kevlar pieces cut to size and sewn to prevent fraying. Briefly etched to create surface roughness.
- Part 1: SDS, KPS, and MWCNTs are added to a flask with H_20_2. Stirred in ice bath for 4 hours, and stored overnight in Fridge.
- Part 2: SDS, water, Butyl Acrylate, and CNTs from Part 1 added to flask under N_2. Ferrous Sulfate added to initiate reaction. The solution is gently mixed at 80^0C for 3 hours and 30 minutes.
- Part 3:CNTs from Part 2 filtered and sonicated. One third of the CNT solution is poured into a jar with THF and DVB. Solution sonicated and poured into a stainless steel dish. A Kevlar sheet is soaked for 30 minutes, then dried and cured.
- Samples are rinsed with distilled water to remove any loosely bound CNTs from material.

Part 2 Setup



Kevlar Dip

CHEMICAL MODELING

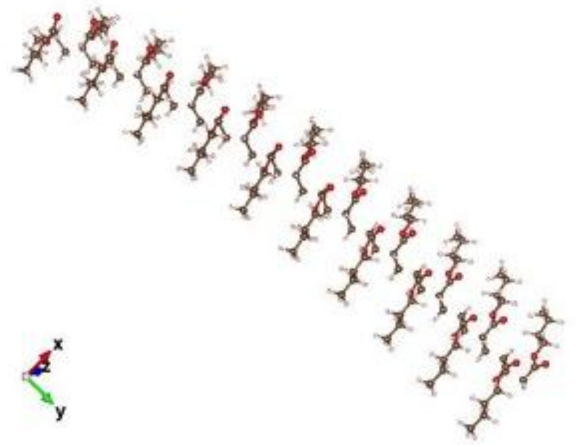
Objectives:

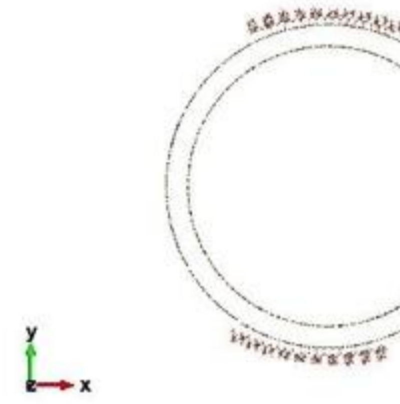
- Understand the surface grafting phenomena that occurs in our Capstone fabrication process
- Capture the reactivity of the CNT-polymer system and model the trajectory and chemisorption of PBA molecules on the CNTs

Method:

- ReaxFF methodology implemented in LAMMPS
- Generate a DWCNT-PBA structure and compile it into a data file
- Compile the input files: data.in, lammps.input, ffield.reax.mattsson
- Submit job to the queue
- Use NVE to equilibrate the system and NVT to obtain production state

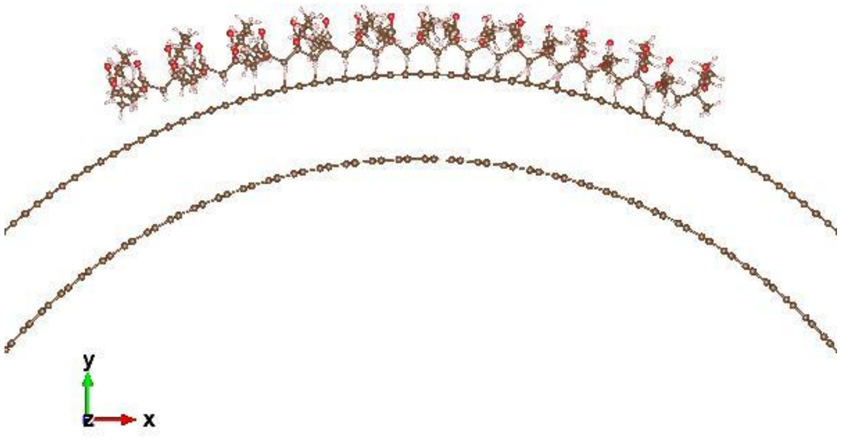
CHEMICAL MODELING



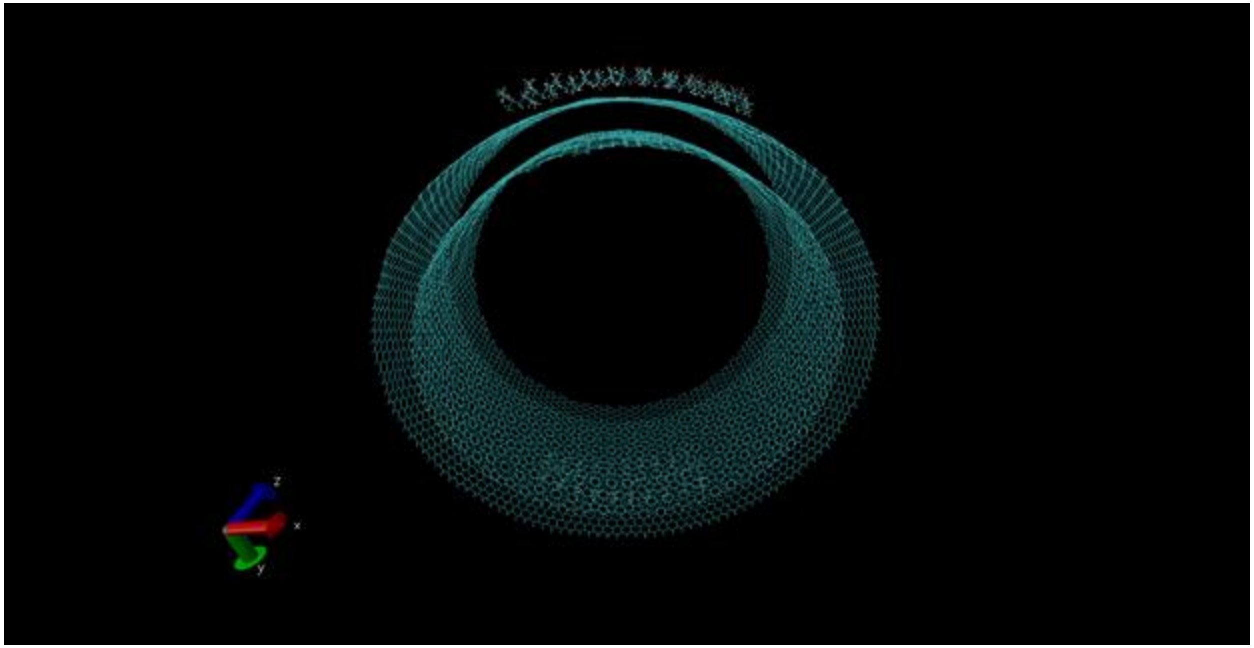


Finite PBA molecule = 422 atoms
DWCNT = ~10,000 atoms
    Inner tube – armchair config. (65,65)
    Outer tube – zigzag config. (130,0)
    Tube diameter – 10 nm
    Tube length – 40 Å

Total system size = 10,984 atoms



SIMULATION



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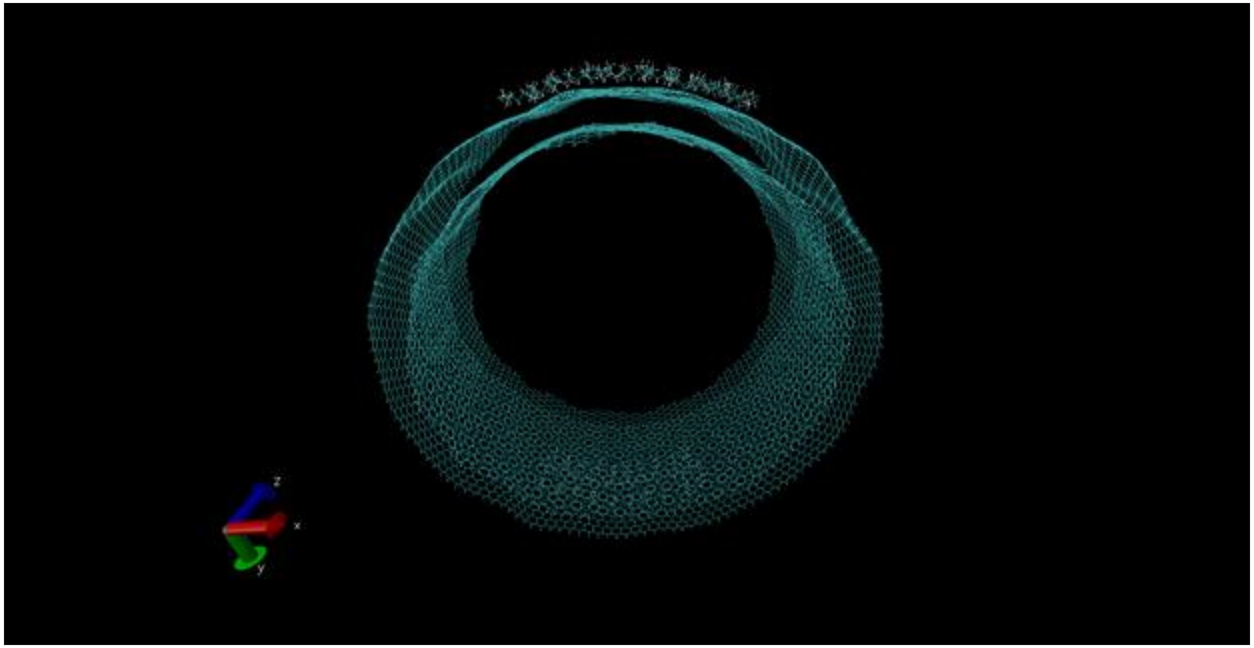

