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Sinan Keten

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Northwestern University Evanston Campus
1801 Maple Avenue

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**14. ABSTRACT**
Engineered nanocellulose assemblies are renewable nanomaterials that exhibit unique properties in paper and film forms, such as molecular mechanisms that concurrently improve both strength and toughness. The objective of this research project was to establish the theoretical link between cellulose nanocrystal (CNC) interface characteristics and the fracture toughness of engineered CNC neat films and nanocomposites. In pursuit of this objective, we carried out two research thrusts. Thrust I aimed to explain the role of CNC surface functionalization on interfacial (IF) and interphase (IP) characteristics. Thrust II focused on establishing predictive models of IF & IP

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## Report Title

Final Report: Validated Predictive Modeling of Engineered Cellulose Materials


## ABSTRACT

Engineered nanocellulose assemblies are renewable nanomaterials that exhibit unique properties in paper and film forms, such as molecular mechanisms that concurrently improve both strength and toughness. The objective of this research project was to establish the theoretical link between cellulose nanocrystal (CNC) interface characteristics and the fracture toughness of engineered CNC neat films and nanocomposites. In pursuit of this objective, we carried out two research thrusts. Thrust I aimed to explain the role of CNC surface functionalization on interfacial (IF) and interphase (IP) characteristics. Thrust II focused on establishing predictive models of IF & IP characteristics for nanocomposites. We developed an atomistically informed multi-scale modeling strategy for CNC neat films and nanocomposites that allows us to now predict how CNC interface chemistry, dimensions, and alignment influence the strength, toughness, and elasticity of neat films, as well as key thermomechanical properties of nanocomposites. Fundamental studies carried out helped us describe strategies to best utilize nanocellulose for applications such as ballistic protection materials and structural nanocomposites of great relevance to the US Army.

**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

| Received | | Paper |
|---|---|---|
| 04/01/2017 | 4 | Wenjie Xia, Sinan Keten. Size Dependent Mechanical Behavior of Free-Standing Glassy Polymer Thin Films, Journal of Materials Research, (07 2014): 36. doi: 332,359.00 |
| 04/01/2017 | 15 | Wenjie Xia, Jake Song, Zhaoxu Meng, Chen Shao, Sinan Keten. Designing multi-layer graphene-based assemblies for enhanced toughness in nacre-inspired nanocomposites, Mol. Syst. Des. Eng., ( ): 40. doi: 1,036,803.00 |
| 04/01/2017 | 11 | Brendan Abberton, Wing Kam Liu, Sinan Keten. Anisotropy of Shear Relaxation in Confined Thin Films of Unentangled Polymer Melts, Macromolecules, (07 2015): 0. doi: 366,822.00 |
| 04/01/2017 | 10 | Xin Qin, Wenjie Xia, Bobby Sinko, Sinan Keten. Tuning Glass-Transition in Polymer Nanocomposites with Functionalized Cellulose Nanocrystals through Nanoconfinement, Nano Letters, (07 2015): 0. doi: 366,820.00 |
| 04/01/2017 | 9 | Chen Shao, Sinan Keten. Stiffness Enhancement in Nacre-Inspired Nanocomposites due to Nanoconfinement, Scientific Reports, (05 2015): 0. doi: 366,814.00 |
| 04/01/2017 | 14 | Robert Sinko, Matthieu Vandamme, Zden?k P. Bažant, Sinan Keten. Transient effects of drying creep in nanoporous solids: understanding the effects of nanoscale energy barriers, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science, ( ): 20160490. doi: 1,036,800.00 |
| 08/31/2014 | 1 | Dominique Derome, Jan Carmeliet, Karol Kulasinski, Sinan Keten, Sergey V. Churakov. A comparative molecular dynamics study of crystalline, paracrystalline and amorphous states of cellulose, Cellulose, (03 2014): 0. doi: 10.1007/s10570-014-0213-7 332,356.00 |
| 08/31/2014 | 3 | David D. Hsu, Sinan Keten, Wenjie Xia. Dependence of Polymer Thin Film Adhesion Energy on Cohesive Interactions between Chains, Macromolecules, (08 2014): 0. doi: 10.1021/ma5006974 332,358.00 |
| 08/31/2014 | 2 | Robert Sinko, Shawn Mishra, Luis Ruiz, Nick Brandis, Sinan Keten. Dimensions of Biological Cellulose Nanocrystals Maximize Fracture Strength, ACS Macro Letters, (01 2014): 0. doi: 10.1021/mz400471y 332,357.00 |
| 08/31/2015 | 7 | Robert Sinko, Sinan Keten. Effect of moisture on the traction-separation behavior of cellulose nanocrystal interfaces, Applied Physics Letters, (12 2014): 0. doi: 10.1063/1.4904708 366,799.00 |
| 08/31/2015 | 8 | Wenjie Xia, Sinan Keten. Size-dependent mechanical behavior of free-standing glassy polymer thin films, Journal of Materials Research, (02 2015): 0. doi: 10.1557/jmr.2014.289 366,800.00 |
| 08/31/2015 | 5 | Robert Sinko, Xin Qin, Sinan Keten. Interfacial mechanics of cellulose nanocrystals, MRS Bulletin, (04 2015): 0. doi: 10.1557/mrs.2015.67 366,796.00 |
| 08/31/2015 | 6 | Robert Sinko, Sinan Keten. Traction–separation laws and stick–slip shear phenomenon of interfaces between cellulose nanocrystals, Journal of the Mechanics and Physics of Solids, (05 2015): 0. doi: 10.1016/j.jmps.2015.02.012 366,797.00 |

