# REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188



| 1. REPORT DATE (DD-MM-YYYY) | 2. REPORT TYPE | 3. DATES COVERED (From - To) |
|---|---|---|
| 25-06-2022 | Final Report | 1-Sep-2017 - 31-Mar-2022 |

**4. TITLE AND SUBTITLE**
Final Report: Engineering Nanocellulose Materials for High Ballistic Impact Performance

**5a. CONTRACT NUMBER**
W911NF-17-1-0430

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**
611102

**6. AUTHORS**

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAMES AND ADDRESSES**
Northwestern University Evanston Campus
1801 Maple Avenue

Evanston, IL 60201 -3149

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)**
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

**10. SPONSOR/MONITOR'S ACRONYM(S)**
ARO

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**
71604-EG.14

**12. DISTRIBUTION AVAILIBILITY STATEMENT**
Approved for public release; distribution is unlimited.

**13. SUPPLEMENTARY NOTES**
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

**14. ABSTRACT**

**15. SUBJECT TERMS**

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | Sinan Keten |
| UU | UU | UU | UU | | 19b. TELEPHONE NUMBER 847-491-5282 |

# RPPR Final Report
as of 29-Jun-2022

Agency Code: 21XD

Proposal Number: 71604EG **Agreement Number: W911NF-17-1-0430**
**INVESTIGATOR(S):**

**Name:** Sinan Keten
**Email:** s-keten@northwestern.edu
**Phone Number:** 8474915282
**Principal:** Y

Organization: **Northwestern University Evanston Campus**
Address: 1801 Maple Avenue, Evanston, IL 602013149
Country: USA
DUNS Number: 160079455 EIN: 362167817
**Report Date:** 30-Jun-2022 Date Received: 25-Jun-2022
**Final Report** for Period Beginning 01-Sep-2017 and Ending 31-Mar-2022
**Title:** Engineering Nanocellulose Materials for High Ballistic Impact Performance
**Begin Performance Period:** 01-Sep-2017 **End Performance Period:** 31-Mar-2022
**Report Term:** 0-Other
Submitted By: Sinan Keten Email: s-keten@northwestern.edu
Phone: (847) 491-5282
**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 4 **STEM Participants:** 8

**Major Goals:** The goal of our research over the first three years was to investigate the size, microstructure, and surface chemistry dependent mechanics of neat nanocellulose thin films from a molecular viewpoint, and establish design principles for maximizing the performance of these nanostructured materials under microballistic impact. Our first aim was to establish a coarse-grained molecular dynamics (CG-MD) modeling framework for nanocellulose fibrils. Building on this capability, our second aim was to relate nanocellulose fibril microstructure in thin films to ballistic impact performance, mimicking laser-induced projectile impact tests (LIPIT) with coarse-grained molecular simulations.

The goal of the add-on thrust in Year 4 was to understand the mechanics of atomically layered nanocomposite films (ALNFs) under high-strain rate deformation and impact conditions using chemistry-specific multi-scale modeling approaches. The knowledge gaps we wish to address here are how strain rate or projectile speed influences dissipation in ALNFs and how different microstructures attainable with these systems should be tailored to maximize performance in extreme mechanical deformations. As a model material system, we focused on reduced graphene oxide - polymer nanocomposites subject to high-strain rate impact deformations.

**Accomplishments:** Please see the attached PDF document.

**Training Opportunities:** This project provided partial funding support for 7 PhD students and 5 postdoctoral fellows, and one undergraduate student. They received training in molecular simulations, coarse-grained modeling, ballistic impact and theoretical modeling of the mechanics of materials. Weekly team and invidual meetings were held, as well as web-conferences and discussions with external collaborators at UMass-Amherst and ARL. Trainees involved in the project attended conferences such as the APS March meeting to present their work.

Of the 5 postdoctoral fellows involved in the project, 3 have taken tenure-track faculty positions in prestigious institutions in the US and abroad. 4 PhD degrees were awarded, and 3 students are progressing on track towards completion of their doctoral degree. The graduates have taken positions in industry including companies such as Intel and 3M. All participants of the project continue to work in STEM related fields, with the majority of them contributing to the U.S. economy and STEM workforce.

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**Results Dissemination:** This project resulted in 13 peer-reviewed journal publications (others in preparation) that appeared in the most highly regarded interdisciplinary and solid mechanics journals. The PI and trainees presented this work in annual conferences such as the SES Meeting, USNCTAM meeting, MRS Spring Meeting, ACS meeting, and APS March meeting. The PI has given departmental seminars on this research at UC San Diego, Cornell, Northwestern, Bogazici University (Turkey), Sabanci University, Stevens Institute, Texas A&M.

**Honors and Awards:** Sinan Keten

ASME Thomas J.R. Hughes Young Investigator Award (2020) (early career award from the Applied Mechanics Division)
Young Observer, US National Committee on Theoretical & Applied Mechanics (2020-2022)
ASME Sia Nemat-Nasser Early Career Award (2019)
ASCE Huber Research Prize (2019)
DOE Distinguished Achievement Team Award (2019) (Project PI: Jian Cao)
JMBBM Early Career Award (2018)
Society of Engineering Science Young Investigator Award (2018)

Nitin Hansoge:

Selected as a finalist for the APS Frank J. Padden Award, the prestigious national award for graduate students working in the polymer science field.

Received the terminal year fellowship.

Zhaoxu Meng:

Became a faculty member at Clemson University.

Andrea Giuntoli:

Became a faculty member at Groningen University

Yao Zhang:

Became a faculty member at Huazhong University

**Protocol Activity Status:**

**Technology Transfer:** The work focuses primarily on fundamental mechanics problems and computational method development. There are no patents or licenses to report from this project at the time of this writing.

The add-on segment of this project facilitated close interactions with an ARL team (Muge Fermen Coker , Brian Barnes, Debjoy Mallick and Jim Berry). To facilitate these collaborations, we have been holding bi-weekly meetings with ARL team members. Additionally, we have implemented automated setup and simulation codes we developed in house on Centennial, DoD HPC resource. We have shared these codes with ARL team members (Brian Barnes) for implementation of high-throughput simulations on atomically layered graphene - polycarbonate and graphene silk nanocomposites, which will be used to generate large material design data sets for their internal HTMDEC project. We anticipate additional publications may come from these ongoing efforts in the near future.

**PARTICIPANTS:**

**Participant Type:** PD/PI
**Participant:** Sinan Keten
**Person Months Worked:** 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

# RPPR Final Report
as of 29-Jun-2022

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)
**Participant:** Andrea Giuntoli
**Person Months Worked:** 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Nitin Hansoge
**Person Months Worked:** 8.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)
**Participant:** Ben Marchi
**Person Months Worked:** 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)
**Participant:** Zhaoxu Meng
**Person Months Worked:** 9.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Subhadeep Pal
**Person Months Worked:** 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Xin Qin
**Person Months Worked:** 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Ao Wang
**Person Months Worked:** 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)

# RPPR Final Report
as of 29-Jun-2022

**Participant:** Heather White
**Person Months Worked:** 7.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)
**Participant:** Zhenghao Wu
**Person Months Worked:** 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Graduate Student (research assistant)
**Participant:** Xinyan Yang
**Person Months Worked:** 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**Participant Type:** Postdoctoral (scholar, fellow or other postdoctoral position)
**Participant:** Yao Zhang
**Person Months Worked:** 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

**ARTICLES:**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Carbon
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.carbon.2017.10.068
Volume: 126 Issue: First Page #: 611
Date Submitted: 8/27/18 12:00AM Date Published: 1/1/18 6:00AM
Publication Location:
**Article Title:** Spalling-like failure by cylindrical projectiles deteriorates the ballistic performance of multi-layer graphene plates
**Authors:** Zhaoxu Meng, Jialun Han, Xin Qin, Yao Zhang, Oluwaseyi Balogun, Sinan Keten
**Keywords:** multi-layer graphene, ballistic impact, spalling
**Abstract:** Through coarse-grained molecular dynamics simulations, we show that beyond a critical plate thickness, a cylindrical projectile penetrates the plate at a lower velocity than a spherical one. This counterintuitive phenomenon is explained by spalling-like failure for thicker plates, where the graphene layers at the bottom section undergo a wave-superposition induced failure in the cylindrical case. Finite element simulations are carried out to show that in-plane tensile stress concentrates at the bottom section, resulting from the superposition of incident and reflected stress waves. A mechanics relationship is then proposed to describe the resisting pressure of the graphitic plate during ballistic impact. The analytical relationship indicates that the intensity of stress wave, which affects the spalling-like failure, depends on the projectile initial velocity, plate compressive modulus, and density.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

