Novel PBA-Grafted Carbon Nanotube Soft Body Armor

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Abstract:
Kevlar fabric used in soft body armor provides protection from projectiles for service men and women, though often such a large amount of Kevlar layers is required that the flexibility of soft body armor is lost. By modifying Kevlar fabric with the addition of an embedded crosslinked network of carbon nanotubes (CNTs), the mechanical properties of Kevlar are increased such that less layers are needed to protect from projectiles, thus leading to greater flexibility. This report presents a three phase chemical fabrication process for producing modified Kevlar fabric via functionalizing CNTs with poly(butyl acrylate) (PBA) molecules, embedding functionalized CNTs in Kevlar fibers, and curing to form a crosslinked network of CNTs. Chemical modelling implementing the ReaxFF methodology in LAMMPS code is used to characterize the grafting reaction of PBA molecules onto the CNTs. The impact of a projectile onto a modified Kevlar body armor sample is modelled using ballistics modelling in excel in order to predict projectile penetration depth. Tensile tests and live ballistic testing indicate that modifying Kevlar with a CNT network leads to twofold increase in projectile impact resistance, thus indicating this method may be used to strengthen standard Kevlar and achieve the goal of greater armor flexibility.

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Motivation

Various types of body armor are used to protect men and women serving in the military and local law enforcement. There are two main types of body armor: hard and soft. Hard body armor is composed of ceramic plates inserted into a fabric vest and is used to stop higher caliber rounds. Because of the ceramic plates the vests are really heavy and the reusability is very low. Once one bullet strikes the ceramic plate, the plate cracks and is weakened to additional impacts. Soft body armor is made up of layers of flexible Kevlar fabric sewn into a vest, and is used as a lightweight substitute for the hard body armor when possible. Because the fabric is flexible, a hole in one area of the vest will not affect the strength of another area of the vest. While soft body armor has its benefits, it takes 20 to 50 layers of Kevlar to stop a bullet, and is typically used to stop lower caliber rounds [1]. This many layers causes the vest to lose its flexibility, which is a major disadvantage in applications where quick reflexes are required. Soldiers in combat already carry average weights over 100 pounds in equipment and supplies [2]. This much weight slows a soldier down considerably, and heavy, bulky body armor reduces speed and flexibility even more. The main purpose of body armor is to interact with the bullet, slowing it down and blunting it before it reaches the wearer. By improving the strength of the Kevlar fibers, we can increase the amount of time the bullet interacts with each layer, which will allow for a reduction of layers in the vest. Additionally, a stronger vest with the same number of layers, while bulky, may be able to replace the much heavier ceramic plates. A lighter vest will aid in reducing the amount of weight carried by our service men and women and provide more flexibility, which could be the determining factor for survival in a life threatening situation. Our group wants to better protect the men and women fighting to protect us.

Materials Science Aspects

The objective of this project is to modify the properties of Kevlar fabric, which relies heavily on materials science principles. The main points of the project rely on a knowledge of the mechanics of materials. CNTs are known for having outstanding mechanical properties while being lightweight. Body armor also functions on the basis of being strong and lightweight. Through the use of one strong and light material with another, we will create a composite material that is even stronger while still being light. The use of CNTs in the project also draws on knowledge of nanosized materials, and how to use them safely. The purpose of surface grafting poly(butyl acrylate) (PBA) onto CNTs is not only to make a protective network, but also to keep the nanotubes from aerolizing when the Kevlar is shot. Characterization of our treated samples is also required. This involved the use of various macro and nanoscale characterization techniques. Optical microscopy, tensile testing, TGA, AFM, and SEM were all used to try and understand our new material more fully. Our ballistics modeling also made use of our materials properties to predict how well the treated fabric would perform in ballistics testing. Additionally, our project makes use of macroprocessing concepts to scale up small sample fabrication into vest manufacturing.

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Previous Work

Kevlar vests have been incorporated in industry since its creation in 1971 [5]. The ballistic Kevlar that is used in armor is made from tightly woven para-aramid fibers. The patterns and techniques have been refined throughout the lifetime in order to achieve greater fabric

density and optimize energy dissipation to increase impact resistance.

The use of shear-thickening fluid for body armor applications is currently being evaluated. This fluid becomes much more viscous to flow in the presence of an applied force. This has shown promise to decrease the necessary layers of Kevlar needed to protect against bullets [6]. The shear-thickening fluid design uses a suspension of the fluid with kevlar layers in between. This innovation could be used in conjunction with what the proposed fabricated product to further increase the high strength and low density properties desired for body armor.

Dupont has experimented with CNTS in a layered design with Kevlar, and is part of their new research efforts. They are working on creating pure CNT fabrics rather than using the CNTs to strengthen the Kevlar fabrics [7]. Amendment II is a company that is currently using CNTs in body armor and selling it commercially. They use a proprietary processing of CNTs to make the body armor. They have been able to achieve very good test results with their design, but they keep their process secret to protect their design, so we do not know how they use the CNTs [8].

Intellectual Merit and Broader Impact

The basis of our project is founded on the research conducted by Yuyang Liu and his research associates. They surface grafted PBA molecules onto CNTs through a free radical reaction and dip dyed cotton in the resulting solution to strengthen it. They reported great results showing a significant increase in mechanical strength, without a sacrifice in flexibility [3]. Ian O'Connor and his research group have used unmodified CNTs to functionalize Kevlar. They soaked their Kevlar samples in NMP - CNT solutions and reported an increase in mean strength from 4 GPa to 5 GPa for Kevlar with 1 wt% CNT deposition [4]. Similar studies are currently being done at Johns Hopkins Applied Physics Lab by Dr. Morgan Trexler and her research group. They are currently working on replicating O'Connor's work and has seen 35% improvement.

We took the framework of our chemical processing from Liu’s work and applied to it Kevlar instead of cotton. Because cotton and Kevlar are two very different fabrics, we needed to modify the process to meet our needs. We modified the process based on advice provided to us by Dr. Nie’s research is all polymer based, and he was able to provide insight on how to get better CNT deposition and infiltration. From acting on his suggestions to find a solvent to swell the fibers we found Dr. O’Connors research. They used NMP to swell the Kevlar. When we consulted Dr. Nie about this solvent he suggested we use THF instead, as it interacts better with the PBA molecules. Dr. Nie also suggested that we etch our samples, a process that was not seen in any of the other research, but yielded good results.

The potential impact for improving the strength of Kevlar body armor affects all service men and women, both those in the armed forces and police departments. By modifying Kevlar through the addition of an embedded network of crosslinked CNTs, its strength and toughness may be significantly increased. This increase in mechanical properties will allow military grade vests to be scaled down in thickness, thus giving greater flexibility and range of motion for wearers, or if the same vest size is used the increase will provide greater protection from projectiles. This will undoubtedly offer greater protection to service men and women, thus saving lives and reducing the amount of serious injuries suffered by projectiles. Additionally, this research paves the way for future study into the area of modifying Kevlar to improve its performance in body armor. The results indicated in the report support the feasibility and potential of Kevlar modification, and the technical approach may serve as a springboard for

future investigations.

Ethics Consideration

The potential benefits of CNT modification of Kevlar body armor are quite attractive. Through increasing the mechanical properties of body armor, wearers have a better chance of survival in combat situations. Thus this research directly leads to improving the safety of service men and women. The ethical concerns associated with this research are mainly related to the toxicity of CNTs. The foremost concern is that the aerolization behavior of CNTs in the embedded polymer network is poorly understood. It is unclear how many CNTs may be released into the air when the modified body armor is impacted with a projectile. Aerolized CNTs are toxic when breathed as they may become lodged in the lungs, eventually causing symptoms associated with mesothelioma. Theoretically, the poly(butyl acrylate) network should keep the CNTs embedded and prevent aerolization, though the air quality after ballistic impact should be tested to ensure low CNT concentration. Another concern is the amount of CNT contaminated waste produced during the large scale production of modified vests. This waste must be disposed of properly to prevent CNT contamination of the environment and drinking water. This concern can be addressed simply by following proper waste disposal techniques during processing.