| | | |
|---|---|---|
| 10/28/2016 | 12 | Robert Sinko, Matthieu Vandamme, Zden?k P. Bažant, Sinan Keten. Transient effects of drying creep in nanoporous solids: understanding the effects of nanoscale energy barriers, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science, ( ): 20160490. doi: 1,018,999.00 |

**TOTAL:** **14**

**Number of Papers published in peer-reviewed journals:**

## (b) Papers published in non-peer-reviewed journals (N/A for none)

| Received | Paper |
|---|---|

**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

## (c) Presentations

**Number of Presentations:** 0.00

## Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

| Received | Paper |
|---|---|
| 04/01/2017 | 13 Xin Qin, Shizhe Feng, Sinan Keten. MECHANICAL AND FRACTURE PROPERTIES GOVERNED BY CRITICAL LENGTH SCALES OF CELLULOSE NANOPAPER, International Conference on Fracture. 21-JUN-17, Rhodes, Greece. : , |

**TOTAL:** **1**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

## Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

**TOTAL:**

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

## (d) Manuscripts

Received Paper

**TOTAL:**

**Number of Manuscripts:**

## Books

Received Book

**TOTAL:**

| Received | Book Chapter |
|---|---|

**TOTAL:**

## Patents Submitted

## Patents Awarded

## Awards

Sinan Keten
Presidential Early Career Award for Scientists and Engineers (PECASE), DoD, 2017
Elected as an American Physical Society Fellow, 2016
ONR Director of Research Early Career Award, 2016
ONR Young Investigator Award, 2015

Wenjie Xia (graduate student)

Best poster award at the 2nd Midwest Workshop on Mechanics and Materials, Evanston, IL, 2016

Selected for the ACS Padden Symposium on Polymer Physics as a finalist at the American Physical Society Meeting, 2016

Robert Sinko (Graduate Student)

Selected as an NDSEG Fellow

Jake Song (undergraduate student coauthor on some of the work conducted)

2nd place prize on the Notre Dame Undergraduate Research Competition
Outstanding Junior in Materials Science and Engineering Award, Northwestern University

## Graduate Students

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED |
|---|---|

**FTE Equivalent:**
**Total Number:**

## Names of Under Graduate students supported

| NAME | PERCENT_SUPPORTED |
|---|---|

**FTE Equivalent:**
**Total Number:**

## Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

| | |
|---|---|
| The number of undergraduates funded by this agreement who graduated during this period: ..... | 1.00 |
| The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... | 1.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... | 1.00 |
| Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... | 1.00 |
| Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... | 1.00 |