# RPPR Final Report
as of 29-Jun-2022

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Extreme Mechanics Letters
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.eml.2017.06.001
Volume: 15 Issue: First Page #: 70
Date Submitted: 8/27/18 12:00AM Date Published: 9/1/17 12:00AM
Publication Location:
**Article Title:** Reduced ballistic limit velocity of graphene membranes due to cone wave reflection
**Authors:** Zhaoxu Meng, Amit Singh, Xin Qin, Sinan Keten
**Keywords:** Cone wave reflection Size-dependent Molecular dynamics simulation Analytical relationship
**Abstract:** We discover a particular size effect due to the reflection of cone wave that has not been previously observed or considered. We present molecular dynamics simulations showing that there exists a critical membrane size below which the cone wave reflections from the boundaries induce perforation; a phe- nomenon that is particularly relevant for microballistic testing of graphene membranes. We present an analytical relationship, verified by simulation data, which predicts the critical membrane size simply as a function of the projectile size, membrane thickness and the ratio of the projectile and membrane densities. Our findings provide timely guidance for future microscale experiments and atomistic simulations for accurate characterization of the impact performance of 2D nanomaterials.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Journal of Applied Mechanics
Publication Identifier Type: DOI Publication Identifier: 10.1115/1.4041041
Volume: Issue: First Page #:
Date Submitted: 8/27/18 12:00AM Date Published: 8/1/18 12:00AM
Publication Location:
**Article Title:** Unraveling the Effect of Material Properties and Geometrical Factors on Ballistic Penetration Energy of Nanoscale Thin Films
**Authors:** Zhaoxu Meng, Sinan Keten
**Keywords:** Ballistic impact, thin films, molecular dynamics, impact propagation zone, geometrical factor
**Abstract:** We employ atomistic and coarse-grained molecular dynamics simulations to measure the ballistic limit velocity (V50) and penetration energy (Ep) of these nanoscale films and investigate their distinctive failure mechanisms over a wide range of impact velocities (Vi). For local penetration failure mechanism observed in polymer and metal films, we find that the intrinsic mechanical properties influence Ep at low Vi, while material density tends to govern Ep at high Vi. MLG films uniquely show a large impact propagation zone (IPZ), which transfers the highly localized impact energy into elastic deformation energy in a much larger area through cone wave propagation. We present theoretical analyses that corroborate that the size of IPZ should depend not only on material properties, but also on a geometrical factor, specifically, the ratio between the projectile radius and film thickness.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

# RPPR Final Report
as of 29-Jun-2022

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Advanced Functional Materials
Publication Identifier Type: DOI Publication Identifier: 10.1002/adfm.201800032
Volume: 28 Issue: 26 First Page #: 1800032
Date Submitted: 8/27/18 12:00AM Date Published: 6/1/18 12:00AM
Publication Location:
**Article Title:** Binary Cellulose Nanocrystal Blends for Bioinspired Damage Tolerant Photonic Films
**Authors:** Bharath Natarajan, Ajay Krishnamurthy, Xin Qin, Caglar D. Emiroglu, Amanda Forster, E. Johan Foster,
**Keywords:** tunicate, cellulose,mechanical properties, thin films, molecular dynamics
**Abstract:** Herein, we present a simple strategy to fabricate superior helicoidal CNC lms with mechanical properties that rival those of the best natural materials and are some of the best reported for photonic CNC materials thus far. Assembling the short w-CNCs with a minority fraction of high aspect ratio CNCs derived from tunicates (t-CNCs), we report remarkable simultaneous enhancement of all in-plane mechanical properties and out-of-plane exibility. The important role of t-CNCs is revealed by coarse grained molecular dynamics simulations where the property enhancement are due to increased interaction lengths and the activa- tion of additional toughening mechanisms. At t-CNC contents greater than 5% by mass the mixed lms also display UV re ecting behaviour. These damage tolerant optically active materials hold great promise for application as protective coatings.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Cellulose
Publication Identifier Type: DOI Publication Identifier: 10.1007/s10570-017-1367-x
Volume: 24 Issue: 8 First Page #: 3289
Date Submitted: 8/27/18 12:00AM Date Published: 6/1/17 12:00AM
Publication Location:
**Article Title:** Optimizing the mechanical properties of cellulose nanopaper through surface energy and critical length scale considerations
**Authors:** Xin Qin, Shizhe Feng, Zhaoxu Meng, Sinan Keten
**Keywords:** Cellulose nanocrystals Nanopaper Overlap length Strength and toughness Coarse- grained molecular dynamics
**Abstract:** We predict how the mechanical properties of CNC nanopaper with nacre-inspired brick-and-mortar structure depend on CNC overlap length and interfacial energy. We show that the modulus and strength both increase with increasing overlap length, but saturate at different critical length scales where a transition from non-covalent interfacial sliding to CNCs fracture is the key influencing mechanism. Maximum toughness is achieved when the interface and CNC failure are tuned to occur at the same time through balanced failure. We propose strategies for maximizing nanopaper mechanical performance by tuning interfacial interactions of constitutive CNCs through surface modifications that improve shear transfer capability.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

# RPPR Final Report
as of 29-Jun-2022

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Nanoscale
Publication Identifier Type: DOI Publication Identifier: 10.1039/C7NR08879E
Volume: 10 Issue: 10 First Page #: 4761
Date Submitted: 8/23/19 12:00AM Date Published:
Publication Location:
**Article Title:** Ballistic impact response of lipid membranes
**Authors:** Yao Zhang, Zhaoxu Meng, Xin Qin, Sinan Keten
**Keywords:** membranes, ballistics, penetration
**Abstract:** Our simulations reveal that upon impact, the projectile can pursue one of three distinct pathways. At low velocities below the critical penetration vel- ocity, projectiles rebound off the surface. At intermediate velocities, penetration occurs after the projectile deforms the membrane into a tubular thread. At very high velocities, rapid penetration occurs through localized membrane deformation without tubulation. Membrane tension, projectile velocity and size govern which phenomenon occurs, owing to their positive correlation with the reaction force generated between the projectile and the membrane during impact. Two critical membrane tension values dictate the boundaries among the three pathways for a given system, due to the rate dependence of the stress generated in the membrane.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Nanoscale Advances
Publication Identifier Type: DOI Publication Identifier: 10.1039/C8NA00232K
Volume: 1 Issue: 4 First Page #: 1351
Date Submitted: 8/27/19 12:00AM Date Published:
Publication Location:
**Article Title:** Impact resistance of nanocellulose films with bioinspired Bouligand microstructures
**Authors:** Xin Qin, Benjamin C. Marchi, Zhaoxu Meng, Sinan Keten
**Keywords:** ballistics, Bouligand, cellulose nanocrystals, LIPIT
**Abstract:** We present atomistically- informed coarse-grained molecular dynamics simulations to measure the ballistic performance of thin films with helicoidally assembled nanocrystals by subjecting them to loading similar to laser-induced projectile impact tests. The effect of pitch angle on the impact performance of CNC films was quantified in the context of their specific ballistic limit velocity and energy absorption. Bouligand structures with low pitch angles (18–42¶) were found to display the highest ballistic resistance, significantly outperforming other pitch angle and quasi-isotropic baseline structures. Improved energy dissipation through greater interfacial sliding, larger in-plane crack openings, and through-thickness twisting cracks resulted in improved impact performance of optimal pitch angle Bouligand CNC films. Intriguingly, decreasing interfacial interactions enhanced the impact performance by readily admitting dissipative inter-fibril and inter-layer sliding events.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