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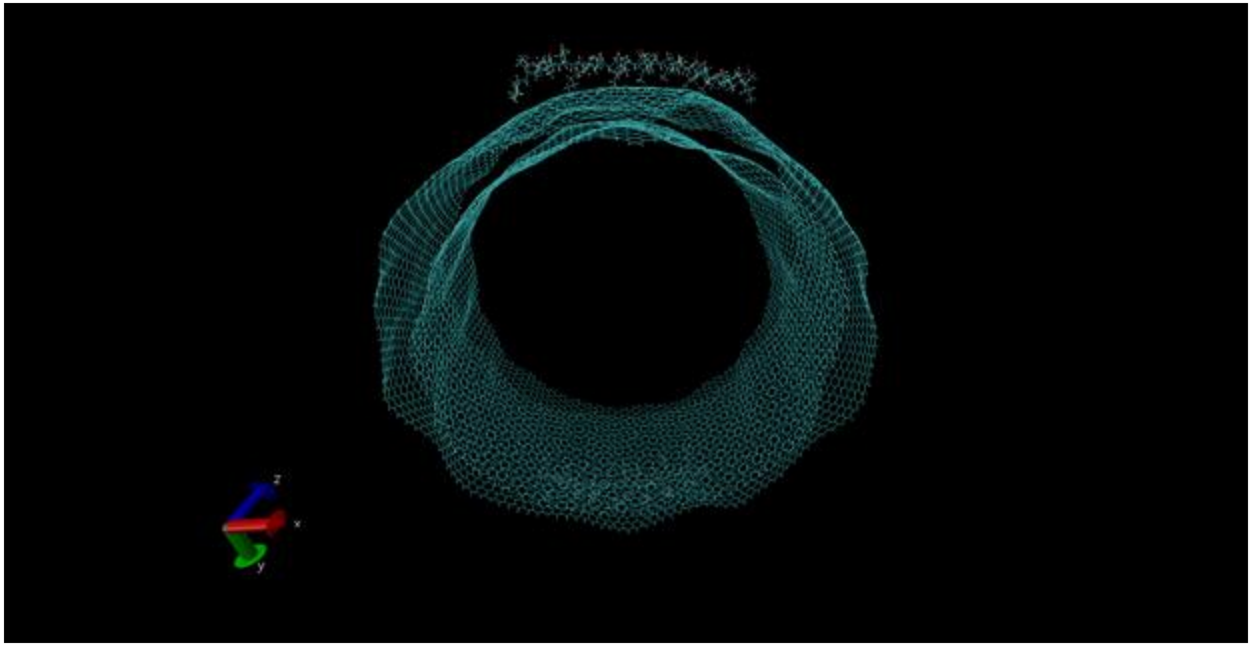

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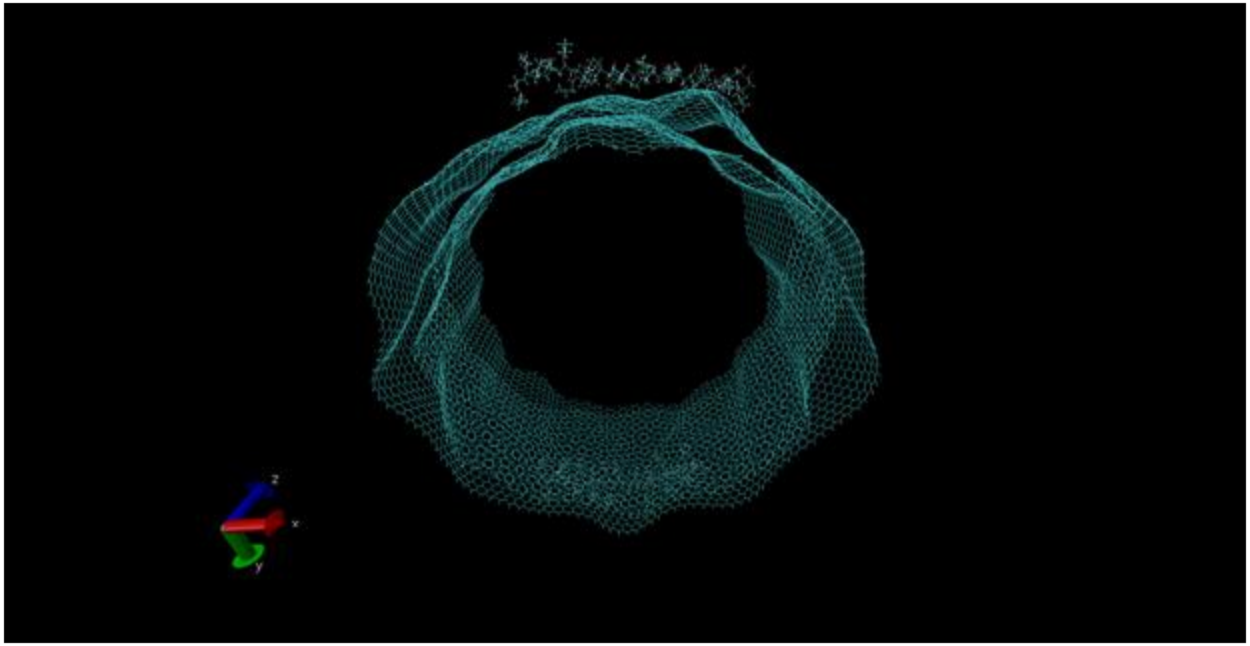

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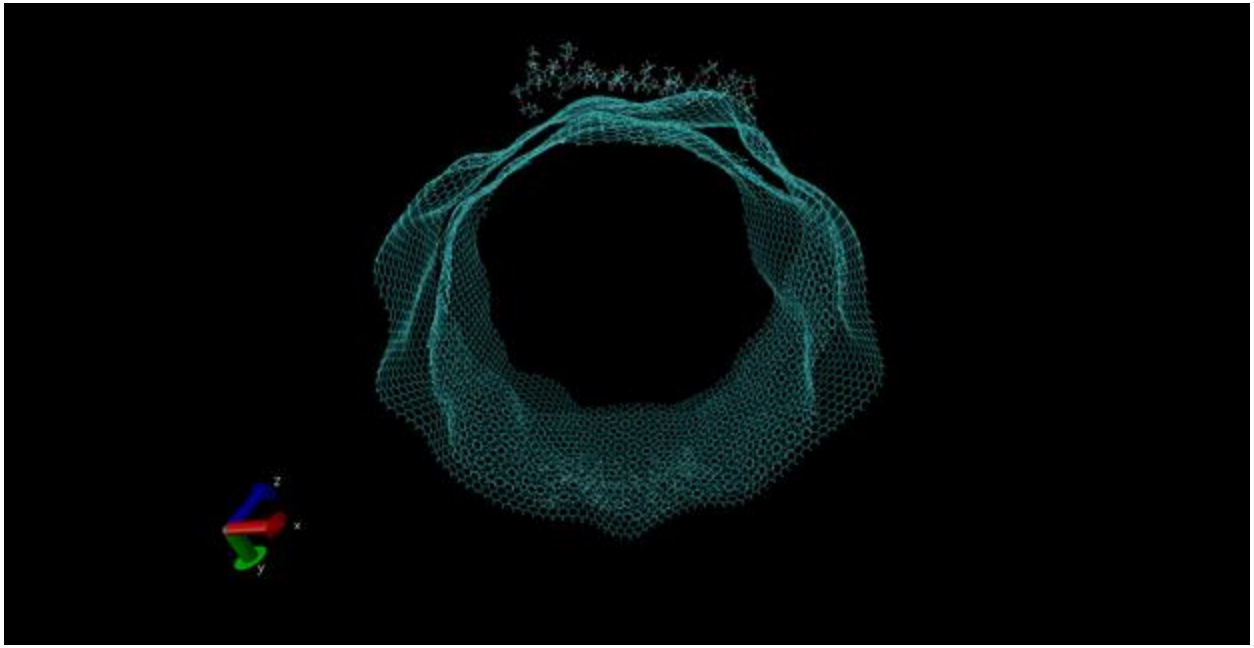

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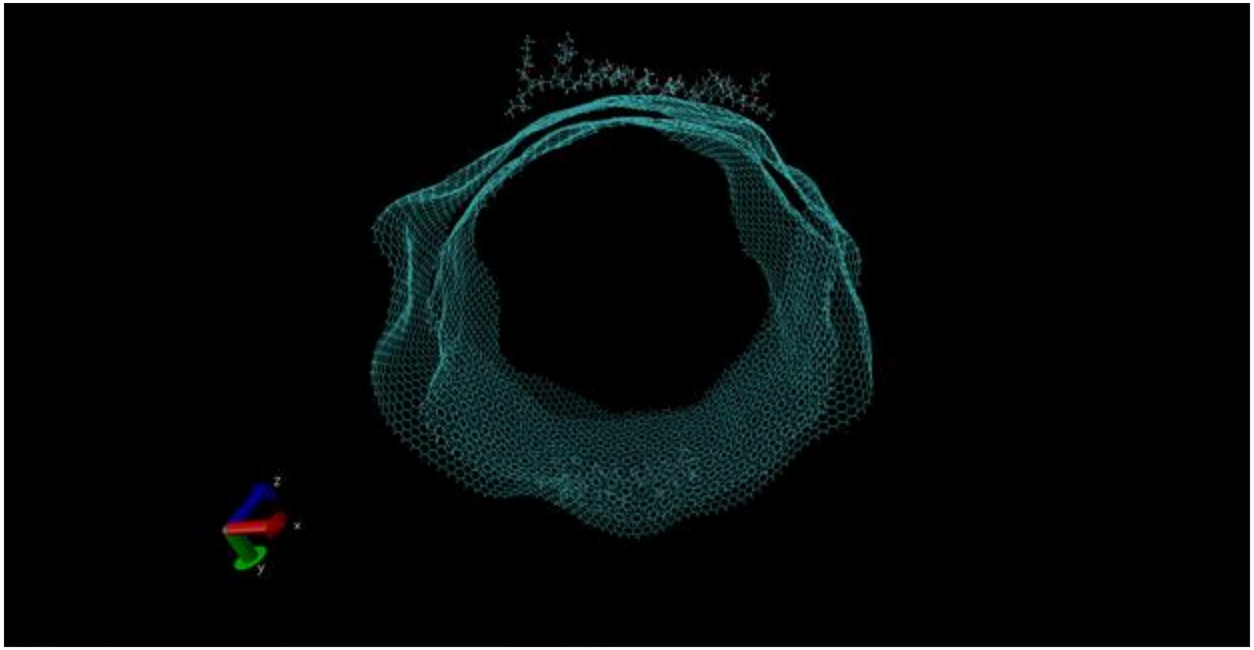