## Names of Personnel receiving masters degrees

| NAME |
|---|

**Total Number:**

## Names of personnel receiving PHDs

| NAME |
|---|

**Total Number:**

## Names of other research staff

| NAME | PERCENT_SUPPORTED |
|---|---|

**FTE Equivalent:**
**Total Number:**

## Sub Contractors (DD882)

# Inventions (DD882)

# Scientific Progress

Problem Statement:

Objectives: The objective of this research project was to establish the theoretical link between cellulose nanocrystal (CNC) interface characteristics and the fracture toughness of engineered CNC neat films and nanocomposites. In pursuit of this objective, we carried out two research thrusts. Thrust I aimed to explain the role of CNC surface functionalization on interfacial (IF) and interphase (IP) characteristics. Thrust II focused on establishing predictive models of IF & IP characteristics for nanocomposites.

Approach: Specifically, we first aimed to explain the role of CNC surface functionalization on interface and interphase characteristics using atomistic simulations, a novel systematic coarse-graining approach, combined with continuum mechanics theory of composites. These analyses were geared towards capturing the link between surface chemistry and interfacial traction-separation laws for neat films, and interphase effects in polymer CNC nanocomposites. Using this information, we aimed to derive scaling relationships of the fracture strength of CNC-CNC interfaces as a function of overlap length and crystallite size, thereby establishing a new fracture model of CNC neat films. One of our main efforts was was to utilize mesoscale simulations and shear-lag theory to estimate the critical overlap length scales and optimal crystal dimension for maximizing the fracture strength of CNC-CNC interfaces that govern the performance of neat CNC films. To explore the longer-range effects of interfacial energy on polymer-decorated CNCs and polymer nanocomposites, mesoscale simulations on interphase thermomechanical properties and polymer chain dynamics will be carried out. Our investigations judiciously focused on the interfacial characteristics of CNCs, as this is the most important and least understood determinant of the mechanical performance of engineered cellulose materials, particularly fracture toughness. At the same time, it was the first study to relate these nanoscale features to macroscopic mechanical properties of nanocomposites and neat CNC films via multi-scale modeling. In this sense, this research broke new ground by establishing a mechanics-based design paradigm for engineering novel nanocellulose materials.

Relevance to Army: Engineered nanocellulose assemblies mark a new class of renewable materials that can be considered as a hybrid between polycrystalline materials (e.g. metals) and polymers that exhibit unique properties in paper and film forms, such as molecular mechanisms that concurrently improve both strength and toughness. However, the lack of knowledge on how to relate grain and matrix interactions of high-aspect ratio crystals to mechanical properties hindered our progress. Through this research, we developed new modeling and characterization tools and key physical insights into these novel, promising materials, while expanding our computational research infrastructure to understand the mechanics of similar heterogeneous nanostructured materials. With the help of this work, we can now predict how surface engineering of CNCs (or other fillers for that matter) influence filler dispersion, composite Tg, and relaxation dynamics in polymer nanocomposites with little or no empirical input. The multiscale modeling approach to capture the important effects of interphases and a description of property gradients in the vicinity of inclusions were critically needed to produce accurate constitutive relations and fracture toughness predictions of engineered materials. Predictive modeling of neat films allowed us to explain how both strength and toughness can be increased in neat films, simply by changing crystal dimensions and through interface engineering. Fundamental studies carried out helped us assess the potential of using engineered cellulose materials for applications such as ballistic protection materials and structural nanocomposites of great relevance to the US Army.