Design Goals

Our design goals focused mainly on increasing the strength of the fabric. Our figures of merit were to increase the tensile strength of the modified Kevlar to twice that of regular Kevlar. We also aimed to decrease the number of layers needed for the vest in half from 30 to 15, making the vest lighter and easier to move in. Finally, we want there be a high enough adhesion force, so that there was no safety hazard in CNT's coming off the fabric through friction or aerolization when the vest was shot.

Technical Approach

Chemical Modeling

One aspect of our design is chemical modeling where our objective was to understand the surface grafting phenomenon that occurs in our experimental process. In our fabrication process, we functionalized the multi-walled carbon nanotubes with poly butyl acrylate (PBA) to prevent aerosolization during ballistic testing and to strengthen the Kevlar fabric's ballistic resistance through the addition and infiltration of strong, lightweight PBA-grafted carbon nanotubes. Capturing the reactivity of this CNT-polymer system and modeling the trajectory and chemisorption of the PBA molecules on the CNTs would be advantageous in understanding the surface grafting phenomenon in our fabrication process.

Numerous computational modeling tools are available to model our CNT-polymer system; however, the ReaxFF methodology implemented in the LAMMPS code was deemed the most useful. LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is a classical molecular dynamics (MD) code that is easily modifiable, highly portable in C++, and has good scalability and performance. LAMMPS is often used to model atomic, polymeric, and mesoscale systems which is advantageous for our CNT-polymer system. The ReaxFF (Reactive Force Field) methodology is a powerful tool due to the fact that it captures reactivity while incurring a relatively inexpensive computational cost. This methodology is used in molecular

dynamics simulations and has the ability to model chemical reactions due to the force field's functional form with bond orders (i.e. bond order potentials). Note that a study by Mirabbaszadeh et al. performed simulations of systems related to this project using ReaxFF implemented in LAMMPS [9]. In his study from 2012, Mirabbaszadeh et al. successfully simulated the adhesion of various polymers (i.e. poly(3-hexythiophene), MDMO-PPV, and MEH-PPV) with single-walled carbon nanotubes (SWCNTs) [9]. For our purposes, we wanted to model a system closely related to our actual fabrication process which is why we chose to create a double-walled carbon nanotube (DWCNT).

One problem we needed to address was what ReaxFF parametrization will accommodate our complex chemical system consisting of both CNTs and PBA molecules. A study by Mattsson et al. extended the original hydrocarbon force field from K. Chenoweth and trained it for polymers [10]. For our simulation, we adopted the Mattsson force field as our ReaxFF parametrization and one of our three necessary input files. The three input files required to run the simulation included a data input file, a LAMMPS input file, and a ReaxFF input file (i.e. the Mattsson force field). The data input file consists of the structure you are using to model with (i.e. the DWCNT with PBA molecules). In this case, we needed to generate both the finite PBA molecule and the DWCNT using modeling software. Some software programs capable of generating CNT structures include TubeGen, VMD, as well as Nanotube Generator. TubeGen has an online interface and is more user friendly compared to VMD however both TubeGen and VMD are limited since they cannot generate DWCNTs at one time. However, it is possible to generate multi-walled CNTs (MWCNTS) using these software programs by creating multiple SWCNTs of increasing diameter as separate files and then append the coordinates to create a master XYZ coordinate file. To generate our DWCNT structure, we requested access to TubeGen's source code repository. After obtaining the source code, we compiled it and generated an XYZ file with translation vectors to show the Periodic Boundary Conditions using TubeGen. Normally, simulations would require PBCs to simulate infinite systems (i.e. an infinitely long CNT) however our DWCNT was composed of an inner and outer nanotube with different chirality. This meant that the inner and outer nanotube terminated at different points causing PBCs to be a formidable challenge. It is imperative that the atoms match up perfectly between each simulation cell to obtain the correct physics and avoid artifacts in the simulation data. To solve the PBC dilemma, we terminated the DWCNT with hydrogens by uploading the structure in Gaussview to satisfy valency. Note that terminating structures with hydrogens is common in the literature when modeling CNTs. This is likely due to the fact that PBCs are an additional computational expense where terminating the structure with hydrogens avoids that unnecessary computational cost. The generated DWCNT shown in Figure 1 closely represents the CNTs we bought for our fabrication process in terms of diameter. The DWCNT shown has a diameter of 10 nm and a length of 40 angstroms. Since we are not using PBCs, the length of the CNT doesn't really matter as long as the finite PBA molecule has room to interact with the CNT's surface. Note that the inner nanotube is in the armchair configuration (65,65) and the outer nanotube is in the zigzag configuration (130,0).

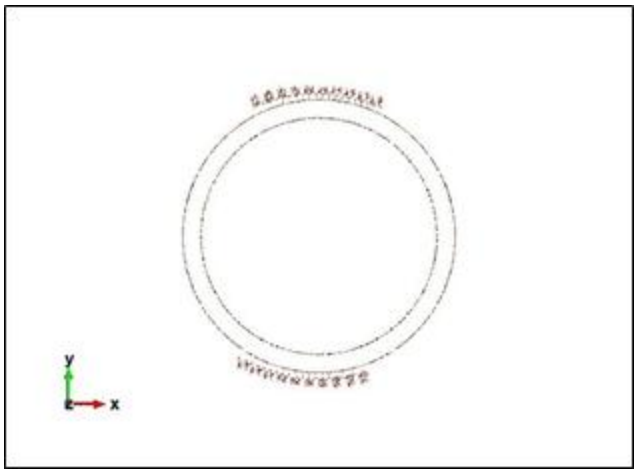


Figure 1: Double-walled carbon nanotube (DWCNT)

To generate the finite PBA molecule, we used Materials Studio. Materials Studio is modeling software package where you can create polymer structures and visualize the simulation results. Note that the finite PBA molecule shown in Figure 2 was comprised of 422 atoms. Our entire system consisted of the DWCNT terminated by hydrogens with 2 PBA molecules (Figure 3). The total system size was 10,984 atoms which is very large for modeling purposes. Typically, ReaxFF is used with systems comprised of a few thousand atoms.

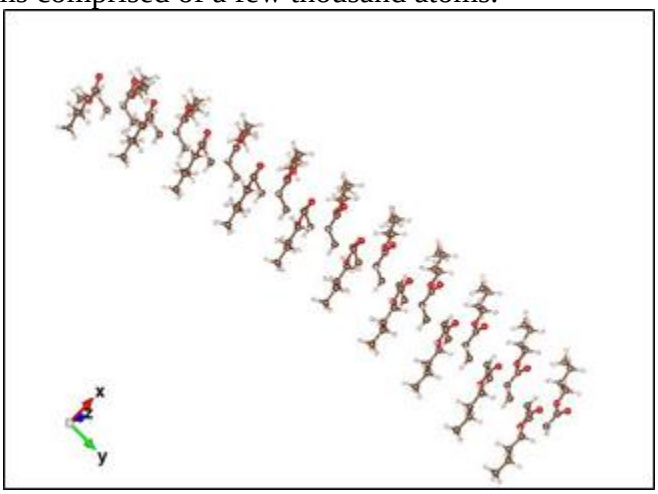


Figure 2: Finite poly butyl acrylate (PBA) molecule

Due to the extent of our CNT-polymer system, we needed to allocate resources on UMD's HPCC (High-Performance Computing Cluster), Deepthought. A request to allocate time on Deepthought was submitted and approved by the Division of Information Technology at UMD. However, after compiling the structural data file as well as the LAMMPS and ReaxFF input files, we submitted numerous jobs to the queue and continuously received error messages explaining how the job was aborted due to inadequate resources (i.e. walltime, memory storage, etc.). We coordinated with a researcher at ARL (Army Research Laboratory in Adelphi, MD), Marco Olguin, to not only compile the proper codes and receive insight into our modeling procedure but also run the simulations using the DoD's HPCC, Garnet. Unlike Deepthought, Garnet did not have many restrictions on the resources needed to run our simulations.