# RPPR Final Report
as of 29-Jun-2022

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Journal of Applied Mechanics
Publication Identifier Type: DOI Publication Identifier: 10.1115/1.4040119
Volume: 85 Issue: 8 First Page #: 081004
Date Submitted: 8/27/19 12:00AM Date Published: 5/1/18 5:00AM
Publication Location:
**Article Title:** Analysis of Cone Wave Reflection in Finite-Size Elastic Membranes and Extension of the Ballistic Impact Problem From Elastic to Viscoelastic Membranes
**Authors:** Amit Singh, Sinan Keten
**Keywords:** Computational mechanics, Impact, Wave propagation
**Abstract:** The cone wave reflected from the finite boundaries of the elastic membrane has been studied analytically. A first-order linear nonhomogeneous differential equation for the ratio of the reflected cone wave front velocity to the speed of tensile waves is derived, which is further used to calculate the traveling time taken by the reflected cone wave to reach to the projectile surface. Since the reflected wave starts when the membrane is already in a deformed configuration, the speed of the reflected cone wave is a function of radius r in the cylindrical coordinates as opposed to almost constant speed of the incoming cone wave studied in the literature. The analytical results are validated with molecular dynamics (MD) simulations of the ballistic impact of projectiles onto a single layer of coarse-grained (CG) graphene. In the second part of the paper, we find that the tensile wave speed under viscoelasticity is the same as that obtained in the case of a linear isotropic elastic material.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Frontiers in Materials
Publication Identifier Type: DOI Publication Identifier: 10.3389/fmats.2019.00174
Volume: 6 Issue: First Page #:
Date Submitted: 8/27/19 12:00AM Date Published: 7/1/19 5:00AM
Publication Location:
**Article Title:** Microstructure and Size Effects on the Mechanics of Two Dimensional, High Aspect Ratio Nanoparticle Assemblies
**Authors:** Benjamin C. Marchi, Sinan Keten
**Keywords:** bioinspired nanocomposites, CNC film, coarse-grained molecular dynamics, size effect, staggered composites
**Abstract:** This work assesses the effects of fiber geometry and in-plane topology on the elastic and failure behaviors of neat CNC thin films using an atomistically informed coarse-grained molecular dynamics model. Short fiber films show a greater dependence on their specific in-plane ordering compared to longer fiber films. Furthermore, aligned, brick, and mortar type CNC films exhibit a remarkable resiliency to random structural perturbations, particularly for films built from long fibers. Finally, simulation size is shown to affect the apparent failure properties of CNC films, with no meaningful impact on elastic property predictions. The relationships between structure and fiber length, as well as the sensitivities to structural randomness and simulation size, elucidated herein provide a comprehensive overview of the expected mechanics of high aspect ratio nanoparticle assemblies.
**Distribution Statement:** 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

# RPPR Final Report
as of 29-Jun-2022

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Extreme Mechanics Letters
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.eml.2020.101038
Volume: 41 Issue: First Page #: 101038
Date Submitted: 8/27/21 12:00AM Date Published: 10/31/20 9:00PM
Publication Location:
**Article Title:** Star topology increases ballistic resistance in thin polymer films
**Authors:** Andrea Giuntoli, Nitin K. Hansoge, Sinan Keten
**Keywords:** LIPIT, impact, star polymers, mechanics
**Abstract:** We study the resistance to ballistic impact of thin polymer films using coarse-grained molecular dynamics simulations, investigating melts of linear polymer chains and star polymers with varying number (2 ? f ? 16) and degree of polymerization (10 ? M ? 50) of the arms. We show that increasing the number of arms f or the length of the arms M both result in greater specific penetration energy within the parameter ranges studied. Greater interpenetration of chains in stars with larger f allows energy to be dissipated predominantly through rearrangement of the stars internally, rather than chain sliding.
**Distribution Statement:** 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Journal of the Mechanics and Physics of Solids
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.jmps.2022.104808
Volume: 161 Issue: First Page #: 104808
Date Submitted: 6/23/22 12:00AM Date Published: 4/1/22 5:00AM
Publication Location:
**Article Title:** Scaling for the inverse thickness dependence of specific penetration energy in polymer thin film impact tests
**Authors:** Yuwen Zhu, Andrea Giuntoli, Nitin Hansoge, Zhongqin Lin, Sinan Keten
**Keywords:** impact, size scaling, molecular dynamics, coarse-graining, ballistics
**Abstract:** We systematically study the effect of polymer film thickness on the impact resistance, quantifying specific penetration energy Ep*, stress wave propagation, and energy absorption processes. The penetration process is broken down into two stages, with Stage 1 involving initial local compression, and Stage 2 corresponding to global film deformation. Specimen thickness greatly influences which stage dominates energy dissipation, with nonlinear deformation in Stage 1 being non-negligible under all circumstances studied. When stage 1 dominates, the stage 1 penetration depth normalized by film thickness is larger in thinner films. This leads to higher Ep* in thinner films, in analogy with indentation phenomena. Higher energy transfer per unit mass is observed for thinner films as they deform in Stage 2. We show that Ep* scales as the inverse of the square root of the thickness based on simulations and experiments, explaining why performance is better for thinner films.
**Distribution Statement:** 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

# RPPR Final Report
as of 29-Jun-2022

**Publication Type:** Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
**Journal:** Cell Reports Physical Science
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.xcrp.2021.100596
Volume: 2 Issue: 10 First Page #: 100596
Date Submitted: 6/23/22 12:00AM Date Published: 10/1/21 5:00AM
Publication Location:
**Article Title:** Tuning star architecture to control mechanical properties and impact resistance of polymer thin films
**Authors:** Andrea Giuntoli, Sinan Keten
**Keywords:** star polymer, ballistics, impact, debye-waller factor, thin film
**Abstract:** Developing materials resistant to high-rate impacts requires an understanding of the molecular mechanism at play during the spatiotemporal scales of these events. Controlling the response of thin films under impact by manipulating their molecular structure is a key challenge for materials science applications and fundamental understanding of the material behavior under high-rate deformations. Using coarse-grained molecular dynamics, we tune the mobility and mechanical properties of star polymer films by varying the number of arms of the star and their length. We subject the films to nanoballistic impacts and identify two components of the penetration energy and corresponding to the early-stage compression (Ep1*) and late-stage deformation (Ep2*) of the film. Ep1* correlates with Young's modulus and the Debye-Waller factor of the films, and Ep2* correlates with the toughness of the films.
**Distribution Statement:** 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

**DISSERTATIONS:**

**Publication Type:** Thesis or Dissertation
**Institution:** Northwestern University
Date Received: 23-Aug-2019 Completion Date: 9/2/18 12:27AM
**Title:** Biomimetic Design of Cellulose Nanomaterials via Multiscale Modeling Approaches
**Authors:** Xin, Qin
Acknowledged Federal Support: **Y**

**Partners**

,

I certify that the information in the report is complete and accurate:
Signature: Sinan Keten
Signature Date: 6/25/22 2:00PM

**Accomplishments**

To link the nanoscale properties of rod-like wood CNCs (w-CNCs) and their structural arrangements to the macroscale performance of nanopaper in a predictive manner, we established an atomistically informed coarse-grained model for CNCs via a strain energy conservation paradigm. Using this model, we predicted how the mechanical properties of CNC nanopaper with nacre-inspired brick-and-mortar structure depend on CNC overlap length and interfacial energy. We showed that the modulus and strength both increase with increasing overlap length but saturate at different critical length scales where a transition from non-covalent interfacial sliding to CNC fracture is the key influencing mechanism. Maximum toughness can be achieved when the interface and CNC failure are tuned to occur at the same time through balanced failure. We discovered strategies for maximizing nanopaper mechanical performance by tuning interfacial interactions of constitutive CNCs through surface modifications that improve shear transfer capability. Our model generated broadly applicable insights into factors governing the performance of self-assembling paper materials made from 1D nanostructures. [1]

Building on the findings of this paper, we then focused on improving the mechanical properties of CNC nanopapers in synergy with experiments carried out at NIST by our collaborators. To overcome the shortcoming of shear transfer between w-CNCs, we considered the self-assembly of short w-CNCs with a minority fraction of high aspect ratio CNCs derived from tunicates (t-CNCs). These systems resulted in remarkable simultaneous enhancement of all in-plane mechanical properties and out-of-plane flexibility. The role of t-CNCs was revealed by coarse grained molecular dynamics simulations where the property enhancements were identified to be due to increased interaction lengths and activation of additional toughening mechanisms. The mechanical properties of films were comparable to mineralized biomaterials like bone, despite the lack of a hard mineral phase. Owing to their chiral nematic structures, these damage tolerant films were optically active and could be prospected for applications such as protective coatings. More broadly, we expect the strategy of using length-bidispersity to be adaptable to mechanically enhancing other matrix-free nanoparticle ensembles. (**Fig. 1**). [2]

In addition to our efforts to study nanocellulosic systems, we also provided fundamental insights into the mechanics of microballistic experiments, focusing on a broad range of materials to understand differences in mechanisms activated in these tests. For instance, recent microscale ballistic experiments have revealed that multilayer graphene membranes exhibit exceptionally high ballistic limit velocity and specific penetration energy. A key feature contributing to the exceptional performance of these systems is the cone wave that develops at impact, which propagates radially at a very high speed for ultra-light and stiff graphene membranes, distributing the kinetic energy of the projectile away from the impact zone. Current theories on ballistic impact consider infinitely wide membranes, and atomistic simulations involve very small projectiles and specimen dimensions, and thus cannot ascertain whether microscale ballistics observations are scalable or size-independent. We discovered a particular size effect due to the reflection of cone wave that had not been previously observed or considered. We carried out molecular dynamics simulations which showed that there exists a critical membrane size below which the cone wave reflections from the boundaries induce perforation, a phenomenon that is particularly relevant for

microballistic testing of graphene membranes. We found an analytical relationship, verified by simulation data, which predicts the critical membrane size simply as a function of the projectile size, membrane thickness and the ratio of the projectile and membrane densities. Our findings provided timely guidance for future microscale experiments and atomistic simulations for accurate characterization of the impact performance of 2D nanomaterials. [3]

