RICE UNIVERSITY

Push it to the Limit: Investigating the Material Response of Nanostructured Materials under Extreme Mechanical Environments

by

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ABSTRACT

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High velocity impact phenomena range in scale from catastrophic events such as impact of aircraft and missiles into large infrastructures to impact of micron- and sub-micron-sized micrometeorite particles into spacecraft and satellites. Although, events of this nature are not a popular topic in the public community, they play a large role in the material development to meet the technological and protective needs of today.

Materials with length scales in the nanometer range are known to exhibit superior mechanical properties as their unique structure-property relations are drastically different than many macroscopic materials, some examples include: graphene, carbon nanotubes, polymer nanocomposites, and gradient nano-grained metals. When utilized at the macroscale, the unique nanomaterial properties do not always translate due to impurities, defects and inherent flaws in the scaled-up bulk material. Additionally, certain materials may only exhibit unique properties during transformations requiring extremely high pressures.

In this thesis, I employ a micro-ballistic impact test to study the very high strain and strain rate behavior of one-dimensional carbon nanotubes in a non-woven mat, two-
dimensional assemblies of polymer grafted nanoparticles, and three-dimensional silver metallic micro-cubes, to understand the structure-property relations of these nanomaterials and micromaterials. The micro-ballistics technique provides an improved understanding for researchers to scale these materials to the macroscale with tailored properties for different applications, like fracture resistant coatings, impact mitigating protection systems, and reinforcement for large infrastructures.
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This thesis would not have seen the day of light without the crucial help and contribution of several wonderful and helpful persons which is why I would like to take this opportunity to show my appreciation to all the kind people around me, to only some of whom it is possible to give particular mention here.

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My experience at Rice has been memorable, and thank everyone I have crossed paths with for making my short time challenging, exciting, and fun—thank you!
“Blessed is the one who finds wisdom, and the one who gets understanding, for the gain from her is better than gain from silver and her profit better than gold.”

—Proverbs 3:13-14

“The ultimate measure of a man is not where he stands in moments of comfort and convenience, but where he stands at times of challenge and controversy.”

—Martin Luther King Jr.

“We are all faced with a series of great opportunities brilliantly disguised as impossible situations.”

—Chuck Swindoll
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<td>Nanostructured Material</td>
</tr>
<tr>
<td>0D</td>
<td>Zero Dimensional</td>
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<td>hPS</td>
<td>Homopolymer Polystyrene</td>
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<tr>
<td>GNG</td>
<td>Gradient Nano-Grained</td>
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Chapter 1

High Strain-rate Behavior of 1D, 2D, and 3D Nanostructured Materials

1.1 Goals and Motivation of Research

The main goals in this dissertation are: (i) the characterization of the dynamic deformation response, measured at the nanoscale, of nanostructured materials (NSMs)—materials with nanoscale features; (ii) the study of the effects that internal nanostructural features have on material bulk properties and on the material deformation mechanisms; and (iii) examination of the fundamental deformation behavior of NSMs at very high strain rates.

With the continuing discovery of new materials with nanoscale features, researchers are quickly testing their properties to search for suitable improvements to currently available materials. What remains unknown for many of these advanced materials is their response in extreme environments (e.g. thermal, mechanical, or chemical). To succeed in new, high performance applications, the new nanomaterials must not only have superior
properties, but also maintain performance integrity under harsh conditions. Extensive mechanical studies have been conducted under static, quasi-static, and high strain rate regimes. However, to further establish principles for rapid development of new materials technology, materials development should be considered not solely from the viewpoint of bulk properties of NSMs, but also from the coupling effect of bulk properties and deformation mechanisms. By characterizing the active deformation mechanisms, we can deepen our fundamental understanding of the effects that nano- and micro-structures have on a material’s bulk dynamic response. This will lead to the development of better failure-resistant nanomaterial compositions, microstructures, and nanostructures.

This thesis demonstrates this conjecture with three individual cases, of one dimensional, two dimensional, and three dimensional materials with nanoscale features, that allow each system to exhibit formerly counterintuitive properties—e.g. strong and lightweight or strong and tough materials. These property enhancements will create new pathways to greatly improve protection materials and systems.

The three specific materials cases not only promise to exhibit unique properties, but are also viable model systems to better understand the specific structure-property relationships of NSMs with similar structures. Finally, this thesis will discuss dimensionless factors for scaling to macroscopic sizes without adversely affecting structure-property relationships, and hopefully encourage more scientists and engineers to seek methods to improve scalable nanomaterials syntheses and manufacturing conditions.
1.2 Organization and Brief Overview of Dissertation

The remainder of Chapter 1 emphasizes the utility of conducting research using a micro-ballistics testing apparatus. It discusses current challenges in research on protection materials, and what advantages are inherent in miniaturizing impact tests.

Chapters 2, 3, and 4 in this thesis are either verbatim from or written in preparation for journal publications.

Chapter 2 and 3 use impact testing conditions like those used for soft armor to investigate the mechanisms of penetration and perforation of nanoscale thin NSMs at high strain rates (> $10^6$).

Chapter 2 discusses the energy absorption and dissipation ability of entangled 1D carbon nanotubes (CNTs) and CNT ropes in a 2D membrane. It relates the length-scale effects and sample dimensions relative to the impacting object—i.e. the projectile—and the resultant energy dissipation.

Chapter 3 examines the microscale and nanoscale structural changes of a 2D polymer NSM, with 0D grafted particles, under dynamic loading conditions. Then compares it to the homopolymer equivalent of the polymer matrix. Investigation of the governing failure modes allow the construction of a pathway to alter the polymer internal structure to enhance its energy dissipation capacity.

Chapter 4 presents the structural characterization of single crystal microcubes deformed at high strain rates. Analysis using electron microscopy reveals the nanostructural
changes that evolve during and after impact which may lead to the dynamic formation of a new type of gradient NSM.

Chapter 5 concludes the dissertation and provides an outlook on future research directions.

1.3 Introduction

Anthropologists have relied on the use of specific materials to define the culture of mankind. From the stone age to the bronze age, to the iron age and now currently the silicon age, technological advancement has been driven by the ability of the science and engineering community to utilize these materials in ways that advance our human capabilities. In this current decade, rapid progress in technology is pushing current materials to their physical limitations including: lithium’s output (storage) efficiency in lithium-ion batteries, semiconductors’ energy conversion efficiency in solar cells, composite strength-to-weight ratios for protection applications, and the ever-decreasing size of silicon integrated circuits in electronics. The science and technology community now faces the reality that Moore’s law (doubling the capacity of Silicon integrated circuits approximately every two years, with commensurate decreases in cost) has ended[1].

Nanomaterials are pushing the forefront of remedying these challenges. IBM has declared a “major engineering breakthrough” with the ability to create a carbon nanotube transistor that will reduce the number of integrated circuits required for an electronic device to function while increasing the transistor’s efficiency[2]. Professor Mirkin from
Northwestern university has spent over two decades developing methods to attach DNA and RNA strands to nanoparticles with recent notable success as in therapeutic applications[3], [4]. These examples illustrate how the field of nanotechnology is converging multiple disciplines not only to study the world of atoms and nanostructures, but also to develop solutions to our most pressing human and world problems. [Malcolm Gillis, “21st Century Technology and the Nano-Bio-Info Convergence,” seminar on Nanotechnology, The Royal Institution of Great Britain, London, June 3, 2014.]

Ultimately, the realization of truly unprecedented products that incorporate nanotechnology, such as nanorobotics, remains unknown—many believe it is decades away; some believe the future draws close. [Ray Kurzweil, “Nanotechnology and Change”, Keynote on Impact of Nanotechnology, Foresight Institute.] As it stands now, nanotechnology is firmly embedded in the basic research and development of nanomaterials in academia and other laboratories across the globe. Thus, revolutionary research and development in the field of nanomaterials or NSMs is constantly “pushing the limit” of our fundamental understanding of “nano”.

1.3.1 Nano-Route for New Protection Systems

At the heart of this thesis lies the first fundamental question: What is the “nano” contribution to macroscopic mechanical properties. First, let’s clearly define “nano”. It is commonly accepted that “nano” refers to the smallest length scale associated with a material. By definition, “nano” is relevant when materials have lengths scales that are either intrinsic or extrinsic ranging from 1 nm to 100 nm[5]. At this scale, the percentage of atoms at the surface of a material significantly increases along with the
surface area per unit volume. An example is in 1D materials where we would expect 3 orders of magnitude increase in specific surface area, given by Equation 1.1, when the radius, $r$, decreases from the micron level to the nanoscale.

\[
\text{Specific Surface Area} = \frac{4\pi r^2}{3\pi r^3 \rho} = \frac{3}{\rho r} \quad (1.1)
\]

**Equation 1.1—Specific Surface area; $r$ denotes radius**

Understanding the “nano” effect on mechanical properties, will require investigations of the defining mechanisms that develop on nanometer length scales, that influence the microscale, and that impact the macroscale. These mechanisms can include the enhancement of internal energy-dissipating interactions in a structure, the enhancement in stress transfer between materials with relatively similar properties due to the existence of nanofillers, and the creation of new microstructures through dynamic evolution.

Researchers have previously explored the static (time independent)[6], [7], and quasi-static (low strain rate)[8], [9] mechanical properties of nanomaterials. But, there is an increased need to conduct very high strain rate experiments (greater than 10,000 s$^{-1}$, so that new materials can be identified as possible candidates for applications requiring material that can serve in an extreme mechanical environment. The field of high velocity impact of nanomaterials, which includes the ballistic velocity impact regime (200-1500 m/s), has remained minimally explored since the expansion of “nano” research started back in the late half of the 1980s when Smalley, Curl and Kroto discovered the C-60 fullerene[10]. The field has mainly focused on nanomaterials as reinforcing agents, with comparison of the materials composition, density, and bulk properties against the
material response to impact using a statistical approach to material optimization[11]. While this is useful for device comparisons, it neglects a general discussion on the basic laws of mechanics and physics coupled with the behavior of materials to further understand the complex problems associated with impact events at ultra-high strains rates.

1.3.2 Classification of Dimensions

The second fundamental question asks, “how do we classify NSMs as 1D, 2D, and 3D?” The rapid growth in NSM development and discoveries have given reason for the necessity in the general classification of NSMs. In 2000, Gleiter first classified NSMs as low dimensional structures with submicron or nanoscale microstructures in at least one direction, which display size effects as a result[12]. However, Gleiter’s model did not consider 0D, 1D, 2D, and 3D carbon NSMs such as fullerenes, nanotubes, graphene, and nanoflowers. Thus, Pokropivny and Skorokhod detailed a modified classification outline for NSMs[13], and I classify the NSMs based on the outline of Pokropivny et al.

0D nanomaterials

Classified as point like objects with dimensions only observed in the sub 100nm range, 0D materials are generally denoted as objects in a matrix or as repeating units of an array. A variety of physical and chemical methods have been used to develop new 0D materials to include: quantum dots[14], plasmonic particles[15], core–shell nanoparticles[16], metal nanoparticles[17], ceramic nanoparticles[18], and hollow spheres[19].
0D NSMs, such as ceramic nanoparticles, which serve as fillers for polymer composites, approach the length scale of a single polymer coil and allow unique interactions that enable optimal control of mechanical properties[20].

1D nanomaterials

In this case, I refer to line like objects were two dimensions are sub 100 nm with a third dimension greater than a micron. This class includes nanotubes[21], nanowires[22], and nanofibers[23] to name a few. Figure 1.2 below captions a few different types of 1D materials.

Nanofibers and nanotubes are expected to play a major role in defining the next generation of soft armor material due to the increase in strength, toughness, and surface area of the fiber that results in greater mechanical properties and interactions between fibers for improved load transfer in the protection system.

2D nanomaterials

Continuing the classifications, nanomaterials are denoted as 2D when they have only one dimension in the nanoscale with the remaining two extending above the micron level. For, simplicity I only consider the idea that a flat plane material such as graphene or a polymer/metallic thin film to be 2D. For my thesis, I incorporate 0D nanomaterials into a 2D membrane, and configure a 2D membrane from 1D nanomaterials to study as my 2D NSMs.
3D nanomaterials

The last classification, requires a material to have dimensions between $10^2 - 10^3$ nm such that the study conducted is solely on a single 3D NSM, and does not consist of multiple 3D nanomaterials in an array or composite.

1.3.3 Designing New Protection Systems

In designing new protection systems, the common approach remains to incorporate materials with the combination of high strength and toughness, since such materials are expected to improve impact resistance against incoming objects. However, according to Cunniff [24], impact resistance tests suggest strength and toughness are not the only criteria necessary to produce a high performing material. Cunniff suggest that the combination of the material’s properties relative to the density of a material allow a more comprehensive understanding of a material performance. He sought out to answer very important questions; (1) Do other properties offer better guidance in material selection for development of new protection systems, if conventional bulk properties do not? (2) Does the materials behavior rely on individual properties or the synergistic effect of multiple properties, and, if so, how can they be identified, measured, and even enhanced? These fundamental questions are later discussed in, Chapter 2. Nevertheless, with Cunniff’s findings, I can now ask deeper questions related to nanomaterials to include: (1) Whether the chemical make-up and processing of materials can be tailored to achieve microstructures that exhibit nonconventional mechanical properties once they have been identified? (2) And can such control improve strength, toughness, impact resistance, and overall performance of a material?
To answer these questions, I view the development of novel material from the dual perspective of the influence of the conventional bulk material properties and the micro- and nanomechanical mechanisms coupling contribution to the deformation behavior of a material. Defining the behaviors associated with different micro- and nanostructures—including the chemical and phase composition that make up the building blocks—can assist in narrowing materials that are more resistant to penetration and will lead to protective materials with better performance.

This thesis will integrate all components associated with energy dissipation in a material, by investigating the mechanical properties of nanomaterials at very high strain rates using a previously developed micro-ballistic system[25], [26]. Post-impact analysis will identify key deformation mechanisms associated with the energy storage and dissipation in each of the nanomaterials. Ejected material, separated material, and material near the penetration hole provide an informative illustration with which our framework of analysis is built. Capturing the projectile, sectioning the penetrated material, or inspecting using high resolution microscopy, will reveal the damage features to help uncover the mechanisms of material failure.

1.4 High Strain Rate Dynamic Deformation

The initial important concept involves strain rate—not velocity—as the essential parameter to observe dynamic deformation. Strain rate ($\dot{\varepsilon}$) is defined as the rate of change of strain ($\varepsilon$) with respect to time ($t$)[27].

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt}$$  \hspace{1cm} (1.2)
Equation 1.2—Specific Surface area; \( r \) denotes radius

Much of the inelastic, specifically the plastic, deformations occur from impacting material at rapid velocities to generate high strain rates. High temperature spikes and large strains near impact often occur because of the material’s deformation. The high-strain-rate behavior of many polymers, metals, ceramics, and nanomaterials is generally dependent on parameters such as strain, strain rate, and temperature[28].

A variety of experimental techniques for quantifying the rate-dependent properties of different materials are listed in Figure 1.1. Note that the stress states developed by the techniques may be different.

![Figure 1.1—Experimental techniques to control strain-rate deformations in materials [28]–[30].](image-url)
Detailed reviews of the current methods can be found in many literature articles and books.[27], [28], [31]–[34] Classification as high strain rates occurs at $10^2$ s$^{-1}$, then to very high strain rates above $10^4$ s$^{-1}$, and then to ultrahigh strain rates above $10^6$ s$^{-1}$[34]. Quasi-static strain rates are below $10^{-3}$ s$^{-1}$, and strain rates are referred to as creep once they drop below $10^{-6}$ s$^{-1}$. The emphasis for this thesis is using micro-ballistics testing to generate impact conditions at ultra-high strain rates ($>10^6$ s$^{-1}$).

1.4.1 Current Challenges of Testing at High Strain Rates

The need to engineer and optimize protection material to survive high-strain rate conditions is constantly rising as technology expands the applications requiring protection against incoming objects, to include: spacecraft and satellite protection from incoming micrometeorites[35], large-scale infrastructure protection from missiles and hijacked aircraft[36], automobile protection against high speed collisions[37], personnel protection against high-velocity bullets and flechettes[38], and even human bodies against head-to-head impact in sports[39]. An important consideration when enhancing the capabilities of protective systems is the ability to rapidly develop and apply technology to meet the challenges of today. There is a current gap in the design practice for material development, where materials are not considered for testing unless they are readily accessible in large quantities[33]. This sets limitation, especially for nanomaterials, as synthetic chemists, who may lack the knowledge to predict material macroscopic performance, may not focus their attention on scalable methods for incorporation of nanomaterials into real-world applications. Additionally, once these materials are available in macroscopic quantities for testing, generally above the cubic
centimeter scale, they follow a “make then impact” iterative process which allows only a few samples to be tested over a given week. In the case of studies that seek to vary compositions to find the optimum performance, this can drastically extend the necessary time and cost to complete the series of studies.

This thesis uses a micro-ballistics testing apparatus to overcome these challenges and provide a new paradigm for testing nanomaterials for potential use in commercial applications. By reducing the scale, multiple samples can be mounted such that rapid testing (> 100 impact events per day) is available. Moreover, the reduction in scale allows high resolution characterization of samples’ nano-/micro-structures, behaviors, and deformation mechanisms with electron microscopes— not reasonably performed in depth with macroscopic samples because of large sample size vs. the small size of high resolution images. Indeed, capturing the deformation field in a 10 mm x 10 mm event vs a 1000 nm x 1000 nm event is a factor of $10^8$ difference. Most importantly, micro-ballistic testing offers a solid pathway to explore the properties of advanced materials that are not available in large quantities, which will serve as a useful prototyping technique. The principal objective of this new paradigm is to improve the “design and test” iterative process for nanomaterials and materials with nanoscale features with suggested superior properties and to accelerate their implementation in protection systems.

1.5 Laser Induced Projectile Impact Test (LIPIT)

The Thomas research group has a unique experimental method for investigating the high-strain-rate and high-strain characteristics of nano-materials, known as the laser induced projectile impact test (LIPIT), first coined in 2012 by Lee et al.[25]. The LIPIT system
was first used to characterized the impact response of alternating glassy-rubbery nanocomposites.[25] Clusters of projectiles were launched at various angles and velocities and imaged after impact (Fig. 1.2).

![Image](image_url)

**Figure 1.2**—Optical image of hundreds of micron sized silica projectiles launched over a large range of angles. Double exposure photograph with a 22-ns interval at 250ns after the excitation laser pulse. The scale bar is 200mm, image taken from Lee et al [25].

While this provided a suitable method for initial study, expansion of LIPIT’s capabilities was greatly enhanced by the selective launching of individual projectiles. Thus, the Thomas group’s development of the alpha LIPIT ($\alpha$-LIPIT) to selectively impact nanometer thin films of multi-layer graphene to examine their mechanical properties under ultra-high strain rates using impact velocities of up to 1000 m s$^{-1}$ (Fig. 1.3)[25], [26].
In the LIPIT setup (Fig. 1.4), a delay generator, which controls two lasers, triggers the 1064nm laser to ablate a local area of a highly absorbing thin metal film, and launches the µ-projectile from a “launch pad”, and triggers the 532 nm laser to image the event. The launch pad consists of a ~20 µm thick polydimethylsiloxane (PDMS) film on a gold coated glass slide (~50 nm thick gold layer). The thickness of gold was used such that there is no optical transmittance of the laser through the gold, preventing any heating from excitation by the laser[26]. The 1064 nm ablation laser rapidly heats the gold film to create a plasma, causing the PDMS film to very rapidly expand and propel the projectile forward. PDMS top layer is used to capture gold debris, absorb shock wave generated from impact, and prevent heat transfer from gold to projectiles[26]. At a user defined delay time after triggering the 1064nm laser, the delay generator triggers the second 532
nm green imaging laser to send three probe pulses that generate a transmission image of the projectiles in flight. Each pulse was directed to a dye laser cavity to convert the coherent pulse to a series of incoherent pulses at a wavelength of 620 nm and prevent interference in collected image from any scattering of the laser pulse. Time gaps of 34.5 ns were established by the optical delay path. Once images are recorded by a CCD camera, the velocity during flight is calculated by taking the calibrated distance traveled from the pixel line length over the time gaps between each pulse. Details of the experimental system and its improvements are in [25], [26], [40], [41].