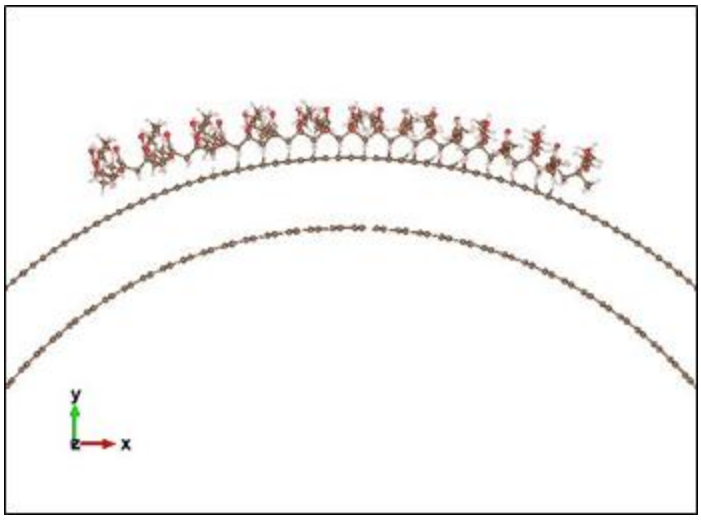


Figure 3: Finite PBA molecule on DWCNT surface

Our procedure to capture the reactivity of the CNT-polymer system consisted of two main ensembles, NVE and NVT. The NVE ensemble is a microcanonical ensemble that keeps the system's total energy (E) constant (as well as the number of moles (N) and the volume (V)). NVE is used to equilibrate the DWCNT-PBA system. After equilibration, the NVT ensemble is used to obtain the production state and observe the trajectory of the PBA molecules. Note that the NVT ensemble is a canonical ensemble where moles, volume, and temperature are conserved. The specified temperature for our simulation was 300K.

Chemical Process

Materials

- Kevlar 29, cut to size and sewn to prevent fraying
- MWCNTs
  - Outer Diameter: 10 – 30 nm
  - Length: 10 – 30 μm
  - Purity: Industrial Grade , 90%
- Poly(butyl acrylate) (PBA) – Polymer network
- Divinyl Benzene (DVB) – Crosslinker
- Sodium Dodecyl Sulfate (SDS) – Surfactant
- Ferrous Sulfate – Initiator
- Potassium persulfate (KPS) – Initiator
- Hydrogen Peroxide (H_2O_2) – Solvent
- Water – Solvent
- Hydrochloric Acid (HCl) – Etchant

The majority of the materials used in this process were chosen based on the process used in Liu's research. We selected the industrial grade MWCNTs for budgetary reasons. High purity CNTs are very expensive. We wanted our product to be viable for eventual scale up into a vest.

Process Scale Up

The process was initially done with small tensile specimens that weighed approximately 2g. This was relatively easy to accomplish because the amounts of constituents for the reactions were very small. When we scaled up the process for 12" x 12" sheets the processing was much harder. For maximum fabrication efficiency, one batch of solution contained enough CNTs for 3

sheets of Kevlar. This was the largest amount of CNTs we could modify at one time with the given lab equipment. In order to make the large scale process work we needed to buy gallon sized jars to hold solution, and had to find a 2 L three neck flask, for the reaction done under N_2.

Initial Kevlar Preparation

The Kevlar sample is dipped into HCl for 5 seconds. Once removed it is immediately rinsed in distilled water to stop the etching process. The sample is allowed to dry before dipping in the CNT solution.

We chose to etch the samples with HCl prior to dipping because we were very interested in achieving implantation of CNTs into the fabric of the Kevlar, as we felt it would be the best way to see increased ballistic properties. The team hypothesized that a dip of less than 5 seconds in an acidic solution that was known to break the covelant bonding on the aramid polymer but is a strong enough acid to break hydrogen bonds between the molecules might loosen the fibers and allow for better CNT deposition and implantation. The team decided on HCl with 37% concentration due to its little impact on breaking strength of Kevlar fabric after immersion **[KEVLAR Tech guide...not sure if we reference this elsewhere]**.

The thought was that after limited exposure to the HCl the aramid molecules and would rebond at often-different than the original Hydrogen Bonding sites, and dangling hydrogen bonds would be left exposed. These bonds would have a lower activation energy for the bonds to form. These dangling bonds would interact favorably with the CNTs for a higher bonding rate. The results were successful. This A side-by-side comparison of etched versus non-etched fabric is shown in Kevlar fibers are noticeably less wound in the etched sample in the samples.

The addition of the etch phase in the fabrication was shown to significantly increase the mechanical properties of the CNT implanted Kevlar. The team tested this by comparing tensile tests from the same fabrication batch for etched and non-etched Kevlar and found an increase of 1 KN. This result caused the team to decide to incorporate this into the large-scale sample that was eventually implemented.

Part 1

Relative weights for constituents in this part of the procedure are based on the weight of CNTs. Each batch consisted of enough constituents for 3 12” x 12” sheets that weigh about 46 g each. The amount of CNTs added was determined from the weight of the Kevlar samples. To get the desired deposition of 1 wt% CNTs we have used approximately 3.7g of CNTs per sheet (a total of about 11 g per batch), this is about 8 wt% of one Kevlar 12”x12” panel.

Approximately 3 wt% of sodium dodecyl sulfate (0.11 g of SDS per sheet, 0.33g per batch) is added to a flask with 0.9 L of hydrogen peroxide, along with about 2 wt% of Potassium persulfate (0.739g of KPS per sheet, 2.2g per batch). 11g of CNTs are added to the solution and the solution is gently stirred in an ice water bath for about 4 hours. This setup is shown in Figure 4. After 4 hours the sample is stored overnight in a fridge to allow for complete adsorption.

Figure 4. Part 1 reaction setup.

Part 2

Relative weights for constituents in this part are based on the weight of the butyl acrylate monomers added. Each batch contained enough constituents for 3 12" x 12" sheets. The amount of the butyl acrylate added was determined from the volume of PBA needed to make an adequate network across the samples. We determined this to be about 12 wt% of one Kevlar sheet.

About 3 wt% of SDS (about 0.16g per sheet, 0.49g per batch) is added to 0.9L of water in a flask equipped with magnetic stirring. Approximately 6.5mL per sheet (19.5mL per batch) of Butyl Acrylate monomers are added to the solution and the flask is put under N2. The solution from Part 1 is filtered with filter paper and rinsed into a flask with distilled water and then poured into the butyl acrylate solution. The filtered solvent in disposed of in a waste container. About 2 wt% of Ferrous Sulfate (0.108g per sheet, 0.325 per batch) is dissolved in a small amount of water and then added to the flask. The mixture is gently mixed in a water bath at 80ºC for 3 hours and 30 minutes. The setup for Part 2 is shown in Figure

Figure 5. Part 2 reaction setup.