We moved on to address two open questions in LIPIT experiments, namely, how graphitic plates behave when they can no longer be treated as a thin membrane, and how the projectile shape influences the perforation resistance of plates of varying thicknesses. Through coarse-grained molecular dynamics simulations, we showed that beyond a critical plate thickness, a cylindrical projectile penetrates the plate at a lower velocity than a spherical one. This counterintuitive phenomenon was attributed to spalling-like failure for thicker plates, where the graphene layers at the bottom section undergo a wave-superposition induced failure in the cylindrical case. Finite element simulations were carried out to show that in-plane tensile stress concentrates at the bottom section, resulting from the superposition of incident and reflected stress waves. A relationship was then proposed to describe the resisting pressure of the graphitic plate during ballistic impact. The analytical relationship indicated that the intensity of stress wave, which affects the spalling-like failure, depends on the projectile initial velocity, plate compressive modulus, and density. Our findings revealed the existence of a new failure mechanism for multi-layer graphene systems and provided theoretical guidance for future dynamic mechanical property characterization of graphitic barriers. (**Fig. 2**) [4]

LIPIT experiments on rubbery materials showed quite intriguing mechanisms, such as arrest of projectiles and rebounding within the film. Thus, we extended our impact analyses to softer viscoelastic materials. Our simulations revealed that upon impact, the projectile can pursue one of three distinct pathways in viscoelastic thin films. At low velocities below the critical penetration velocity, projectiles rebound off the surface. At intermediate velocities, penetration occurs after the projectile deforms the membrane into a tubular thread. At very high velocities, rapid penetration occurs through localized membrane deformation without tubulation. Membrane tension, projectile velocity and size govern which phenomenon occurs, owing to their positive correlation with the reaction force generated between the projectile and the membrane during impact. Two critical membrane tension values dictate the boundaries among the three pathways for a given system, due to the rate dependence of the stress generated in the membrane. Our findings provided broad physical insights into the ballistic impact response of soft, highly deformable thin films. [5]

To understand how material properties influence cone wave dynamics and impact resistance, we conducted a comparative analysis of the dynamic behavior of nanoscale thin films made from multilayer graphene (MLG), polymer, gold, and aluminum under high-speed projectile impact. We employed atomistic and coarse-grained molecular dynamics simulations to measure the ballistic limit velocity (V50) and penetration energy (Ep) of these nanoscale films and investigate their distinctive failure mechanisms over a wide range of impact velocities (Vi). For local penetration failure mechanism observed in polymer and metal films, we found that the intrinsic mechanical properties influence Ep at low Vi, while material density tends to govern Ep at high Vi. MLG films uniquely showed a large impact propagation zone (IPZ), which transfers the highly localized impact energy into elastic deformation energy in a much larger area through cone wave

propagation. We developed theoretical analyses that corroborate that the size of IPZ should depend not only on material properties, but also on a geometrical factor, specifically, the ratio between the projectile radius and film thickness. This study clarified how material properties and geometrical factors relate to ballistic penetration energy, thereby allowing quantitative comparison of the nanoscale ballistic response of different materials. [6]

Our later work focused primarily on predicting the response of cellulose nanocrystal thin films to high-strain rate impacts. We examined two specific aspects, the effect of the length and in-plane staggered arrangement of crystals, and also the out-of-plane pitch angle effects on mechanical behavior. Despite the exceptional properties of CNC films, accurately linking their nanoscopic properties to macroscale performance remains a challenge. Therefore, our work assessed the effects of fiber geometry and in-plane topology on the elastic and failure behaviors of neat CNC thin films using an atomistically informed coarse-grained molecular dynamics model. Short fiber films showed a greater dependence on their specific in-plane ordering compared to longer fiber films. Furthermore, aligned, brick, and mortar type CNC films exhibited a remarkable resiliency to random structural perturbations, particularly for films built from long fibers. Finally, simulation size was shown to affect the apparent failure properties of CNC films, with no meaningful impact on elastic property predictions. The relationships between structure and fiber length, as well as the sensitivities to structural randomness and simulation size, elucidated in our work provided a comprehensive overview of the expected mechanics of high aspect ratio nanoparticle assemblies.[7]

Next, we examined the effect of helicoidal arrangement of cellulose nanocrystals on their mechanical behavior. The Bouligand structure features a helicoidal (twisted plywood) layup of fibers that are uniaxially arranged in-plane and is a hallmark of biomaterials that exhibit outstanding impact resistance. Despite its performance advantage, the underlying mechanisms for its outstanding impact resistance remain poorly understood, posing challenges for optimizing the design and development of bio-inspired materials with Bouligand microstructures. Interestingly, many bio-sourced nanomaterials, such as cellulose nanocrystals (CNCs), readily self-assemble into helicoidal thin films with inter-layer (pitch) angles tunable via solvent processing. Taking CNC films as a model Bouligand system, we carried out atomistically-informed coarse-grained molecular dynamics simulations to measure the ballistic performance of thin films with helicoidally assembled nanocrystals by subjecting them to loading similar to that of laser-induced projectile impact tests (LIPIT). The effect of pitch angle on the impact performance of CNC films was quantified in the context of their specific ballistic limit velocity and energy absorption. Bouligand structures with low pitch angles (18–42 degrees) were found to display the highest ballistic resistance, significantly outperforming other pitch angle and quasi-isotropic baseline structures (**Fig. 3A**). Improved energy dissipation through greater interfacial sliding, larger in-plane crack openings, and through-thickness twisting cracks resulted in improved impact performance of optimal pitch angle Bouligand CNC films. Intriguingly, decreasing interfacial interactions enhanced the impact performance by readily admitting dissipative inter-fibril and inter-layer sliding events without severe fibril fragmentation (**Fig. 3B**). This work breaks new ground in the field because it revealed, for the first time, structural and chemical factors that govern the optimal mechanical design of Bouligand microstructures made from high aspect ratio nanocrystals, paving the way for sustainable, impact resistant, and multi-functional films. [8]

We also carried out further work on the fundamental mechanics of wave propagation and its influence on materials performance in LIPIT experiments. The transverse ballistic impact on a two-dimensional (2D) membrane causes a truncated deformation cone to develop in the wake of tensile implosion waves. The cone wave reflected from the finite boundaries of the elastic membrane was studied analytically. A first-order linear nonhomogeneous differential equation for the ratio of the reflected cone wave front velocity to the speed of tensile waves was derived and further used to calculate the traveling time taken by the reflected cone wave to reach to the projectile surface. Since the reflected wave starts when the membrane is already in a deformed configuration, the speed of the reflected cone wave is a function of radius $r$ in the cylindrical coordinates, as opposed to almost constant speed of the incoming cone wave studied in the literature. The analytical results were validated with molecular dynamics (MD) simulations of the ballistic impact of projectiles onto a single layer of coarse-grained (CG) graphene. In the second part of the paper, we analyzed the membrane impact problem for linear isotropic viscoelastic materials and found that the tensile wave speed for stresses and displacements is the same as that obtained in the case of a linear isotropic elastic material. We also showed that only under special conditions, self-similar solutions for the cone wave are possible in viscoelastic materials modeled by Maxwell, Kelvin–Voigt, or a combination of similar models. Our findings lay some grounds on which further studies on the ballistic response of viscoelastic materials can be performed. A particularly important outcome of this analytical study was the explanation of the importance of viscoelasticity on the minimum dimensions of membranes that should be selected to avoid cone wave reflection in LIPIT experiments on thin films.[9]

Understanding the interactions between polymer grafted nanoparticles is important for predicting the macroscale mechanical properties of the nanocomposites they form. Grafted nanocellulose is prospected for improving the toughness of cellulosic films, which is critical for valorization of these systems and also for creating impact resistant materials. Previous coarse-grained molecular dynamics (CG-MD) simulations by our group captured the interfacial effects of grafting on structure and mobility. However, simulating ballistic impact at micron length scales of relevance to LIPIT was extremely challenging even with these models. A hierarchical coarse- graining strategy that builds upon the computational efficiencies of CG-MD is critically needed for describing impact physics at mesoscopic scales in nanoparticle thin films. As a step towards addressing this challenge, we developed a computational framework to predict the effective pairwise interparticle interactions between polymer grafted nanoparticles with different design parameters, i.e., polymer chain length, grafting density and polymer chemistry. In this work, we idealized the particles as two flat surfaces from which brushes emerge **(Fig. 4)**. Using CG-MD simulations, we evaluated the potential of mean force (PMF) between two nanoparticles by varying their radial distance under affine deformations, from which an effective interaction can be derived. We found a universal analytical form of the PMF that captures the differences between 4 different polymer types (polybutadiene (PB), poly(methyl methacrylate) (PMMA), polystyrene (PS), and polycarbonate (PC)) over a broad range of grafting densities and graft lengths. We quantified how the empirical constants obtained from CG-MD depend on molecular design parameters. The PMF curves of all different designs were collapsed onto a single curve, proving the universality of the approach. The fitting parameters from the PMF could be converted in to strain energy density functions, which yielded reasonable predictions of modulus and toughness for the nanocomposites **(Fig. 5).** With the development of this interatomic potential between the nanoparticles, we paved

the way for a mesoscopic model for nanoparticle assemblies that circumvents the need to explicitly simulate polymer chains, significantly improving the computational efficiency by extending the spatiotemporal scales by many orders of magnitude relative to atomistic simulations. [10]