![Schematic of LIPIT optical path.](image)

**Figure 1.4—Schematic of LIPIT optical path.** [26]

### 1.6 Penetration and Perforation Assumptions

Chapter 2 and 3 of this thesis focus on the penetration and perforation of 2-D membranes. Previously, Backman and Goldsmith define penetration as the embedding of an incoming
object into a target resulting in a residual velocity of zero.[42] In contrast, perforation occurs via the complete piercing through a target by the incoming object.[42] Based upon analytical approximations, each of the following assumptions are used throughout the impact events in this thesis:

(1) The penetrated and perforated membranes in chapters 2 and 3 are thin targets, such that the stress and deformation gradients through the thickness of the specimen are minimized;

(2) For thin membranes, only small local regions with dimensions a few times the projectile diameter are affected by impact, such that they behave as free standing membranes and boundary effects are not considered;

(3) The thin membranes are initially stress free;

(4) Projectiles are undeformable rigid bodies such that no energy dissipation occurs through hard projectile deformation.

1.6.1 Importance of Impact Physics

Currently, the research community has not created technology with the capacity to record high resolution video of materials deformation behavior during microscale impacting. Most updated research has developed multi-frame technique to better track the projectile flight path, but does not allow for the high resolution imaging of the deforming sample in the process[43]. For this reason, simplified analytical models are used to examine the complex stress wave in the solids, enabling the explanation of the response of the materials and structures under dynamic loading events. The key physical phenomenon to consider at these strain rates are: (i) wave propagation theory (elastic, plastic, shock) and
material deformation (elastic, plastic, hydrodynamic) as functions of strain rates.[28]

Exploration of stress wave propagation is in each of the subsequent chapters as it relates to the specific material.
High Rate Deformation Behavior and Energy Absorption characteristics of Nanotube Mats

Carbon nanotubes (CNTs) have exceptional intrinsic mechanical properties with high axial stiffness up to 900 GPa [44] and tensile strength of up to 150 GPa[6]. Their ultra-high aspect ratios (~ $10^5$) [45] and surface area[46] >300 m²/g allow a significant level of physical interactions between tubes in a network over many length scales. Herein, we investigate the energy absorption characteristics and associated deformation behavior of porous, nonwoven CNT films having approximately 2D planar isotropic symmetry using a laser-induced micro-projectile impact test[25], [26]. Micron size silica spheres impact thin CNT mats with thicknesses between ~50-250 nm at velocities from 300 ms⁻¹ to 900 ms⁻¹. Electron microscopy characterization of the deformed CNT mats is used to deduce energy dissipation mechanisms operative at high strain rates (~$10^7$). Our results suggest the potential for nanoscale non-woven fabrics to raise the performance standard of protection material.
Disclaimer

The results shown in this study are not transferable to the macroscopic scale for use in ballistic fabrics or government armor grade vehicles. A requirement for fiber based materials is for fiber lengths to well exceed the diameter of an impacting object. Our CNTs have lengths of \(~1-2\text{mm}\) which is well below even the standard bullets used in pistols. Therefore, our research serves to merely show how the synergistic effect between fiber diameter reduction, fiber mechanical property enhancement, and use of nonwoven morphology can lead to superior performance.

2.1 Protective Materials

Protection materials that are comfortable, compatible, and easily incorporated into clothing are highly desirable today. Modern protection materials are categorized as hard and soft. Hard protective materials are can be made of thick ceramic or metal plates which are hard enough to deflect impacting objects such as bullets to prevent penetration[33], [47], [48]. Typically, hard protective materials offer more protection, but their weight reduces the functionality of these protective systems [33]. On the contrary, soft protective systems offer more flexible, comfortable, and mobile alternatives which can provide much greater protection than a standard t-shirt or jacket.

2.1.1 Soft Fiber-Based Protective Materials

Polymeric fiber based materials comprised of long, thin one dimensional filaments are one type of soft protective material that offer flexible, lightweight material with high strength and modulus[49]. Although the individual fibers exhibit high mechanical properties, they do not alone enable the protection against impacting foreign objects, rather it is the yarns (i.e. strand of fibers) that are made into woven and nonwoven fabrics that enable the interaction between fibers to collectively provide the necessary
mechanical properties[31]. These high-strength, impact resistant fabrics are desirable in applications such as protective clothing for military and law enforcement personnel, protective layering in turbine fragment containment and other similar applications involving protection resistance against high velocity projectiles[33], [50].

In recent years, several high-performance fabrics arose and drastically improved fabric physical performance to include: highly oriented polyethylene (e.g. Spectra®, Dyneema®), aramids (e.g. Kevlar®, Twaron®, Technora®), and PBO (e.g., Zylon®)[33]. Researchers developed the fabrics to outperform previous nylon based fabrics by increasing stiffness, retaining flexibility, increasing strength to weight ratios, and reducing fabric strain to failure below 4% [51].

A unique feature in the new generation protective fabrics are their ability to undergo large plastic deformation without diminishing their tensile load carrying ability at low and high strain rates[52]. To date, aramid fibers such as Kevlar 129®, KM2, and Twaron are the most common fibers used as soft protective systems. The aramid fibers previously mentioned consist of highly aligned Polymer chains that result in superb modulus values; which makes them ideal for ballistic applications that require soft protective systems. Additionally, the lightweight properties of the material is another advantageous feature.

### 2.1.2 Classes of Fabrics

Based on their structures and manufacturing methods, fabrics are categorized into three major classes: woven, nonwoven, and knitted fabrics.
Woven

Based on their structures and manufacturing methods, fabrics are categorized into three major classes: woven, nonwoven, and knitted fabrics. Woven fabrics are formed by repeatedly weaving yarns together in a specific pattern. Yarns can be classified as 1D solid structures, or twisted and untwisted bundles of 1D solid structures called fibers.

They are further broken down into “warp yarns”, which are in the lengthwise direction of the fabric that are held in tension, and “weft yarns”, which are woven in the perpendicular direction to warp yarns (Fig 2.1)[49].

Figure 2.1—left) a typical woven fabric (indicating the two principal directions of the aligned fibers/yarns (right) a typical woven fabric (indicating the two principal directions of the aligned fibers/yarns

The weaving patterns determine the types of woven fabrics. For impact resistance fabrics, a plain-weave fabric (Fig 2.1) is commonly used, and has only one cross over point of warp and weft yarns in the repeating pattern[49][53], [54]. The interaction between yarns are optimized in this configuration[31], [33]. The mechanical properties of woven fabrics ultimately depend on multiple factors including fiber material, yarn geometry, and weave.
pattern, but these comparisons are not discussed in this thesis because the focus is on plain-weave materials vs. nonwoven nanostructured materials (NSMs). Moreover, knitted fabrics are not used in ballistic protection, therefore, will not be discussed in the thesis.

**Nonwoven**

Nonwoven fabrics contain solid 1D structures that are not woven in two primary directions, but instead contain randomly entangled fibers (Fig 2.1). Currently, High porosity in nonwoven fabrics drastically decreases the interaction between neighboring yarns. Therefore, yarn and fiber fusing processes are generally required to achieve sufficient mechanical properties for use in different applications (e.g. clothing[55], filter paper[56]).

### 2.1.3 Impact Response of Nonwoven vs. Woven Materials

When considering the use of protective materials factors such as lightweight, flexibility, and physiological comfort are often compared. Both nonwoven fabrics and woven fabrics meet these specifications, but studies have continually showed the ability of nonwoven fabrics to outperform their counterparts. A study by the U.S. Department of Defense demonstrated an 80% retention in ballistic resistance using a needle-punched nonwoven fabric made of nylon fibers while reducing the weight to a third of the woven fabric [57]. Another study by Thomas, demonstrated the ability of a nonwoven structure composed of blended Kevlar and high density polyethylene (50/50) to outperform a 100% Kevlar plain woven structure [58].
To understand how a change in internal structure influences the performance of the fabric we can look at the deformation behavior of the two woven and nonwoven structures. A biaxial woven fabric, when impacted, will deform in two principal directions resulting in a diamond shaped cone during deformation (Fig 2.2a). On the other hand, the non-woven morphology, due to the approximately 2D random fiber orientations, will deform in a axi-symmetric fashion [59] (Fig. 2.2b).

![Fig. 2.2—Schematics of spherical or hemispherical projectile impact onto a biaxial and an isotropic fabric. (a) square-shaped deformation cone of biaxial plain woven fabric, and (b) axi-symmetric deformation cone of nonwoven, isotropic fabric. Adopted from Wang et al.[60]](image)

A calculation can be made of the dimensions of the base of the deformation cone produced as an object impacts the biaxial and multi-axial fabric (Fig. 2.2a,b). If we assume that half of the diagonal of the square base is equal to the radius of the circular base, then the length of the edge of the square base is $\sqrt{2R}$, resulting in an area ratio of 1.57:1 for the circle and square area respectively. Thus, for the same cone base lengths,
the fabric structure in Fig. 2.2b has more material volume involved and therefore, given the same material is used to compare Fig 2.2a and Fig. 2.2b, will increase the amount of energy absorbed through strain and kinetic energy loss[60]. When only considering strain energy, the maximum energy absorption increase is about 57%. The increase in material volume suggest non-woven mats could have a greater potential to mitigate impact normal to their plane than woven fabrics if the design considerations that include fiber diameter, length, and fiber entanglements—controlled by density—allow the most fiber-fiber interactions in the system[61].

Although studies have shown nonwoven structures can potentially outperform their counterpart, Afshari et. al. realized adequate fiber entanglements, and fabric weight are crucial for nonwoven materials to remain competitive with woven materials. But, an increase in weight is not advantageous for lightweight materials, therefore, we are limited to finding opportune ways to increase fiber interactions in non-woven structures.

A clever solution can arise from the reduction in fiber diameter. This will result in an increase in total surface area of the fabric as more fibers can pack into the same size fabric. Typical fibers have diameters in the range of ~ 10-40 microns, thus, diving into the realm of nanomaterials to utilize materials with diameters $10^3$ times smaller would be of great interest.

2.2 CNTs as Fibers in Soft Protective Materials

Carbon nanotubes (CNTs) are suitable candidates because of the drastically reduced diameter (~10-80nm) and remarkable quasi-static mechanical properties. To date, CNTs
have some of the highest values of axial/ in plane stiffness and tensile strength for any material and due to their inherent low densities, are very attractive for several applications where performance per unit weight is critical. Treacy et al. first noted the high elastic modulus (i.e. stiffness) of CNTs by measuring the thermal vibrations of individual carbon nanotubes over a range of temperatures. By relating the vibrational frequency, length, and density of CNTS they deduced an average axial modulus value of 1.8 TPa for CNTs[62]. Although the value obtained in this experiment varied quite substantially from 0.4 TPa to 4.15 TPa, another experiment, in which an anchored carbon nanotube was deflected by an atomic force microscope tip, recorded the force as a function of displacement to calculate an axial elastic modulus of 1.22 TPa[44]. These modulus and strength values of CNT are amongst the highest reported for any material to date.

Previous research by Lee et al. has shown the flat 2D representation of CNTs, denoted as graphene, demonstrates remarkable penetration resistance, and up to 10x higher energy dissipation per unit mass than steel during high strain-rate loading[26]. These findings have sparked new research on graphene and engineering of new graphene composites[63]–[65]. For CNTs, there is little investigations on the very high strain rate (>10⁴ s⁻¹) deformation behavior.[66] Only, unique deformation modes of sequential collective buckling have been found in aligned carbon nanotube arrays in static,[67], [68] quasi-static[8], [69] and dynamic[9] (10³-10⁴ s⁻¹)[27] loading regimes, but not at strain rates of 10⁷ s⁻¹. Here we explore the ballistic penetration behavior of a carbon nanotube (CNT) nonwoven mats using the miniaturized high speed laser induced projectile impact test (LIPIT).
2.3 Performance of Soft Protective Materials

Although the tensile strength, modulus, and even strain-to-failure of CNTs are impressive, each have an important role in the performance of materials against high velocity impacting objects, and no individual property can control penetration performance of the fabric containing CNTs. If the ballistic performance was based on fiber/yarn toughness, nylon would be a better performer than Kevlar[31]. Instead, Cuniff developed an equation based on fiber properties to predict ballistic performance of fiber based materials to address this concern.

Cuniff introduced the parameter $U^*$ to predict the ballistic impact resistance in fibers. The specific toughness $(\sigma \varepsilon / 2\rho)$ and stress wave speed $(c = \sqrt{E/\rho})$ of a material are combined to define $U^* = \left(\frac{\sigma \varepsilon}{2\rho} \cdot c\right)$ where $\sigma$ is the ultimate axial tensile strength, $\varepsilon$ is the ultimate tensile strain of the target material, $E$ is the axial elastic modulus, and $\rho$ is the bulk density[24]. The quantity $(U^*)^{1/3}$ is a velocity and Cuniff found that $(U^*)^{1/3}$ is proportional to a material's $V_{50}$, the velocity where 50% of incident projectiles penetration through a target and 50% are stopped. Thus, developing material with a higher $(U^*)^{1/3}$ corresponds to improved $V_{50}$ values and ultimately better energy absorption capacity.[70]

Table 2.1 below lists the $(U^*)^{1/3}$ for multi-walled carbon nanotubes (MWCNTs), graphene, metal plates, and many common fabrics used for ballistic protection.
Table 2.1—List of CNT, Graphene, textile fiber, and metal protection plate impact properties used to predict ballistic performance.

<table>
<thead>
<tr>
<th>Fiber type</th>
<th>Strength (σ) (GPa)</th>
<th>Failure Strain (e) (%)</th>
<th>Modulus (E) (GPa)</th>
<th>Density (ρ) (kg/m³)</th>
<th>Wave Speed (c) (km/s)</th>
<th>Cunniff velocity (U)¹/³ (m/s)</th>
</tr>
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<tbody>
<tr>
<td>MWCNT[71]</td>
<td>150</td>
<td>5</td>
<td>900</td>
<td>1250</td>
<td>28.2</td>
<td>4036</td>
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<td>Graphene[26], [63]</td>
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<td>6ₐ</td>
<td>981</td>
<td>2210</td>
<td>21.0</td>
<td>2978</td>
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<tr>
<td>PBO[24]</td>
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<td>3.10</td>
<td>169</td>
<td>1560</td>
<td>10.4</td>
<td>813</td>
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<tr>
<td>Spectra®[24]</td>
<td>2.57</td>
<td>3.50</td>
<td>120</td>
<td>970</td>
<td>11.1</td>
<td>801</td>
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<tr>
<td>Dyneema[63]</td>
<td>3.38</td>
<td>3.6</td>
<td>88</td>
<td>980</td>
<td>9.5</td>
<td>784</td>
</tr>
<tr>
<td>600 denier Kevlar® KM2[24]</td>
<td>3.40</td>
<td>3.55</td>
<td>82.6</td>
<td>1440</td>
<td>7.5</td>
<td>682</td>
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<tr>
<td>Twaron⁵[61]</td>
<td>3</td>
<td>3.3</td>
<td>90</td>
<td>1440</td>
<td>7.9</td>
<td>607</td>
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<tr>
<td>Steel Alloy[63]</td>
<td>1.86</td>
<td>12</td>
<td>196</td>
<td>7850</td>
<td>5.0</td>
<td>390</td>
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<tr>
<td>Aluminum Alloy[63]</td>
<td>0.317</td>
<td>16</td>
<td>70.3</td>
<td>2660</td>
<td>5.1</td>
<td>344</td>
</tr>
</tbody>
</table>

a Lee et al.[26]

b [http://www.teijinaramid.com](http://www.teijinaramid.com)

Spectra is an ultrahigh molecular weight gel spun polyethylene fiber from Honeywell.

Dyneema is an ultrahigh molecular weight gel spun polyethylene fiber from DSM.

Kevlar is a liquid crystalline solution spun poly(paraphenylene terephthalamide) fiber from DuPont.

Twaron is a liquid crystalline solution spun poly(paraphenylene terephthalamide) fiber from Teijin.

For multi-walled carbon nanotubes (MWCNTs) fibers, (U*)¹/³ is approximately 5 times greater than many commercial protection fibers such as Kevlar or Dyneema (Table 2.1).

The penetration resistance indicator, (U*)¹/³, suggests a CNT fabric may even be able to outperform graphene (Table 2.1) but since a fabric consists of fibers oriented in various directions, the value of (U*)¹/³ for the fabric needs to be suitably averaged for the fiber arrangement. The relationship between the mechanical properties of a fiber and the ballistic performance of a fabric is rather complex. There are other factors that should
also be considered such as temperature resistance, friction from CNT inner wall shear-sliding[71], [72], and interaction between fiber and impacting objects. Nonetheless, a careful and detailed study of nanoscale failure phenomenology in CNT nanostructured materials (NSMs) would be most useful in developing fibers with better penetration resistance performance.

2.4 Experimental Methods

For these reasons, we have decided to investigate nonwoven MWCNT mats, a 2D NSM made of 1D components (Fig. 2.3a), by examining the coupling structural and mechanical property influence on the MWCNT mat behavior. During the impact loading event, the fiber-fiber interactions in the mat will generate local friction that dissipates energy and the fiber-projectile interactions control how the stress is distributed. These will be the determining factor of whether complete penetration (Fig. 2.3b) or partial penetration (Fig. 2.3c) occurs in the impact region. The MWCNTs, are reported to have diameters in the range of, $d_{\text{CNT}} \sim 10$-50nm, which are up to $\sim 300$ times narrower than the projectile diameter used ($d_p \sim 3.72 \mu$m). During impact, the projectile can now directly interact with hundreds of nanotubes in the mechanically loaded region. This large contrast in diameters is promising as studies have found that the impact resistance of protection material can increase as the fiber-fiber and projectile-fiber interactions increase [49][73].
Figure 2.3—SEM Images of undeformed, completely penetrated, and partially penetrated MWCNT mats and the experimental LIPIT setup. SEM images of (a) as-received MWCNT mat (b) penetrated thin MWCNT mats and (c) embedded SiO$_2$ (~3.72 µm) projectile in thin MWCNT mat. (d) Schematic of the experiment from projectile launch to penetration of target to capture of projectile; PDMS-polymethylidisiloxane, Au-gold, PS-polystrene. PS-PDMS.[25]
2.4.1 Impact Conditions

The thin MWCNT mats range in thicknesses from 50-250 nm, and are each impacted by 3.72-micron diameter silica spheres at average velocities of 300, 600, and 900 m/s. The mats consist of long (~ 1.5-2 mm) individual multi-walled carbon nanotubes (MWCNTs) overlaid in the x and y plane (Figure 2.3a). SEM (and some TEM) is used to characterize the as received materials and the morphologies developed following impact (e.g. Fig. 2.3b-c). The laser induced projectile impact test (LIPIT)[25], [26] accelerates an individual SiO$_2$ sphere to various velocities (Fig. 2.3d). The in-flight projectile velocities are measured before and after penetrating the target to determine the loss in kinetic energy ($\Delta$KE) due to interaction with the MWCNT mat. A capture plate comprised of a 500 µm thick polystyrene-polydimethylsiloxane (PS-PDMS, 22k-24k g mol$^{-1}$) block copolymer is placed ~300 µm behind the target to collect the projectile after perforation of target. Lee et al. previously demonstrated the ability of PS-PDMS thick films to capture similar micron size silica projectiles.[25]

2.4.2 Penetration Threshold

The material was impacted at three different velocities to cross the three energy absorption regimes (i.e. (1) below the ballistic limit, (2) lower velocity perforation regime, and (3) high velocity perforation regimes (Fig. 2.4). Near the ballistic limit—as previously mentioned is denoted as the material’s penetration threshold which describes where 50% of the events lead to complete penetration[74]. As the ballistic limit is surpassed, energy absorption increases until a critical impact velocity after which it starts to show maximum energy absorption capacity is reached (Fig. 2.4). Impacting at
velocities below, near, and above the penetration threshold allows the observation of a range of deformation modes for the target material.

Figure 2.4—Model plot of energy absorption as a function of impact velocity. Figure taken from Kocer[58].