Part 3

The solution from Part 2 is filtered using filter paper and the CNTs are rinsed with distilled water into a flask. The flask is placed into a sonicator for about 30 minutes to get a uniform dispersion. About 7 wt% (of the PBA weight) of Divinyl Benzene (0.413 mL) is added to about 1 L of THF in a jar. Once the flask of CNTs is well dispersed a third of the volume is measure and poured into the THF solution. The solution is placed in a sonicator for 30 minutes to

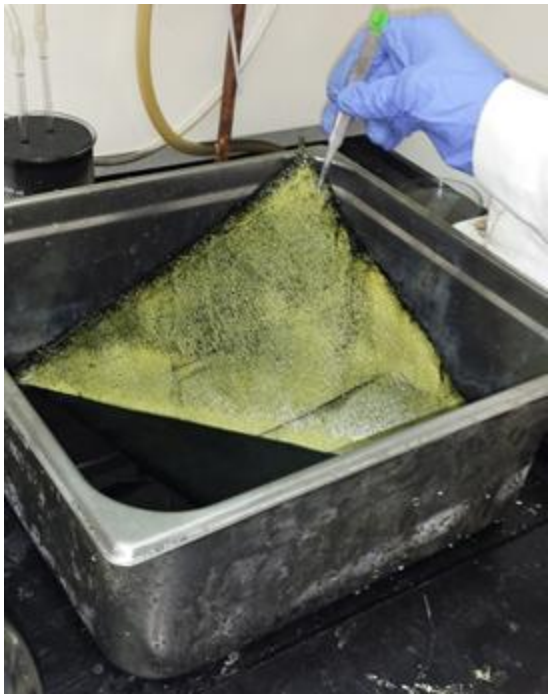


Figure 6. Image of Kevlar dipping

obtain a uniform dispersion. The solution is then poured into a stainless steel container and one Kevlar sheet is placed inside and allowed to soak for 30 minutes. The sheet is turned over halfway through to ensure even deposition on both sides of the sample. This setup is shown in Figure 6. After 30 minutes, the Kevlar is removed and placed on aluminum foil and moved to an oven at 100ºC. The samples are dried for 10 minutes and then the oven temperature is raised to 120ºC and the sample is allowed to cure for an additional 3 minutes. After 3 minutes, the sample is removed from the oven and allowed to cool. After cooling the sheets are rinsed with distilled water to remove any loosely attached CNTs.

Sample Structure Characterization

The main method of sample characterization used was optical microscopy. The Kevlar samples were observed at 200x magnification before the process began, after the HCl etch step, and after the CNT deposition step. The intent of this characterization was to qualitatively determine the effect of HCL etching on the surface roughness of the Kevlar fabric (as a higher surface roughness should allow greater CNT penetration), and to determine the appearance of the Kevlar threads after CNT deposition.

The previously chosen methods of surface characterization were scanning electron microscopy (SEM) and then atomic force microscopy (AFM). The intent of these higher resolution techniques was to determine qualitatively how well the CNTs had penetrated past the Kevlar surface and what the network of functionalized CNTs looked like on the surface of the Kevlar. However, the use of the SEM was not very helpful as was hoped. Since the Kevlar substrate is insulating, electronic charging due to the electron beam of the SEM was a hindrance to obtaining informational images of the Kevlar surface. Additionally, those few pictures that could be taken by adjusting SEM focus parameters and finding a “good spot” on the sample did not provide much insight into the supposed network structure of the functionalized CNTs. It would be possible to prevent charging and obtain better SEM images if the samples were first coated in a conductive material (such as gold), if the beam energy were precisely tuned to a value such that the flux of primary and secondary electrons were equal, or if copper or carbon tape were used to ground the sample. However, the team did not have a chance to attempt SEM again with these charge prevention techniques due to constraints in the budget and timeline. Additionally, some of these charge prevention techniques may not have been helpful, as the carbon nanotubes may not have been conductive themselves (grounding would be ineffective), and coating the sample in gold may have prevented a clear analysis of the underlying CNT

network structure. AFM was attempted after SEM, though with a similar lack of results. The AFM data was largely unphysical and provided no topographical information. A potential reason for this is the low stiffness of the Kevlar fabric, which could have caused the fabric to crease up on itself while the tip rastered across it.

Ballistic Modeling

Originally, the group planned to perform computational ballistic modelling using LS-DYNA software; however, after further research and meeting with Dr. Phoenix at Cornell University, the group discovered research combining both computational and experimental results to derive an analytical model of impact on fibrous systems[13][14][15][16][17][18]. Based on the coherence of the curves with experimental results, it was decided that this empirical modeling is superior to the computational modeling. The systems of equations, which are used to determine various values, depend on three main variables: density of the fabric, thickness, elastic modulus, and the yield strength. When performing ballistic testing on the body armor, we used a 9 mm bullet weighing 7.5 grams with a cross sectional area of 0.025 mm. These values were used as some of the parameters in our analysis, when finding Γ_0, which is a comparison of the areal density of the fabric to the bullet. All the other variables related to the fabric were determined through tensile testing.

The main way of characterizing the performance of a fibrous system is creating what is called a master curve which is V_{50} vs. 100Γ.

$$\Gamma_0 = \rho h/(M_p/A_p). \quad \text{and} \quad V_{50} = (1+\Gamma_0)\sqrt{(2A_p h\sigma_{max})/(M_p\Gamma_0)\varepsilon_{max}^{1/4}} \qquad (1)(2)$$

where V_{50} is the speed below which the layer will break, σ_{max} is the tensile strength of the fabric, ε_{max} is the maximum strain the fabric can withstand before on fiber breaks, ρ is the fabrics' density, h is the material's thickness, and M_p and A_p are the mass and cross-sectional area of the bullet [13][14][15].

For this characterization to correctly model the fibrous system, we assumed that the fabric had an infinite extent and was quasi-isotropic with the same linear elastic properties in the plane [6][8]. We neglected Poisson effects in these equations because local buckling and bending in the fibrous structure can be approximated to relieve all its stresses [13]. From this curve and the values found during weighing, dimensional characterization, and tensile testing of the fabric, we could predict the velocity need to break a single layer of the fabric. From these graphs, the Kevlar with the highest velocity needed to break, and therefore the highest performance, was predicted.

Ballistic Impact Physics of Fibrous Systems

When a bullet strikes a piece of fabric, the force of impact creates a cone in the fabric, as the material deflects and stretches to absorb the force[13][14][15][17]. In addition, the force induces a strain wave over the fabric which radiates out from the bullet. Three characteristic variables used to describe this wave movement are the tensile wave velocity, the transverse cone wave speed relative to the ground, and ψ, which is the

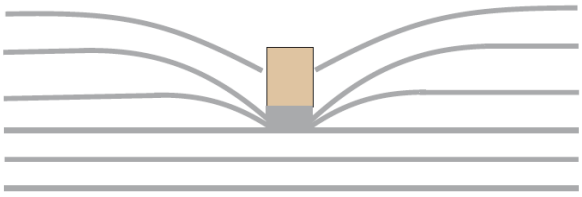


Figure 7. A schematic showing the cone shape created by a bullet hitting multiple layers of fabric. In this depiction layer 1 is broken through and layer 2, 3, and 4 are activated. [15]

ratio between the radius of the cone wave initiated and the bullet radius[13][14][15][17]. Ψ is the most important characterization with respect to ballistic modelling. With multiple sheets of fabric the bullet becomes less and less likely to penetrate the fabric. The multiple layers of fabric work together to reduce stress on the fabric by sharing the loading, as seen in Figure 7. But when each new layer of fabric is activated by the bullet, a new strain wave is created in this layer with a differing velocity and position then the wave above it. This can cause interference which is detrimental to the system's $V_{50.}$ For the purposes of this model, we assume that the interference is negligible because the layers have enough friction between them to prevent strong difference in waves [15][18].

For this part of the model we also assumed each layer had inplate, isotropic elastic mechanical properties, [8] and that there was no bonding between layers. The force of the fabric against the bullet is given by

$$F = -\varphi \pi r_p^2 \rho h V \frac{d\psi^2}{dt} = -\varphi m_p V \frac{d\psi^2}{dt}, \tag{3}$$

And the mass and thickness (h) increases with increasing layers [13][15][17]. There is also a certain amount of force given by friction between the bullet and the fabric and some thermal energy contributes to absorbing the energy from impact [13][17].