Major Accomplishments

- We built a meso-scale model to study the fracture behavior of aligned neat CNC films, using atomistically-informed coarse-grained models. This study is currently in submission, but revealed the size-dependence of the fracture behavior of layered CNC nanomaterials and allowed us to contrast this with existing micromechanics theories such as shear-lag models. Interestingly, we discovered that increasing the aspect ratio of CNCs (i.e. length) increased their strength and toughness simultaneously, explaining recent experimental observations on nanocellulose papers. We developed a general description of how the optimal overlap length, which balances fibril slip-out with fibril fracture, depends on surface energy. Our preliminary investigations on the ballistic response of these aligned systems showed that forming a Bouligand structure (chiral nematic) in nanocellulose films improved the V50 performance of these materials compared to orthogonally aligned systems.
- We investigated interfacial mechanics of nacre-inspired layered nanoparticle - PMMA layered nanocomposite systems by performing pull-out simulations using coarse- grained molecular dynamics (CG-MD) approach. Our simulations uncover two different deformation and failure mechanisms, which greatly influence the toughness and energy dissipation of the system: pull-out failure, which occurs along the particle–PMMA interface, and yielding failure, which occur within the nanofillers, where multi-layer graphene and nanocellulose are examples. Taking graphene as a simpler model than CNCs, we built a theoretical model validated by the simulation data to determine the critical number of layers Ncr of graphene that governs the mode of failures as a function of MLG length and graphene- polymer interfacial interactions. We find that when the number of graphene layers N = Ncr, significant energy dissipation is observed via yielding failure mode, a direct result of the staggered arrangement of MLG. This staggered architecture allows sliding between graphene sheets, resulting in higher toughness compared to that of pull-out failure mode when N > Ncr. We also find that increasing the system length L and the interfacial interaction strength between the layers will enhance the energy dissipation of the nanocomposite, which is a direct result of the nacre-like layer-by-layer arrangement of hard and soft phases. We anticipate that a similar mechanism can be achieved in layered CNC- PMMA nanocomposites. (Figure 1) [1]
- Moisture is known to be a very important parameter in dictating the mechanical properties of CNC based layered

nanocomposites, where water trapped between layers can lower strength, and also cause drying creep type of phenomena more commonly associated with cementitious materials (known as the Pickett effect). We built a coarse-grained model based on the dissipative particle dynamics approache where the behavior of nanoconfined water and its impact on the creep behavior of layered materials was investigation in a generic fashion. In collaboration with Z. Bazant and M. VanDamme, we examined how creep deformations in a slit pore are accelerated by the motion of water due to drying forces. We found that the drying that drives water flow in the nanopores lowers both the activation energy of pore walls sliding past one another and the apparent viscosity of confined water molecules. This behavior and related shear-thinning phenomena can be captured with an analytical Arrhenius relationship accounting for the role of water flow in overcoming the energy barriers. Notably, we used this model and simulation results to demonstrate that the drying creep strain is not linearly dependent on the applied creep stress at the nanopore level. Our findings establish the scaling relationships that explain how the creep driving force, drying force and fluid properties (e.g. viscosity under nanoconfinement) are related. Thus, we establish the nanoscale origins of the Pickett effect and provide strategies for minimizing the additional displacements arising from this effect. [2]