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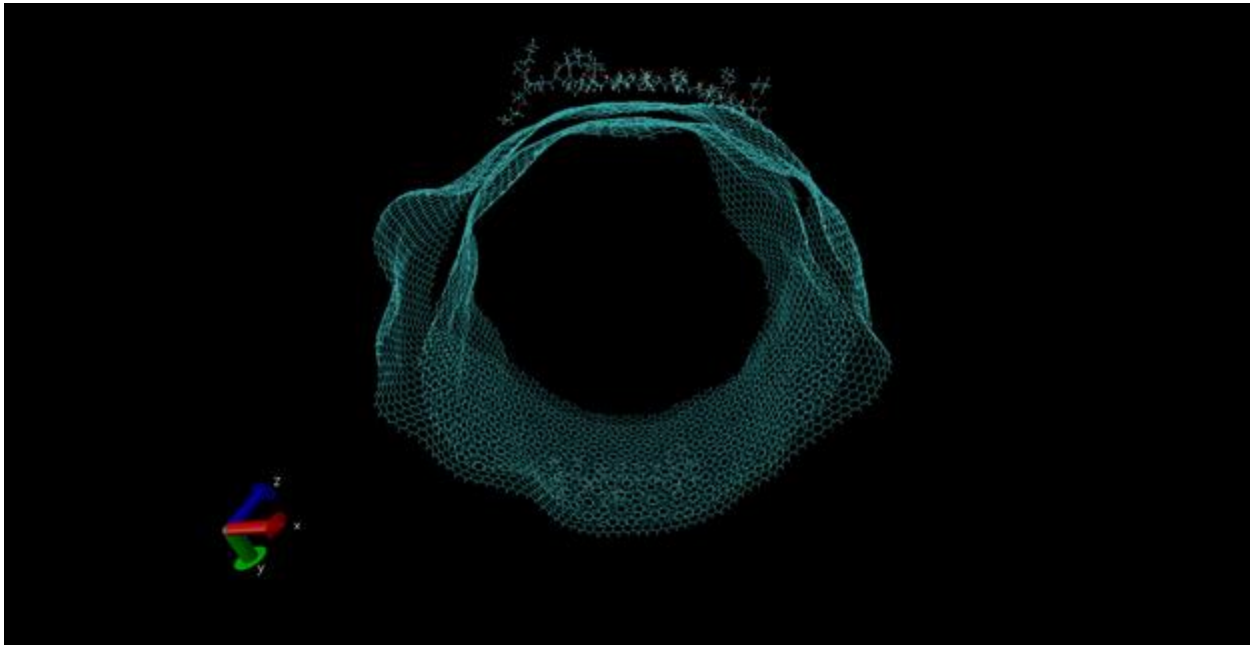

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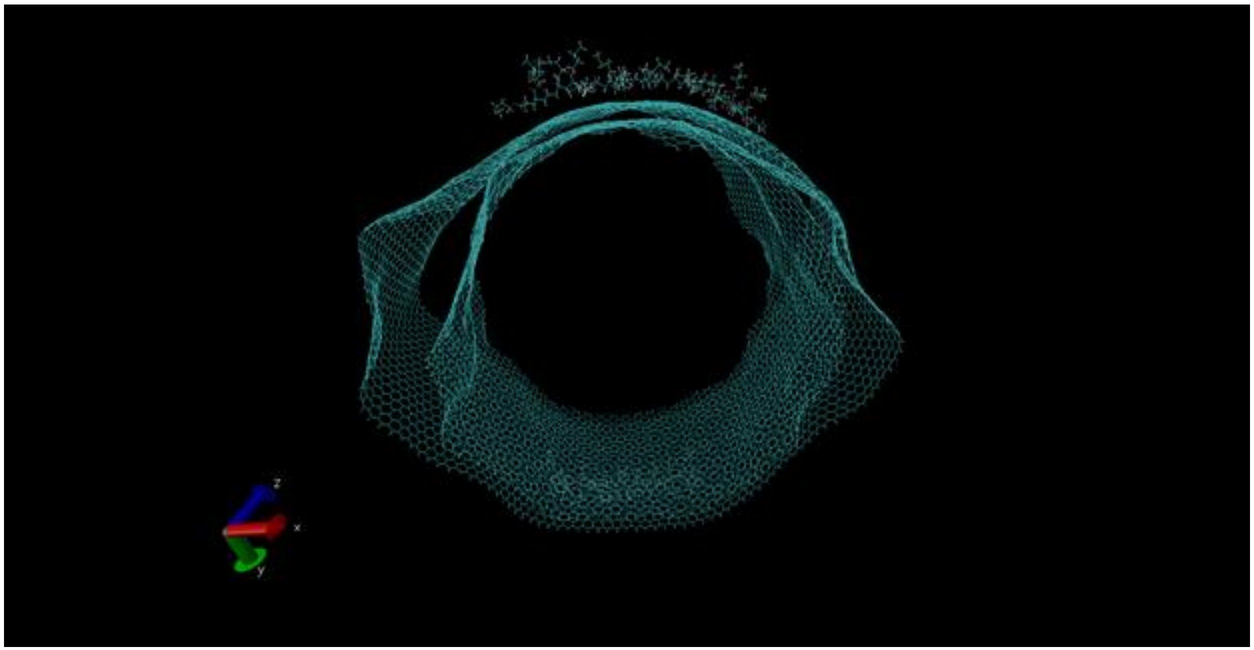
SIMULATION



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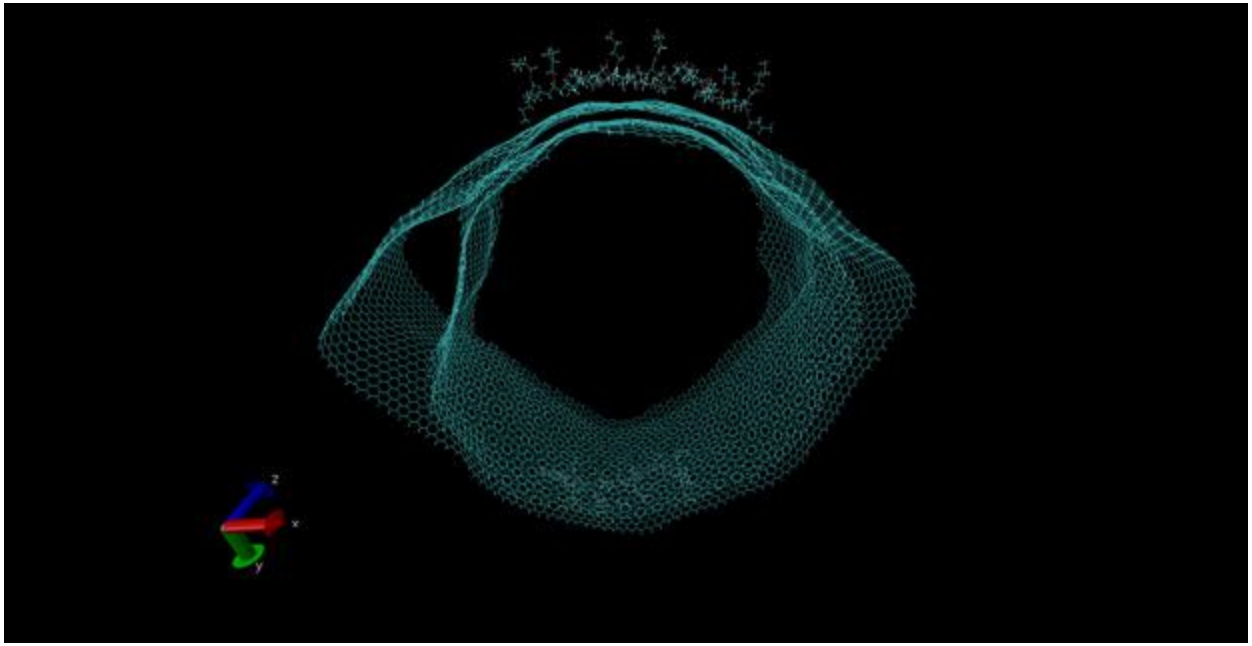

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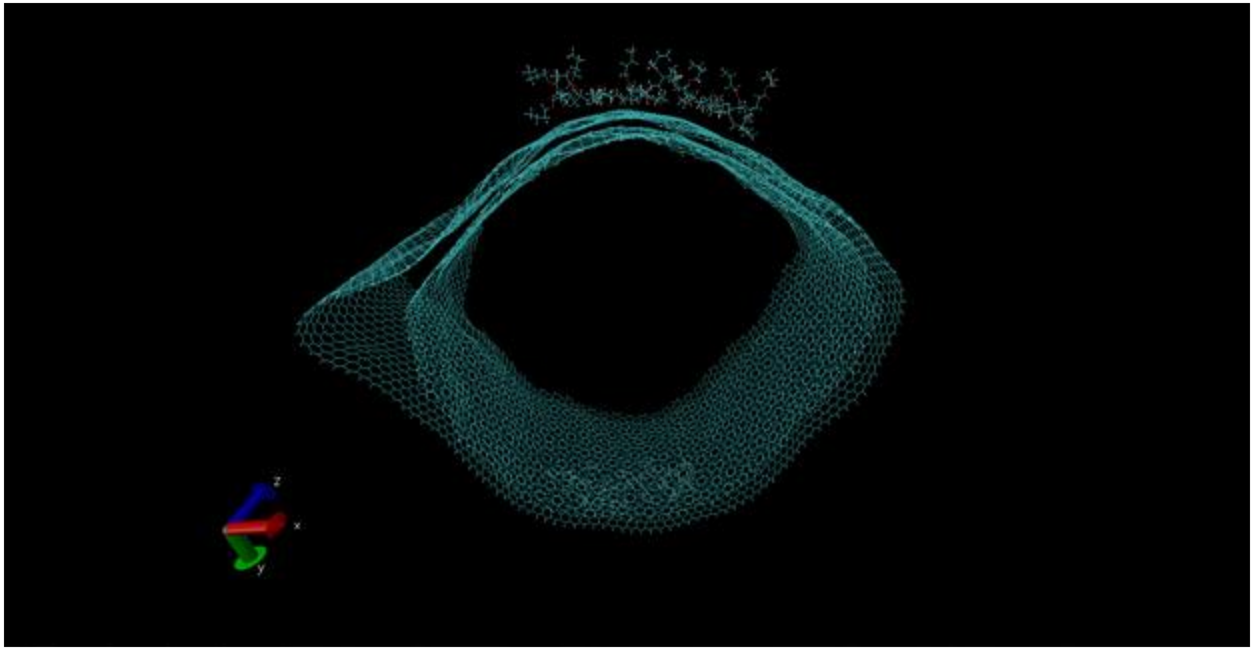