2.4.3 Physical properties of CNT mats

A non-woven mat has an approximately 2D randomly entangled arrangement of MWCNTs. Figure 2.5a shows a normal incidence SEM image of a nonwoven MWCNT mat. This material was supplied from the company Tortech, a joint venture between Q-Flo (UK) and Plasan Sasa Ltd (Israel). The MWCNTs are synthesized from a gas phase catalytic reaction which uses floating metal catalyst to nucleate CNT growth (Fig. 2.5a)[75], [76]. As CNTs grow and flow out the chamber they form an aerogel network (Fig. 2.5b) which is form continuously drawn out of the reaction zone of the furnace onto a rotating drum to form a nonwoven mat with thicknesses of up to $10^3$ microns (Fig. 2.5c).
Figure 2.5—Synthesis of CNTs using gas phase catalytic reaction. (a) progression of reaction from CNT nucleation and growth to material collection. (b) Optical image of CNT aerogel denoted as “Sock” exiting the furnace. (c) Nonwoven CNT mat collected on drum. Image provided by Tortech Nanofibers.

The final product is hundreds of centimeters long in length and width (Fig. 2.6a). The overall morphology of the entangled nanotube network comprising the mat is important (Fig. 2.6a-insert). Other woven and nonwoven fabrics are often made from individual fibers that have diameters defined during the melt or solution spinning process and may be combined to form yarns containing many fibers[77]. Thus, the diameter is a very well defined entity. The yarns or the fibers can be combined in various weave patterns or more randomly agglomerated into mats by a variety of processes, followed sometimes by thermal spot bonding, or they are needle-punched to improve fiber-fiber interactions[78].
In the MWCNT mats we study, the gas phase process forms MWCNTs that can mutually impinge during growth, leading to a resultant dual phase entangled (Fig. 2.6a insert) and interconnected (Fig. 2.6b) network of MWCNTs due to the bonding together (bundling) and splitting apart (debundling) of individual nanotubes each having a diameter of 5-15nm. The “entanglement” is akin to that of the entanglement network of isotropic 3D flexible chain polymers that entangle in the x, y, and z direction. In such normal synthetic polymer systems, every chain is identical in diameter, differing only in overall length, according to the molecular weight distribution. Contrary to a 3D network, the MWCNTs in the mats have trajectories that are mostly confined to the x, y plane with no significant component of their contour length along the z (thru-thickness direction). Figure 2.6c, confirms this statement as a cross-section of the CNT mats show several layers inside of the mat collected on the drum, thus suggesting minimal entanglement in the z-direction.
Figure 2.6—Final Production of CNT mat. (a) Optical image of large CNT mat; insert—SEM image of CNT network. (b) TEM images of interconnected CNTs. (c) Cross-section of CNT mat collected on drum.
Table 2.2—Physical properties of as-received MWCNT mats.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Sample Thickness</td>
<td>~42 µm</td>
</tr>
<tr>
<td>Bulk Areal Density (kg/m²)</td>
<td>0.016 ± 0.001</td>
</tr>
<tr>
<td>Bulk Volume Density (kg/m³)</td>
<td>380 ± 10</td>
</tr>
<tr>
<td>Porosity</td>
<td>~66%</td>
</tr>
<tr>
<td>Surface Area (m²/g)</td>
<td>300</td>
</tr>
<tr>
<td>Raman (I_D / I_G)</td>
<td>0.15</td>
</tr>
<tr>
<td>MWCNT Diameter</td>
<td>varies from 5-50 nm (see fig. 6)</td>
</tr>
<tr>
<td>MWCNT Length</td>
<td>~ 1-2 mm*</td>
</tr>
<tr>
<td>Nanotube Type</td>
<td>Non-chiral (zig-zag and armchair) multiwall CNT with an average of 3-6 walls</td>
</tr>
</tbody>
</table>

* Data retrieved from Tortech Nanofibers

The measured physical properties of MWCNT mats and individual properties of MWCNTs are detailed in Table 2.2. Details of techniques to measure values are discussed later. Areal density is the mass per unit area and is used for thin films or plate type specimens undergoing impact to acquire information of impact resistant properties relative to weight of the protection material. Often, experimental studies will compare the penetration resistance of materials with equal areal density and layer laminates of
equivalent areal densities to assess the effects of thickness on energy absorption[79].

Bulk areal density is a measurement from the as received ~42 microns thick Tortech sample. The areal densities of the much thinner films prepared for LIPIT are mentioned later.

2.4.4 MWCNT Characterization and Target Fabrication

CNT Fiber Diameter

Transmission electron microscope (JEOL 2100 Field Emission Gun TEM) images were used to estimate the range of MWCNT diameters (Table 2.2). Amorphous carbon (Fig. 2.7) from the growth procedure is found on the surface of the MWCNTs[80].

![Figure 2.7—Bright field transmission image of an individual 12nm diameter MWCNT with amorphous carbon on the outer surface, and diameter distribution of MWCNTs.](image)

The fiber diameter distribution above includes both the diameter of individual MWCNTs as well as bundles of MWCNTs to retrieve the effective diameter of a CNT “fiber”. The
areal density of the MWCNT mat taken was estimated by razor sectioning a 5 cm x 5 cm sample and weighing. The bulk density of the as-received sample was estimated by microtoming to determine mat thickness using an optical microscope (32x objective lens, NA 0.9). Quantachrome Autosorb-3b BET Surface Analyzer was employed to measure the surface area of the bulk MWCNT mat. A 15mg sample was placed in glass container and liquid nitrogen adsorbate at 77k filled small pores in sample, and calculations based on the Brunauer–Emmett–Teller (BET) isotherm provides an estimate of the surface area of the sample as 300m$^2$/g. The MWCNT mats average four to eight times more surface area then other ballistic fabrics (average surface area between 40-80 m$^2$/g with highest reported at 190 m$^2$/g) which suggests more interactions within the given area to produce more internal friction during impact by MWCNT mats. Measuring the lengths of MWCNTs is a non-trivial issue. The Windle group at the University of Cambridge conducted detailed experiments using TEM to follow along the axis of individual nanotubes searching for tube ends while noting the total length traversed and found the range of tube length to be between 1-2 mm. This corresponds to very long (millimeters) individual MWCNTs with correspondingly high aspect ratios of L/d ~ 2mm/20 nm =10$^5$ (Value reported Tortech Nanofibers).

**CNT Fiber Alignment**

Since the production of the MWCNT can result varied alignment of CNTs in the mat, we used Raman spectroscopy (Renishaw InVia Microscope) at $\lambda= 785$nm to characterize the anisotropy of the MWCNT mats.
Figure 2.8—Characterization of the alignment of the tubes in the mats using polarized Raman. a) Polarization angles of $\theta = 0, 30, 60, 90^\circ$, that describe the angle between the most aligned CNT direction and the polarization direction of the incident laser beam. b) Using a 785nm excitation wavelength with 10s exposure time produced a polar diagram that illustrates the G-band intensity as a function of $\theta$.

The excitation beam was polarized and passed through a half-wave plate to control the polarization direction. After passing the half-wave plate, the excitation beam was focused onto the sample using a 100x objective lens with NA 0.9. The Raman spectrum of the MWCNT mat was collected over a 180$^\circ$ span by 30$^\circ$ increments. The intensity of the G peak was normalized by the highest value and is plotted in Fig. 2.8. Herman’s orientation factor (HOF), a common alignment quality factor, was used to assess the orientation [9],[81]. The orientation of the nanotube backbone direction relative to the polarization direction of the incident beam is defined by the formula

$$f = \frac{1}{2} \left( 3 < \cos^2 \theta > -1 \right)$$

Equation 2.1—Herman’s orientation factor
The values of $f$ range between 1 for complete alignment and 0 for random orientation. The mats received from Tortech exhibited a $f$ value of 0.47 indicating some preferred orientation along the production direction.

**Nanometers Thin CNT Mat Preparation**

In order to create mats that could be penetrated by the silica projectiles, we used a derivative of the Lee et al. method for making multi-layer graphene from millimeter thick sections of highly ordered pyrolytic graphite.[26] The as received MWCNT mat was placed on the surface of a Kapton tape with a water soluble adhesive and subsequently the mat pulled away to delaminate a thin layer without compression to avoid densification effects. Continued mechanical exfoliation of the MWCNT films could produce 50 – 250nm thick MWCNT specimens (Fig. 2a). Next, an organic based liquid adhesive (Scotch Super™ 77, 3M) was diluted in toluene (~10 wt%) and applied to a nickel TEM grid (200 Mesh, Electron Microscopy Sciences) to coat the grid frame with a non-water soluble adhesive. Before drying, air was blown through grid holes to eliminate any adhesive spanning across grid holes, to coat the TEM grid frame only. The MWCNT/tape laminate was then mounted onto the TEM grid and then placed on surface of deionized water for 24 h. After dissolution of the adhesive, the Kapton film was removed with the MWCNT film remaining on TEM grid which was then dried in vacuum at 60 °C for 2 h before LIPIT testing.

**Launch Pad Preparation**

The particle launch pad was prepared following the procedure of Lee et al. [13] using a 22x22 mm microscope cover glass (Fisherbrand 12-541-B) with 30 nm of gold coated
onto the cover glass using a sputter coater (Denton Desk V Sputter System). A PDMS solution was prepared using a two-part PDMS kit (Sylgard 184, Dow Chemical), consisting of a PDMS monomer solution and a PDMS hardener. The two-part PDMS kit was combined at a 10 to 1 ratio of PDMS monomer to PDMS hardener. A Laurell WS-400BZ-6NPP/LITE spin coater was employed to give a 20 µm thick PDMS top layer. Due to the possible formation of air pockets, the cover slides were placed in a vacuum (Lab-Line 3628-1 S Quaroid Duo-Vac Vacuum Oven) for 30 minutes and then thermally cured (60°C for 24 hrs). A suspension of 3.72 µm diameter silica particles in ethanol was prepared (microParticles GmbH). After thermal curing of the PDMS, a drop of the SiO$_2$ particle/ethanol suspension was applied to the gold/PDMS-coated cover slide. A standard lab wipe sheet (Kimberly-Clark Kimwipe) was then used to spread the silica particles across the surface of the PDMS and Au coated cover glass.

*Projectile Capture*

To capture the SiO2 projectiles after penetration of the target films, a PS-PDMS film was spin-coated at 1500 rpm for 1 min onto a silicon wafer to produce an approximately 5 mm diameter, 20µm thick capture plate. Both the projectile capture plate and the TEM target grid were mounted onto another microscope cover glass slide using carbon tape to create ~0.3mm distance between each component. After impact, the capture plate and projectile were coated with 3nm gold and analyzed in SEM. Transmission optical microscopy employing a Zeiss Axioskop microscope with 20x, NA 0.4 was used to map out the target locations on each TEM grid before LIPIT testing to avoid shooting highly nonuniform or fractured film areas.
Deformation Analysis Instruments

To understand the deformation of the MWCNTs, we again use spatially resolved Raman spectra (Renishaw InVia Microscope, $\lambda = 633\text{nm}$ 100x objective lens, NA 0.9) to quantify the defects induced in individual tubes from the impact. The estimated spot size of the 633nm Raman laser is $\sim 1\mu\text{m}$ in diameter, thus measurements were taken in multiple micron steps away from the previous measurement to ensure no overlap in data collection. The ratio between the peak intensity of the defect band, D, and the graphite-like planar vibration of carbon atoms resonance band, G, indicated the damage induced by projectile impact. The actual impact region and the back-surface deformation was viewed using a FEI Helios NanoLab 660 SEM. Samples were characterized in immersion mode at 2kV and viewed at tilts ranging from $0^\circ$ to $55^\circ$.

Thickness Measurements

The thicknesses of the peeled MWCNT mats were measured by cross-sectioning each thin mat with a focused gallium ion beam (30kV, 40 pA). Several impact thickness measurements were conducted on two sides of each sample to obtain an average thickness for each sample (Fig. 2.9).
Figure 2.9—SEM images of Ga+ ion beam milled MWCNT exfoliated mat cross-sections. The cross sections appear solid due to the redeposition of the ion milled material.

2.5 Results and Discussion

MWCNT mats subjected to an impact velocity at 900 m s\(^{-1}\) recorded residual velocities \((V_r) > 0 \text{ m s}^{-1}\), indicating perforation across all thickness values impacted at 900 m s\(^{-1}\) (Fig. 2.10a). At 600 m s\(^{-1}\), the MWCNT mats at lower thicknesses show \(V_r > 0 \text{ m s}^{-1}\), but as mat thickness increases above 200 nm \(V_r\) shows \(V_r = 0 \text{ m s}^{-1}\) and \(V_r > 0 \text{ m s}^{-1}\) (Fig. 2.10a). These values are observed for near equivalent thicknesses, and indicates the crossing of the penetration threshold at the thickness range of 180-220 nm for this velocity range. Within this range ~30\% of projectiles perforate the MWCNT mat (Fig. 2.10b). To confirm this event, another set of MWCNT mats were impacted at 300 m s\(^{-1}\) within this thickness range, and \(V_r = 0\) were recorded for all samples.
Figure 2.10—(a) Plot of residual velocity vs. MWCNT mat thickness at velocities of \( \sim 600 \) and \( \sim 900 \) m s\(^{-1}\). (b) Ballistic penetration upper limit of 200nm thin MWCNT mat as a function of velocity and fitted with a Boltzmann sigmoidal curve.

From the percent penetration at the varying velocities we estimate the MWCNT mats breaking point (i.e. upper limit for ballistic protection), also denoted as the \( V_{50} \) (ballistic limit) at \( h_{ave} = 200 \pm 10 \) nm. The \( V_{50} \) ballistic limit estimates the velocity at which projectiles penetrate the target 50% of the time\[^{49}\] \[^{74}\]. Complete penetration of the MWCNT mat was observed when the residual velocity of the projectile, after penetration, was greater than zero. Other ballistic test methods approximate the \( V_{0} \), no complete penetration will occur below velocity, and \( V_{100} \), penetration occurs 100% of the time above velocity\[^{82}\]. The inability to precisely control velocity of projectile, and instability of penetration results within the \( V_{0}-V_{100} \) zone make it difficult to accurately estimate these values. Thus, the \( V_{50} \) statistical approximation more accurately depicts the likelihood that complete and incomplete penetration are likely to occur at the \( V_{50} \) velocity. The data was fit to Boltzmann sigmoidal curve. Many different methods are used to predict the ballistic limit of materials. We choose an approximation based on the
predicted trend of penetration events as a function of velocity. This sigmoidal fit is commonly used to predict the V_{50} ballistic limit.[49]

For these impact velocities and corresponding residual velocities, the ballistic limit is displayed at 535 m/s (Fig. 2.10b). Although, a range of thickness values were impacted, to understand the relevance of our residual velocities and the ballistic limit on performance we limited our characterization discussion to the samples impacted at \( h_{\text{ave}} = 200 \pm 10 \) nm, and we characterize the deformation behavior of the MWCNT mats using scanning and transmission microscopy analysis.

### 2.5.1 Impact Assumptions

Two impact approximations are first noted to include: (1) the diameter of the projectile, \( d_p \), is much larger than the MWCNT mat thickness (\( d_p/h_{\text{ave}} >> 1 \)) such that as the MWCNT films are loaded in tension and the stress gradients through the target thickness are negligible (2) The silica projectiles can also be assumed as rigid and non-deformable (SEM images of spheres on the capture plate and back surface of MWCNT mat do not show any cracking or shape deformation, Fig. 2.11). Angular momentum (i.e. the rotation of the projectile) is evident by the unidirectional alignment of tubes pulled from the mat to become perpendicular to the rotation axis. The launching mechanism does not call for controlled angular momentum in projectile, which is evident in a later discussion. The alignment direction of the MWCNT along the projectile surface is in the projectile spin direction. The high frictional force from the extensive contact length of the extended MWCNTs on the projectile surface prevents significant amount of slip of the tubes across the projectile surface.
2.6 Deformation mechanisms and multiscale interactions

Post-impact morphological analysis can be used to construct hypothetical sequences of how the MWCNT mat and the projectile interact as a function of incident velocity for the $h_{\text{ave}} = 200 \pm 10\ \text{nm}$ targets.

At 300 m s$^{-1}$, MWCNT mats incur microscale tensile strain in the incident particle direction. The forward motion of the spherical projectile results in the formation of a hemispherical cone shape by the mat (Fig. 2.12a). Like aPGN film analysis in Chapter 2, MWCNT mats incur $\sim 10^7\ \text{s}^{-1}$ strain rates.
Doubling impact velocity further progresses the projectile through the MWCNT mat. At 600 m s\(^{-1}\), the projectile starts to wedge through the entangled MWCNTs, and pull tubes
along its path (Fig. 2.12b). Nanotubes are straightened along the surface of the projectile, and translated through the MWCNT mat, while others begin slipping around the projectile. According to Kirkwood et al. who studied yarn pullout as a method to dissipate energy in Kevlar KM2 fabric against ballistic impact, the straightened and translated MWCNTs were first uncrimped (i.e. detangled) around the periphery of the impact site to allow nanotube translation[54]. Both translation and slip of CNT fibers are suggested to increase the CNT-CNT and CNT-projectile interactions, and thus will contribute towards energy absorption by generating friction[54].

Inconsistency in projectile rotation is shown at 600 m s⁻¹. Depending on rotation velocity of projectile, projectile penetrates according to Fig. 2.12b; ideally from projectile with lower rotational velocity, or Fig. 2.12c.; generated by projectile with higher rotational velocity. Some tubes are nearly completely wrapped around the sphere, suggesting the surface rotational velocity can reach up to roughly 10⁴ m s⁻¹. Please note that linear momentum and angular momentum are not interchangeable. They have separate conservations laws that require different units, and measure fundamentally different quantities. However, energy from angular momentum of projectile has shown to be negligible regarding impact, and is only considered for optimizing the ballistic trajectory of a bullet[31].

At the same velocity, we also observe complete penetration of the CNT mat (Fig. 2.12d). As mentioned, the very high fracture stress of MWCNTs allows significant lateral motion of individual tubes to dissipate energy through tube–tube friction, but near the estimated ballistic limit of ~535 m s⁻¹ the fracture stress may be occasionally surpassed.[51]
As the velocity is increased to 900 ms$^{-1}$, the ability of the MWCNTs to reconfigure and translate to relieve the rapidly increasing stress is surpassed and the increased stress levels cause tubes to fracture consistently and complete penetration occurs without debate (Fig. 2.12d). Images of projectiles that have completely penetrated and been impinged onto the PS-PDMS capture plate display tubes near the central region of the projectile undergoing tensile fracture (Fig.2. 11a2). Within the local impact region, we observe not only MWCNT fracture but also kinking, tube-tube fibrillation and shear sliding (telescoping) of MWCNT inner walls (Fig. 2.13a-i).

Fibrillation (i.e. the splitting of CNTs along their longitudinal axis) is a damage behavior attributed to abrasive action across the CNT length[51]. In multiply industry materials, fiber-fiber friction results in abrasion perpendicular to the fiber axis. Research states that all projectiles with the capacity to wedge through the a fabric (e.g. hemi-spherical, ogival, and conical shaped projectiles) cause a splitting of the fiber[51].

Telescoping, also observed in CNTs at the impact site, is a unique deformation credited to the MWCNT geometry that consists of a set of nested tubes of different diameter. “Telescoping” is a deformation made by shearing and sliding of the inner tubes with respect to the outer tubes within the MWCNT (see Fig. 2.13f). The known repetitive breaking and reforming of the van der Waals interactions from inner-wall slippage contributes to energy dissipation[83], [84].
Figure 2.13—Post impact relaxation features of due to elastic recoil of the MWCNTs. (a-e) SEM images depicting fibrillation (f) High magnification TEM image of fibrillation (g) SEM image of nanotube diameter reduction also denoted as telescoping (h-i) SEM (h) and TEM (i) of highly bent (i.e. kinked) individual CNTs. All images collected from MWCNT mats impacted at 900 m s⁻¹.

One deformation event, CNT kinking, is only realized post-impact when relaxation of CNTs (i.e. after complete penetration of projectile initiates recoil (snapback) of the highly elastically strained CNTs). Kink formation leading to abrupt, localized fiber bending is attributed to formation of defects sites along the CNT axis or it may be that the high stresses and strains induce defects and subsequent kink formation[85].
2.6.1 Intrinsic Damage

Identification of fracture mechanisms in individual CNTs brings forth more questions concerning the induction of defects and degradation of CNTs into carbon. Therefore, the potential damage to the graphene wall structure of the MWCNTs due to impact was investigated by tracking Raman intensity ratio of D—defect band and G-vibrational mode of nanotube along its length ($I_D/I_G$), representing the percent defects in the sample. The Raman intensity ratio ($I_D/I_G$) is related to the density of defects in carbon materials, and is used to assess any disorder in the sp$^2$ (C=C) structure[21], [86], [87].