- In a similar vein, we investigated the mechanical behavior of nanoconfined polymers, showing that significant stiffening can be attained when the interfacial energy between filler layers and polymers are large. This effect is more dramatic when the polymers have low internal cohesive energy, and also when the polymer layer thickness is relatively small. We demonstrated this approach again using our CG models for PMMA and multi-layer graphene (MLG). CNCs exhibit similar properties to MLG in terms of mechanical properties and layered structure, and thus a direct connection exists between these systems. This study ascertained the importance of surface chemistry of CNCs to achieve greater benefits from nanoconfinement of polymers between fillers. [3]
- To further our understanding of the shear relaxation behavior of confined polymers, we examined unentangled melts confined between nanolayers. We found that the classical Rouse model¿unsurprisingly fails to predict the thin polymer layer relaxation functions¿in response to out-of-plane shear, due in part to non-Gaussian¿ conformation statistics in the dimension perpendicular to the¿sub/superstrate. Using an alternate empirical model for the out-¿of-plane response, we quantified decreases in the plateau modulus, relaxation time, and viscosity and an increase in the¿logarithmic relaxation rate as functions of film thickness, and¿we described these anisotropic changes in stress-relaxation properties in terms of structural/conformation changes on the microscopic level, namely the relative contraction and non-Gaussian quality of polymer conformations in the dimension normal to the substrate and the resulting phenomenon of cooperative relaxation. We then incorporated these into a semiempirical extension to the Rouse model, which closely predicts our computational results and which will be useful for further study of polymer thin films and layered nanocomposites[4]. We also extend these studies to understand how free surfaces reduce the elastic properties of polymer layers, looking at the size-dependence of layers and understanding the dependence on surface-induced free-volume effects on mechanical properties as a function of polymer cohesive energy [5].
- Using a thin film nanocomposite analogy, we extended our efforts to predicting glass-transition temperature (Tg) in CNC-PMMA nanocomposites. We discovered that increasing the volume fraction of CNCs results in nanoconfinement effects that lead to an appreciation of the composite Tg provided that strong interfacial interactions are achieved, as in the case of TEMPO-mediated surface modifications that promote hydrogen bonding. The upper and lower bounds of shifts in Tg were predicted by fully accounting for nanoconfinement and interfacial properties, providing new insight into tuning these aspects in nanocomposite design. Our multiscale framework explains recent experiments and breaks new ground in predicting, without any empirical parameters, key structure-property relationships for nanocomposites (Figure 2). [6]
- We developed analytical relations that describe the shear and tensile failure of the interfaces between Iß CNCs, providing new insight into factors governing the mechanical behavior of neat films. Analytical models to describe the energy landscapes are developed using energy scaling relations for van der Waals surfaces in combination with a modification of the Prandtl–Tomlinson model for atomic friction. Our simulations paved the way for tailoring hierarchical CNC materials. (Figure 3) [7]
- Prior efforts [8-12] elucidated CNC-CNC interfaces and the impact of moisture on traction and separation behavior. We wrote an invited review article on this issue. We also developed models for describing polymer adhesion to nanofiller surfaces, assessing the dependence of interfacial energy on cohesive behavior of the polymers. We also found that small wood-based CNCs should perform better than other CNC types because they offer a small size that allows maximum surface area per unit volume while achieving a large-enough fracture surface energy.

Bibliography:

W. Xia, J. Song, Z. Meng, C. Shao, and S. Keten*, “Designing multi-layer graphene- based assemblies for enhanced toughness in nacre-inspired nanocomposites”, 2016, Molecular Systems Design and Engineering, 1, 40.
2. R. Sinko, M. Vandamme, Z. P. Bažant, S. Keten*, "Transient effects of drying creep in nanoporous solids: understanding the effects of nanoscale energy barriers", 2016, J. Roy. Soc. A., 472: 20160490.
3. C. Shao, S. Keten*, “Stiffness Enhancement in Nacre-Inspired Nanocomposites due to Nanoconfinement”, 2015, Scientific Reports, 5, pp. 16452.
4. B. Abberton, W. K. Liu, S. Keten*, “Anisotropy of Shear Relaxation in Doubly Confined Thin Films of Unentangled Polymer Melts”, 2015, Macromolecules, 48 (20), pp. 7631- 7639.
5. W. Xia, and S. Keten*, "Size-dependent Mechanical Behavior of Free-Standing Glassy Polymer Thin Films", 2015, Journal of Materials Research, 30(1) pp. 36-45, invited contribution for the Focus Issue on Soft Nanomaterials.
6. X. Qin, W. Xia, B. Sinko, S. Keten* “Tuning Glass-Transition in Polymer Nanocomposites with Functionalized Cellulose Nanocrystals through Nanoconfinement”, 2015, Nano Letters, 15(10), pp. 6738–6744.
7. R. Sinko, S. Keten*, “Traction-separation laws and stick-slip shear phenomenon of interfaces between cellulose

nanocrystals”, 2015, Journal of the Mechanics and Physics of Solids 78, pp. 526-539.
8. R. Sinko, X. Qin, S. Keten*, “Interfacial Mechanics of Cellulose Nanocrystals”, 2015, 40(04), pp. 340-348, invited article for MRS Bulletin, special issue on “Mechanics of biological materials”.
9. R. Sinko, S. Keten*, “Effect of moisture on the traction-separation behavior of cellulose nanocrystal interfaces”, 2015, Applied Physics Letters, 105, pp. 243702.
10. K. Kulasinski, S. Keten, S. Churakov, R. Guyer, J. Carmeliet, D. Derome "Molecular Mechanism of Moisture-Induced Transition in Amorphous Cellulose”, 2014, ACS Macro Letters, 3 (10), pp. 1037–1040.
11. W. Xia, D. Hsu, S. Keten*, "Dependence of Polymer Thin Film Adhesion Energy on Cohesive Interactions between Chains", Macromolecules, 2014, 47 (15), pp. 5286–5294.
12. B. Sinko, S. Mishra, L. Ruiz, N. Brandis, S. Keten*, “The dimensions of biological cellulose nanocrystals maximize fracture strength”, ACS Macro Letters, 2014, 3, pp. 64– 69.