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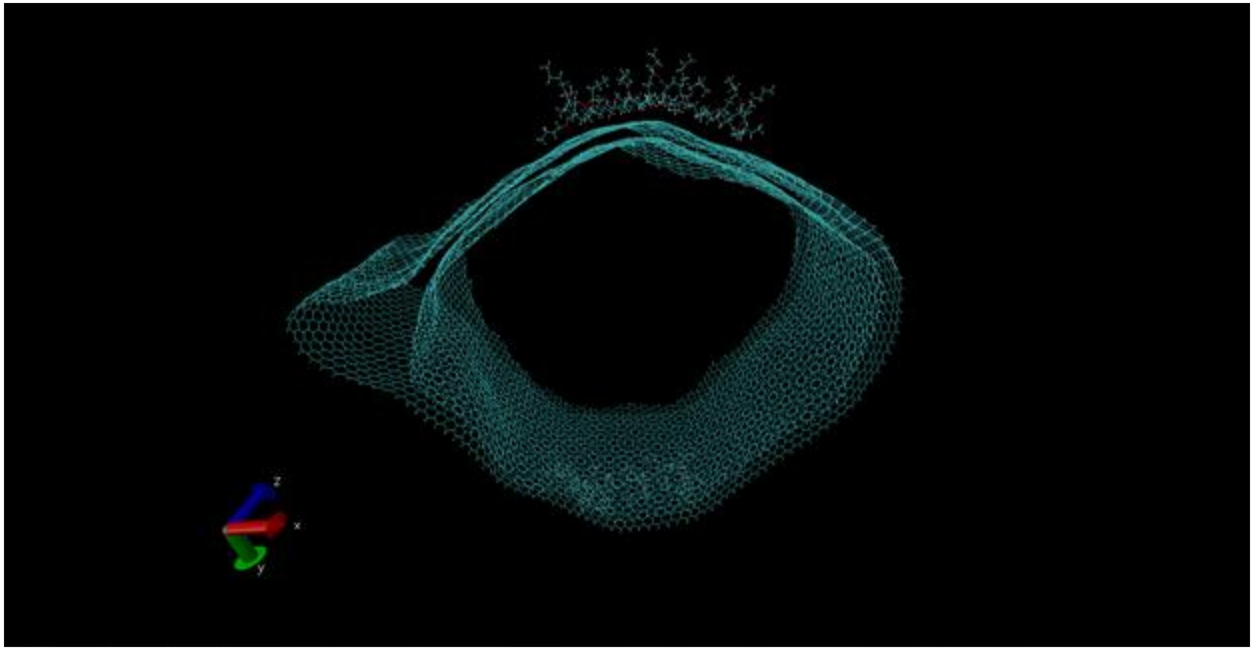

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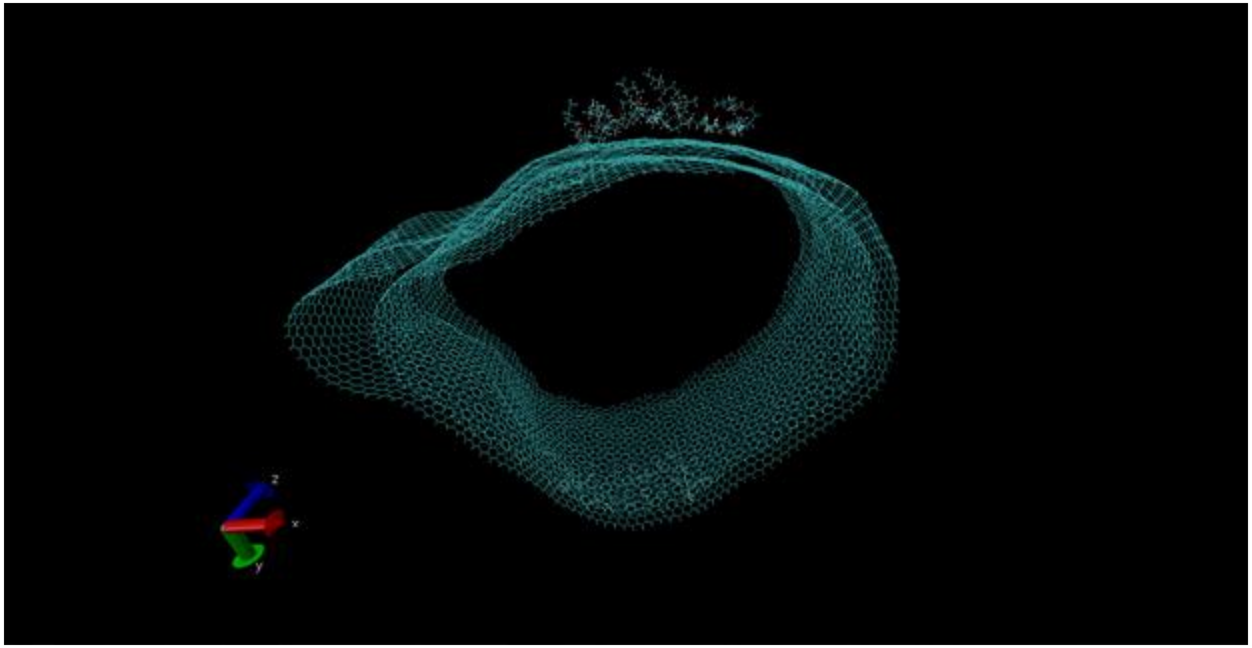

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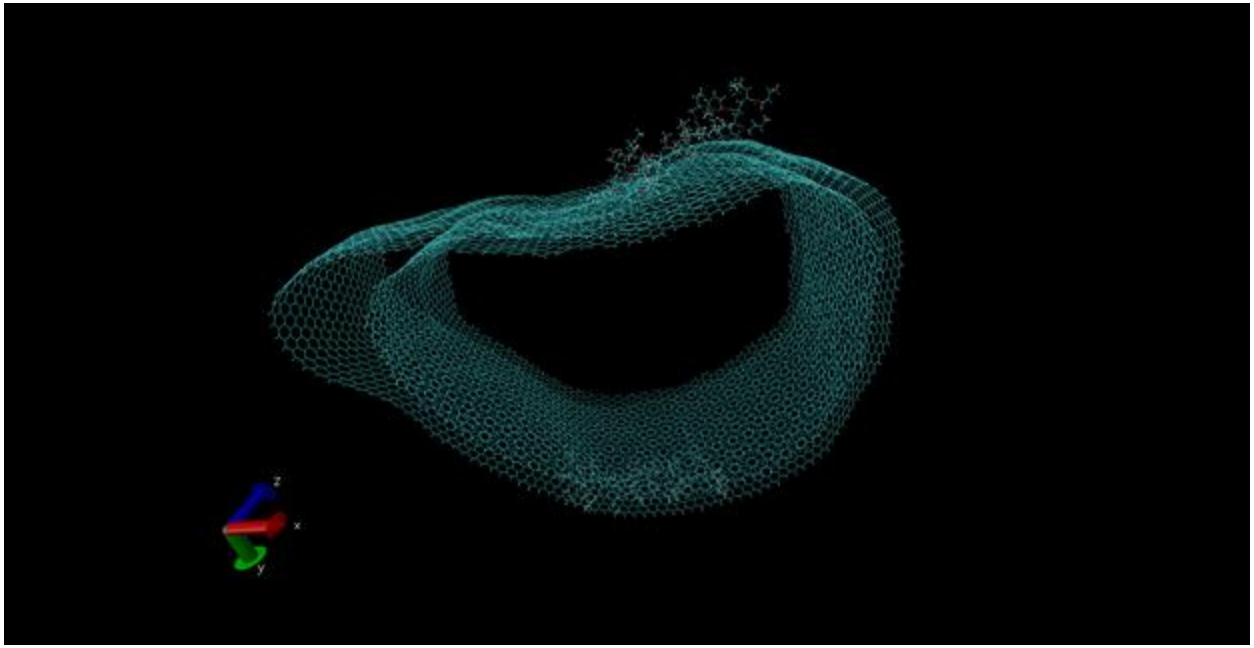
SIMULATION



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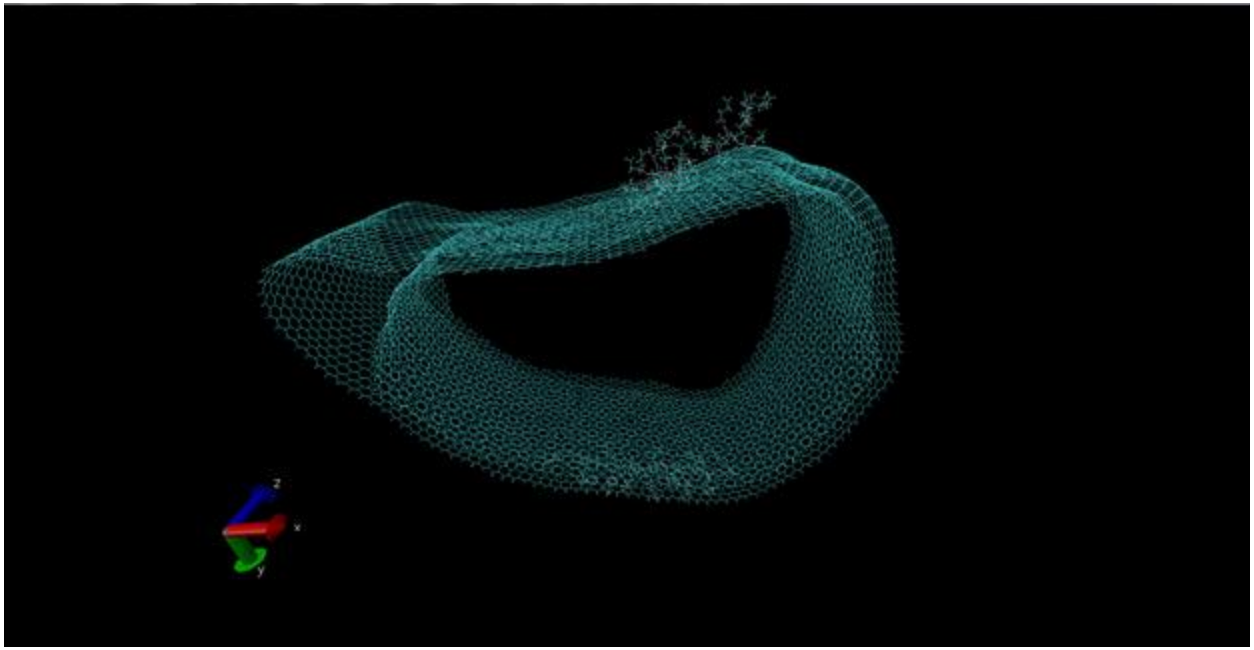