Previous work by Ozden et. al. impacted a sphere of compact MWCNTs at hyper velocities near 6 km s$^{-1}$, and used Raman to confirm the formation of large numbers of defects in the nanotubes[66]. Rapid atom evaporation, and defect formation lead to nanotube unzipping along the longitudinal axis to form graphene nanoribbons[66]. Although our experiment is not conducted at hypervelocity, investigation of potential unzipping or defect generation can be explored using the same principles. To start, the original $I_D/I_G$ value of CNTs in mat is 0.25[21], [87][88]. Scanning the collective Raman response of impacted CNTs progressing away from the impact site shows nearly a two-time decrease in ($I_D/I_G$), Fig. 2.14, suggesting defect generation is a direct consequence of impact. Given a ~1 µm spot size for the Raman beam, and an impact diameter of ~4 µm, the data collected does not provide detailed analysis of individual nanotube damage. The measurements simply show the general assembly of MWCNTs induced defects during the impact process, but were not destroyed within the impact region as an ($I_D/I_G$) > 1 had not been reached [86].
Further analysis of CNT mat deformation is reserved for a later date. Discussion of individual CNT fiber translation through the mat as the projectile pulls the CNT fiber in the impact direction, and the friction associated with CNT-CNT interaction will provide greater understanding of the impact phenomena. This discussion is reserved for a later publication, and the current chapter, which is written in preparation for a publication journal, primarily seeks to highlight the energy absorption capacity of the nonwoven CNT mats.

Moreover, deformation characterization was restricted to $h_{\text{ave}} = 200$ nm CNT mats, but an array of impacted sample SEM images at different thicknesses can be found in the Chapter Appendices. Ultimately, each of the deformation mechanisms described above are like those found in fiber deformation when industry fabrics are impacted. Therefore,
we must assess the energy absorption capacity of the materials, and relate them to the industry standards to conclude if the material outperforms current fabrics given the same deformation history.

2.7 Analysis of Energy Absorption

The focus behind analyzing the quantitative measurements is to later compare to current materials in academia, and industry. Complete penetration 100% of the time is required to prevent bias information since it has been shown that the highest energy absorption values occur near the ballistic limit. Therefore, as we go forward only data from impacts at 900 m s\(^{-1}\) will be displayed and compared.

2.7.1 Penetration Energy

The energy required to penetrate the MWCNT mats, \(E_p\), can be directly measured by measuring the incident and exit projectile velocities while accounting for energy lost from air drag. Following our earlier paper on the penetration of silica projectiles through multilayer graphene [26], the energy to penetrate the MWCNT mat, \(E_p\) can be expressed in terms of the change in projectile kinetic energy \(\Delta KE = \frac{1}{2} m_p (v_i^2 - v_f^2) = E_p + E_{air}\), where \(E_{air}\) is the energy loss due to air drag, where \(m_p\) is the projectile mass (kg), \(v_i\) is the initial projectile velocity (m s\(^{-1}\)), and \(v_f\) is the residual projectile velocity (m s\(^{-1}\)). The energy loss associated with air resistance, \(E_{air} = m_p a_{air} d\), is \(\sim 1.07\) nJ at 900 m s\(^{-1}\) (\(m_p\)-projectile mass, \(a_{air}\)-deceleration of projectile, \(d\)- travel distance of projectile past target, 310 \(\mu m\)). For the perforated samples, a linear trend in the plot of \(\Delta KE\) is observed as a
function of film thickness (h) for the MWCNT targets (Fig. 2.15). The intercept for $h_{ave} = 0$ reflects $E_{air}$ for that velocity.

Figure 2.15—Plot of kinetic energy loss vs. MWCNT mat thickness for incident impact velocities of ~900 m s$^{-1}$.

The linear trend of $\Delta KE$ as a function of thickness can be converted to find the specific penetration energy of the CNT mats[26]. $E_p^*$ addresses the ability of the material to absorb energy relative to the mass of the minimum plug region (hole) and is defined as $E_p^* = E_p/A_sA_d$ where $A_s$ describes the strike face area which is equivalent to the cross-sectional area of projectile, and $A_d$ denotes the areal density of the target material[26]. Specific penetration energy of the MWCNT mats was calculated using details in Table 2.3 and then compared to multilayer graphene (MLG), various woven ballistic fabrics, non-woven ballistic fabrics, and metals in Table 2.4.
Table 2.3—Targets used and impact specifications.

<table>
<thead>
<tr>
<th>Target</th>
<th>Target Areal Density (kg/m²)</th>
<th>Projectile Type</th>
<th>Projectile Diameter (m)</th>
<th>Projectile Mass (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT mat</td>
<td>4.90E-05</td>
<td>Silica</td>
<td>3.72E-06</td>
<td>5.10E-14</td>
</tr>
<tr>
<td>Graphene</td>
<td>2.2 E-04</td>
<td>Silica</td>
<td>3.72E-06</td>
<td>5.10E-14</td>
</tr>
<tr>
<td>Kevlar Neat</td>
<td>0.4</td>
<td>FSP-steel</td>
<td>0.00556</td>
<td>0.0011</td>
</tr>
<tr>
<td>Kevlar STF</td>
<td>5.704</td>
<td>FSP-steel</td>
<td>0.00556</td>
<td>0.0011</td>
</tr>
<tr>
<td>Dyneema Fraglight</td>
<td>1.2</td>
<td>Steel Sphere</td>
<td>0.006</td>
<td>0.00867</td>
</tr>
<tr>
<td>Twaron multilayer</td>
<td>2.8</td>
<td>Steel Sphere</td>
<td>0.00635</td>
<td>0.00105</td>
</tr>
<tr>
<td>304 Stainless Steel</td>
<td>23.4</td>
<td>Steel Sphere</td>
<td>0.0125</td>
<td>0.0084</td>
</tr>
<tr>
<td>2024 T4 Al</td>
<td>17.7</td>
<td>Steel Sphere</td>
<td>0.00953</td>
<td>0.00353</td>
</tr>
</tbody>
</table>

* STF-shear thickening fluid

Table 2.4—Targets used in X parameter calculations.

<table>
<thead>
<tr>
<th>Target</th>
<th>Impact Velocity (m s⁻¹)</th>
<th>SPE (MJ kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT</td>
<td>900</td>
<td>5.09 ± 1.04</td>
</tr>
<tr>
<td>Graphene</td>
<td>900</td>
<td>1.26 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>1.11± 0.15</td>
</tr>
<tr>
<td>Dyneema Fraglight</td>
<td>640</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>505</td>
<td>0.98</td>
</tr>
<tr>
<td>Twaron multilayer</td>
<td>700</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.43</td>
</tr>
<tr>
<td>Kevlar Neat</td>
<td>1135</td>
<td>0.64</td>
</tr>
<tr>
<td>Kevlar STF*</td>
<td>1053</td>
<td>0.67</td>
</tr>
<tr>
<td>304 Stainless Steel</td>
<td>997</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.43</td>
</tr>
<tr>
<td>2024 T4 Al</td>
<td>903</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* STF-shear thickening fluid **estimated using 100nm multilayer graphene
Compared to other protection materials in Table 2.3, MWCNT mats exhibit remarkable $E_p^*$ values of almost ten times that of ballistic armor like Kevlar, three to five times that of nonwoven fabric like Dyneema Fraglight, and again almost 5 times that of MLG, which had previously been reported as an excellent energy absorbing material.[26] This suggest, the impressive values of the MWCNT mats originate from the various mechanisms contributing to the ability to delocalize the deformation and absorb large amounts of energy at a significant reduction in areal density due to the low density of MWCNTs and the high porosity of the mat (i.e. CNT mat $\rho = 380$ kg/m$^3$ vs 1250 kg/m$^3$ of individual CNT, yielding a porosity of 66%),

Individual carbon nanotubes influence the energy absorption properties through their intrinsic properties and their multiscale interactions with neighboring tubes. The speed that an individual MWCNT can delocalize the impact stresses along its longitudinal axis can be estimated by $c = \sqrt{E/\rho}$ where $c$ is the speed of the elastic stress wave through an individual CNT, and $\rho$ and $E$ are the density and axial modulus of the MWCNT [89]. The elastic wave speed in a material demonstrates its capacity to engage material outside of the impact zone to assist with energy absorption[24], [31], [52]. The unique intrinsic properties such as a very high axial stiffness approaching ~1 TPa[62] and low density of ~1250 kg m$^{-3}$ [90] for multi-walled carbon nanotubes (a density of 1250 kg m$^{-3}$ assumes 10nm diameter CNTs having on average 3-5 walls) shows that the individual MWCNTs can propagate elastic stress waves at speeds up to 28 km/s, which is ten times higher than other protection materials (Table 2.1)[49], [63]. However, the highly porous nature of the CNT mat would generate a low elastic wave speed in air (~343 m/s at room temperature) such that the impact energy is not delocalized rapidly like with graphene[26]. Instead, the
network junctions/branches of the MWCNTs will split/transmit (and partially reflect) the stress waves along the fibers to engage multiple CNT fibers within the local area to contribute to dissipate impact energy, thereby, maximizing the ability to dissipate energy in the network.

2.7.2 Comparison of Ballistic Fabric $X$ values for Scaling

Not only does the ability to dissipate energy matter in designing the next protection system, but also the weight at which it can dissipate the energy. In an effort to compare the advanced nanostructured materials (NSMs) not available in the commercial market with current protection materials, we used a non-dimensional parameter that was also previously established by Cunniff [24] such that the target can be altered in size and thickness, and projectile in size and mass as long as the $X$ is keep constant. The dimensionless parameter allows the objective assessment and optimization of materials based on the trade-off between mechanical properties of the material and weight of the material to provide the demonstrate the impact resistant capabilities based on the application.

Parameter denoted as $X = A_s A_d/m_p$ compares each targets strike face area ($A_s$) and areal density ($A_d$) relative to the projectile mass to form a non-dimensionless parameter. The dimensionless feature of $X$ desensitized the length scale effects that come in to play—e.g. millimeter size projectile diameter compared to micron size projectile diameter—during impact testing (e.g. micro- vs. macro-). For this reason, we can consider performance relative to only the mechanical properties and structure of target material.
Comparison of a materials specific penetration energy against \( X \), showed how even at significantly low \( X \)—suggesting low areal density of target material or highly dense projectile for impact—CNT mats exhibit unparalleled SPE values in relation to material with much higher \( X \) values (Table 2.5).

### Table 2.5—Targets used in \( X \) parameter calculations.

<table>
<thead>
<tr>
<th>Target</th>
<th>( X ) ((A_dA_s/m_p))</th>
<th>SPE* ((MJ kg^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar Neat</td>
<td>0.0122</td>
<td>0.64</td>
</tr>
<tr>
<td>Kevlar STF</td>
<td>0.0131</td>
<td>0.67</td>
</tr>
<tr>
<td><strong>MWCNT</strong></td>
<td><strong>0.96</strong></td>
<td><strong>5.09 ± 1.04</strong></td>
</tr>
<tr>
<td>Dyneema Fraglight</td>
<td>2.69</td>
<td>1.79</td>
</tr>
<tr>
<td>Graphene</td>
<td>4.7</td>
<td>1.26 ± 0.15</td>
</tr>
<tr>
<td>Twaron</td>
<td>5.3</td>
<td>1.12</td>
</tr>
<tr>
<td>304 Stainless Steel</td>
<td>34.2</td>
<td>0.66</td>
</tr>
<tr>
<td>2024 T4 Al</td>
<td>35.7</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* SPE values from velocities closes to 900 m s\(^{-1}\) were selected to minimize discrepancies.

#### 2.7.3 Material dependent Energy Absorption Comparison

To further, on the unprecedented behavior of the CNT mat, we decoupled penetration energy to mass dependent \( (E_{Mass}) \) and material dependent \( (E_{Mat}) \) components.

\[
E_p = (E_{Mat} + E_{Mass})
\]

\( E_p \) - Energy required to penetrate target

\( E_{Mat} \) - Energy dissipated by mechanisms associated with structural deformation processes and mechanical property of material
$E_{mass}$—the minimum energy required to accelerate a plug with a given mass directly under cross-sectional area of projectile.

CNT mats superior performance to MLG and other known protective material is non-trivial, but from Fig. 2.16 it can be attributed to the large $E_{Mat}$ contribution to $E_p$.

Coupling of the individual CNT mechanical properties and the structure of the CNT mat show remarkable $E_p$ values because of the CNT mat ability to significantly reconfigure its structure during impact to dissipate energy.

![Figure 2.16—Plot of material dependent and mass dependent contributions to SPE](image)

Figure 2.16—Plot of material dependent and mass dependent contributions to SPE
Summary

To conclude, our use of the micro-ballistic LIPIT test [25], [26] enabled the experimental investigation of the properties of MWCNT mats at ballistic velocities. This chapter illustrated how the structural components of the CNT mat lead to designated deformation routes to dissipate an unprecedented amount of energy from impact. The random network associated with the non-woven structure enables several CNT-CNT interconnections and cross-over points, which results in an enhancement of the friction-dominant dissipation mechanisms associated with fabrics. These unique features support the high-energy absorption capacity of the CNTs. In the macroscopic sense, faults in common woven fabrics such as “windowing”[91]—projectile pushes yarns to periphery of impact zone and penetrates without causing serious fiber failure—can be negated as even the sharpest tip bullets induce interaction of several CNTs preventing slippage around the macroscopic penetrator.

Along with the non-woven morphology, the intrinsic mechanical properties of CNTs and their multiscale deformation modes from micro to atomistic scales in a non-woven mat result in excellent impact properties that are 5 times greater than multilayer graphene films and more than 10 times greater than common ballistic fabrics. Micro-, nano-, and atomistic deformation modes such as CNT mat’s tensile strain, CNT-CNT friction, CNT-projectile friction, and fracture of CNTs enhance the energy absorption properties of the non-woven CNT mats. Complementing the multiscale deformation modes is the high modulus and low density of the individual CNTs that results in rapid stress transfer between CNTs and an increase in the number of CNTs contributing to energy absorption.
As previously stated in the disclaimer, comparisons between fiber lengths and projectile diameters offer insight into aspect ratio effects relative to other textile fibers that are commonly used in protective fabrics. Our experiments examine the response of CNTs when the length of the individual CNTs are significantly greater than the diameter of the projectile (~ 270 times). We expect similar results may not hold for macroscopic testing of the CNT mats used in this chapter unless growth procedures can produce CNTs with lengths ratios significantly larger than the millimeter range diameter of macroscopic projectiles. Nevertheless, the microscopic high velocity impact platform offers a means to observe the novel properties of nanomaterials such as CNTs and compare them to current material for development of new lighter weight energy absorbing material.
Additional Impact

Figure 2.17—Front side normal views of MWCNT mat deformation.  a) ~50nm thick CNT mat at a1-900, a2-900, a3-600 ms$^{-1}$; scale bars are equally 2um. b) ~200nm thick CNT mat impacted at b1-900, b2-600, b3-600 ms$^{-1}$; scale bars are equally 2 μm. c) c1- 60 nm thick CNT mat impacted at 600 ms$^{-1}$ and imaged at 45° tilt, c2- ~200 nm thick CNT mat impacted at 900 ms$^{-1}$ and imaged at 20° tilt; Scale bars is 7um and 2um for c1 and c2 respectively. d) ~200 nm thick CNT mat impacted at d1-300, d2- 300, d3-600 ms$^{-1}$; scale bars are equally 2 μm.
Figure 2.18—SEM images of the backside of the MWCNT mat for samples where the projectile did not completely penetrate or was entangled and arrested by the tubes. (a1-b3) SEM images of CNT mats impacted at 600 ms\(^{-1}\) with thickness values of ~200nm, ~150nm, and ~100nm from left to right for (a1-a3) and (b1-b3). (c1-c2) ~120 nm thick CNT mat impacted at 900 ms\(^{-1}\). Image a1 is taken at 0° tilt and all the other images are at 45° tilt. All scale bars are 2 \(\mu\)m.
Figure 2.19—Backside view of penetrated MWCNT mat. All images are at 45° tilt
a) ~100-150nm thick CNT mat at a1-600, a2-600 ms⁻¹; scale bars are equally 5 µm.
b) ~100-150nm thick CNT mat impacted at b1-900, b2-900 ms⁻¹; scale bars are 2 µm and 5 µm respectively. c) ~100 nm thick CNT mat impacted at 600 ms⁻¹; Scale bars are 5 µm and 2 µm for c1 and c2 respectively.
Matrix-free single-component nanocomposites overcome many challenges faced in uniformly dispersing nanofillers in a polymer matrix. Moreover, the anchoring of several hundred polymer chains to individual particles through covalent bonds improves the stress transfer through the composite, allowing us to create polymer nanocomposites with improved mechanical properties. We present the dynamic response of nanocomposite thin films consisting of matrix-free assemblies of polymer grafted silica nanoparticles as well as their corresponding homopolymer subjected to supersonic micro-bullet impacts. Deformation micro- and nanostructure characterized using scanning and transmission electron microscopy revealed film thinning, plastic flow, and biaxial crazing that have occurred due to impact. The relation between energy dissipation and nanostructural changes during
impact identified in this study provides fundamental insights that are critical to designing energy absorbing composite materials for protective applications.

3.1 Introduction

Polymer nanocomposites afford high tunability in their mechanical, electrical, and thermal properties through the choice of the polymer matrix, the reinforcing material(s), and their synergetic interactions. This enables the design of polymer composites with multifunctional attributes that are suitable for applications such as high-energy capacitors,[92] quantum dot films,[93] biocidal coatings,[94] flexible electronics,[95] or photovoltaics and solar cells[96], [97]. Moreover, polymer composites are commonly used in sports, military, and structural environments where the ability to resist high strain rate deformations is a necessity[98]–[100]. Polymer composite fillers with length scales at the nanoscale are strong candidates for impact resistant applications as they increase internal interactions which improves the moduli, yield strength, and strain-to-failure of a polymer matrix, ultimately enhancing the toughness of the material.[20]

Unfortunately, the nanofiller-polymer interactions that are enthalpically unfavorable often results in the aggregation and phase separation of nanofillers in the polymer matrix. Such non-uniformly dispersed nanofillers in the polymer matrix result in nucleation of voids and poor transfer of stresses at the nanofiller-polymer interface during external loading[92], [101], [102]. “Matrix-free” assemblies of polymer-grafted nanoparticles (aPGN) circumvent these issues in the traditional ‘two-component’ nanoparticulate polymer composites[92], [103]–[108]. Covalently grafted polymer chains
on the surface of nanoparticles eliminates demixing and allows uniform dispersion of particles in polymer matrices during self-assembly of aPGNs[92], [109], [110].

Previous nanoindentation[103], [111] and film buckling[112], [113] tests have provided an understanding of the variation in properties as a function of size and volume fraction of particles, density of grafted chains on the particle surface, and length of polymer chains. Adequate chain entanglement of polymers is required to provide efficient internal load transfer in aPGNs as the polymer chain molecular weight must be greater than 18 kg mol\(^{-1}\) [103], [114]. Indentation studies on glassy amorphous polymers such as polystyrene and polymethylmethacrylate have shown a six-fold increase in toughness for aPGNs in comparison to the homopolymer as well as a two-component polymer blend with similar particle volume fractions[103]. Also, distinct increases in fracture toughness and elastic modulus were observed as the polymer chain length was increased, resulting in more chain entanglements and a deformation transition from brittle fracture to crazing—a dilational plastic deformation enabling greater energy dissipation in glassy polymers[103], [115].

### 3.1.1 Current Limitations of aPGNs

While major advances have been made to control the synthetic capabilities of aPGNs, several challenges remain evident for chemist and prohibit large scale production for implementation of these aPGNs into real world applications. Issues often arise from the inability to control aPGN architecture, i.e. the particle radius as well as the degree of polymerization (length of polymer chain) and density of grafted chains, represented by number of chains per square nanometer on particle surface area.[115], [116] Polymer
chains diffuse past previously grafted chains on a slow logarithmic time frame as the reactive ends of the polymer chain attach to the nanoparticle surface, thus the dramatically reduced grafting kinetics and random grafting of chains on particle surface can lead to variations in grafting densities.[92], [117] In addition, literature illustrates a Gaussian distribution in polymer size relative nanoparticle, in which distribution or variability in polymer chain size widens and increases as projectile diameter increases.[118] These grafting kinetic limitations create significant hurdles in scale-up synthesis of large volumes when trying to retain consistency from the micro to macroscale in the recently emerging “materials-by-design approach.” In this perspective, use of techniques to examine the properties of aPGNs at smaller scales to demonstrate their performance is crucial for scientist and engineers to understand the need to establish new methods to produce large scale quantities of aPGNs.