Appendices: Illustrations are provided as an attachment.

## Technology Transfer

Throughout the research project, we frequently exchanged our progress and other relevant information with ARL scientists. The nanocellulose group was updated on progress through web conferences, and research efforts were tailored towards developing a better understanding of nanocellulose composites relevant for the studies by Jim Snyder's group. We also interacting with modeling experts at ARL (Jan Andzelm's research group), for instance to share our coarse-grained modeling algorithms and simulation findings on the effects on nanoconfinement on polymer film and composite mechanical properties.

**Related Figures**

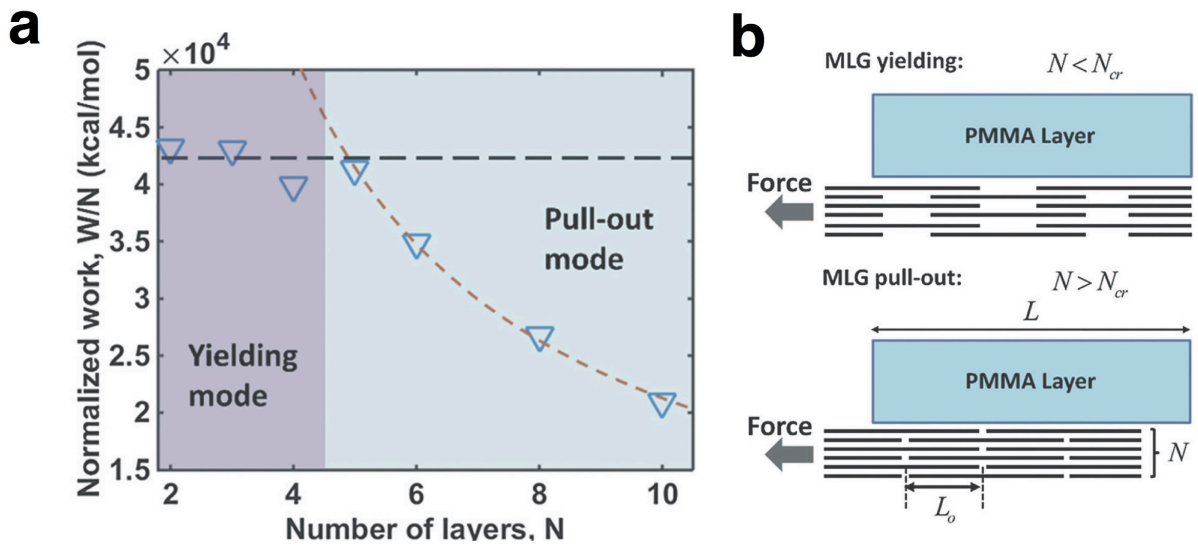


**Figure 1.** Failure behavior of layered nanocomposites. When a multi-layer filler like graphene or CNCs are employed in polymer matrices, failure mechanism depends on the number of layers and interfacial chemistry. Specifically, there exists a critical number of layers below which failure will be ductile, as it will facilitate yielding of the fillers, as opposed to simple pull-out of the fillers. This is contrary to most composites, where pull-out is considered a relatively dissipative failure mechanism, but for layered nanofillers yielding of the fillers further increases work to fracture due to creation of more failure surfaces. [1]