Through solving the differential equation of the force, the velocity of the bullet at each layer after it breaks can be described. To determine the velocity through each layer of our two potential systems, the solution of

$$V = \frac{V_p}{1+\tilde{\Gamma}_0} \exp\left[-\frac{\sum_{i=2}^{n} \Gamma_{0i} \psi_i^2 + \Gamma_{01} \psi_{1,fl}^2 - \tilde{\Gamma}_0}{1+\tilde{\Gamma}_0} \right] \tag{4}$$

where V_p is the velocity of the projectile (≈900 m/s), ψ_i is the ψ for active layers and ψ_{fl} is the ψ of the other active layers [15]. Immediately after the bullet strikes an area and activates it ψ=1, since the radius of the cone wave and the bullet are the same. As time progress the radius increases until a maximum ψ is reached, which creates the ε_{max} required to break through the fabric layer[13][17]. The equation for ψ_{max} is given by

$$\psi_{max} \approx \sqrt{\frac{1+\Gamma_0}{2\Gamma_0}} \tag{5}$$

The other layers activated have ψ falling between 1 and $\psi_{max.}$. It must be noted that once a layer is penetrated it no longer interacts with the bullet, other than through friction. Therefore, its value becomes 0 after penetration

One of the problems with this form of modeling is it only determines the number of layers penetrated based on the strain and areal density of the fabric; however, other factors such as absorption of energy and toughness of the material must be taken into account. The energy absorbed by the fabric at impact is given by

$$E_0 = M_0 * \frac{(V_p - V_2)^2}{2} \tag{6}$$

where V_1 the velocity after striking layer 1[15]. The toughness of the fabric is given by

$$\Omega = \frac{\sigma_{ymax}\epsilon_{ymax}}{2\rho_y}\sqrt{\frac{E_y}{\rho_y}} = \frac{\epsilon_{ymax}^2 a_{0y}^3}{2} = \frac{1}{2}\left(\frac{\sigma_{ymax}}{\rho_y}\right)^{3/2} \tag{7}$$

We performed multiple iterations of this equation in excel to find the velocity at each layer, taking the case of a bullet penetrating layer i and activating layer i+3, such that $\psi_i=\psi_{max}$, $\psi_{i+3}=1$, and $1 \leq \psi_{i+2} \leq \psi_{i+1} \leq \psi_{max}$ [15].

Results and Discussion

Chemical Modeling

Modeling our DWCNT-PBA system shed light on the surface grafting phenomena that occurs in our fabrication process when we functionalize the CNTs with PBA. To run the chemical modeling simulations, we used the ReaxFF methodology implemented in LAMMPS to capture the chemical reactivity of the PBA molecules on the CNT surface. Since we wanted to model a CNT closely related to our actual fabrication process, the total system size of the DWCNT-PBA molecule was very large, approximately 11,000 atoms. We needed to allocate resources for UMD's Deepthought HPCC (High-Performance Computing Cluster) due to the computational cost of modeling our complex CNT-polymer system. We submitted a request form to UMD's Division of Information Technology to allocate time to run the molecular dynamics simulations on Deepthought and our small allocation of 20 kSUs was approved. Marco Olguin, an ARL researcher, helped us provide the estimates of the necessary resources and identify other computing requirements we required to model our CNT-polymer system using UMD's HPCC. The following are the estimated resources and computing requirements detailed in the approved UMD allocation request: the estimated RAM usage per core is 0.05 GB, the estimated file space required is 6 GB, the parallelization strategy is to use a message passing interface (MPI) designed to handle distributed-memory systems, the expected job queues include narrow-long, wide-debug, and wide-med, and the required size on the cluster is large (approximately 20 kSUs). Due to our group's ties to ARL, we also had access to the DoD's HPCC to run our simulations. This access to DoD supercomputing capabilities was priceless since we were not necessarily limited by the allocation size (like we were using UMD's HPCC) and our simulations could run for longer periods of time relative to UMD's HPCC (i.e. in excess of a week if need be). After submitting numerous jobs to Deepthought, we continuously received error messages describing how our jobs were aborted due to inadequate resources (i.e. walltime, memory storage, etc.). Due to the DoD's impressive supercomputing capabilities, we ran our simulations using the DoD's HPCC, Garnet. To simulate our CNT-polymer system, we used 96 processors (32 processors per node for 3 nodes). Our simulation runtime was 168 hours (i.e. a week) for approximately 0.4 ns of production run due to our large system size and the small timestep required for ReaxFF (which adds extra computational cost). Even on Garnet, we needed to increase the memory allocation to store the larger matrices for our simulation to run smoothly. This was done by adding a line in the LAMMPS input file.

Three input files are required to run the simulations: a data/structure file, a LAMMPS input file, and a ReaxFF input file described by Mattsson et al. [10]. Our modeling procedure consisted of equilibrating our system using the NVE ensemble before using the NVT ensemble to obtain our production run. After the job is submitted to the queue and the simulation runtime continues for a week, the output files can be visualized by loading them in VMD (Visual Molecular Dynamics). The simulation demonstrated the chemical reactivity of the PBA molecules on the CNTs. When the simulation commences, the CNT curvature begins to distort due to the equilibration process in NVE as shown in Figure 4a. Towards the end of the equilibration process, the DWCNT begins to distort from its original cylindrical curvature to maximize the pi-pi stacking between the inner and outer nanotube as shown in Figure 4b. As the

NVT ensemble progresses, the DWCNT continually twists and compresses (i.e. torsion and bending) as shown in Figure 4c due to the chemical reactivity of the PBA molecules as well as the local conformation strain on the CNTs described by Brenner et al. Brenner et al. called this phenomena "kinky chemistry" where there is a shift in hybridization of the atoms from sp^2 to sp^3 as well as enhanced reactivity of the adsorbate due to the nonlinear distortions of the CNTs [19]. Our simulation demonstrated how the adsorption of two PBA molecules impacts the structure of the DWCNT. The DWCNT tends to distort from its original shape due to the chemisorption reactivity to maximize the pi-pi stacking between the inner and outer nanotube. We also observed that the hydrogen bonds of the PBA molecules seemed to favor the DWCNT surface throughout the entire simulation. The distortion shown in our model closely resembles the theoretical and computational predictions documented in a study from Brenner et al. [19]. Note that Brenner modeled the adsorption of hydrogen molecules on the surface of SWCNTs and also noticed this distortion effect enhances chemical reactivity.

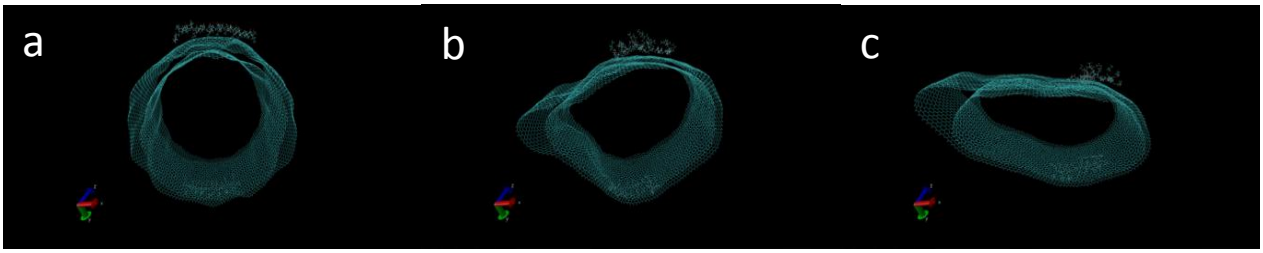


Figure 8: CNT-PBA system at the (a) beginning of equilibration, (b) the beginning of CNT distortion, and (c) as the NVT ensemble progresses

Optical Microscopy Characterization

The optical microscopy characterization was used to qualitatively determine the effect of HCl etching on the Kevlar surface roughness as well as the appearance of the Kevlar threads after CNT deposition. The optical microscopy images are shown in Figure 9 below. A comparison of (b) and (c) indicate that there is some increase in the surface roughness due to the HCl etching step, as the fibers in (c) are much less ordered and less tightly woven as compared to those from (b). Image (d) shows that the CNTs do indeed deposit on the Kevlar threads. Additionally, they are fairly evenly distributed along the fibers, without noticeable agglomeration on one side of the thread.