Polymeric nanocomposite films with enhanced impact and ballistic resistance are highly desired for numerous applications, but molecular configurations that best address this need remain subject to debate. It has been envisioned that polymer grafted particles could outperform other materials since they offer a broader material design space than traditional composites. As a model for these atomically ordered nanocomposites, we studied the resistance to ballistic impact of thin polymer films using coarse-grained molecular dynamics simulations, investigating melts of linear polymer chains and star polymers with varying number ($2 \leq f \leq 16$) and degree of polymerization ($10 \leq M \leq 50$) of the arms. We showed that increasing the number of arms f or the length of the arms M both result in in greater specific penetration energy within the parameters range studied. Greater interpenetration of chains in stars with larger f allows energy to be dissipated predominantly through rearrangement of the stars internally, rather than chain sliding. During film deformation, stars with large f show higher energy absorption rates soon after contact with the projectile, whereas stars with larger M have a delayed response where dissipation arises primarily from chain sliding, which results in significant back face deformation (**Fig. 6**). Our results suggest that stars may be advantageous for tuning energy dissipation mechanisms of ultra-thin films. These findings set the stage for a topology-based strategy for the design of impact-resistant polymer films. [11]

The development of materials resistant to high-rate impacts requires an understanding of the molecular mechanism at play during the spatiotemporal scales of these events. Controlling the time-dependent response of thin film under impact by manipulating their molecular structure is a key challenge for material science applications and for the fundamental understanding of the material behavior under high-rate deformations. Using coarse-grained molecular dynamics simulations, we tuned the molecular mobility and the mechanical properties of star polymer thin films by varying the number of arms ($2 \leq f \leq 16$) and length of the arms ($10 \leq M \leq 50$) of the star. We also subjected the films to nanoballistic impacts and identified two components of the penetration energy, which correspond to the early-stage compression and late-stage back face deformation of the film, respectively. We found that early-stage dissipation correlates with the Young's modulus and the Debye-Waller factor of the films, and that late-stage dissipation correlates with the films' toughness, governed by chain pullout mechanisms (**Fig. 7**). These correlations between dynamics, mechanical properties and ballistic resistance established important guidelines to develop new polymer-based, impact-resistant nanomaterials. [12]

Recent LIPIT studies on nanoscale polymeric films suggest that the specific penetration energy Ep*, a key metric of impact performance, scales inversely with film thickness, making thinner films more resistant per unit mass. This is a puzzling observation that remained unexplained with mechanistic principles. We employed coarse-grained molecular dynamics (CG-MD) to explain this counterintuitive observation. We systematically studied the effect of film thickness on the impact resistance, quantifying penetration energy, stress wave propagation, and energy absorption processes. The penetration process was broken down into two stages, with Stage 1 involving initial local compression and Stage 2 corresponding to global film deformation. Specimen thickness was found to greatly influence which stage dominates energy dissipation, with nonlinear deformation in Stage 1 being non-negligible under all circumstances studied. When stage 1 dominates, the stage

1 penetration depth normalized by film thickness is larger in thinner films. This led to higher Ep* in thinner films, in analogy with indentation phenomena. In addition, higher energy transfer per unit mass was observed for thinner films as they deform in Stage 2. We proposed that Ep* scales as the inverse of the square root of the thickness based on our nanoscale simulations. Remarkably, this scaling also agreed very well with existing impact experiments conducted at larger scales. Our findings revealed the shortcomings of Ep* as a simple metric for comparing the impact resistance of thin films, and provided important scaling arguments and molecular insights that will aid the design and interpretation of nanoscale impact tests. [13]

Shifting our focus to graphitic materials in the add-on (4$^{th}$ year) period of the project, we investigated polymer nanocomposites with multi-layer graphene or graphene oxide fillers arranged in a lamellar fashion. Multilayered graphene oxide (MLGO) is an intriguing material for use in ballistic barriers, combining the phenomenal strength of graphene with enhanced resistance to inter-layer sliding provided by hydroxyl and epoxide functionalization. These groups not only allow the material's mechanical properties to be tailored by adjusting the degree of oxidation but also provide anchoring points for grafted polymers and other materials. Previous works have shown that the degree of oxidation significantly impacts the mechanical performance of GO, reducing the elastic modulus and tensile strength of the individual sheets while increasing the friction and interfacial shear strength between sheets. Laser induced projectile impact tests (LIPIT) allow evaluation of thin films as ballistic barriers. However, it is difficult to explore the films' precise failure mechanism since the projectiles are traveling at around 1000 m/s. We implemented coarse-grained molecular dynamics to simulate LIPIT (**Fig. 8**) and evaluate the performance of MLGO thin films as ballistic barriers, accessing previously unavailable timescales and evaluating the effects of oxidation level on the thin films' ability to dissipate ballistic energy. Additionally, we explored the effects of varying flake size on these systems as previous computational studies on GO films generally do not consider their microscopic arrangement. The primary failure mechanism of these thin films is sliding of the GO flakes, as no bonds were broken. We discovered that elevated levels of oxidation increase the amount of energy required to penetrate the film, as do larger GO flake sizes as they increase energy dissipation via friction. These findings ascertained the potential for MLGO films to be tailored to maximize ballistic energy dissipation, providing a starting point to design impact-resistant GO materials for applications including not only projectile resistance but also space debris protection. (manuscript under preparation)

Nacre, a biological composite commonly found in mollusk shells, is composed a combination of brittle but strong aragonite bricks and elastic but weak biopolymer, the specifics of which vary by species. This combination results in a protective layer that retains most of aragonite's stiffness but increases its toughness by a factor of nearly 1000, despite the composition containing only about 5% biopolymer. When replicating this structure in composite materials, graphene is a very popular choice for the "brick" component due to its phenomenal mechanical properties. In ongoing work in collaboration with ARL researchers, we are using a coarse-grained molecular dynamics (CGMD) model for layered graphene and polycarbonate (PC) to evaluate the nanocomposite's impact resistance and failure mechanisms. Polycarbonate was chosen for its high toughness and strength relative to other polymers, which marks a shift in focus from the original proposal that reflected new priorities as communicated by our collaborators at ARL. As polymers in composite materials are highly tailorable, we intend to vary the PC chain lengths and layer thicknesses to study the effects on the composite performance as a ballistic barrier. Additionally, we will vary

the number of graphene sheets per graphene layer in addition to the number of repeat units (a repeat unit being a layer of graphene plus a layer of PC) in the composite. Automation codes for preparing these hierarchical structures, equilibrating them, and running them on DoD HPC resources have been developed and shared with our collaborators. These CG-MD simulations will allow for high-throughput characterization of these systems, which will be tied into machine learning and data-driven methods to design better ballistic barrier materials. The time-series of a LIPIT test from our developmental work on this project is shown in **Fig. 9**.