To date, literature has vaguely investigated the mechanical response of aPGNs[103], [116], while leaving the effects of temperature and strain rate on their deformation mechanisms completely unexplored[119]–[124]. In this study, I investigate the high-strain-rate (>10^7 s^{-1}) deformation behavior of thin films (~157 nm) of aPGNs (Fig 1a) and compare it to that of the thin film (~150 nm) homopolymer polystyrene (hPS).

3.2 Experimental Methods

The aPGN films consist of high molecular weight linear PS (~230 kg mol^{-1}) covalently bonded to silica nanoparticles (16 ± 5.6 nm diameter, 1 vol%) with a polymer chain grafting density of ϕ=0.57 chains/nm2 (~470 chains/nanoparticle), Fig.3.1a,b. Polymer-grafted nanoparticles (PGN) were synthesized using surface-initiated atom transfer
radical polymerization (SI-ATRP)—details of the synthesis have been well summarized in recent publications[103], [104]. In short, polymer chains were polymerized from the particle surface after covalently binding a low molecular weight initiator to the particle surface by means of a coupling reaction. A detailed description is supplied in the following section.

Figure 3.1— Specimen characteristics and illustration of LIPIT. a) Bright Field TEM (Titan, 300 kV) of the aPGN film with 1% volume fraction of nanoparticles, b) schematic representation of a polymer grafted nanoparticle (PGN and aPGNs).

3.2.1 Materials and Synthesis

Silica Nanoparticles and Polystyrene

Silica nanoparticles (30%) were received in methyl isobutyl ketone (MIBK) solution. Particles were used as received by Nissan Chemical Corp.

Neat poly(styrene) was obtained from Polymer Source ($M_w$: 267 kg/mol, $Dispersity$: 1.12).
Synthesis of Initiator for Particle Surface Polymerization

A previously reported method was used to synthesize the initiator 1-(chlorodimethylsilyl) propyl-2-bromoisobutyrate for atomic transfer radical polymerization (ATRP), which is the method used to grow polymer chains on nanoparticle surface[125].

Synthesis of Initiator-Modified Silica Nanoparticles

Detail synthesis methods for initiator-modified silica nanoparticles is described by Pyun et al[126]. A reaction mixture of silica nanoparticles in MIBK (52 g) and the initiator 1-(chlorodimethylsilyl) propyl-2-bromoisobutyrate (6.0 mL, 27 mmol) was refluxed for 24 h in 100 mL three-pronged flask. Mixture is then cooled to room temperature and Hexamethyldisilazane (HMDZ) (6.0 mL, 28 mmol) was added, stirred for 3 h at room temperature, and heated for another 6-8 h. Precipitant formed during reflux was removed using centrifugation and dropwise additions of orange supernatant was added to methanol/H₂O (4:1 vol) to precipitate initiator-modified silica nanoparticles. Filtration was used to recover particles. Tetrahydrofuran (THF, 50 mL) was used to redissolve particles that were subsequently washed with hexanes for 12 cycles.

Surface Initiated Atomic Transfer Radical Polymerization of Styrene on Silica Nanoparticles

Choi et al. have thoroughly explained reaction steps in previous report[103]. A reaction mixture of 1.48 g initiator-modified silica nanoparticles (0.353 mmol Br per g silica; 0.524 mmol ATRP initiator sites) and anisole (12.0 mL) was stirred in a charged Schlenk flask for 24 h to prepare short chain PS-grafted silica nanoparticles (SiO₂-S10). Styrene (6.0 mL, 52.4 mmol) and PMDETA ligand (21.9 mL, 0.105 mmol) were then added to
the flask. The resulting mixture was immersed in liquid nitrogen after three freeze–
pump–thaw cycles, and then 15.0 mg (0.105 mmol) of CuBr was added while the flask
was filled with nitrogen gas. The flask was evacuated and purged with nitrogen, five
times. After warming to room temperature, the sealed flask was placed in an oil bath and
heated to 90 °C. To stop polymerization, the catalyst was stopped exposed to the air after
5 h of reaction time. The product was precipitated by adding the reaction mixture to
methanol and the solid was filtered and washed with methanol prior to drying in a
vacuum oven at 60 °C.

3.2.2 Film Preparation on TEM Grid

Approximately monolayer films were prepared by flow-coating dilute polymer solutions
in toluene (2.5 wt% in toluene) on 5 x 7 cm$^2$ glass slides that were cleaned with UV-
Ozone (Novoscan Tech., Inc.). After evaporating toluene, these films were thermally
annealed under vacuum for 24 h at 120 °C. Equilibrium films were lifted off by water
immersion and transferred onto nickel TEM grids for imaging.[127]

The grafted PS chains and the hPS chains both have a molecular weight well above the
entanglement molecular weight of ~ 18 kg mol$^{-1}$[114] and create an efficient load-
transferring network.

**Thickness Measurements**

The thickness of the films on silicon was measured with a Bruker DektakXT
profilometer.
Particle-Particle Distance

Previous research by Koerner et al. published particle-particle distance for polymer grafted nanoparticles.[104] Small angle X-ray (SAXS) experiments were carried out on a Rigaku S-MAX 3000 pinhole SAXS system in transmission mode at a sample to detector distance of 150 cm. The SAXS data for aPGN films was analyzed and fitted using a combination of sphere form factor (obtained from solutions) and a Percus and Yevick hard sphere model.[128] The average center-to-center distances between the PGNs in the film is ~35 nm (Fig. 1c) as determined from the first-order-structure-factor peak from (SAXS) measurements (Figure 3.2) [127]

![Diagram of PGN structure](image)

**Figure 3.2**—Nanostructural configuration of PGNs. Descriptors relevant to aPGN: radius of particle, \( r_p \) is ~8 nm, particle-particle distance[104] is ~35nm, and non-entangled region (NER) in which polymer chains grafted on adjacent particles are not able to entangle due to high density of grafted chains (\( N \sim 250 \), where \( N \) is the number of repeating units in polymer chain with a single unit of PS having a molecular weight of 104 kg-mol\(^{-1}\)) [103], [108].

3.2.3 Impact Testing

Details of launch pad preparation are previously discussed in Chapter 2 section 2.9. A schematic of the experimental technique denoted as LIPIT is shown below (Figure 3.3).
Figure 3.3— Schematic of the advanced laser induced projectile impact testing (α-LIPIT) of the aPGN and hPS thin films.

Deformation Analysis

*Scanning Electron Microscope (SEM)*

Impact surface and back surface deformation was viewed by FEI Helios NanoLab 660. Samples were coated with 5nm Carbon on each side and characterized in Immersion (High-Resolution) mode at 2kV.

*Transmission Electron microscope (TEM)*

Thin film deformation was also observed from bright-field electron transmission images (JEOL 1230 High Contrast TEM-80kV)
3.3 Mechanical Properties of Thin Films

All low strain rate low strain rate measurements were conducted by our Collaborators at the Air Force Research Laboratory under Dr. Vaia.

Table 3.1—Thin Film Mechanical Properties

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
<th>Strain to Failure</th>
<th>Poisson Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>aPGN</td>
<td>3.3</td>
<td>22</td>
<td>9</td>
<td>0.34</td>
</tr>
<tr>
<td>hPS</td>
<td>3.3</td>
<td>30</td>
<td>15</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Elastic modulus was previously obtained using a strain-induced elastic buckling instability test for mechanical measurements[112], [129]. Thin films are transferred to relatively thick polydimethylsiloxane (PDMS) substrate, and a compressional strain is applied to the thin film/PDMS laminate to induce the buckling instability. Buckling is a result of the imbalance in energy required to bend the stiff film and deform the soft PDMS substrate[112]. Each film displays a material dependent periodic buckling wavelength, \(d\), defined by

\[
d = 2\pi h \left[ \frac{(1-\nu_s^2)E_f}{3(1-\nu_f^2)E_s} \right]^{1/3}
\]

Equation 3.1—Periodic buckling wavelength
where \( h \) is thin film thickness, \( \nu \) is Poisson’s ratio, and \( E \) is the Elastic modulus (subscripts \( f \) and \( s \) denote the film and substrate, respectively). Rearranging Equation (3.1) to solve for \( \varepsilon_f \) and we get

\[
E_f = 3E_s \left( \frac{\lambda}{2\pi h_f} \right)^3
\]

Equation 3.2—Plane-strain modulus of thin films

where \( E = E/(1 - \nu^2) \) is the plane-strain modulus. The thin films strain to failure was approximated by using the inverse relation between buckling wavelength and applied strain after cracking of film, \( \varepsilon_f \), due to buckling, thus enabling the final estimate of yield strength from the following equation[129].

\[
\sigma_f = \frac{dE_f\varepsilon_f}{2h_f}
\]

Equation 3.3—Estimation of thin film yield strength

where \( \sigma_f \) is the fracture strength of the film.

3.4 1D approximations of thin film impact response

According the Rankine stress criterion, plastic flow takes place in a complex state of stress until the greatest principal direction reaches the flow stress values in uniaxial tension[130]. Thus, due to the complexity of the impact event, we only consider 1-D elastic-plastic deformation in an isotropic solid along the greatest principal direction for
analytical approximations. Elastic wave speed \( c \), impact strain \( \varepsilon_i \), strain rate \( \dot{\varepsilon} \), and penetration time \( t_p \) calculations are based on 1-D approximations relative to the primary principal stress axis in a biaxial stress state and are valid for isotropic, linearly elastic 2D thin membranes.[52] Statistical averages of measured hole radius, \( r_h \) and average radial deformation length away from impact site were used to calculate radius of region influenced by impact, \( r_i \).

**Elastic Wave Equation**

Elastic stress wave, composed of Young’s modulus \( E \) and density \( \rho \).

\[
c_E = \sqrt{\frac{E}{\rho}}
\]  

(3.4)

**Equation 3.4—Elastic wave speed in thin film**

**Radius of influenced Region,**

Radius of total area influenced is a combination of radius of hole generated, \( r_h \), and deformation extending past hole in radial direction, \( L_R \)

\[
r_i \cong r_h + L_R
\]  

(3.5)

**Equation 3.5—Distance of deformation from center of impact**

**Penetration Time,** \( t_p \)

\[
t_p \cong \frac{r_i}{v_c}
\]  

(3.6)
Equation 3.6—Estimated penetration time

**Strain-to-Failure, \( \varepsilon \)**

\[
\varepsilon = \left( \frac{1}{2} \right) \left( \frac{v_l t_p}{r_i} \right)^{2} \quad (3.7)
\]

Equation 3.7—Estimated strain-to-failure

**Strain Rate, \( \dot{\varepsilon} \)**

\[
\dot{\varepsilon} = \left( \frac{1}{2} \right) \left( \frac{v_l}{r_i} \right)^{2} t_p \quad (3.8)
\]

Equation 3.8—Estimated strain rate

3.5 Estimation of local heating in thin films

The thermal energy required to heat material in the impact zone is governed by:

\[
E_{Tg} = \int_{RT}^{Tg} c_p m_{plug} dT \quad (3.9)
\]

Equation 3.9—Thermal energy required to heat a material

\( E_{Tg} = \) amount of energy to raise temperature (J)

\( c_p = \) heat capacity of polymer, polystyrene \( \sim 1300 \) (J/kg\(^\circ\)C)—Lower bound of literature value

\( dT = \) temperature difference \(^\circ\)C
\[ m_{plug} = \text{mass of plate directly under cross-sectional area of projectile, } \sim 2.6 \times 10^{15} \text{ (kg)} \]

\[ m_{plug} = A_p h \rho \quad (3.10) \]

Equation 3.10—Mass of a plug

Refer to Schematic below

Figure 3.4—Schematic illustration of minimum perforated mass of thin film

Heat capacity of the composite is given by the expression

\[ c_c = \left( c_m \rho_m V_m + c_n \rho_n V_n \right) / \rho_c \quad (3.11) \]

Equation 3.11—Specific heat capacity of a composite

where \( \rho \) represents the material density and \( V \) designates the volume fraction, with subscripts \( c, m, \) and \( n \) denoting the composite, matrix, and nanoparticle reinforcement.
The significantly low volume fraction of silica makes the particle contribution to \( c_c \) negligible, thus \( c_p \) for polystyrene was used for calculations.

Assuming all kinetic energy loss in projectile is dissipated through thin film deformation and not projectile deformation, equation can be simplified to solve for temperature rise in film from impact.

\[
\Delta KE = c_p m_{plug} (T_{\text{Final}} - T_{\text{RT}})
\]  

Equation 3.12—Kinetic energy loss relative to rise in temperature

- \( T_{\text{Final}} \) – Temperature rise from impact
- \( T_{\text{RT}} \) – Room temperature

### 3.6 Results and Discussion

Films are impacted at a kinetic energy ratio of 1:2:4 by increasing the projectile impact velocity from ~350 to 500 to 700 m s\(^{-1}\). The impact velocity of the projectile is highly reproducible within a standard deviation of 10 m s\(^{-1}\), for a given laser energy.

The residual velocity of the projectile increases with the impact velocity linearly (Fig. 3.5a). Additionally, the kinetic energy loss of the projectile also increases with the impact velocity (Fig. 3.5b). This increase in energy absorbed by both aPGN and hPS films with increasing impact velocity suggests that the deformation response of both materials is strain rate dependent.
Figure 3.5—Quantitative measurements of the performance of aPGN and hPS films: a) residual velocities of micro-projectiles penetrating aPGN (~157 nm) and hPS (~150 nm) films as a function of the impact velocity. b) Kinetic energy loss of projectiles as a function of impact velocity. c) Kinetic energy loss in aPGN as a fraction of that of in hPS films.

Relative to hPS, the aPGN films show up to a 50% increase in energy absorption (Fig. 3.5c). To understand the dynamic deformation mechanisms in micro- and nanoscales contributing to the enhanced energy absorption of aPGN and their strain-rate-dependent response, I performed detailed post-impact analysis using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3.6.1 Micro- and nanoscale deformations and rate effects in aPGN films

The SEM images of the impacted aPGN films show near-circular perforations that are at least 6 µm² larger than the cross-sectional area of the projectiles for all high-velocity impacts, Fig. 3.6(a-c). Additionally, characteristic features such as radial and tangential crazes as well as highly stretched and ‘folded’ regions on the back surface are found near the impact site, Fig. 3.6(a-c). Rate-effects are found in the craze structure where the
formation of tangential crazes increases with increasing velocity, and additionally, substantial localized plastic stretching of films occurs at the highest velocity, Fig. 3.6(a-c).

Figure 3.6—Micrographs of perforated aPGN films (a-c) SEM images of aPGN impacted at velocities of ~350, 500, and 700 m s\(^{-1}\).

Measurements of the perforated site were collected, and a schematic depicting the measure items is shown in Fig. 3.7. Refer to tables 3.2 and 3.3 for values.

Figure 3.7—Schematic of deformation event and measured descriptors used in analysis where \(r_p\) represents the projectile radius; \(r_h\) denotes the radius of the perforated hole; \(L_R\) signifies the average distance of each radial craze.

Table 3.2—Quantification of aPGN Deformation descriptors
Further observations show a folded region of the polymer film that elongates up to \( \sim 4.8 \) \( \mu \text{m} \) at the highest impacted velocity of 700 ms\(^{-1}\) (Figs. 3.8a,b). Previous literature suggest that high-strain-rate deformation leads to adiabatic heating in the impact region, and results in the local thermal softening[131] of the aPGN to cause severe film stretching and thinning in the impact zone. If the entire kinetic energy loss of the projectile is assumed to have resulted in adiabatic film heating, the estimated temperature rise is hundreds of degrees above the glass transition temperature \( (T_g) \) of PS \((\sim 102 \degree \text{C})[130]\), see section 3.4 for calculations. Since the energy is also lost into mechanical deformations the actual temperature rise is much less, but certainly far exceeds the \( T_g \).
Figure 3.8—Impact analysis and micrographs of perforated aPGN films (a-b) SEM and TEM images biaxial crazing in raidal and tangential directions, respectively.

Outside the perforated region, we see biaxial crazes in the radial and tangential direction of the films, see Fig. 3.9a, b. They propagate perpendicular to the principal stress directions (Fig. 3.9c). Crazes are comprised of load bearing fibrils that are aligned along the principal stress axis and are bounded by micro-voids on either side in between the craze surfaces, Fig. 3.9d[132]. The crazes nucleate at stress levels below what is necessary to induce shear yielding[133], but high enough to cause chain scission and intermolecular slip[132]–[134]. The crazes result from constraints—i.e. chain entanglements—along the film thickness direction that prevent the volume-preserving free flow of polymer along the film plane and instead causes repeated Tailor meniscus instabilities[132], [135], [136]. These repeated instabilities during stress propagation leave behind fibrils along the crazing direction. Each craze fibril contains oriented polymer chains that provide work hardening and carry the load preventing rapid full crack opening[137].
Figure 3.9—Biaxial craze formation. (a-b) SEM and TEM images of biaxial crazes, and (c) Illustration of biaxial craze formation: two principal directions affected by impact are the tangential and radial directions. Craze formation exist perpendicular to the direction of stress such that the tangential stresses produce radial crazes and radial stresses produce tangential crazes [133]. (d) High magnification SEM image of craze fibrils.

The measured crazes in aPGN and hPS films consist of fine fibrils between 15 and 25 nm in diameter with a mean value of 20 nm, as measured by High magnification (100k) SEM images (Fig. 3.10 and Table 3.4).
Figure 3.10—aPGN 100k magnification image, 2kV, 50pA. Numbers correspond to individual fibrils measured in Table 3.4.

Table 3.4—Fibril Width Measurements

<table>
<thead>
<tr>
<th>Fibril Number</th>
<th>Fibril Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>23</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>23</td>
</tr>
<tr>
<td>7</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>17</td>
</tr>
<tr>
<td>10</td>
<td>19</td>
</tr>
<tr>
<td>11</td>
<td>18</td>
</tr>
<tr>
<td>12</td>
<td>19</td>
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<tr>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>16</td>
<td>23</td>
</tr>
<tr>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>Avg.</td>
<td>20</td>
</tr>
<tr>
<td>Std.</td>
<td>3</td>
</tr>
</tbody>
</table>
These craze fibrils are wider than the craze fibrils previously reported for PS films (4-10 nm)[138] with comparable film thicknesses. It is likely that at these high strain rates the characteristic time for disentangling a chain becomes long with respect to the time scale of the experiment causing more chain breakage then at much lower strain rates, thereby reducing the potential lengthening and narrowing of the craze fibrils[136]. Additionally, stress levels surpass the craze initiation stress to produce several crazes, but the short loading event does not sustain stress levels for sufficient time to initiate long periods of craze widening that would have also reduced fibril diameter and increased fibril aspect ratio during widening.

Craze lengths were measured using the descriptors noted in Fig. 3.11a. Radial crazes propagate an average distance of $\sim$3.1 ± 1.2 $\mu$m away from the edge of the hole with no differences in average length as velocity varies (Fig. 3.11b). The angle between neighboring radial crazes ($\theta_R$) is about $\sim$15° with $\sim$24 radial crazes per perforation (Fig. 3.11c). The tangential crazes are closely spaced nearest the hole then separate from one another with the furthest distance averaging out between 1-1.2 $\mu$m away from impact edge (Fig. 3.11d). The distance to the tangential craze furthest from the hole ($L_\theta$) is less than the distance to the tip of the average radial craze ($L_r$). This implies a stress bias where radial crazes propagate faster than tangential crazes. Additionally, the $L_\theta$ for the aPGN films increases with increasing impact velocity suggesting rate-effects on the craze formation.
Figure 3.11—Craze length and angle analysis. (a) illustration of relevant distances and angles measured using SEM. (b) histogram of radial craze length distribution. (c) histogram of radial craze angle distribution. (d) Furthest tangential craze lengths were measured in 4 locations per sample.