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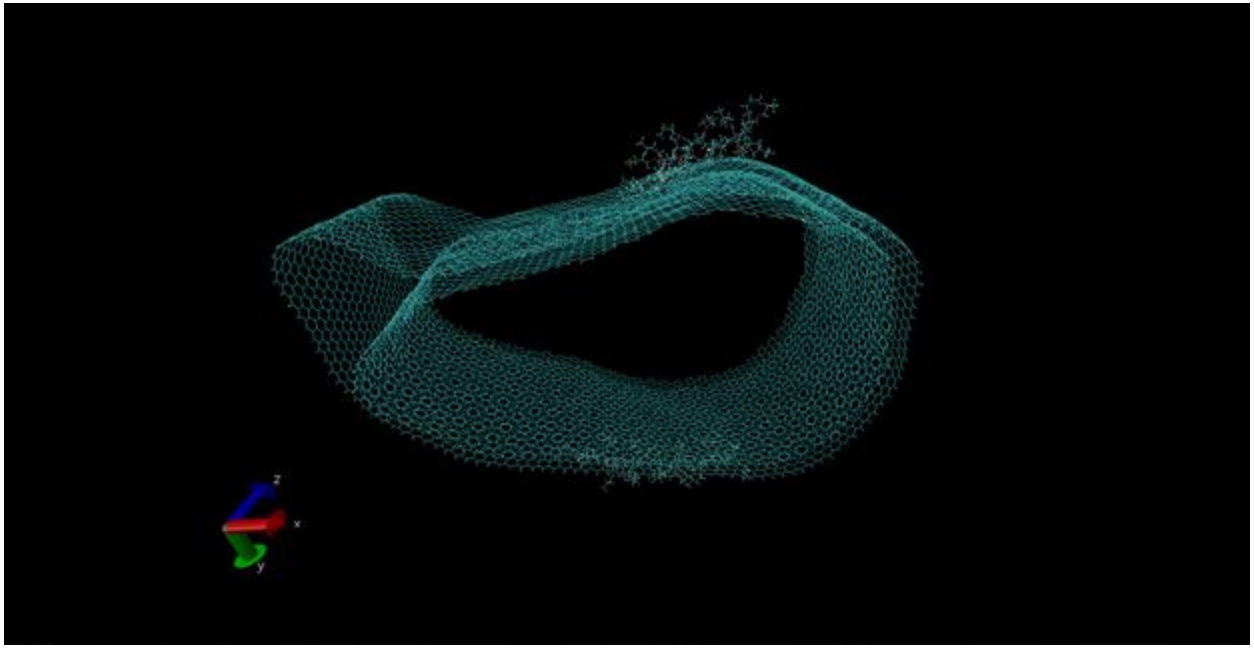

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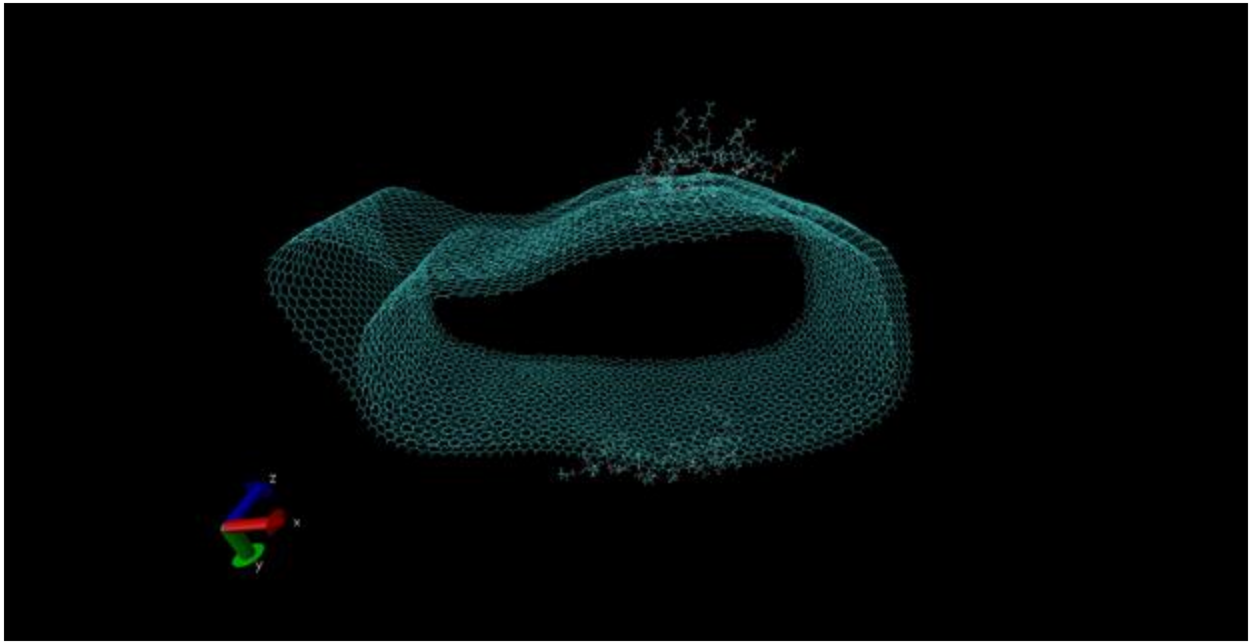

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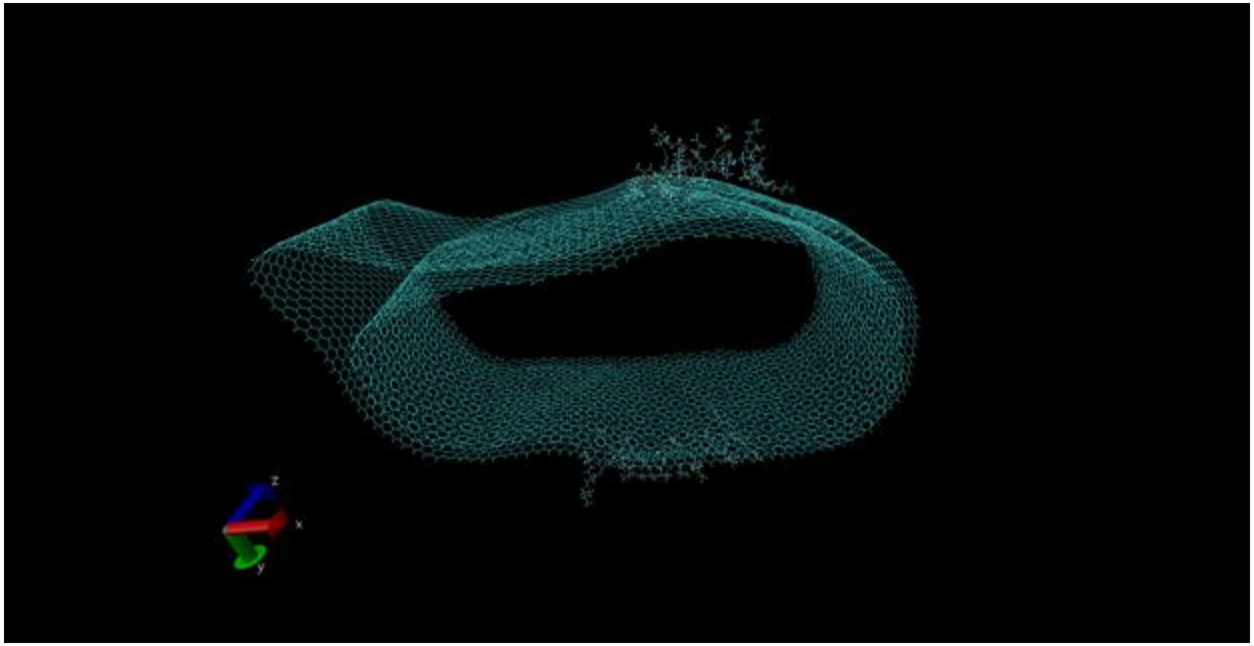

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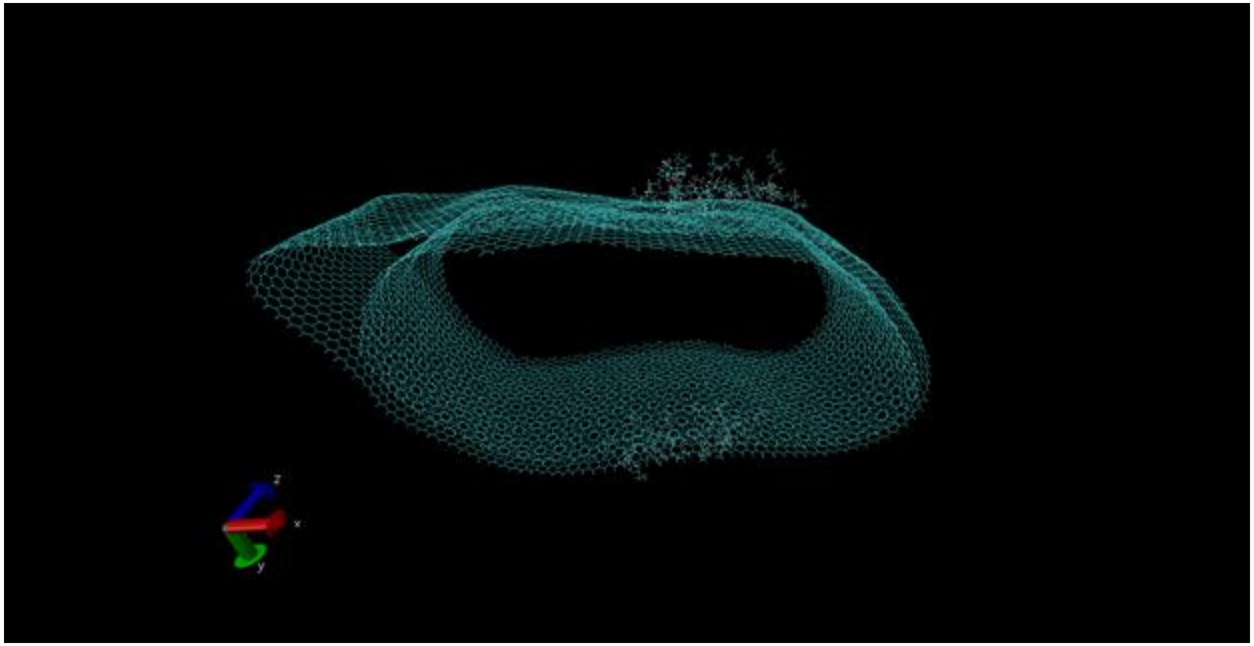