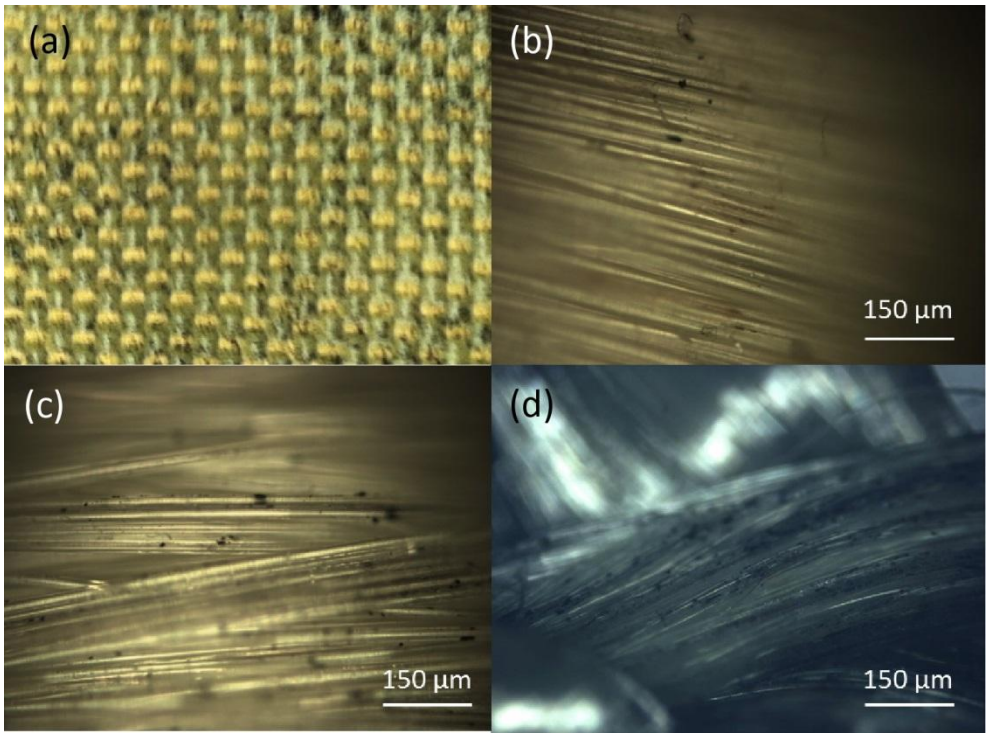


Figure 9. **(a)** Digital image of modified Kevlar 29. Optical microscope images at a magnification of 200X of Kevlar 29 **(b)** before treatment, **(c)** after HCl etching, and **(d)** after full CNT treatment.

Tensile Testing Results

To improve the performance of the vest, the fabric had to show an increase in tensile strength and elastic modulus. Originally, we were not sure whether adding an HCl etching step to our process would increase or decrease these properties. The results of a tensile test between unmodified Kevlar 29, modified Kevlar 29, and Kevlar29 modified with an etching step are shown below in Figure 10. The results show that the treatment of the fabric increased the desired properties. Furthermore the etched Kavlar 29 had the highest tensile strength of 466 MPa compared to the tensile strength of modified Kevlar 29 (283 MPa) and unmodified Kevlar 29 (116 MPa). Therefore, the etching step was added to the treatment procedure. These results showed that the modification process with HCl dip increased the tensile strength of the fabric by 4 times its original value with only a small amount of weight gain.

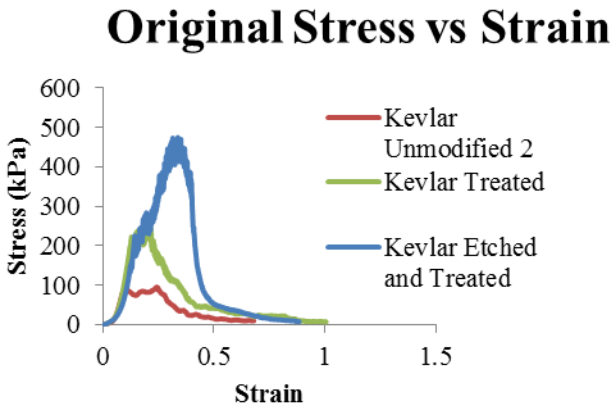


Figure 10. Stress vs Strain curve of initial tensile testing, used to determine the validity of the treatment process and if an etching step should be used.

During manufacturing of

the prototype, a tensile testing specimen was prepared for each batch of 3 layers created. The results from testing these specimen showed the range of properties between the different layers of the vest, which were caused from refining the scale up process. The results for these specimens and an unmodified Kevlar 29 specimen are shown in Figure 11a). The tensile strength and elastic modulus for the modified samples ranged from 443 MPa to 205 MPa and 2.29 GPa to 1.74 GPa, respectively. Although there was a large range in values, all of the modified specimens mechanical properties improved upon the unmodified Kevlar 29 with a tensile strength of 94.7 MPa and an elastic modulus of 1.4 GPa.

During ballistics testing the modified Kevlar 29 15 layer vest was compared with a control KM2 15 layer vest. We did not use KM2 because it is military grade and not commercially available. To prove the treatment process would improve the performance of KM2, we treated a sample of KM2, provide by APG, and used tensile testing to compare it against an unmodified KM2 specimen. The results are shown in Figure 11b). The tensile strength of the treated specimen compared to the unmodified specimen increase from 213 MPa from 142 MPa. Therefore, the treated KM2 is predicted to perform better in ballistics testing. The increase in KM2's tensile strength is smaller than that seen in Kevlar 29. We believe this is a result of KM2 having a finer denier and tighter weave, which made it harder for the CNT to penetrate into the fibers.

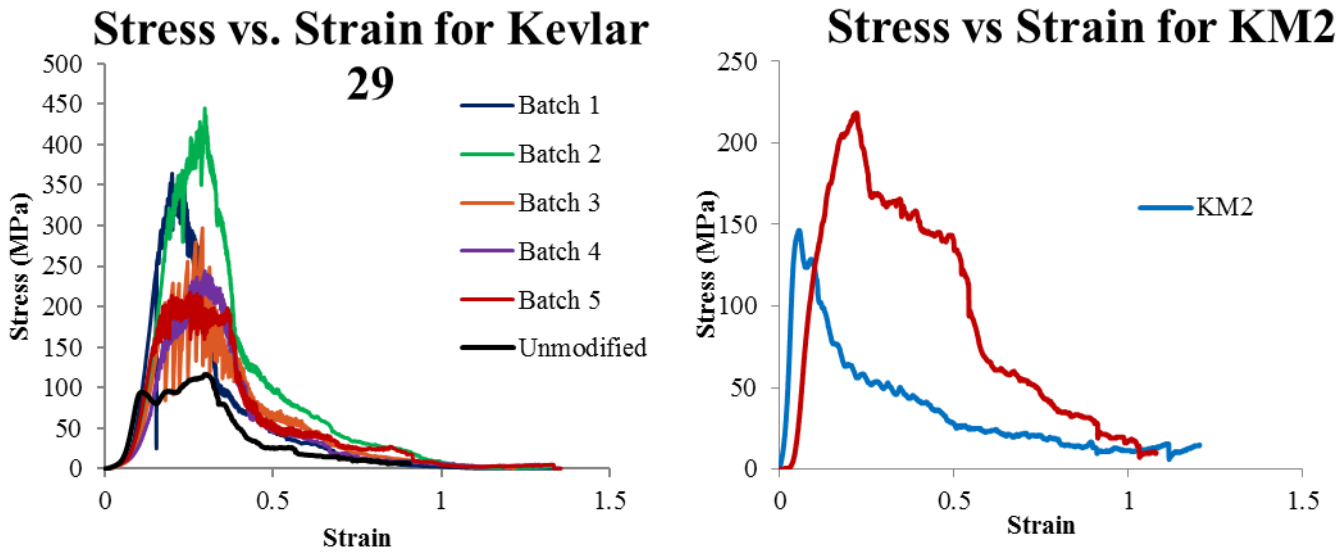


Figure 11a) Kevlar 29 stress strain curves for a specimen from every batch of solution created to modify three layers and an unmodified specimen and b) KM2 stress strain curves for a modified and unmodified specimen.

Ballistic Modeling

Table 1 shows the properties of each piece of fabric, found through tensile testing and calculations, that are necessary for ballistic modeling.

Table 1: Properties of each type of fabric both treated and unmodified.