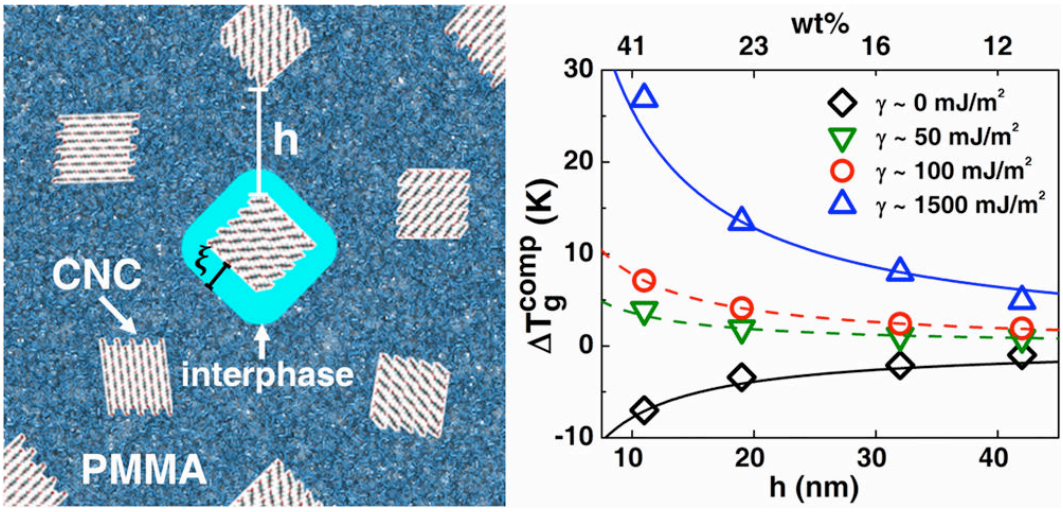


**Figure 2.** Predicting the glass-transition shifts in CNC-PMMA nanocomposites using a thin-film nanocomposite analogy. CNC surface modifications that improve adhesion to the matrix can lead to increases in the glass-transition temperature ($T_g$)at relatively high wt %, whereas lowering surface interactions with the matrix typically leads to lowering $T_g$. [6]

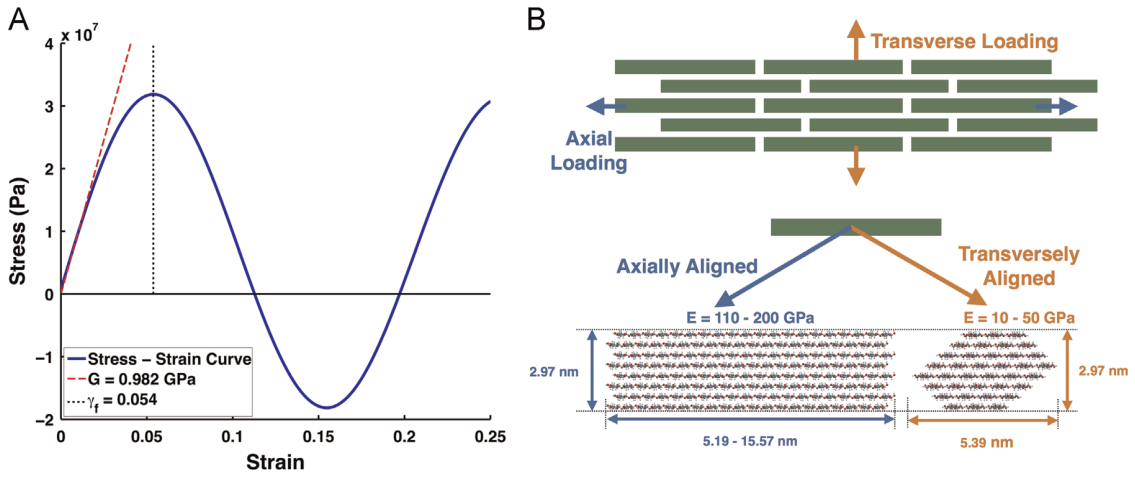


**Figure 3.** (A) Stress–strain plot for the shearing of two CNC crystals ((110)-(110) interface along the width) based on the traction potentials developed. The interlayer shear modulus is estimated by taking the initial slope of the stress–strain curve and the strain at failure initiation is taken as the strain at the maximum stress. (B) Illustration of a CNC neat film where each of the rectangles represents a CNC crystal. A shear-lag model is used to predict the overall performance of this system based on the dimensions, mechanical properties of individual CNCs, and the interfacial shear properties obtained from stress–strain plots shown in panel (A). [7]