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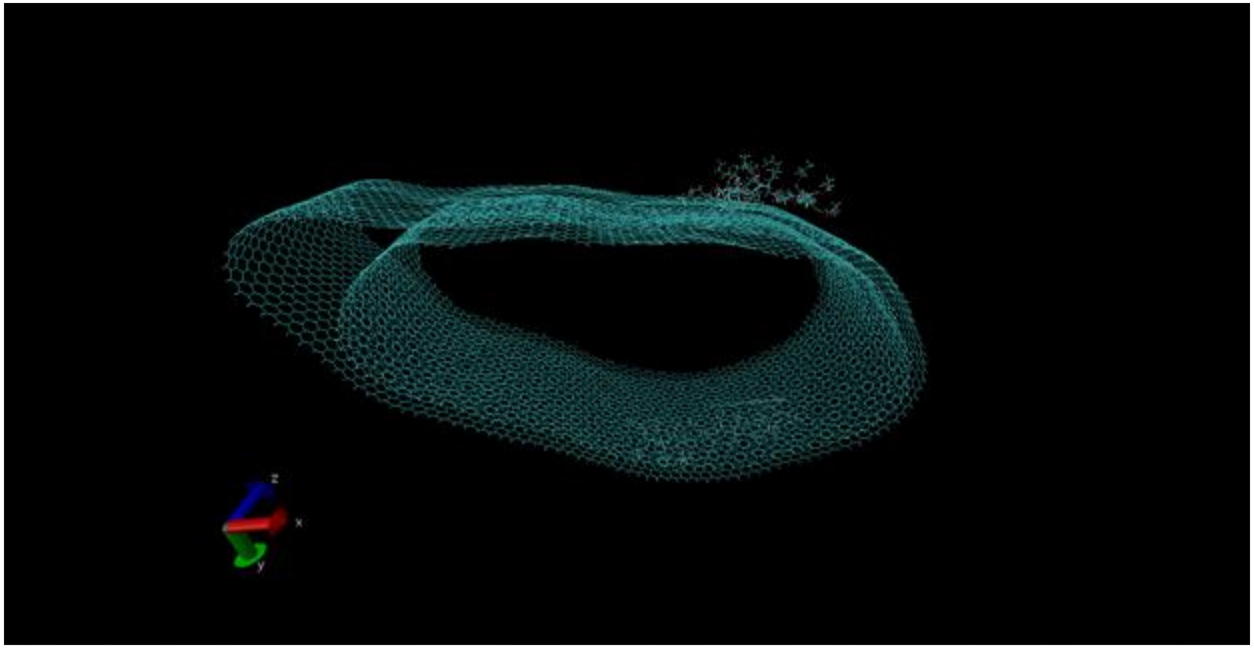
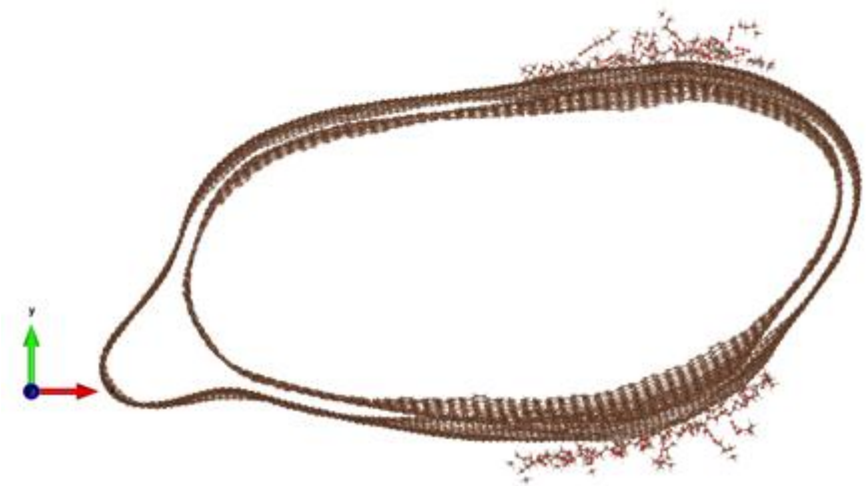


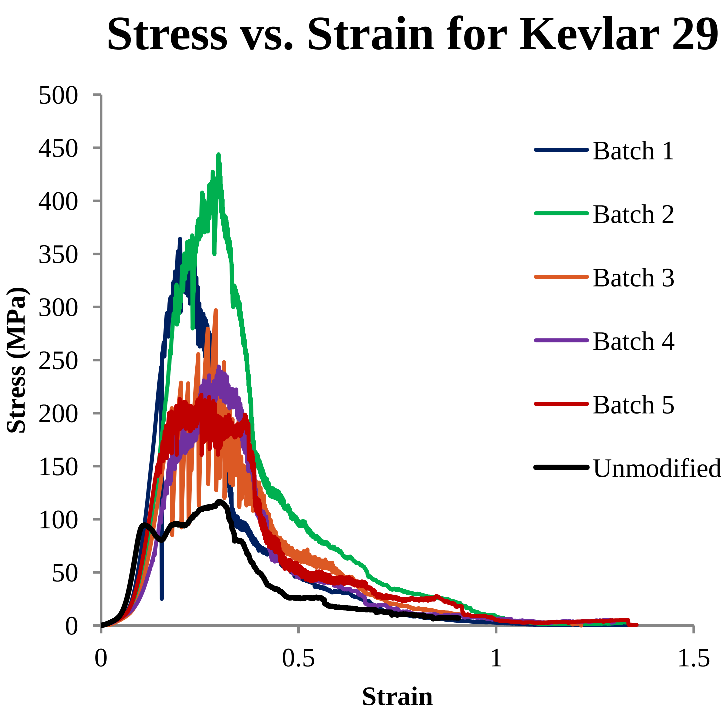
CHEMICAL MODELING



__Results__:

- **Adsorption of 2 PBA molecules impacts the structure of the DWCNT**
- **DWCNT distorts the original cylindrical curvature due to chemisorption reactivity**
- **DWCNT distorts to maximize pi-pi stacking**
- **Hydrogen bonds of PBA molecules seem to favor the DWCNT surface**
- **Closely resembles the theory in Brenner paper where SWCNTs were distorted due to adsorption of H_2 molecules [5]**

TENSILE TESTING RESULTS



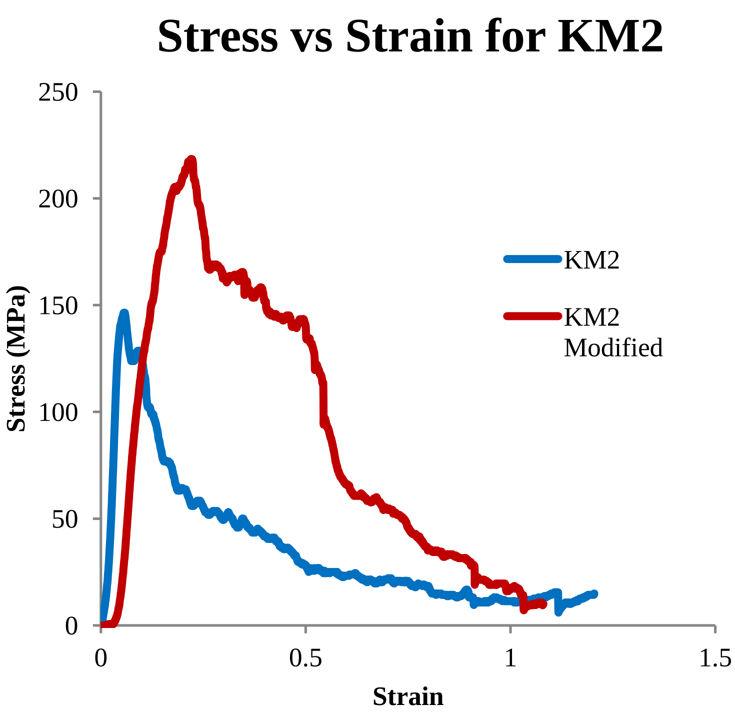


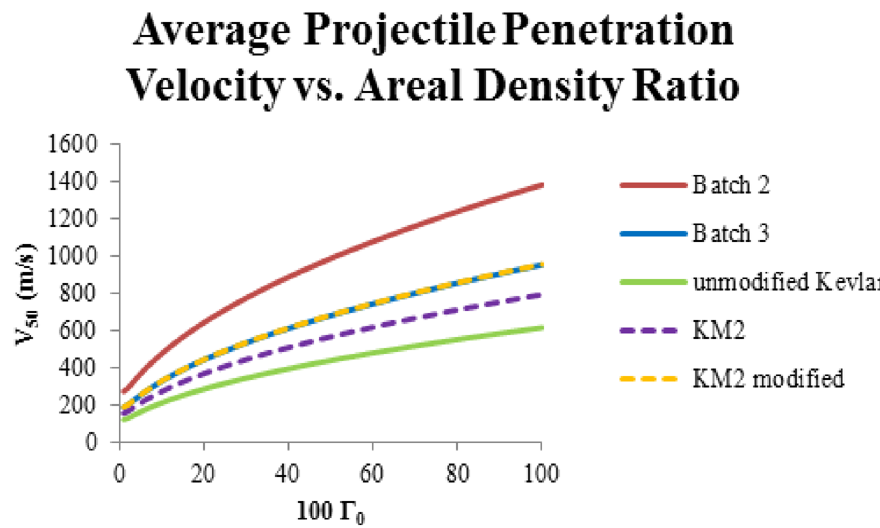
TABLE 1: CALCULATED FABRIC PROPERTIES

Fabric Type	Tensile Strength (MPa)	Elastic Modulus (GPa)	Strain	Density (kg/cm^3)	Toughness (MJ/kg)	Areal Density (Γ_0)	V_{50} (m/s^2)
Kevlar 29 unmodified	94.7	1.4	0.905	669	92.66	0.01383	526.14
Kevlar 29 Modified Averaged	292.6	2.106	1.106	395.42	344.96	0.01504	931.44
K2 Unmodified	142	5.2	1.11	983.56	184.24	0.02034	562.77
K2 Modified	213	1.349	1.04	829.57	170.26	0.01716	736.08