Fabric Type	Tensile Strength (MPa)	Elastic Modulus (GPa)	Strain	Density (kg/cm³)	Toughness (MJ/kg)	Areal Density (Γ_0)	V_{50} (m/s)
Kevlar 29 unmodified	94.7	1.4	0.905	669	92.66024	0.01383	526.14
Kevlar 29 Modified Averaged	292.6	2.106	1.106	395.422	344.962	0.01504	931.44
K2 Unmodified	142	5.2	1.11	983.560	184.239	0.02034	562.77
K2 Modified	213	1.349	1.04	829.573	170.2575	0.01716	736.08

Figure 12 shows the master curve relating V_{50} to Γ_0 for the best and worst performing treated Kevlar 29, unmodified Kevlar 29, treated KM2 and untreated KM2 . The curve shows that the treated Kevlar 29 (red and blue lines) have much higher velocity needed to penetrate them than the unmodified Kevlar 29. The average V_{50} for the modified specimens was 931.44 m/s. This correlated well with the findings from the ballistic testing at APG, given a degree of error. The bullet penetrated the first layer because its velocity of 914 m/s was enough to penetrate through the first layer, but the dissipated energy was not. Similar to what was seen with Kevlar 29, modified KM2 (dashed orange) also has a higher V_{50} than unmodified KM2 (dashed purple).

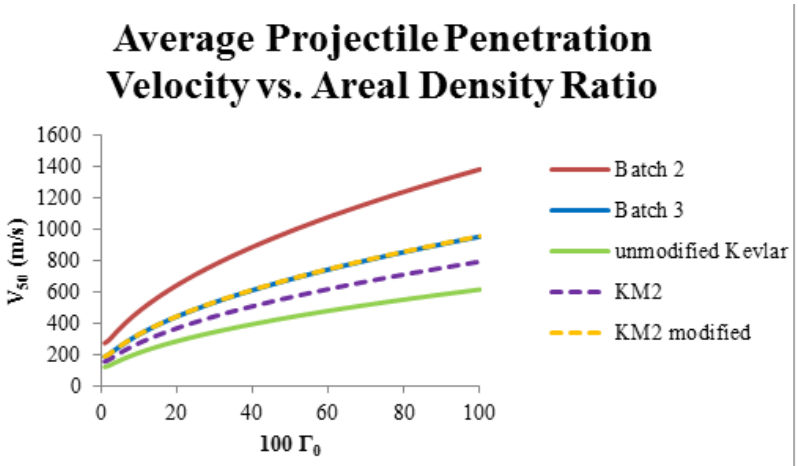


Figure 10. Plot of V_{50} in m/s vs. Γ_0 for a single sheet of the unmodified Kevlar 29 sample, treated Kevlar 29 samples from batch 2 and batch 3, which displayed the highest and the lowest tensile stress out of the samples made, unmodified KM2, and treated KM2.

Figure 11 shows the ballistic modelling curve that uses V_p to determine the residual velocity of the bullet after penetrating a number of layers for the sample modified Kevlar 29, the reference KM2, and the prediction for modified KM2. The model closely matches the results from ballistic testing with an error of 1 layer. The number of predicted penetrated layers for the modified sample is 3, determined by the low residual velocity, which is considered to be negligible due to the effects of friction not taken into account. The bullet for both the unmodified and modified layers of KM2 is predicted to penetrate 2 layers. Although they both penetrate the same number of the layers, the modified KM2 is predicted to perform better by an

increased dissipation of energy in the vest, caused by the higher calculated toughness values.

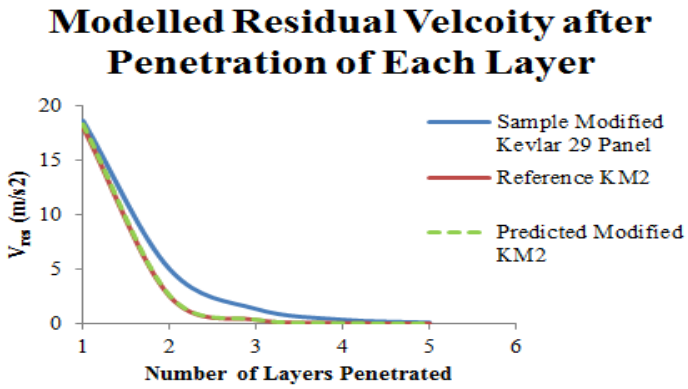


Figure 11 model of the residual velocity of the bullet versus the projectile velocity with which it hits a layer based on a 15 layer shot sample inside a nylon pouch

Ballistics Testing

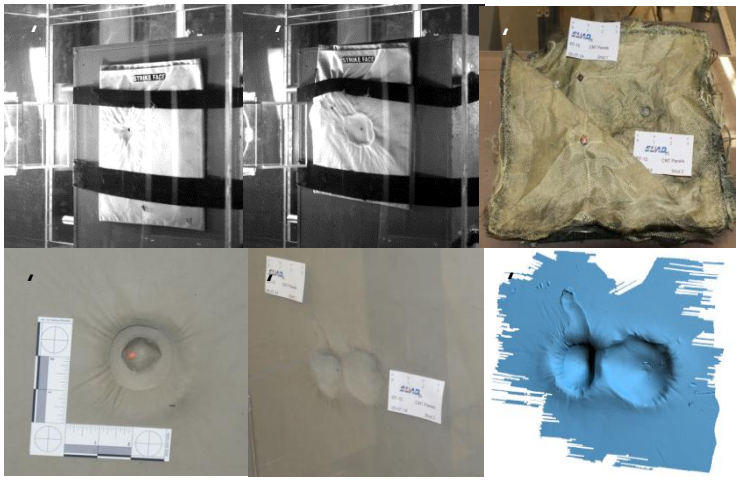


Figure 12. a) Digital image of first shot on CNT panel, b) of second shot on CNT panel, c) the CNT panel after shots with two layers folded back, d) Digital images of clay backing material for K2 reference panel after 2nd shot, and e) our CNT panel. f) 3D Faro Scan of clay backing material post-shot.

The ballistics testing was conducted at the Army Research Lab at the Aberdeen Proving Grounds. The testing was done in with cooperatio as a part of their newly implemented open campus policy. The lab dedicated over 10 individuals to test the sample that day, as well as many hours of multiple personnel to set up the shot.

The test was done to maintain the strictest adherence to NIJ standards and controls were minimized. The clay that is used is a sculptor's clay that is temperature controlled. This is to maintain repeatability of impact response. This clay is then tested for impact response within a

certain tolerance, and then is flattened. This flattened clay is then imaged using a faroscan machine to establish a baseline for the clay shown in figure 12 f).

The test was done in an access-controlled room with a custom ventilation system that was designed specifically for the team's samples. There were concerns by the safety office about exposure to aerolized CNTs after the sample was shot, so they took drastic precautions. The clay was shot in a customized box that experienced air changes, and the room itself experienced air changes. The technicians who were responsible for setting up and shooting the sample were in full cleanroom suits and wore respirators in the room after the initial shot. Filters in the room are currently being examined in TEM by the safety office to determine if there was any CNTs aerolizing off of the fabric.

Prior to testing, the team had done a control test using 15 layers of KM2 fabric. This fabric has a much finer denier than the Kevlar 29 that the team used for fabrication, but it was an effective baseline to determine testing conditions. The team decided on 900 ft/s as the velocity for the test. This is slower than the NIJ standards for Type IIA body armor, but their goal was to leave safety factor to make sure the bullet did not penetrate through the fabric. If the bullet penetrated, it would ruin any data for backface deformation that can be analyzed. The bullet was shot twice at different locations on the pack. Images of the bullet hitting our sample are shown in Figure 12 a) and b). The first shot penetrated three layers of our fabric while the second only penetrated two as shown in Figure 12 c). The bullet hitting the KM2 only penetrated 1 layer.