**Figures and Captions**

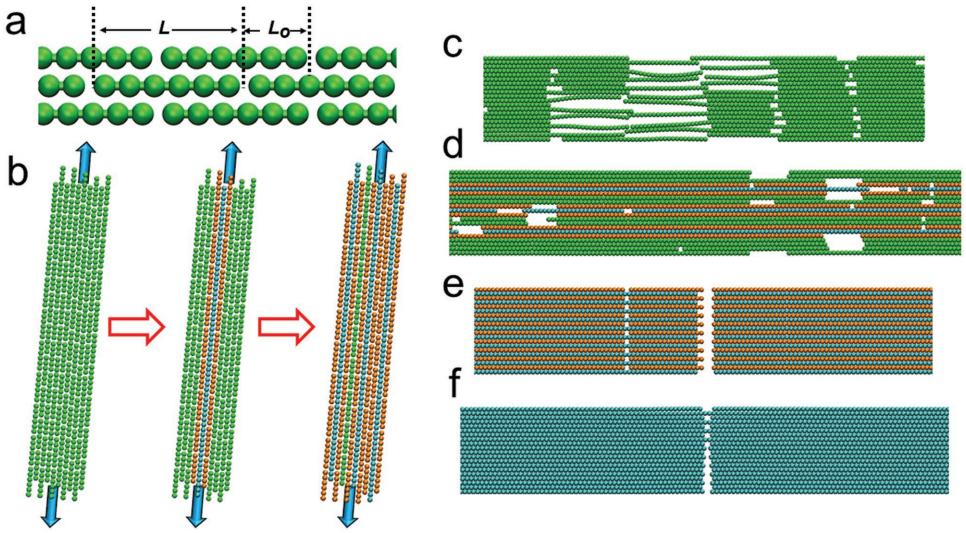


*Figure 1. By introducing tunicate CNCs between wood CNCs, better shear stress transfer in thin films. Optimal fraction of t-CNCs vs. w-CNCs was found to be around 50%, beyond which a transition from pullout to brittle fracture occurred. These observations were validated with experimental data, resulting in CNC-based photonic thin films with extraordinary mechanical properties comparable to bone.*

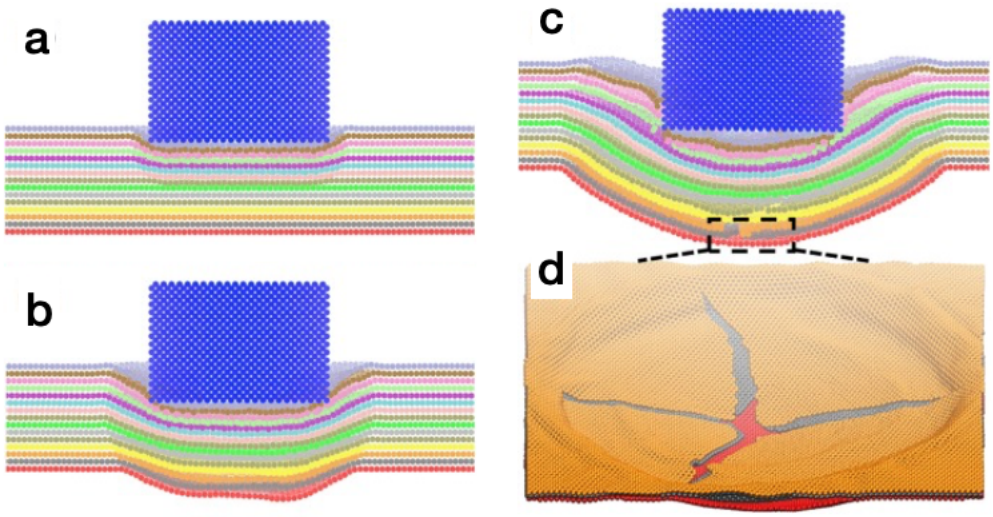


*Figure 2. Spalling failure of multilayer graphene films subject to flat projectiles.*

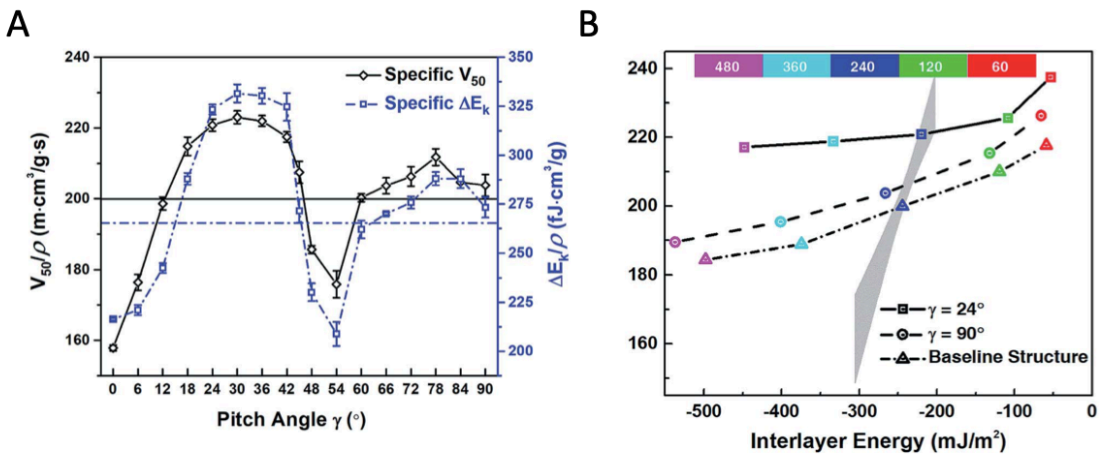


*Figure 3. (A) Specific ballistic limit velocity and specific energy absorption as a function of pitch angle for a Bouligand CNC film. The solid black line and dashed blue line correspond to the specific ballistic limit velocity and specific energy absorption of the quasi-isotropic baseline structure, respectively. (B) The sensitivities of various pitch angles (denoted by different shapes and line styles) to changes in interfacial energy; each point along the curves colored according to its specific interfibril interaction energy value, D0. From this analysis, it can be seen that the higher performance of Bouligand structures cannot be explained simply by changes in interfacial energy between layers.*

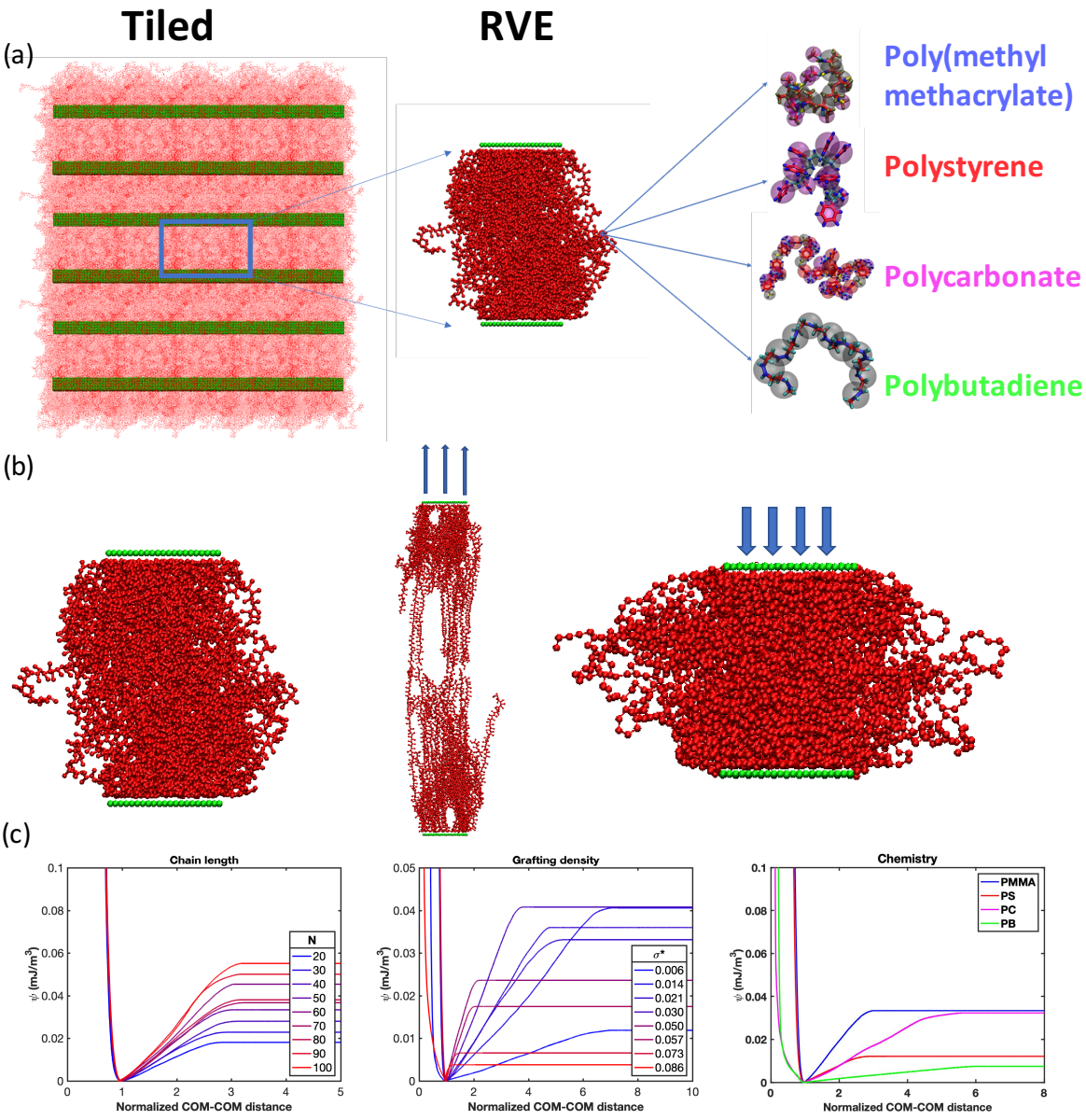


*Figure 4. a) Schematic of the polymer-grafted high aspect ratio nanoparticles arranged in a lamellar configuration. A representative volume element (RVE) is used to analyze the transverse properties of these assemblies. The different polymers studied, and their atomistic and coarse-grained representations are shown on the right. (b) CG-MD simulations are carried out by fixing the bottom plate and pulling/pushing on the top plate with a constant velocity. (c) Representative plots of potential of mean force (ψ) with respect to center of mass (COM) distance between the nanoparticles normalized by their equilibrium distance. The three plots show the variation with chain length, grafting density and polymer chemistry.*