BALLISTIC MODELING: MASTER CURVE

Analytical equations in research based off computational and experimental data

- Parameters: elastic modulus, areal density, and maximum stress
- Assumption: infinite extent and quasi-isotropic
- Equations:[6][7]



Plot of V_{50} in m/s vs. Γ_0 for a single sheet of the unmodified Kevlar 29 sample, treated Kevlar 29 samples from batch 2 and batch 3, which displayed the highest and the lowest tensile stress out of the samples made, unmodified KM2, and treated KM2.

$$\Gamma_0 = \frac{m_p}{M_p} = \frac{\rho_y h \pi r_p^2}{M_p}$$

$$V_{50} = (1+\Gamma_0)\sqrt{(2A_p h\sigma_{max})/(M_p\Gamma_0)}\varepsilon_{max}{}^{1/4}$$

BALLISTICS MODELING: VELOCITY AT EACH LAYER

Impact causes:

•Cone in fabric

•Radial wave outward characterized one way by ψ, the ratio radius of the cone wave initiated: the bullet radius

•Ignore wave interference assume negligible due to friction

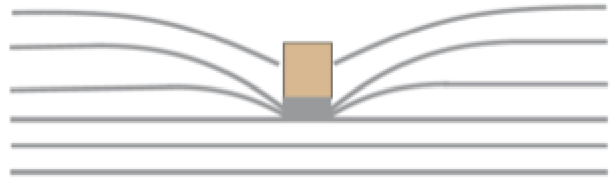
Finding Velocity

•Solved based on differential equation of the force the fabric exerts on the bullet

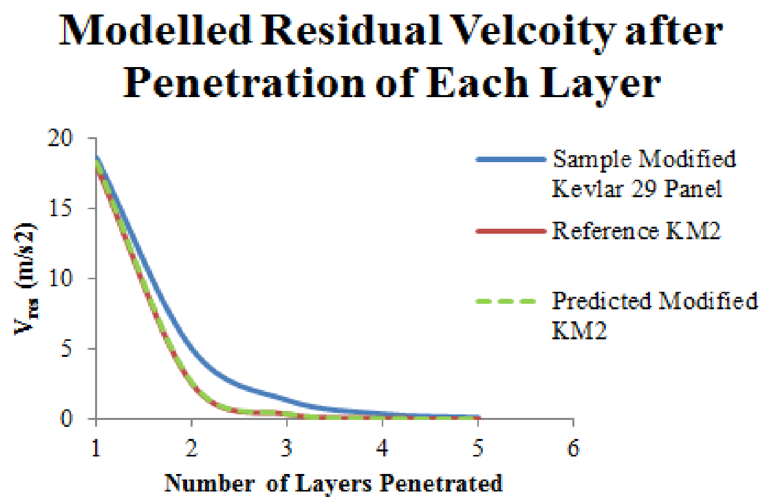
•Iteration of the equation [8]

$$V = \frac{V_p}{1+\tilde{\Gamma}_0}\exp\left[-\frac{\sum_{i=2}^{n}\Gamma_{0i}\psi_i^2 + \Gamma_{01}\psi_{1,f1}^2 - \tilde{\Gamma}_0}{1+\tilde{\Gamma}_0}\right]$$

a)



b)



(a) A schematic showing the cone shape created by a bullet hitting multiple layers of fabric. In this depiction layer 1 is broken through and layer 2, 3, and 4 are activated. [8] b) model of the residual velocity of the bullet versus the projectile velocity with which it hits a layer based on a 15 layer shot sample inside a nylon pouch

BALLISTIC TESTING

CONDUCTED BY ARL/SLAD IN EXPERIMENTAL FACILITY 10 (EF-10)

MAY 8,2014

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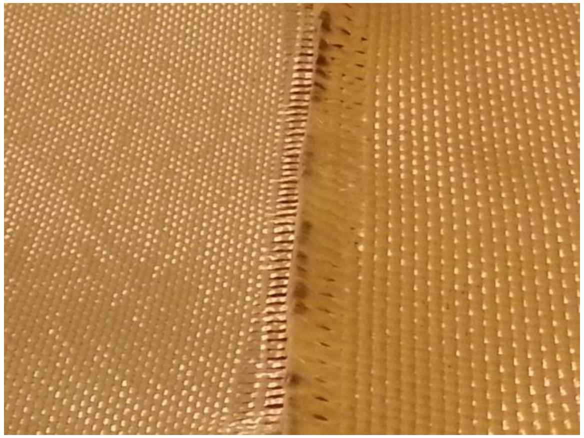
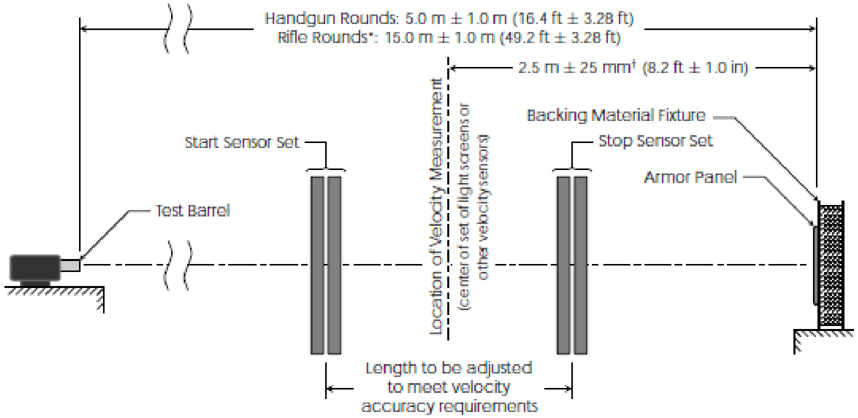
BALLISTIC TESTING



- **Reference Panel**
  - KM2 – 15 layers of military grade Kevlar
- **CNT Panel**
  - 29 Style 745 – 15 layers of PBA-functionalized CNT Kevlar
- **Performed Clay Drop Test and Test Range Configuration based on NIJ Standard-0101.06**
- **High speed footage captures the two 9 mm shots**



SHOT 1

VELOCITY = 914 FT/S

Frame 1

Frame 2

Frame 3

Frame 4

Frame 20

Frame 50

Frame 75

Frame 125

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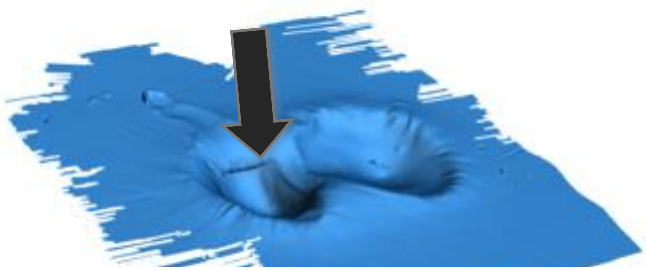
RESULTS