The CNT modified Kevlar 29 the team showed a significant improvement over the KM2 that was used in backface deformation. It is important to note that the acceptable backface deformation is 43mm. The unmodified KM2 was close to within this regime. The NIJ standard bases this based on permanent damage that can occur at these force levels on the body. At similar speeds, the CNT-Kevlar was shown to have much more shallow backface deformation than the unmodified KM2 as shown in Figure 12d) and e).

These results should be taken with caution though since the KM2 control sample has some key different properties than unmodified Kevlar 29. For one, the KM2 is much thinner than the Kevlar 29, so there should be an expectation that the Kevlar 29 unmodified would perform better than the KM2 when comparing the samples based on their layers. Therefore, it is more appropriate to compare these results based on overall thickness. The 15 layers of Kevlar 29 were 9.15mm and the 15 layers of KM2 was 2.35mm. Under these conditions, the improved results to the control sample should be considered.

The team decided to use a sample of KM2 that was shot to examine their mechanical properties in a tensile test. The sample that was used was from the back of the pack and there was not observable deformation from the shot. The goal was twofold in this experiment: one was in order to view unmodified behavior in relation to Kevlar 29 in tensile testing, and the other was to see if the CNT implantation used for Kevlar 29 would be successful for the KM2.

The results show that the Kevlar 29 has a greater than 250% higher tensile strength compared to the KM2. This further shows that the data from the ballistic tests comparing the KM2 and Kevlar 29 are not valid. However, the process of the CNT-deposition into the KM2 showed a 50% increase in the tensile tests as compared to the unmodified sample. This shows that there would be probable improved ballistic resistance if a full KM2 vest was used in a similar process as the modified Kevlar 29 that was implemented.

Future Work

There were several areas of interest that the team was unable to explore due to monetary or time constraints. These include issues with the chemical fabrication process, sample characterization methods, and ballistic testing. Future work could focus on analyzing the waste of the chemical process in hopes of determining the final concentrations of reactants and CNTs on the Kevlar fabric. This would give greater insight into the properties of the final sample while simultaneously optimizing the process to reduce waste. The HCl etching step could also be investigated further in order to improve the HCl exposure time to achieve optimal conditions for CNT penetration.

There are several characterization tests that should be performed on the modified Kevlar prototype in order to determine its long term durability, the structure of the CNT network on its surface, and the aerolization behavior of embedded CNTs. The effects of UV and moisture exposure should be investigated, as Kevlar body armor in the field will surely be exposed to these conditions. The CNT quality of the CNT deposition and structure of the CNT surface coating could be analyzed via SEM, using one of the charge neutralization techniques described previously in the report. This analysis would indicate if the CNTs deposited as expected, and if the CNTs were penetrating into the Kevlar fibers or if the deposition was limited to the surface. The air quality around the modified Kevlar during ballistic testing could be analyzed immediately after a projectile impact in order to determine the concentration of aerolized CNTs. This experiment is critical because airborne CNTs are toxic, and it is a primary concern to ensure CNTs remain embedded while the body armor is being worn.

There are also some additional experiments that could be done to test other techniques for improving the strength of Kevlar fabric that may be used in conjunction with the CNT modification method described in this report. One such experiment is to investigate the effect of different denier (linear mass) values and thread orientations on the capability of Kevlar to dissipate impact energy. Additionally, it may be worthwhile to research the possibility of including a non-Newtonian fluid layer in the vest as well as a CNT modified layer. For example, a layer containing a shear-thickening fluid could potentially dissipate a good deal of energy during impact, thus further strengthening Kevlar body armor. Given a greater budget and timeline, these are all lines of research that are worth pursuing and that could lead to even stronger and tougher Kevlar body armor, providing greater protection for service men and women.

Budget

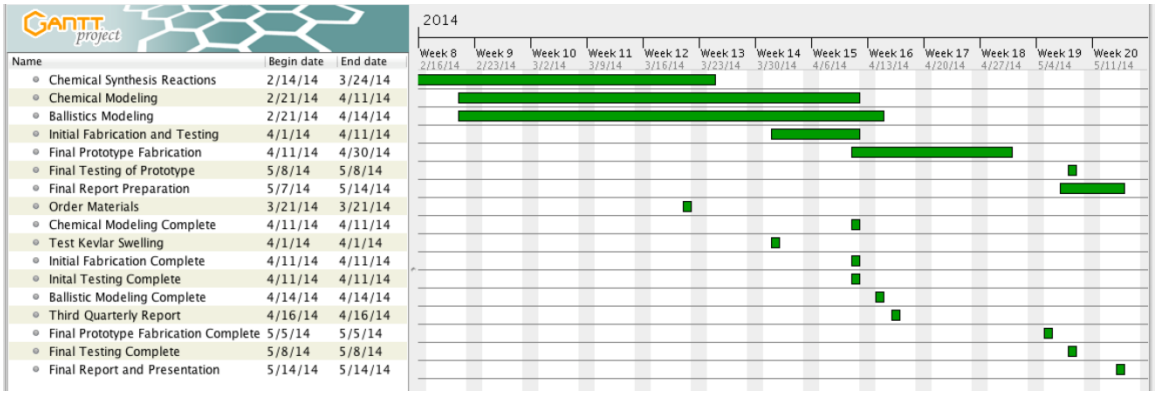
The final budget was barely under the $1000 budget. There were substantial changes from the original budget as the project evolved to accommodate scale-up procedures for the larger sheets. The majority of the budget was spent on supplies for the chemical processing. The other costs that should factor in but did not cost any money were the characterization equipment used, the lab space at the University of Maryland over the team's one hundred plus

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

man hours in the fabrication process, and the ballistic test at Aberdeen Proving Grounds. They fired 4 rounds into the vest. Initial estimates from them were that it is $1000 per shot before they offered to do it pro bono. They also had to fabricate special equipment in a short timeframe, and there were over 10 people on site to test the samples. Their cost far exceeded our budget for the entire project.

Milestones and Deliverables

The team was able to accomplish all of the milestones and deliverables through all phases of the process. There were areas of the project that took longer than expected, but time was made up in sections that followed. All of the major phases were completed within one week of their original timeline. The major milestones and deadlines that the team worked under are in the gantt chart below.



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

In conclusion, the team achieved several of its goals and made a great deal of progress towards meeting the objective of fabricating CNT modified Kevlar vests with a higher strength than standard grade body armor. The team successfully designed and fabricated a 12” by 12” ballistic panel with 15 layers of modified Kevlar fabric. To accomplish this, the processing procedure was first developed and tested on small samples meant for tensile testing before being dramatically scaled up. This modified Kevlar prototype was tested in a ballistics lab at APG. The results of this test indicated that CNT modification enhanced ballistic resistance of Kevlar fabric by twofold based on backface deformation measurements. Additionally, the mechanical properties of the modified Kevlar were determined through tensile testing. These tests showed that the team successfully modified Kevlar 29 Style 745 and KM2 Ballistic Fabric with PBA functionalized CNTs, thereby increasing their tensile strengths from 94.7 MPa to 443 MPa and 142 MPa to 213 MPa, respectively. Furthermore, the effect of reactivity on CNTs during the PBA surface grafting process was demonstrated and the grafting reaction described in greater depth through chemical modeling. The ballistics modeling predicted the amount of layers a small ammunition round would penetrate, thus informing the team of how many layers must be fabricated. The ballistics modeling prediction was very close to experimental results, thus validating the success of the model. Overall, the team successfully tested a CNT modified Kevlar prototype, created through a well-designed fabrication process informed by both chemical and ballistic modelling, all while remaining within the timeline and budget.

Acknowledgements
Special thanks to:

APG Ballistics Lab: This team worked tirelessly to meet the strict deadlines and test our CNT panel at EF-10. They developed all the safety protocol proposed from ARL's Industrial Hygiene Office and completed all the necessary paperwork to constitute our ballistic testing.

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

Johns Hopkins Applied Physics Lab: Dr. Morgan Trexler for providing us with CNT body armour information

NIST: Dr. Amanda Forster and ballistics testing group for providing us with ballistics testing information and referencing us to additional contacts

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