Effects of thermal softening are also evident when observing deformation as it travels away from the impact site. Careful inspection of the biaxial crazes nearest the hole show smooth nanostructures without evidence of fibril or void formation (Fig. 3.12). The film thickness decrease resulting from thermal softening prevents constraints such as chain entanglements or nanoparticle anchors along the film thickness direction to generate instabilities during polymer flow that would leave behind fibrils in the craze region[139]. Similar behavior was observed for uniaxially stretched polystyrene films when the film thickness was below ~100 nm[140]. The length of this region (~1.89, ~1.75, and ~1.61 µm at 350, 500, and 700 m s⁻¹) is also dependent on strain rate induced
on the film by the projectile (Table 3.50. At the elevated temperatures generated from impact, chain relaxation becomes relatively faster compared to the time scale of the deformation process, and intermolecular separation—i.e chain slippage—and chain disentangling dominates the deformation event enabling more noticeable deformation events within the impact region at higher velocities as seen in Fig. 3.6.

![Image of SEM analysis of distance between perforated edge and onset of fibril formation.]

Figure 3.12—SEM analysis of distance between perforated edge and onset of fibril formation.

Table 3.5—Speed of Impact Cone

Measured values neglect any curvature in the film. This allows a simplified comparison between the potential influence of velocity and sample type.

<table>
<thead>
<tr>
<th>Initial Velocity (m-s⁻¹)</th>
<th>Speed of Cone Growth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>1.89 ± 0.60</td>
</tr>
<tr>
<td>500</td>
<td>1.75 ± 0.40</td>
</tr>
<tr>
<td>700</td>
<td>1.61 ± 0.37</td>
</tr>
</tbody>
</table>
3.6.2 Sequence of events during impact

Based on these observed deformation characteristics, we infer that the sequence of events during impact starts with an outward propagation of an elastic tensile wave \( (c_E \approx 1488 \text{ m s}^{-1}) \)—governed by the elastic modulus \( (E = 3.3 \text{ GPa}) \) and density \( (\rho \approx 1050 \text{ kg m}^{-3}) \)—as the forward motion of the projectile stretches the film into a conical shape, see Fig. 3.13(i and ii). The base of the cone expands at a velocity of \( v_c = 1.23c_E(v_i/\sqrt{2c_E})^{2/3} \), where \( v_i \) is the projectile impact velocity, until tensile stresses exceed the material’s yield strength \( (\approx 30 \text{ MPa which increases with strain rate}) \), refer to section 3.2 and 3.3 for approximation methods[141]. Rapid stretching that occurs at estimated strain rates of \( \approx 10^7 \text{ s}^{-1} \), Table 3.6, causes adiabatic film heating and thermal softening of the aPGN film. This lowers the flow stress and promotes smooth craze formation initially during plastic flow. Eventually, microvoids form at the periphery of the impacted area due to stress concentrations at heterogeneities in polymer network and nanoparticles (Fig. 3.13ii)[134], [136]. These microvoids coalesce and leads to Tailor meniscus instabilities[135] that creates tangential or radial crazes containing fibrils (Fig. 3.13iii) that propagate along the two principal stress directions. As the crazes nucleate, grow and intersect, the stresses are relieved. There is a trade-off between the increasing stress from the forward motion of the projectile and the decreasing stress from crazing. Eventually, the forward motion of the projectile leads to puncture of the thin film due to chain slip, disentanglement, and scission of polymer chains within the impact site (Fig. 3.13iii). As the projectile exits the film (Fig. 3.13iv), a tensile release wave recoils the films and relieves the residual stresses in the film. The elongated film at the center recoils and folds onto the back surface of the film (Fig. 3.13v).
Figure 3.13—Schematic of impact sequence of events.
Table 3.6—Approximations of impact event.

<table>
<thead>
<tr>
<th>Initial Velocity</th>
<th>Speed of Cone Growth (m/s)</th>
<th>Penetration Time (ns)</th>
<th>Maximum Strain</th>
<th>Strain Rate (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>558</td>
<td>10</td>
<td>20%</td>
<td>0.8x10(^7)</td>
</tr>
<tr>
<td>500</td>
<td>706</td>
<td>7.8</td>
<td>25%</td>
<td>1.4x10(^7)</td>
</tr>
<tr>
<td>700</td>
<td>870</td>
<td>6.2</td>
<td>31%</td>
<td>2.1x10(^7)</td>
</tr>
</tbody>
</table>

3.6.3 Comparison of Craze Stability

Although an increase in \(\Delta KE\) is observed in aPGN compared to hPS (Fig. 3.5), the average area of influenced zones (\(~95 \, \mu m\)) measured from an array of impact samples, is similar (Table 3.7 and 3.8). It is interesting to note that the crazing surface features vary between the hPS and aPGN films when looking at an array of perforated samples (Fig. 3.14). Therefore, considering the fact aPGN and hPS films have nearly identical densities (1050 and 1040 kg-m\(^{-3}\) respectively) due to low particle volume fraction in the composite and similar influenced zones, but different deformation characteristics inside the influenced zone, this implies that the energy absorption is primarily determined by the micro- and nanostructural deformation mechanisms during impact.
Figure 3.14—Array of SEM and TEM images of perforated hPS and aPGN samples. The average radial craze length was used to estimate the film area involved in the deformation.
Table 3.7—aPGN Deformation Analysis

<table>
<thead>
<tr>
<th>Initial Velocity</th>
<th>Radius Hole (µm)</th>
<th>Avg. Radial Craze length (µm)</th>
<th>Total Influenced Area (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>2.3</td>
<td>3.3</td>
<td>100</td>
</tr>
<tr>
<td>500</td>
<td>2.5</td>
<td>3.0</td>
<td>96</td>
</tr>
<tr>
<td>700</td>
<td>2.3</td>
<td>3.1</td>
<td>91</td>
</tr>
</tbody>
</table>

Table 3.8—hPS Deformation Analysis

<table>
<thead>
<tr>
<th>Initial Velocity</th>
<th>Radius Hole (µm)</th>
<th>Avg. Radial Craze length (µm)</th>
<th>Total Influenced Area (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>2.4</td>
<td>3.4</td>
<td>96</td>
</tr>
<tr>
<td>500</td>
<td>2.4</td>
<td>2.7</td>
<td>87</td>
</tr>
<tr>
<td>700</td>
<td>2.4</td>
<td>3.1</td>
<td>91</td>
</tr>
</tbody>
</table>

At the micro-level, crazes in the aPGN and hPS films both extend out several microns (~3.1 µm in average) from the periphery of the perforation across all velocities (Table. 3.7 and 3.8) Comparable behavior near the impact site, with the generation of the smooth craze structure, is seen for the (hPS) films (~267 kg mol⁻¹, ~150nm) impacted at high strain rates as well, see Fig. 3.15(a1,a2 and b1,2). As deformation propagates away from the impact site, the unfibrillated crazed region transitions to void-fibril crazing in the aPGN films, see Fig. 3.15(c1, c2, and c3), with evidence of craze buckling due to the post-perforation relaxation event. The existence of craze buckling indicates the dramatic decrease in the load bearing capacity of fibrils in this region as the tensile release wave
can induce a deformation event. Mid-rib formation, region with low-volume fraction of polymer, just beyond the buckled region suggests the onset to which the load bearing capacity of the fibrils is being diminished, See Fig 3.15c2. As we approach the craze tip, mature and stable—i.e. load-bearing—crazes with void-fibril structures exist, see Fig. 3.15c3. This void-fibril structure is a dominant feature in aPGN deformed microstructures accounting for 60% of the deformation along the length of the craze, with the other 40% having smooth craze structure. Unlike the aPGN, hPS films undergo a different deformation mechanism that starts from a large region of unfibrillated crazes (Fig. 3.15d1) to a narrow craze region of ~75% reduction in craze width, see Fig. 3.15d2. Closer to the tip, immature void-fibril crazes are found (Fig. 3.15d3) in hPS films, suggesting the crazes lack the ability to alleviate impact stress through craze initiation and craze widening relative to the aPGN films see Fig. 3.15(e,f). The formation of large mature crazes in the aPGN films indicates greater stress transfer capability relative to hPS films. It is likely that the covalent anchoring of nanoparticles to several hundreds of chains in the aPGN film converts nanoparticles into cross-linking agents that link one polymer chain to another. The stress from chains on one end can be distributed across particle cross-links and onwards to adjacent entangled grafted chains. This increases the number of chain slips, and disentanglements required for individual chains to translate past one another, thus potentially increasing resistance to plastic flow relative to the homopolymer, providing a mechanism to improve stress transfer. An estimated average reduction in nominal strain rate of 26% across all velocities (Table 3.9) is found with the use of grafted nanoparticles, which demonstrates the better load transferring ability of the aPGN films relative to hPS films.
Figure 3.15—Progression of Nanostructural Changes from Impact Site to Tip of Craze. Images were collected from 700 m s\(^{-1}\) impact event for both aPGN and hPS. (a1,a2) TEM of aPGN's deformation at periphery of impact site; The radial and tangential crazes can intersect to form “square film islands.” These islands form due to the continued stretching of the polymer in the impact area after the initiation of craze formation. (b1,b2) TEM of hPS deformation at periphery of impact site. (c1-c3) progression of craze nanostructure for aPGN films; c2 displays a midrib, a region with low polymer fibril volume fraction that are commonly found in the centerline of crazes, and originate from high surface stress region just behind the craze tip, and indicate the onset of craze breakdown\[134\]. (d1-d3) progression of craze nanostructure for hPS films. (e,f) comprehensive view of aPGN and hPS craze nanostructure from impact site to craze tip, respectively.
Table 3.9— Strain Rate Reduction

<table>
<thead>
<tr>
<th>Initial Velocity</th>
<th>hPS Strain Rate (s⁻¹)</th>
<th>aPGN Strain Rate (s⁻¹)</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>1.1x10⁷</td>
<td>0.8x10⁷</td>
<td>27%</td>
</tr>
<tr>
<td>500</td>
<td>1.9x10⁷</td>
<td>1.4x10⁷</td>
<td>26%</td>
</tr>
<tr>
<td>700</td>
<td>2.8x10⁷</td>
<td>2.1x10⁷</td>
<td>25%</td>
</tr>
</tbody>
</table>

3.7 Conclusion

In summary, aPGN films exhibit enhanced energy dissipation compared to their homopolymer counterpart, hPS films, primarily due to the distinct craze structures that form during impact. The polymer grafted nanoparticles in aPGN potentially induce void growth during dynamic stretching of the material while transferring load efficiently. Such void growth acts as precursors to Taylor meniscus instability that forms mature crazes having a void-fibril structure at very high strain rates (10⁷ s⁻¹). The formation of mature void-fibril crazes results in enhanced energy dissipation compared to the hPS films in which majorly unfibrillated and immature crazes form in this strain rate regime. Our study offers insight into the effects “single” component nanocomposites have on energy absorption capabilities. There remains several challenges to reproducibly control the grafting density of the nanoparticles as it relates to polymer chain size and nanoparticle diameter[92]. When such control of grafting density is developed, later studies should seek to optimize performance of aPGNs by varying number of crucial parameters such as particle diameter, grafting density, and molecular weight of grafted polymer chains. The
enhanced energy absorption and resistance to failure of aPGN that we demonstrated in study show their potential use in several high-strain-rate applications such as in body armor, helmets, automobile, aircraft, and spacecraft components that particularly require high strength and low-strain to failure materials. Additionally, aPGN films are highly attractive materials for ambient protection environments that utilize materials with high ductility at stand-off distances for impact mitigation[142].
Dynamic Creation and Evolution of Gradient Nanostructures in Single-Crystal Metallic Microcubes

We demonstrate the dynamic creation and subsequent static evolution of extreme gradient-nano-grained structures in initially near-defect-free single-crystal silver micro-cubes. Extreme nanostructural transformations are imposed by high strain rates, strain gradients, and recrystallization in high-velocity impacts of the micro-cubes against an impenetrable substrate. We synthesized the silver micro-cubes in a bottom-up seed-growth process, and use an advanced laser induced projectile impact testing apparatus to selectively launch them at supersonic velocities (~400 ms\(^{-1}\)). Our study provides new insights into the fundamental deformation mechanisms, and the effects of crystal and sample-shape symmetries resulting from high-velocity impacts. The nanostructural transformations produced in our experiments show promising pathways to developing gradient-nano-grained metals.
for engineering applications requiring both high-strength and toughness—for example, in structural components of aircraft and spacecraft.

This chapter has been recently published in Science. Permission to publish in thesis has been requested and granted.


4.2 Contribution to Research

My contribution to this collaborative effort initially focused on developing a technique to remove polymer wax on the Ag cube surface as to reduce the effects the polymer coating may have on deformation. Cleaning process involving water, ethanol, and a centrifuge allowed us to obtain cubes with negligible polymer coating. Once initial step was complete, I impacted Ag cubes at velocities of ~200, 300, 400, 500, 600, and 700 m s⁻¹ to obtain the impact conditions that deformed ~70% of sample but allowed it to retain its single crystal nature at the surface away from impact (this occurs at 400 m s⁻¹). Once cross-sectional analysis occurred I investigated the root of rapid structural degradation, which was confirmed by TEM to be the reaction of silver and sulfur. With this discovery, I assisted with creating testing and storage protocol that allowed us to avoid the degradation effects sulfur will have on the silver cubes. Lastly, I worked with building the sequence of impact events including the hydrodynamic stress state, as we initially ruled it out because of this stress state generally occurs at velocities of 3 km s⁻¹ and above, but my later research revealed otherwise.
4.3 Modification to Published Article

Minor modifications were made to make the published article subtle to read in a thesis. Additional headings were included in the chapter as well as the integration of the main text and supplementary information into one coherent chapter.

4.4 Ultra-strong nanocrystal line metals

Creating ultra-strong materials that are also tough enough to resist failure has always been a challenge to material scientists and engineers. In metals, decreasing the grain sizes to the nanoscale has been shown to result in ultra-strong nanocrystalline metals ([143], [144], and references therein). This improvement, however, comes at the cost of increased susceptibility to catastrophic brittle failure as strain localizes in nanocrystalline metals and forms cracks under tensile loading. It has recently been shown [145]–[148] that the creation of spatial gradients in grain structure can potentially alleviate the catastrophic failure through progressive ductile behavior under applied uniform tensile stresses (Fig. 4.1). Previous methods for creating a gradient-nano-grained (GNG) structure require multi-step surface mechanical grinding [145] or surface mechanical attrition treatment (SMAT) [147]. Surface mechanical grinding results in a GNG structure with grain sizes increasing from the nanocrystalline (~20 nm) to the coarse-grained (~10 µm) scales from the surface to the interior over a depth of ~0.5 mm, leading to a gradient of grain size ~0.02 [145]. The SMAT has been shown to produce a GNG structure with grains increasing in size from the ~100 nm nanocrystals to the ~35 µm coarse-grains over a depth of ~120 µm, leading to a gradient of grain size ~0.3 [147].
Figure 4.1—Competitive battle between ductility and strength. As strength increases ductility decreases (blue line), and vice versa. Homogenous plastic deformation of coarse-grained (CG) metals or homogeneous refinement to nanosized grains (NG) will enable only the transition between strength and ductility, but gradient nanograined (GNG) structures will generate a new level of mechanical properties (red line). [146]

4.5 High-Strain Rate Deformation of Metals

A clear understanding of the fundamental deformation mechanisms in materials exposed to high-velocity impacts and shock compressions is critical to the development of advanced protective technologies for applications in automobile and aircraft crashes [37], sport-related collisions [39], and body and vehicle armors [149]. Impact and shock compression are also used for advanced material processing techniques such as shot peening [150], laser shock peening [151], and explosive welding [152]. Supersonic
velocity micro-particle impacts are especially relevant in cold spray technologies [153], collision of undetectable small-sized space debris and micrometeorites with spacecraft [154], and micro-particle impacts on turbine blades [155]. However, to date, most of the studies on the size-effects of nano and micro grains in metals have been limited to quasi-static loading rates of micro-pillars [143], [144], [156], due to the challenges in conducting short-timescale experiments on small-sized samples.

4.6 Experimental Technique

Laser driven shockwaves have recently been used to probe material responses at small lengthscales and short timescales [157], [158]. Here, we use an advanced laser induced projectile impact testing (α-LIPIT) apparatus [26], [159] to selectively launch individual single-crystal silver (Ag) micro-cubes at supersonic velocities (~400 ms\(^{-1}\)), and allow them to directly impact a rigid impenetrable target—a silicon substrate coated with ~100 nm gold film (Fig. 4.2(A)). The laser ablation of a gold (Au) thin film produces Au vapor—trapped between the glass substrate and the thin crosslinked polydimethylsiloxane (PDMS) layer—that locally expands the PDMS layer, and launches the room temperature projectile (Ag micro-cube, Fig. 4.2(B)) at controlled velocities that are proportional to the laser pulse energy [159]. The Ag micro-cube samples were preserved in ethanol and drop-cast on top of the PDMS layer and air-dried on the launch pad before LIPIT. The PDMS layer also thermally isolates the Ag projectile during laser ablation. This technique allows the sample to deform in an unconstrained manner, and enables us to investigate the role that the intrinsic crystal symmetries and the extrinsic micro-cube-shape symmetries play on resulting
deformations, when the micro-cube impacts along specific crystal-symmetry directions (Fig. 4.2(C-E)).

4.7 Post-impact characterizations

We performed the high resolution SEM analysis of the impacted samples and the preparation of thin TEM-lamella in an FEI Helios NanoLab 660 DualBeam system. We also prepare thin lamella in the Helios NanoLab system for subsequent S/TEM study. Prior to focused ion beam (FIB) milling, we coated the samples first with a layer of electron-beam deposited Pt and then a thick layer of ion-beam deposited Pt in order to protect the sample from direct Ga ion damage. Then, we cut trenches and performed in-situ lift-out and attached the sample to a TEM half-grid. Finally, we thinned down the sample to below 100 nm using high energy (30keV) FIB milling, and subsequently polished under very low-energy ion beam (2keV) to minimize the damage caused by 30 keV ions. The TEM specimens are analyzed in an FEI Titan Themis Scanning/Transmission Electron Microscope (S/TEM) operated at 80keV (300 keV for HRTEM) immediately after final polishing. We performed selective area diffraction (SAD) (~200 nm diameter probing area) and convergent beam electron diffraction (CBED) analyses to investigate the deformed nano/microstructure.
Figure 4.2—The LIPIT of single-crystal Ag micro-cubes: (A) a schematic of the \( \alpha \)-LIPIT experiment, (B) SEM image of a pristine single-crystal Ag micro-cube, (C-E) top and side (at 60° tilt) views of the deformed Ag micro-cubes showing the crystal and deformation symmetries resulting from high-velocity impact, when impacted approximately along (C) [100], (D) [110], and (E) [111] directions (all scale bars indicate 1 \( \mu \)m), and (F) illustrations of the sequence of deformations in the Ag micro-cube during high-velocity impact along the [100] crystal-symmetry direction.

As we discovered the recrystallization in the deformed Ag micro-cubes, we took special care in sample preparation and TEM analysis. During FIB cross-sectioning of the sample
any damage that may have occurred due to the high energy (30 keV) beam were removed during polishing under low-energy beam (2keV). Similarly, we always performed STEM/CBED/SAD analysis at 80 keV first, and employed 300 keV only for the HRTEM performed at the end. When the sample was exposed for extended periods (>30 minutes) under 300 keV in HRTEM, we did observe microstructural changes in the probed regions. Therefore, under our carefully chosen experimental conditions, we do not expect any significant experimental technique-induced microstructural changes.

4.8 Silver Microcube Synthesis (From SI)

Recent advances in the synthesis of Ag nano/micro-cubes [17] enables us to synthesize near-defect-free single-crystals in near-perfect cubic geometry (Fig. 4.2(B)) and in large quantities. Our bottom-up synthesis contrasts the commonly used top-down sample preparation techniques based on focused ion beam (FIB) milling, which result in substrate bound samples in limited quantities, and with surface damage and gallium contamination incurred from ion-milling. We used a seed-growth process with control of oxygen in the reaction environment [159] to synthesize the near-monodispersed single-crystal Ag micro-cubes (cube edge ~1.4 µm) for this study [159].