Stopped bullet on the 3rd layer

Backface deformation- 20.2mm



SHOT 2

VELOCITY = 902 FT/S


STRIKE FACE


STRIKE FACE
1


STRIKE FACE


STRIKE FACE

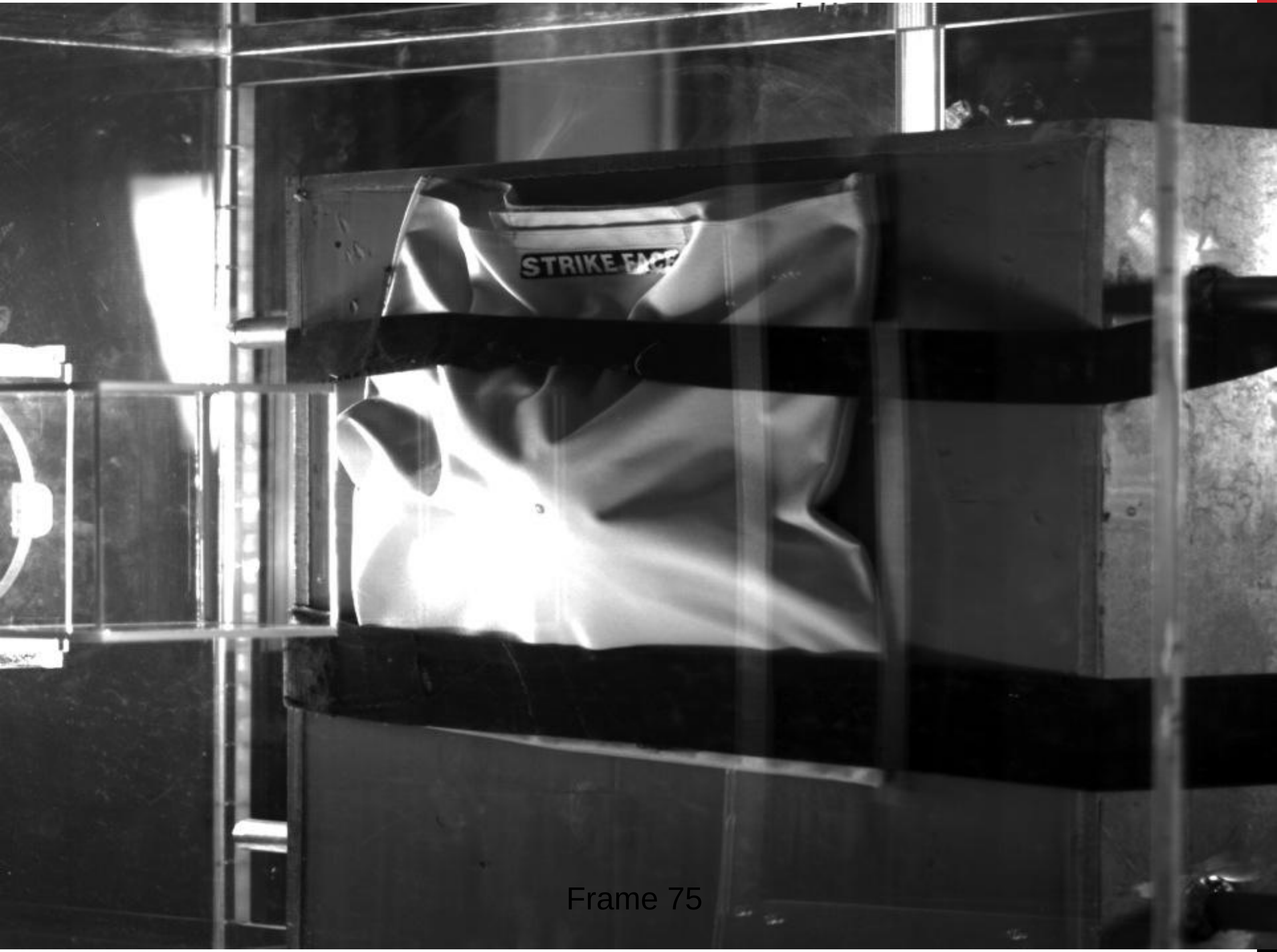

STRIKE FACE


STRIKE FACE


STRIKE FACE


STRIKE FACE


STRIKE FACE

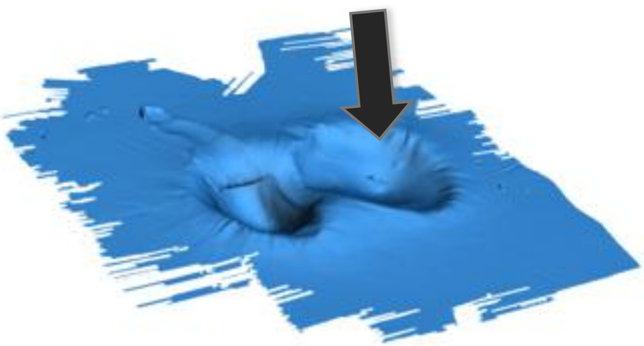


Frame 75


STRIKE FACE

RESULTS

- **Stopped bullet at the 2nd layer**
- **Total Backface Deformation- 14.23mm**



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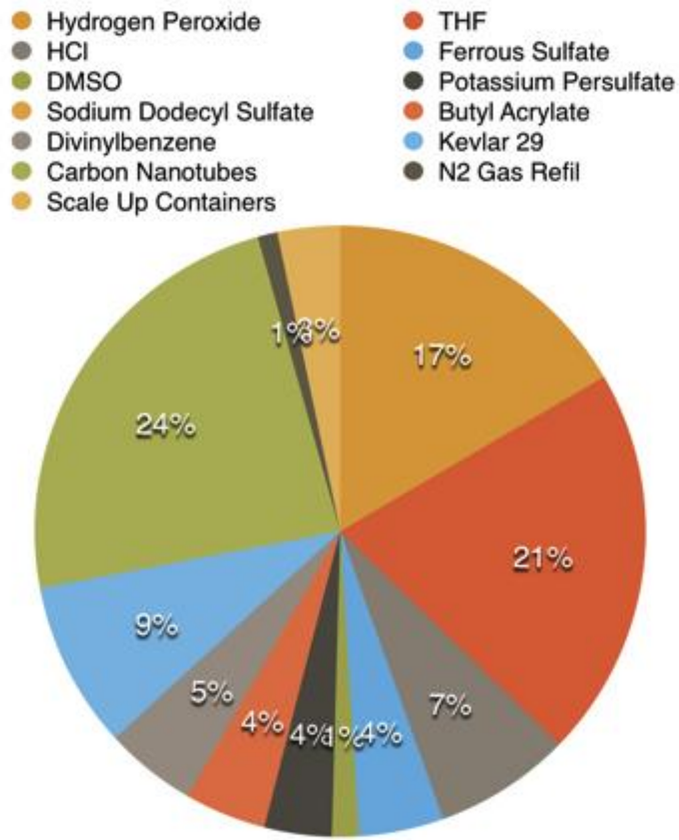
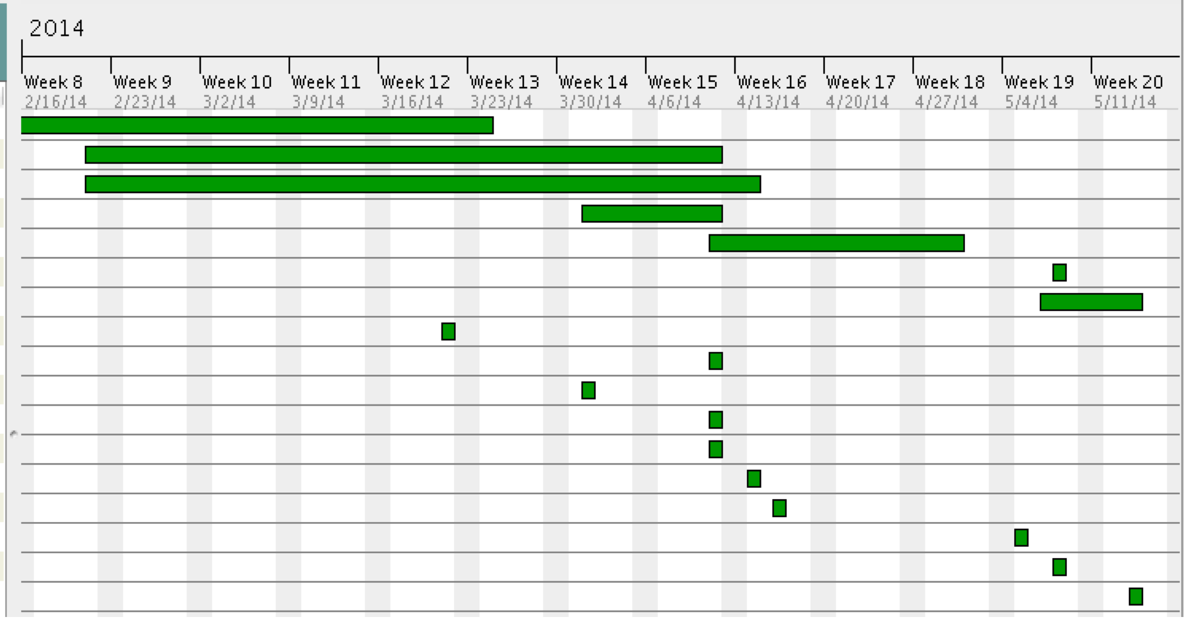
BUDGET

Item	Amount	Cost
Hydrogen Peroxide	4 L	$160.00
THF	16 L	$200.00
HCl	5 L	$70.00
Ferrous Sulfate	500 g	$43.36
DMSO	500 mL	$13.70
Potassium Persulfate	500 g	$34.43
Sodium Dodecyl Sulfate	100 g	0
Butyl Acrylate	1 L	$41.50
Divinylbenzene	250 mL	$47.10
Kevlar 29	127 cm x 189 cm	$85.25
Carbon Nanotubes	120 g	$228.32
N2 Gas Refil	1 tank	$10.00
Scale Up Containers	Various pieces	$32.00
AFM/SEM/TGA	4-hours	0
Ballistics Testing	4 shots	0
Lab Space	100-hours	0
Total		$965.56



TIMELINE

Name	Begin date	End date
Chemical Synthesis Reactions	2/14/14	3/24/14
Chemical Modeling	2/21/14	4/11/14
Ballistics Modeling	2/21/14	4/14/14
Initial Fabrication and Testing	4/1/14	4/11/14
Final Prototype Fabrication	4/11/14	4/30/14
Final Testing of Prototype	5/8/14	5/8/14
Final Report Preparation	5/7/14	5/14/14
Order Materials	3/21/14	3/21/14
Chemical Modeling Complete	4/11/14	4/11/14
Test Kevlar Swelling	4/1/14	4/1/14
Initial Fabrication Complete	4/11/14	4/11/14
Inital Testing Complete	4/11/14	4/11/14
Ballistic Modeling Complete	4/14/14	4/14/14
Third Quarterly Report	4/16/14	4/16/14
Final Prototype Fabrication Complete	5/5/14	5/5/14
Final Testing Complete	5/8/14	5/8/14
Final Report and Presentation	5/14/14	5/14/14



CONCLUSIONS

- Successfully designed and fabricated a 12” by 12” ballistic panel with 15 layers
- Enhanced ballistic resistance of Kevlar fabric by twofold based on backface deformation measurements
- Successfully functionalized Kevlar 29 Style 745 and KM2 Ballistic Fabric with PBA modified CNTs, increasing the tensile strengths from 94.7 MPa to 443 MPa and 142 MPa to 213 MPa, respectively
- Demonstrated the effect of reactivity on CNTs during PBA surface grafting process through chemical modeling
- Ballistics modeling showed amount of layers small ammunition round expected to penetrate was within experimental results

FUTURE WORK

1. Chemical Processing

- Analyze waste to determine final concentrations to determine exact amounts of constituents needed for chemical reactions
- Investigate and optimize exposure to HCl for KM2 fabric
- Maximize materials usage through recycling to minimize waste

2. Sample Testing/Characterization

- Investigate effects of UV exposure and sweat on modified fabric properties
- Evaluate CNT deposition and surface coating
- Evaluate CNT aerolization probability after ballistics test by examining particle concentration in air

3. Ballistic Testing

- Investigate denier orientation for maximum energy dissipation
- Investigate performance of CNT modified Kevlar in conjunction with non-Newtonian fluid layer

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ACKNOWLEDGMENTS

APG Ballistics Lab: This team worked tirelessly to accomplish our testing by the deadline, while meeting all government safety regulations and completing all necessary paperwork.

ARL: David Lowry, John Polesne, and Marco Olguin for coordinating ballistics testing and helping with our chemical modeling.

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SOURCES

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[4] L. O'Connor, H. Hayden, J. Coleman, and Y. Gun'ko, "High-Strength, High Toughness Composite Fibers by Swelling Kevlar in Nanotube Solutions." *Small*, 5, no.4, 466-469 (2009).

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