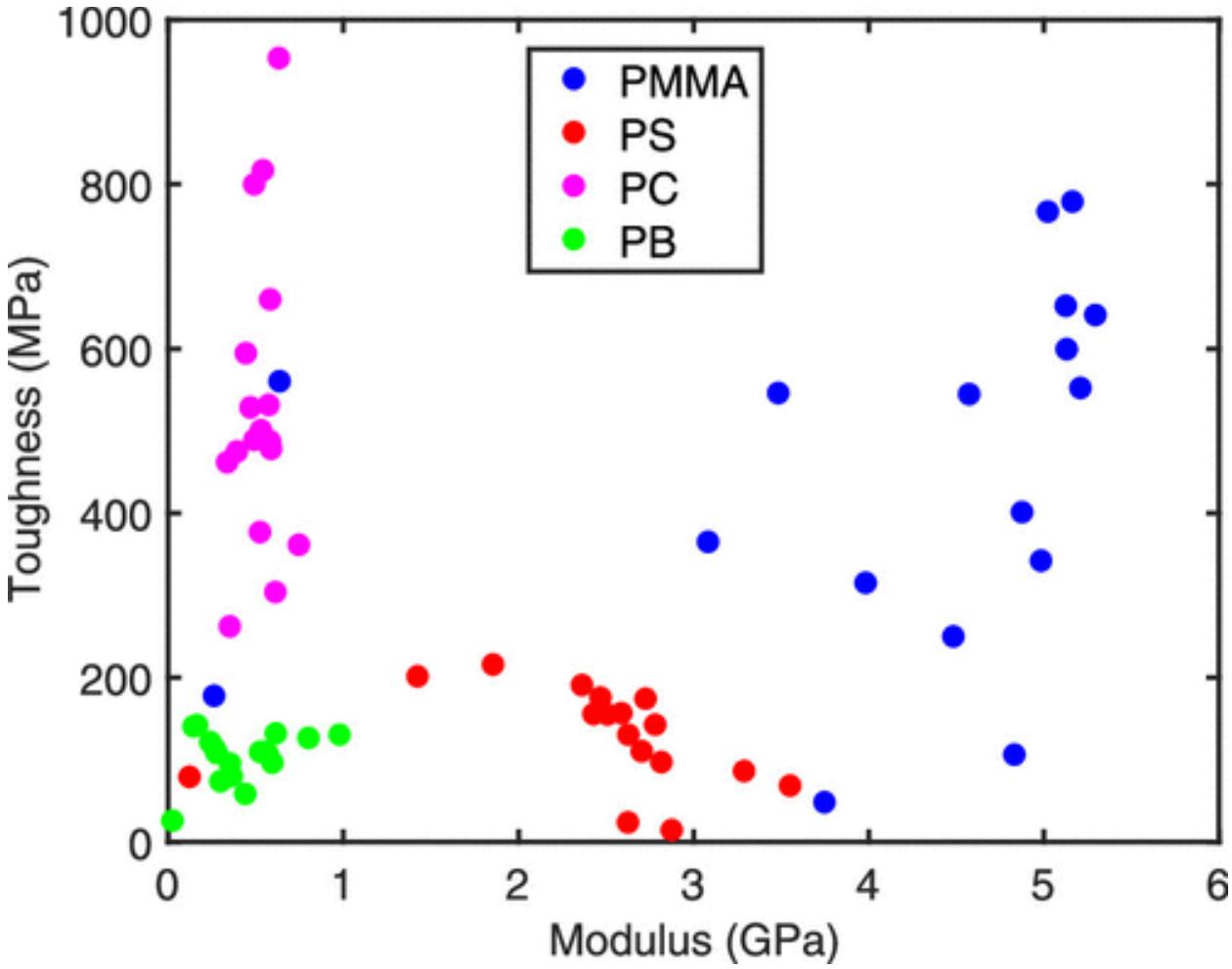


*Figure 5. Ashby plot of modulus vs. toughness in lamellar grafted systems derived from the potential of mean force.*

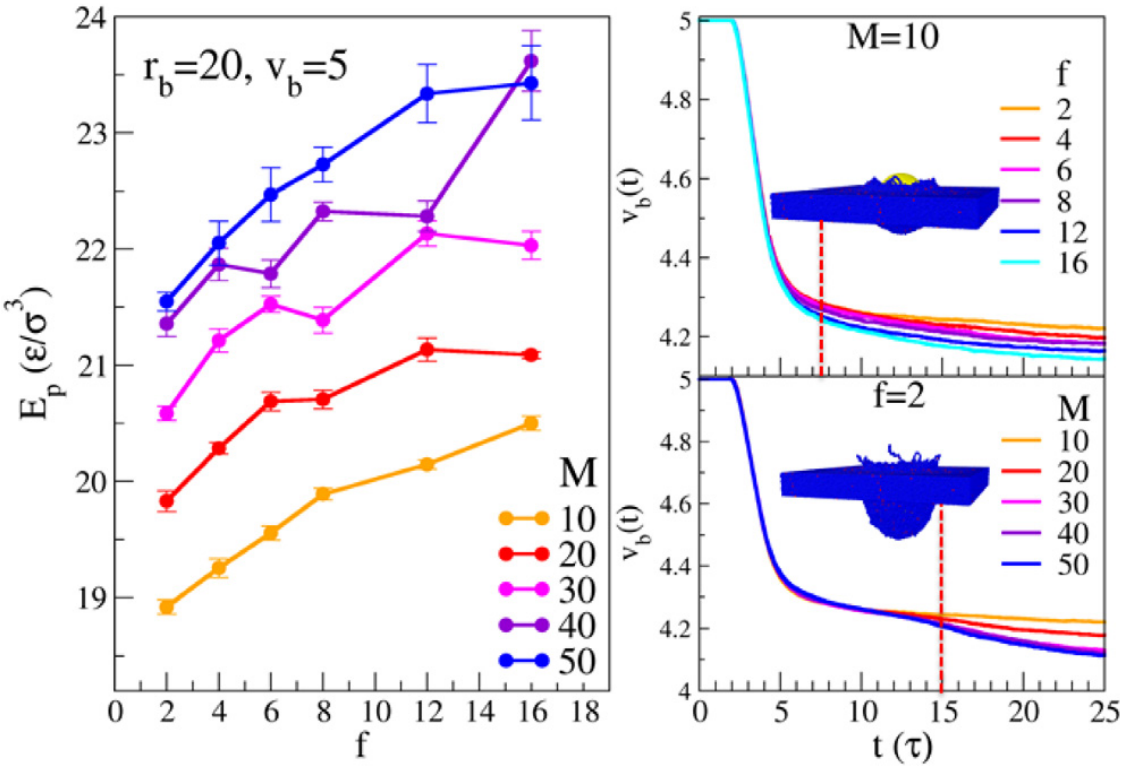


*Figure 6. Superior impact-resistance of star polymers and longer polymer chains. (a) Penetration energy Ep of the films with varying number of arms, f, and length of the arms, M, at fixed bullet radius rb = 20 and velocity vb = 5. For each M, increasing f leads to an increase of absorbed energy, proving a better performance of star polymers with respect to linear chains. Increasing M also leads to increased Ep across all systems, as has recently been experimentally observed for linear chains. The observed fluctuations and outliers (see for example the data point f = 16, M = 40) can be explained by increased molecular interpenetration during the quench. Velocity loss of the bullet in time is higher for stars with higher f (b) during the penetration, while for longer linear chains (c) the increased velocity loss happens at later times, after the membrane penetration.*