4.8.1 Preparation of seed nano-cubes (From SI)

We synthesized the silver nano-cubes in a controlled reaction atmosphere as detailed by Jin-Jeon, Lee, and Thomas [17]. Typically, 1 ml of ethylene glycol (EG, Cl ≤ 0.2 mg/kg and Fe ≤ 0.2 mg/kg, Aldrich) is preheated at 140°C while stirring at ~ 900 rpm in a 22 ml vial for 10 minutes. 50 µl of 60 mM hydrochloric acid (HCl, 37%, Aldrich) solution in
EG is added into the vial. After 2 minutes, 1 ml of 0.2 M silver nitrate (AgNO₃, Aldrich) in EG injected in drops into the vial. Three minutes later, 1 ml of 0.12 M polyvinylpyrrolidone (PVP, MW ~ 55,000, Aldrich) solution in EG is added in drops. 4 hours after the addition of PVP solution, the vial is capped. Seeding starts in an hour as indicated by a yellowish color. Growth is completed in another 35 minutes. The reaction batch is quenched in a water bath at room temperature for 20 minutes. The seed nano-cubes are washed with acetone once, followed by several water washes to remove EG and PVP. Finally, the seed nano-cubes are dispersed in 1 ml of EG for further growth.

4.8.2 First seed-growth (From SI)

The first seed growth under Ar atmosphere is performed as described in Ref. (21). Typically, 3 ml of EG is preheated at 160°C for 10 minutes with Ar introduction (Matheson) and 60 µl of 600 mM HCl solution is added into the vial. A glass pipet is used to introduce a continuous flow of Ar gas above the reaction solution. After 2 minutes, 1 ml of 0.8 M AgNO₃ solution is injected in drops into the vial. After another 2 minutes, 1 ml of 0.4 M PVP solution is added in drops. 120 µl of seed suspension is injected 3 minutes after the PVP injection. After another 35 minutes, the reaction vial is quenched in room temperature water. The product is washed with acetone once, followed by several water washes, and filtered to remove small portion of nano-wires (~ 5%). Finally, filtered particles are dispersed in 1 ml of EG for further seed growth.

4.8.3 Second seed-growth (From SI)
3 ml of EG is preheated at 160°C for 10 minutes under Ar introduction, and 90 µl of 600 mM HCl solution is added into the vial. After 2 minutes, 1 ml of 1.6 M AgNO₃ solution is injected in drops into the vial. 2 minutes later, 1 ml of 0.8 M PVP solution in EG is added in drops. 170 µl of particles synthesized in first seed growth (step b) are injected 3 minutes after the PVP injection. Another 35 minutes later, the reaction vial is quenched in room temperature water and the product is washed with acetone once, followed by several water washes, and filtered to remove small portion of nano-wires. The final product, Ag micro-cubes, are dispersed in 1 ml of distilled water for storage.

4.9 Atomistic Structure of Silver cubes and initially active slip systems in a FCC crystal.

Ag is a face-centered-cubic (fcc) metal having space group $Fm\bar{3}m$ (No.225) that can serve as a model for investigating the dynamic deformation behavior of fcc metals. Moreover, the low-stacking-fault-energy of silver (19 mJ/m²) [160] reduces the mobility of dislocations, which in turn activates numerous intriguing microstructural processes to accommodate large imposed strains such as the formation of stacking faults, partial dislocations, deformation twins, and shear bands, in addition to the conventional slips and cross-slips found in fcc metals with high-stacking-fault-energy [161]–[164].

The fcc lattice presents 12 slip systems, \{111\}(\bar{1}10): each of the densely packed four \{111\} crystal planes—(111), ($\bar{1}1$), (1$\bar{1}$1), and (11$\bar{1}$) (Fig. 4.3(B))—contains three (\bar{1}10) slip directions—for example, [\bar{1}10], [10\bar{1}], and [0\bar{1}1] directions in a (111) plane (Fig. 4.3(C)). Applied loading along different crystal symmetry directions activates specific slip systems when the resolved shear stress on specific slip planes exceeds the
critical resolved shear stress of the material as governed by the Schmid’s law. Schmid’s law states that the critically resolved shear stress is equal to the stress applied on the material multiplied by the Schmid’s factor— the multiplication of the cosines of the angles between the loading direction and the glide plane and glide direction. The slip system with the highest Schmid’s factor is the one that gets initially activated. As shown in the stereographic projections in Fig. 4.3(D-F), the slip planes and the directions that are in close proximity to the impact direction are the ones that constitute the highest Schmid’s factor.

There are 8, 4, and 6 slip systems with equal initial Schmid’s factor that can get simultaneously activated when impacted along [100], [110], and [111] directions, respectively. The active slip systems corresponding to each impact direction and their Schmid’s factors are shown in the Tables 4.1-4.3 below (highlighted in blue).
Figure 4.3—The active slip systems in a FCC single-crystal
### Table 4.1—Impact axis [100]

<table>
<thead>
<tr>
<th>Slip System</th>
<th>$\lambda$ (degree)</th>
<th>$\phi$ (degree)</th>
<th>Schmid’s Factor (Cos $\lambda$, Cos $\phi$)</th>
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<td>54.74</td>
<td>0.4082</td>
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<td>54.74</td>
<td>0.4082</td>
</tr>
<tr>
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<tr>
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<td>54.74</td>
<td>0.4082</td>
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### Table 4.2—Impact axis [110]

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Table 4.3—Impact axis [111]

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<th>$\phi$ (degree)</th>
<th>Schmid’s Factor (Cos $\lambda$. Cos $\phi$)</th>
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</tr>
<tr>
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</tr>
<tr>
<td>$(a/2)<a href="111">01\bar{1}</a>$</td>
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</table>

4.10 Results and Discussion

4.10.1 Estimation of key parameters.

The following are the estimates of the average values of important parameters that describe the high velocity ($V = 400$ ms$^{-1}$) impact of Ag micro-cubes (edge length, $a = 1.4 \times 10^{-6} m$). Properties of Ag were obtained from NIST [165] and Meyers [29]

**Mass**

\[ m = \rho a^3 = 10490 \text{ kg m}^{-3} \times (1.4 \times 10^{-6} m)^3 = 28.78 \times 10^{-15} \text{ kg} \]  (4.1)

**Equation 4.1—Mass of Ag cube**

**Momentum**
\[ p = mV = 28.78 \times 10^{-15} \text{ kg} \times 400 \text{ ms}^{-1} = 11.5 \times 10^{-12} \text{ Ns} \quad (4.2) \]

**Equation 4.2—Momentum of Ag cube**

**Kinetic Energy**

\[ K.E = \frac{1}{2} mV^2 = \frac{1}{2} \times 28.78 \times 10^{-15} \text{ kg} \times (400 \text{ ms}^{-1})^2 = 2.30 \times 10^{-9} \text{ J} \quad (4.3) \]

**Equation 4.3—Kinetic energy of Ag cube**

**Melting Energy of Ag cube**

\[ E_{\text{melt}} = \int mC_p \, dT + m\Delta H_f, \tag{4.4} \]

**Equation 4.4—Energy required for melting of the Ag micro-cube.**

where \( C_p \) is the heat capacity at constant pressure and \( \Delta H_f \) is the latent heat of fusion.

Therefore,

\[ E_{\text{melt}} = 28.78 \times 10^{-15} \text{ kg} \left( 240 \text{ J kg}^{-1} \text{ K}^{-1} \right) (1234.9 - 300) + 111 \times 10^3 \text{ J kg}^{-1} \]

\[ = 9.65 \times 10^{-9} \text{ J} \]

Since the \( K.E/E_{\text{melt}} = 0.24 < 1 \), we do not expect any considerable melting of the Ag micro-cubes under our experimental conditions. Though the average temperature is not expected to rise above melting point, the local temperature may indeed reach high values. However, the deformed shape of the sample at the impacted side with upward bent edges suggests that when the tensile waves from top free surface reached the impacted side, the
material that underwent the most severe plastic deformation during compression now behaved like a solid rather than a molten liquid.

**Average temperature rise due to impact**

\[
\Delta T = \frac{K \cdot E}{m \cdot C_p} = \frac{2.30 \times 10^{-9} \, J}{(28.78 \times 10^{-15} \, kg \times 240 \, J/(kgK)^{-1})} = 333 \, K
\]

*(Equation 4.5)* — Temperature rise during impact

**Estimation of nominal strain gradients from nominal strain measurements**

Brief Illustration of estimated strain values measured (Fig. 4.4). Values are listed in Table 4.4-4.6

---

**Figure 4.4** — Deformation of an Ag micro-cube impacted along [100]

\[
\epsilon_1 = \frac{\ell_1 - \ell_0}{\ell_0}
\]

*(Equation 4.6)*
Equation 4.6—Nominal lateral tensile strain at the top of the sample

$$\varepsilon_2 = \frac{\varepsilon_2 - \varepsilon_0}{L_0}$$  \hspace{1cm} (4.7)

Equation 4.7—Nominal lateral tensile strain at the bottom of the sample

$$\varepsilon_{h} = \frac{d\varepsilon}{dh} = \frac{\varepsilon_1 - \varepsilon_2}{L_0}$$  \hspace{1cm} (4.8)

Equation 4.8—Nominal lateral tensile strain gradient along the height

$$\varepsilon_z = \frac{\varepsilon_0 - h}{L_0}$$  \hspace{1cm} (4.9)

Equation 4.9—Nominal axial compressive strain in the sample

Table 4.4—Strain and strain gradient measurements for five different Ag micro-cubes impacted along near [100] direction, x-direction.
Table 4.5—Strain and strain gradient measurements for five different Ag microcubes impacted along near [100] direction, y-direction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$L_0$ (µm)</th>
<th>In x-direction</th>
<th>$\frac{de}{dh}$ (µm$^{-1}$)</th>
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<td>2</td>
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<td>Avg.</td>
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<td>Std.</td>
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Table 4.6—Strain and strain gradient measurements for five different Ag microcubes impacted along near [100] direction, z-direction.

<table>
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<td>Avg.</td>
<td></td>
<td></td>
<td>0.21</td>
</tr>
<tr>
<td>Std.</td>
<td></td>
<td></td>
<td>0.08</td>
</tr>
</tbody>
</table>

It should be noted that the nominal lateral tensile strains were calculated from the lengths measured on the top SEM view of the impacted samples (a projected view of the 3D deformations), which does not account for variations in height. The actual lengths may have some variations. Additionally, though the nominal strains are used to calculate a nominal strain gradient, the strains and the strain gradients experienced by the material during impact will be of much higher values. Therefore, these nominal values should be taken only as lower bounds for the actual strains and strain gradients.

The nominal axial compressive strains were calculated from the tilt-corrected heights measured on the SEM images of the samples obtained at 60-degree tilt. However, it should be noted that the actual axial compressive strain also has a high strain gradient, with extreme compressions at the bottom of the sample and minimal tensile strains at the top free surface of the sample. Our experimental setup currently does not allow for in-situ strain measurements. Additionally, the heights of the specimens were measured on the edge of the sample on the SEM images obtained by tilting the sample, which is slightly higher than the middle region of the sample which underwent more deformation. Therefore, actual axial strains are slightly higher (up to 10%; as seen on TEM lamella) than the values reported in the table.
The variations seen in the strains between x and y directions is due to the deviation of impact direction from a perfect [100]. This slight tilt imposes higher deformations along x-direction compared to the y-direction, resulting in anisotropic nominal lateral strains.

**Duration of impact deformation**

To estimate the impact duration, we assume that the impacted Ag micro-cube decelerates linearly to rest. Therefore, for a linear change in velocity,

\[ t = \frac{2 \Delta h}{V} \]  

Equation 4.10—Impact duration

where \( \Delta h \) is the reduction in the height of the micro-cube \( \Delta h = 0.3 \, \mu m \), on average (Table 4.4).

Therefore,

\[ t = 2 \times 0.3 \times 10^{-6} \, m/400 \, ms^{-1} = 1.5 \times 10^{-9} \, s \]

**Nominal strain rate**

The nominal strain rate can be estimated from the estimated impact duration and the nominal strain in the sample as follows,

\[ \dot{\varepsilon}_z = \frac{\Delta h / h_0}{t} = \frac{0.3 \, \mu m / 1.4 \, \mu m}{(1.5 \times 10^{-9} \, s)} = 1.4 \times 10^8 \, s^{-1} \]

Equation 4.11—Nominal strain rate along impact direction
Derivation of average pressure and shock velocity immediately after impact

For an Ag micro-cube impacted along [100] direction at an impact velocity of 400 m/s,
\[ \frac{\rho V^2}{\sigma_y} = \frac{[10490 \, kg \, m^{-3} \times (400 \, ms^{-1})^2]}{60 \times 10^6 \, Nm^{-2}} = 28 \gg 1. \]
Therefore, Taylor’s plastic analysis is not applicable[29], and a shock wave analysis using hydrodynamic treatment is required. For stress levels that are much higher than the dynamic flow stress, it can be assumed that the solid has no resistance to shear and a hydrodynamic treatment can be used for analysis as details in Meyers[29]:

\[ P_1 = P_2 \] (1)

**Figure 4.5**—Illustration of a planer normal impact of a cube against a stationary substrate.

Consider the projectile (Ag micro-cube) impacting the target (Au-coated Si substrate; only Au is considered as the target for simplicity) at \( V=400 \, ms^{-1} \). A shock wave is generated at the interface, which propagates at velocities \( U_{S1} \) and \( U_{S2} \) into both materials as shown in the Fig. 4.5.

For the equilibrated pressures on both sides,
For continuity,

\[ V - U_{p1} = U_{p2} \]  

(2)

where \( U_{p1} \) is the particle velocity in the projectile in the Lagrangian referential (the moving reference), and \( U_{p2} \) is the particle velocity in the target in the Eulerian referential (the fixed-reference).

Considering the conservation of momentum, for the projectile,

\[ P_1 = \rho_{01} U_{s1} U_{p1} \]  

(3)

**Equation 4.12—Pressure from impact**

for the target,

\[ P_2 = \rho_{02} U_{s2} U_{p2} \]  

(4)

Equations of state (that relates shock velocity to the particle velocity) for the two materials,

\[ U_{s1} = C_{01} + S_1 U_{p1} \]  

(5)

\[ U_{s2} = C_{02} + S_2 U_{p2} \]  

(6)

**Equation 4.13—Shock velocities for Ag cube and rigid substrate**

Substituting (5) & (6) into (3) & (4),

\[ P_1 = \rho_{01} (C_{01} + S_1 U_{p1}) U_{p1} \]  

(7)
\[ P_2 = \rho_{02}(C_{02} + S_2 U_{p2}) U_{p2} \]  

(8)

Substituting (2) into (7),

\[ P_1 = \rho_{01}(C_{01} + S_1(V - U_{p2}))(V - U_{p2}) \]  

(9)

From (1),

\[ \rho_{01}(C_{01} + S_1(V - U_{p2}))(V - U_{p2}) = \rho_{02}(C_{02} + S_2 U_{p2}) U_{p2} \]

\[(\rho_{02}S_2 - \rho_{01}S_1)U_{p2}^2 + (\rho_{01}C_{01} + \rho_{02}C_{02} + 2\rho_{01}S_1V)U_{p2} - \rho_{01}V(C_{01} + S_1V) = 0 \]  

(10)

Solving the quadratic equation,

\[
U_{p2} = \\
\frac{-(\rho_{01}C_{01} + \rho_{02}C_{02} + 2\rho_{01}S_1V)\pm \sqrt{(\rho_{01}C_{01} + \rho_{02}C_{02} + 2\rho_{01}S_1V)^2 - 4(-\rho_{01}V(C_{01} + S_1V))(\rho_{02}S_2 - \rho_{01}S_1)}}{2(\rho_{02}S_2 - \rho_{01}S_1)}
\]

**Equation 4.14**—Particle velocity of Ag cube

The properties of Ag and Au are [29]:

<table>
<thead>
<tr>
<th>Property</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_0 ) (m s(^{-1}))</td>
<td>3230</td>
<td>3060</td>
</tr>
<tr>
<td>( \rho_0 ) (kg m(^{-3}))</td>
<td>10490</td>
<td>19240</td>
</tr>
</tbody>
</table>
Using these properties in equations (11), (2), (4), (5), and (6) for an impact velocity, \( V = 400 \text{ ms}^{-1} \),

**Table 4.8—Shock Parameters**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( U_{p2} ) (m s(^{-1}))</td>
<td>150</td>
</tr>
<tr>
<td>( U_{p1} ) (m s(^{-1}))</td>
<td>250</td>
</tr>
<tr>
<td>( P_1 ) and ( P_2 ) (GPa)</td>
<td>9.52</td>
</tr>
<tr>
<td>( U_{s1} ) (m s(^{-1}))</td>
<td>3630</td>
</tr>
<tr>
<td>( U_{s2} ) (m s(^{-1}))</td>
<td>3296</td>
</tr>
</tbody>
</table>

It should be noted that the above hydrodynamic analysis is performed assuming a planar impact that generates a shock wave (a discontinuous surface with no apparent thickness). The material behaves like a fluid with no shear resistance under high pressure. Therefore, this analysis gives an estimation of the pressure in a perfect planar impact of the silver cube. Additionally, the above analysis neglects the cubic geometry with free-surfaces at the sides that will cause multiple wave reflections and contribute to rapid attenuation. This is reflected in our experiments where the impacted bottom-region shows severe plastic flow of material caused by the hydrodynamic state that arises immediately after impact, whereas the top-region of the projectile shows elasto-plastic behavior that occurs at comparatively low stress levels.
4.10.2 Deformation mechanisms

For impacts approximately along the [100], [110], and [111] crystal-symmetry directions, the deformed samples exhibit distinct deformation features that reflect the interplay of intrinsic and extrinsic symmetries (Fig 4.2) The extrinsic cubic geometry of the sample guides the plastic deformation to follow the cube’s symmetries and results in \( p4mm, p2mm, \) and \( p3m \) plane-point-group symmetries (Appendices; [159]) as seen in the top views of the deformed samples corresponding to the impacts along [100], [110], and [111] directions, respectively (Fig. 4.2C1-E1).

The average pressure-rise of over 9 GPa during the high-strain-rate (>10\(^8\) s\(^{-1}\)) impact far exceeds (>150x) the 60 MPa [165] yield strength of Ag. This generates a hydrodynamic stress state that results in severe plasticity at the impacted side of the sample as the material deforms with no resistance to shear [29], [159].

The initial compressional shock wave generated during impact rapidly attenuates as it moves towards the top-region of the sample due to interactions with free-surface reflections (tensile waves). This results in large deformations at the bottom region of the sample, but far less at the top region, approximately retaining its initial shape. As the amplitude of the propagating compressive stress wave reduces to a few times the yield strength of the material, plastic deformation via crystallographic slips ensues, governed by the intrinsic fcc-lattice symmetry (Fig. 4.6 [159]).
The deformed geometry also indicates high axial and transverse strain gradients during deformation. For example, the impact along [100] direction (impact on a cube face) results in the nominal lateral strains of ~1.45 and ~0.25 at the bottom and top sides of the samples, with greater than $8 \times 10^5$/m lateral strain gradient along the height direction (Fig. 4.4, Table 4.4-4.6, [159]). These observed characteristic deformations suggest extreme micro and nanostructural changes must occur within the crystal.