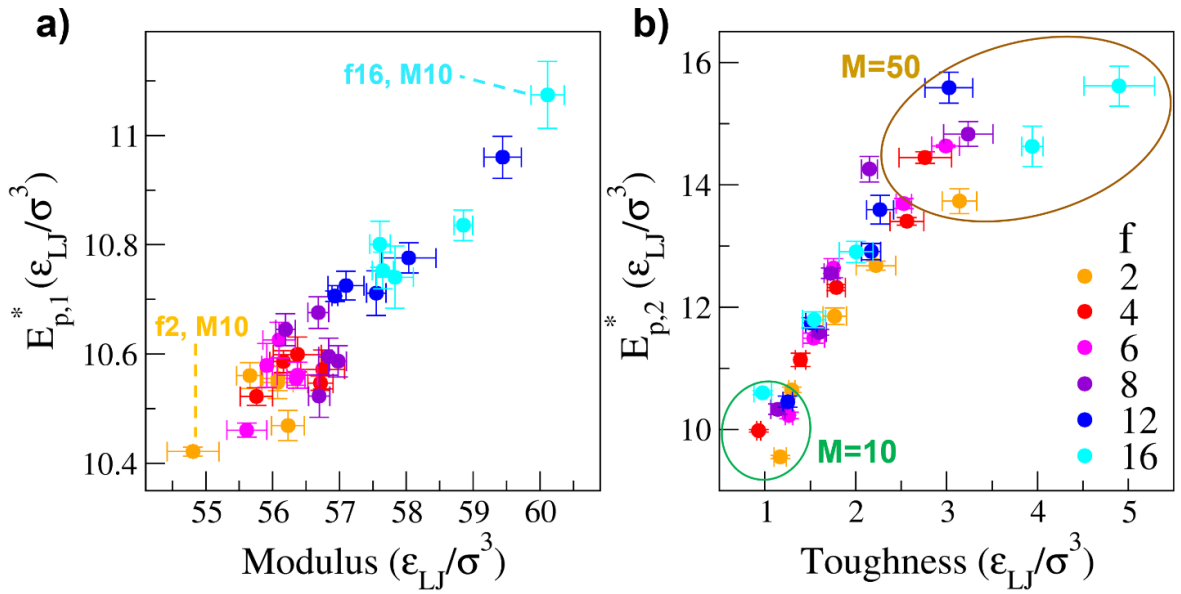


*Figure 7. The early stage and late-stage energy dissipation in thin films correlates with modulus and toughness respectively. Additionally, the Debye-Waller factor, a measure of molecular mobility, is also indicative of energy dissipation in the early-stage behavior due to its inverse correlation with modulus.*

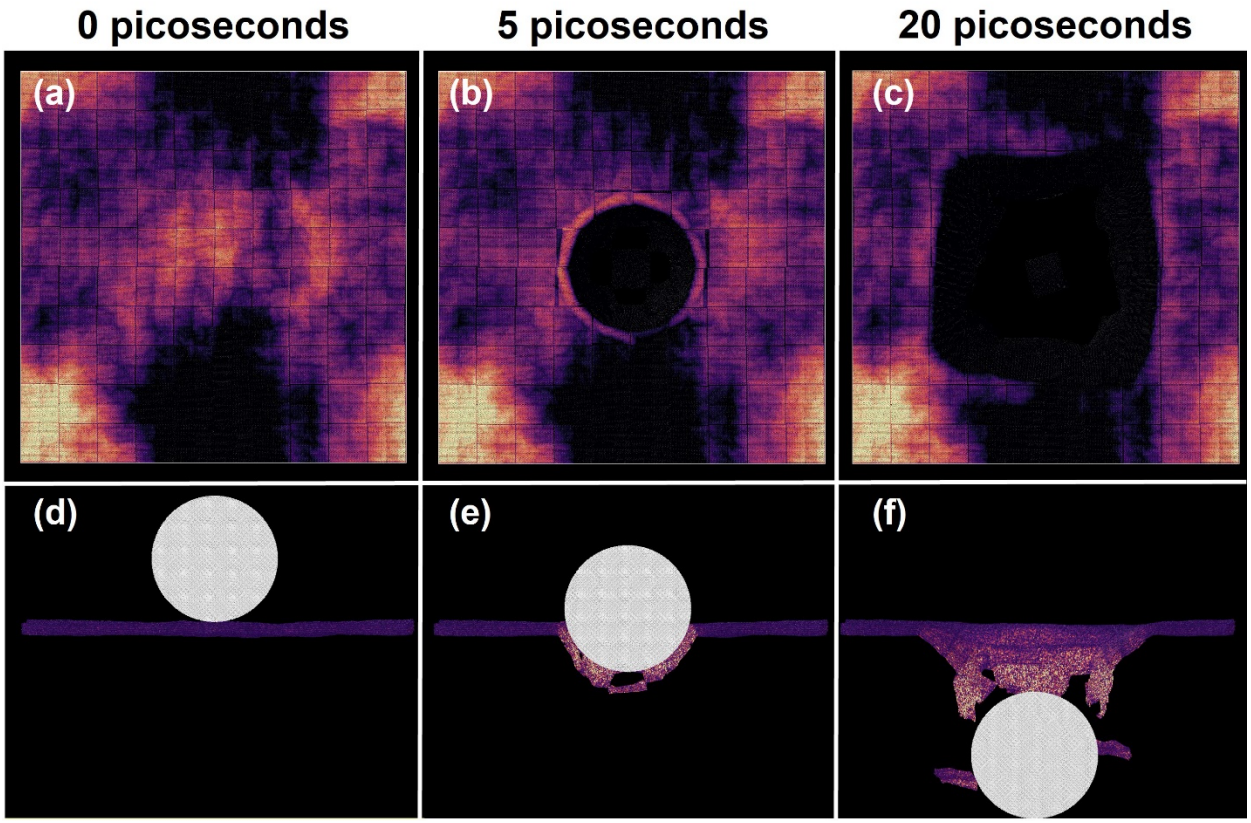


*Figure 8. Laser-induced projectile impact test (LIPIT) on multilayered graphene oxide (GO) thin films. This film contains 6 layers of tiled 15 nm GO flakes impacted at 1 km/s. Panels (a-c) are color-coded by film elevation to show the texture of the film as well as to show the stress wave in panel (b). The bullet is omitted for clarity. Panels (d-f) correspond to (a-c) and show the cross-sectional view of the film as the bullet penetrates. These three panels are color-coded for magnitude of normal stress in the out-of-plane direction.*

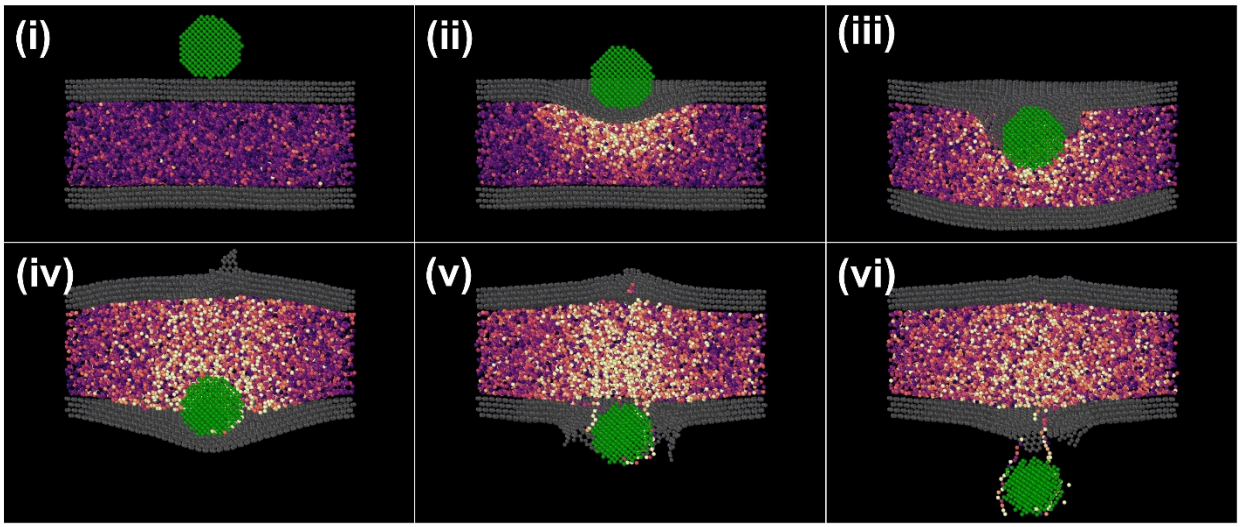


*Figure 9. Time-series cross-sectional view of a laser-induced projectile impact test (LIPIT) simulation on a graphene/polycarbonate nanocomposite, where the polycarbonate is color-coded for particle velocity magnitude. This figure illustrates the transfer of energy from the bullet through the polycarbonate layer, which is part of ongoing work to evaluate this nanocomposite's ballistic performance.*

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