To investigate the nanostructural changes within the sample, we performed transmission electron microscope (TEM) and selective area diffraction (SAD) analyses on a sample impacted along the ~[100] direction (Fig. 4.7(A)), soon after the impact (~20 hours from impact to TEM analysis). The varying SAD patterns (Fig. 4.7(B1-B4)) indicate a strong gradient in grain size along the height of the sample. The top region exhibits a single-crystalline diffraction pattern with negligible distortion arising in the probed ~200 nm diameter region (Fig.4.7(B1-B2)), whereas the bottom impacted region exhibits a nanocrystalline diffraction pattern Fig. 4.7(B4). The high-resolution TEM (HRTEM) images obtained at the bottom region of the sample show nanocrystalline grains that are
~10 nm in size (Fig. 4.7(C-D)). The presence of nanocrystalline structure in the region that underwent severe plastic flow suggests that there may have been dynamic recrystallization during the impact. The nearly adiabatic compression within the short impact time (~1.5 ns) generates material heating, and leads to dynamic recrystallization due to deformation twinning and strain-induced grain boundary migrations during deformation [166], [167]. The average sample temperature is estimated to rise by ~350 K during impact [159], because of the rapid and nearly adiabatic plastic deformation that does not provide enough time for the sample to dissipate heat into the Au-coated Si substrate. Higher temperatures may occur locally, but the overall shape and texture of the deformed cube rules out the possibility of melting. Nanoscale incoherent deformation twins found in the sample (Fig.4.7(E)) and the continuously varying orientation of grains, characterized by varying convergent beam electron diffraction (CBED) patterns, also signify the highly localized deformations in the sample.
Figure 4.7—Deformation modes and GNG structure formation in impacted Ag microcube, examined 20 hours after impact. (A) a cross-sectional image of an Ag micro-cube impacted along ~[100] direction; image is produced by stitching several bright-field TEM (BF-TEM) images (inset shows an SEM image of the impacted sample with a horizontal white dash-line indicating the location from which the TEM lamella was obtained); (B1-B4) SAD patterns taken along the increasingly highly-deformed regions showing a variation from single-crystalline structure in the top-region to the nanocrystalline structure at the bottom-region; (C) HRTEM image of the bottom-region showing nanocrystalline grains; (D) magnified HRTEM image of a nanocrystal grain at a different orientation compared to its surrounding; (E) HRTEM image of the top region of the sample showing deformation twins (insets show the incoherent twin boundaries (ITBs) and the Fast Fourier Transform (FFT) of the selected region exhibiting twin spots).

We performed TEM analysis 8 days’ post-impact and found substantial nanostructural recovery in the form of recrystallization. Two distinct regions are evident in Fig. 4.8(A): the recrystallized highly-deformed bottom region and the top less-deformed region. The
highly-deformed bottom region of this sample now shows 30-150 nm sized grains
(Fig.4.8(B), Fig. 4.9), which have recrystallized from the less than 10 nm sized grains
evident in the sample investigated 20 h post-impact. We also found several sub-grains
and a high density of dislocations in these grains (Fig. 4.8(C)) that suggests a system that
is still far from equilibrium. The top-center region, and the left- and right-side regions of
the sample cross-section exhibit distinct slip planes at ~30° and ~150° to the horizontal
impact plane, which correspond to the {111} crystal planes in the pristine fcc lattice (Fig.
4.8(A)). Though the slip planes also exist in the sample shown in (Fig. 4.7) the
recrystallization in the top region of the sample allows them to be seen more clearly as in
Fig. 4.8(A). Additionally, consistent with the presence of the strong strain gradient, the
thickness of the shear bands bounded by these slip planes gradually reduces from top-
region (~25 nm thick bands) and becomes so thin as to be nearly indistinguishable near
the most-highly-deformed bottom region (Fig. 4.8(D), Fig. 4.10).

The evolution of the GNG structure in the material is also evident in the distinct electron
diffraction patterns obtained in three different regions that have undergone different
extents of deformation and recrystallization. The top region shows a pattern that is similar
to a single-crystal with small distortions caused by the numerous closely spaced slip
systems (Fig. 4.9(E1)). The bottom-center region that was highly deformed and
recrystallized shows the characteristics of a nanocrystalline structure (Fig. 4.9(E2)), and
the bottom-side region that underwent the most severe plastic flow exhibits diffraction
characteristic of even smaller, highly-misoriented nanocrystalline grains (Fig. 4.9(E3)).
Figure 4.8—Partially recrystallized Ag micro-cube, examined 8 days post-impact: (A) cross-sectional BF-STEM image of the Ag micro-cube showing distinct highly-deformed and less-deformed regions, separated by the white dashed line (inset shows an SEM image of the sample), (B) a magnified view of the region labeled “B” in (A) showing nanocrystalline grains that have undergone static recrystallization, (C) a magnified view of the region labeled “C” in (B) showing the smaller-lengthscale sub-grain structure, (D) a magnified view of the region labeled “D” in (A) showing the high density of slip bands, and (E) the diffraction patterns showing the characteristics of (E1) single-crystalline, (E2) nanocrystalline, and (E3) nanocrystalline with much smaller grains.
Figure 4.9—Nanocrystalline-grain-size distribution in a sample 8 days post-impact. (A) the bottom region of the sample showing nano-grains, (B) the length and widths of the identified grains, and (C) equivalent diameter of the grains, calculated from the area of each grain (inset shows the probability of occurrence of grains in different size ranges).
Figure 4.10—Shear bands found in the side-regions of the samples. Such extreme deformations occurring over a short timescale result in high energy storage in the newly formed nanocrystalline grains with high elastic strain and grain misorientations. The stored elastic energy and the recrystallization nucleus formed during dynamic recrystallization together set the stage for continuous (static) recrystallization [167], [168]. The continuous recrystallization at room temperature results in drastic changes in the nanostructure of the sample: the GNG structure formed as a result of impact evolves through grain coarsening by glide and climb dislocation movements, dislocation accumulation at sub-grain boundaries, and coalescence of sub-grains at low-angle grain boundaries, all of which contribute to decreasing the stored elastic energy [167]. It is remarkable that the continuous recrystallization process occurs predominantly due to the stored mechanical energy without any external thermal annealing, in contrast to previous studies [167], [168] that have utilized thermal annealing at ~573 K for 30 s to induce continuous recrystallization in highly deformed Ag.

To further probe recrystallization, we prepared a TEM lamella of another Ag micro-cube impacted along [100] direction, 44 days post-impact. It shows much coarser grained structure indicating that the static recrystallization has continued (Fig. 4.11). The middle region of the sample has a large (~850 nm) grain with an aspect ratio of ~1, whereas the adjacent regions contain elongated grains (up to ~1700 nm in length and ~300 nm in
width; equivalent diameter ~100-750 nm (Fig. 4.11)) inclined at ~27° (right) and ~10° (left) with respect to the impact plane. These unique grain shapes and their preferential orientations imply that the mid-region of the impacted cube has experienced a nearly isotropic state of stress due to initial shock compression, and the large number of \{111\} slip bands crisscrossing in multiple directions, whereas the side-regions have been deformed by \{111\} slip bands oriented predominantly on a preferred plane. The diffraction pattern (Fig. 4.11(C)) obtained in a highly-deformed region exhibits the characteristics of a single-crystal grain structure implying a near-complete nanostructural recovery from the prior severely-deformed nanocrystalline state observed immediately after impact. However, it should be noted that the nanostructural recovery in the form of continuous recrystallization has transformed these single-crystal grains into entirely new orientations compared to the overall single-crystal orientation of the initial micro-cube. CBED analysis performed on the sample showed large misorientations between adjacent grains that exhibit high contrast (Fig. 4.11(B), Table 4.8 [159]), and a gradually varying CBED pattern within each of those grains, consistent with a structure at a lower lengthscale containing defects and small sub-grain misorientations.
Figure 4.11—A highly recrystallized Ag micro-cube examined 44 days post-impact showing a larger grain structure: (A) an SEM image showing the channeling contrast arising from differently-oriented grains (inset shows the SEM image of the sample), (B) Annular Dark Field STEM (ADF-STEM) image of the lamella showing the larger grain structure with high-angle rotations between adjacent grains (the yellow spots indicate the locations where the CBED patterns were obtained for grain orientation measurements), and (C) SAD pattern of the previously-highly-deformed bottom region (labeled as ‘C’ in B) currently exhibiting the characteristics of fully-recovered single-crystalline structure.

The ADF-STEM image (Fig. 4.11(B)) identifies the recrystallized grains from which the grain sizes shown in Fig. 4.12 were measured. We also performed CBED at the locations indicated by the yellow spots in Fig. 4.11(B), and determined the orientations of those grains as given in the Table 4.8. From these orientations, we calculated the relative misorientations between adjacent grains as shown in Fig. 4.11(B).
Figure 4.12—Grain-size distribution in a sample 44 days post-impact: (A) length and width of the grains, and (B) equivalent diameter of the grains, calculated from the area of each grain (inset shows the probability of occurrence of grains in different size ranges).
### Table 4.9—Grain orientations 44 days post-impact

<table>
<thead>
<tr>
<th>Grain</th>
<th>Orientation (plane)</th>
<th>Grain</th>
<th>Orientation (plane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[7 15 105]</td>
<td>7</td>
<td>[14 15 63]</td>
</tr>
<tr>
<td>2</td>
<td>[4 0 19]</td>
<td>8</td>
<td>[63 65 273]</td>
</tr>
<tr>
<td>3</td>
<td>[2 1 18]</td>
<td>9</td>
<td>[1 0 0]</td>
</tr>
<tr>
<td>4</td>
<td>[11 40 220]</td>
<td>10</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>[332 13 2158]</td>
<td>11</td>
<td>[48 39 208]</td>
</tr>
<tr>
<td>6</td>
<td>[5 4 30]</td>
<td>12</td>
<td>[68 13 442]</td>
</tr>
</tbody>
</table>

### 4.11 Summary

Upon impact, the pristine single-crystal single-grain Ag micro-cube undergoes an extreme deformation trajectory of micro- and nano-structural changes due to the high-strain-rate deformation: a highly-deformed external geometry, and creation of nanoscale grains and strong spatial gradients in grain size along the height of the sample. Such a GNG structure has been shown to result in a new gradient-plasticity strengthening and toughening mechanism in metals with spatial gradients in stress and strain under uniform overall deformations [148]. Because of the correlation between the yield strength and the grain size, application of a uniform external load to a material with GNG structure still leads to different strain distributions in different-sized grains, resulting in a spatial gradient of strain and stress [148]. This strengthening and toughening mechanism, which is distinct from the commonly known strain-gradient plasticity, prevents catastrophic failure through progressive yielding and strain hardening [146]–[148].
Our observations of recrystallization driven by the stored elastic energy suggest a microstructural evolution path that progresses from nanocrystalline towards single crystal. The recrystallization processes also soften the hard and brittle nanocrystalline material that results from dynamic deformation [168]. Therefore, the GNG-structured metal with intermediate states of recrystallization should have desirable strength and toughness for mechanical applications requiring high fatigue life and survivability in extreme environments such as automobile and aircraft crashes, sport-related collisions, and body and vehicle armors. The recrystallization process can be retarded by addition of alloying elements that preferentially segregate to grain boundaries for thermodynamic nanostructure stabilization [169].

The GNG-structured materials made by single-step high-strain-rate process, particularly in metallic alloy systems that have the ability to retard continuous recrystallization even at high temperatures [169], will be useful for applications requiring ultra-high-strength and -toughness. Our studies also demonstrate that controlling the impact orientation will provide additional control over tailoring the GNG structure, hence the mechanical properties of the resultant material. Additionally, our findings suggest important roles played by both the intrinsic crystal symmetries and the extrinsic sample geometries, inspiring further fundamental investigations to understand the interplay of intrinsic and extrinsic symmetries.
Summary and Future Outlook

5.2 Summary

Historically, advances in technology, especially those directed towards protective systems, come from the introduction of new or improved materials. However, many challenges to produce new materials with necessary properties that meet today’s needs of new complex systems remain evident. The inability of material development to keep up with technological advancements is not exclusive to protection materials. As mentioned by Thomas et al.[33]

“[In] a recent National Research Council (NRC) study, Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security, describes how, like advances in armor, the vast majority of disruptive technologies since the start of the industrial revolution have been due to materials innovations, but that the insertion of new materials technologies has become much more difficult and less frequent as materials development fails to keep pace with the rapid design process.”
Furthermore, not only must the speed of material development improve, but also the quickness of material testing as this is an integral part of the development cycle. Current methods of testing can be extensive, costly, and excessively time-consuming. Additionally, there is little understanding of how to connect material properties to the behavior of nanomaterials under extreme mechanical conditions. In many cases these advanced nanomaterials have not been well characterized with regards to high strain rate environments, either alone or as part of a protective system. This gap in knowledge greatly limits the ability of nanomaterials to play a significant role in guiding the advancement of new technology. In my thesis, I used a micro-ballistics setup to provide an appropriate pathway that enables the rapid characterization of several types of nanomaterials and materials with nanoscale features to suggest novel materials for the next generation of protective systems.

In Chapter 2, thin (<250nm) mats consisting of pseudo-2D entangled network of millimeter long carbon nanotubes (CNTs) were impacted. During deformation, employing the laser induced projectile impact technique (LIPIT)[25], [26], [40], [41], simultaneous structural changes in the nanotube network were observed under tension from the micron down to the atomistic scale. Typical deformation modes in the CNT networks included microscale tensile straining of the film until strain reached a critical value that forced reconfiguration of the CNTs. During reconfiguration, CNT-CNT and CNT-projectile interactions generate friction in the system, but stress eventually builds and initiates uncramping (straightening) of individual CNTs that translate through the network towards the impact site. As stress continues to build and surpass the fracture strength of individual CNTs the mat transitions to failure mechanisms associated with
CNTs including CNT fibrillation, fracture, and telescoping (i.e. inner-wall sliding). The deformation modes of the CNT mat were dependent on strain rate with evidence from the observed transition from projectile capture to complete perforation of the CNT mat. The mass normalized penetration energy for the CNT mats showed a ten time increase relative to other commercial impact resistance fibrous fabrics and almost a five time increase compared to graphene, which previously showed significant energy dissipation ability due to delocalization of the energy from impact.[26] Additionally, the entangled network of long CNTs breaks the general trend showing that at a ~50 times weight ratio disadvantage relative to the impacting object, the CNT demonstrates higher energy absorption than other ballistic fabrics.

In Chapter 3, a single component composite consisting of thin film assemblies of polymer grafted nanoparticle (aPGNs) was impacted at high strain rates, again using the previously published LIPIT setup. The influence of grafting polymer chains to nanoparticles, that are on similar length scales, on a materials mechanical response and behavior was used to understand the impact resistant capacity of aPGNs relative to a single phase homopolymer. Local straining softening and craze plastic deformation are the two competing deformation mechanisms observed in both materials. Relative to the homopolymer, incorporation of only 1% by volume of the hard silica particles leads to better load transfer through the matrix. This is a result of the increase in the energy required to translate polymer chains through the polymer phase as an applied load strains the material. Increase in required energy originates from the nanoparticles serving as physical cross-links or anchors requiring the movement of $N^3$ chains before polymer grafted particles can flow and show signs of plastic deformation. This phenomenon
enables the material to transfer stress from polymer chains through the nanoparticle cores and prevent stress build up to reduce the effect of strain-softening that leads to reduction in energy dissipation. This chapter did not attempt to provide a comprehensive study of varied nanocomposite parameters, as true identification of fundamental deformation mechanisms is crucial before proceeding to adjust sample variables. This chapter instead, highlighted the significance of utilizing “single-component” assemblies of polymer grafted nanoparticles, such that within the field of polymer science our understanding of the “nano” effect in polymer nanocomposites can be drastically improved.

Research conducted in chapter 4 was a collaborative effort to demonstrate the effective creation of an extreme gradient nano-grained structure with a single-step, high-velocity-impact process. Gradient nano-grained structures have been recently explored because of their unique high strength and high ductility counterintuitive properties. The high strain rates produce pressures in the gigapascal range that far exceed the yield strength of the silver cube, thus generating a hydrodynamic stress state that drastically deforms the Ag cube through shock wave propagation. The impact even creates a gradient nano-grained structure with a gradient of grain size ~1, where the grain size varies from ~10 nm to ~500 nm over ~500 nm. The high elastic energy stored in the material due to impact triggers a continuous (static) recrystallization process that takes place over the course of weeks at room temperature. Experiments were not conducted to kinetically trap the GNG structure in the Ag cube, but if possible would lead to the improvement of the strength and ductility in the silver cube.

In conclusion, this thesis emphasizes the ability to test materials with speculative properties such as lightweight and high strength, or tough and strong. The fundamental
understanding developed in this dissertation related to the nanomaterials, structure, length scales, and properties could help in guiding the design of engineering materials and systems.

5.3 Outlook

The materials presented in this dissertation will undoubtedly enhance the function of technology in a wide range of applications, but this thesis has only scratch the surface to understanding the fundamental mechanisms responsible for these enhanced properties. The mechanical characterization of novel materials for protective applications can be extended in different directions. General ideas for future research are discussed below.

5.3.1 Modification of 1-D networks

Defining the deformation mechanisms associated with an entangled CNT network only establishes a foundation to modify and compare the parameters influencing energy dissipation. Processing methods can be manipulated to create CNT mats with different orientations, or stacking arrangements where uniaxially aligned CNTs are stacked along different directions. Varying CNT orientation and stacking will lead to the understanding of how the interplay between CNT-CNT interactions and density—i.e. defined by porosity—will influence the property and behavior of the material.

There are other materials to replace the 1-D CNT in the network to provide different levels of functionality in the system—e.g. larger band gap for semi-conducting applications[170] and biodegradable for medical applications[56]. Boron nitride nanotubes are another type of 1-D nanostructure that has recently gained interest in the
science community. Literature has shown the multifunctional capability of BNNTs through their piezoelectric properties, high mechanical properties[171] used for structural reinforcement, and Low Z atom configuration making them potential candidates for hydrogen storage[172]. However, little research has been done to understand the behavior of BNNTs at high strain rate. Machado et al. [173] investigated the fracture mechanisms of BNNTs impacted at 5 km s$^{-1}$, and observed the unzipping of BNNTs into nanoribbons, but what still remains is the fundamental understanding of how BNNTs interact in a network to collectively dissipate energy. Investigation of the collective effort of BNNTs in a system will provide a pathway to understand BNNT performance at the macroscale.

Another potential candidate is polymer nanofibers, who have demonstrated both strong and tough properties by reducing the fiber diameter to sub-micron lengths[23]. The tunability of nanofibers expands their potential over CNNTs and BNNTs whose intrinsic properties are set. An interesting discussion can be made to assesses the possibility of using polymer grafted nanoparticles to electrospinning nanofibers. The internal cross-link structure of the aPGNs increase interactions between chains, thus increasing material strength while also demonstrating improved toughness[103]

In both cases, a key requirement is the length of the tube/fiber, which should be sufficient ($L/D > 10^2$) enough to allow entanglements in the network to generate friction through internal reconfiguration to dissipate energy from an incoming object. A schematic of other possible modifications to the non-woven mat are explored in Fig. 5.1.
5.3.2 Modification of 2-D film

Since the nanoparticle sizes approach the length scale of a single polymer coils, unique interactions will give rise to the optimal control of their mechanical properties. Similar to the 1-D non-woven network, several variations in the assembly of polymer grafted nanoparticles (aPGNs) is possible. Discussion of the PGN grafting density ($\sigma$) and particle radius ($R_0$) vs. molecular weight (Mw) can lead to different packing of the composite internal structure, thereby altering the materials mechanical response (Fig. 5.2). Detailed reviews and low strain rates test are available in several literature articles.[92], [103], [104], [107], [115], [116], [118], [174] Below a polymer dependent
molecular weight all other design considerations are irrelevant and the material will undergo cracking, brittle fracture (Fig 5.2). Above this parameter spacing, exploring the effect of internal structure due to less crowding or more crowding as a result of low and high grafting density, respectively, during high strain rate deformation will provide the fundamental understanding of aPGNs under dynamic loading and provide definitive answers to the effect the polymer entanglement variations in loading of aPGNs.

Figure 5.2— Map of different PGN conditions based on models of polymer brushes on curved surfaces[175], $R_0$- particle raidus, $\sigma$-grafting density (ch-nm$^{-2}$), and degree of polymerization of grafted chain, $M$. At the region less crowding and high $M$, PGN forms a mushroom distored region which causes clusters and reduces entanglements.[92] High crowding and High $M$ will result in a crowded particle boudnary (CPB) near the particle surface, composed of rigid and highly alinged polymer chains, and a semi-dilute particle boundary, where chains have more configurational freedom which allows high entanglments in ths regino.

Additional variables in the internal structure of the aPGN will also determine the conformation of densely grafted chains. In this case, there are intriguing opportunities for
the development of innovative hybrid materials that take advantage of the synergistic
effect by controlling the material constituents and surface geometry as well as the
characteristics of the grafted chains. A subset of the design variables of an individual
PGN is illustrated in Fig. 5.3.

![Design variables for a polymer-grafted nanoparticle. Illustration taken from Hui et al.][116]

While this thesis provides a good story for the experiments undertaken and the results
obtained. It does not solve all the problems. I write this thesis with the hope to inspire
further work and research into these areas to gain more of an understanding of materials
structure-property relations in extreme mechanical environments such as high strain rates.
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