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Active, Tailorable Adhesives for Dissimilar Material Bonding, Repair and Assembly

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Composite Vehicle Research Center (CVRC)

Michigan State University

Project ID # : LM087

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OVERVIEW

TIMELINE

- **Start Date:** October 1, 2013
- **End Date:** September 30, 2016
- Percent Complete – 35%

BUDGET

- **Total Project Funding:** $599,999
- **Funding Received in Budget Period 2: (01/2015 – 12/2015) :** $207,282
- **Funding for Budget Period 3: (01/2016 – 09/2016) :** $236,629

BARRIERS ADDRESSED

- **Joining and Assembly**
  - **Light-weight, reversible bonded joints**
- **Performance**
  - **Enhanced damage resistance of joints using nano-materials**
- **Predictive Modeling Tools**
  - **Development of Experimentally Validated Simulations.**

Partners / Collaborations

- **Eaton Innovation Center, MI.**

Project Lead

- **Michigan State University, Composite Vehicle Research Center (CVRC).**

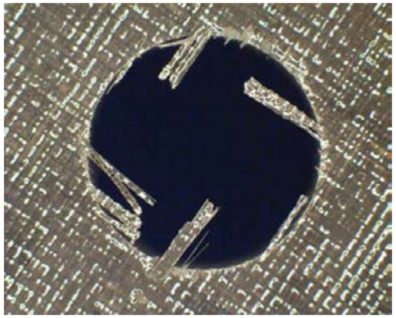
Introduction / Relevance - Joining

- **JOINING / ASSEMBLY**

➢ Joining is inevitable, allows versatility in assembly and repair, reduces costs and time.

➢ Considered a 'weak-link' in the structure due to complex phenomena & interactions.

- ***Mechanical Fastening***
- ***PROS:* *a) Repair and Re-assembly, b) confidence in use as it is commonly used***
- ***CONS :* *a) Adds Weight, b) machining holes, c) delamination in composites, d) stress-concentrations***



Delamination in composites due to hole-drilling, Gardiner, Composites World , (2012)

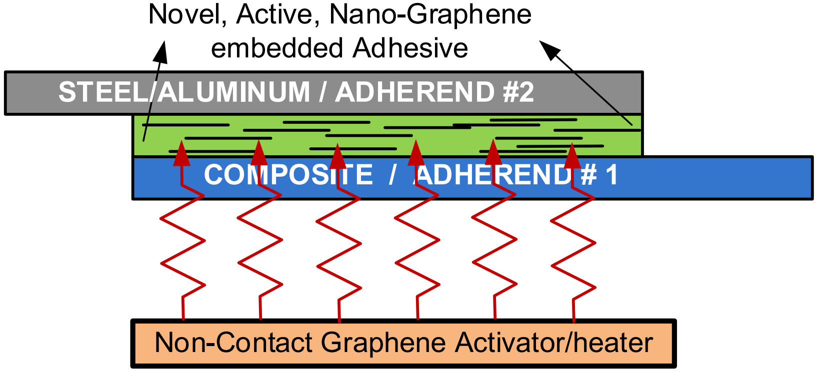
- ***Adhesive Bonding***
- ***PROS:* *a) Light Weight and b) load distribution over larger areas***
- ***CONS :* *a) permanent joint (cannot be repaired or re-assembled), b) lack of confidence in common use to reliability of bonding.***

Examples of Adhesive Joints
a) Lap-Joint , b) Double Lap-Joint

There is a Need for a JOINING TECHNIQUE that can INHERIT the MERITS of BOTH bolted & bonded techniques while still being compatible with current assembly line practices

Global Objective(s) & Approach

- **OBJECTIVE**
  - To demonstrate the feasibility of ACTIVE Adhesive technology for structural joining of similar / dissimilar adherend materials.
- **ACTIVE ADHESIVES**
  - Thermoplastic adhesives reinforced with conductive nano-graphene (GnP) platelets
  - Allow targeted heating of adhesive only using interaction of microwaves and graphene.



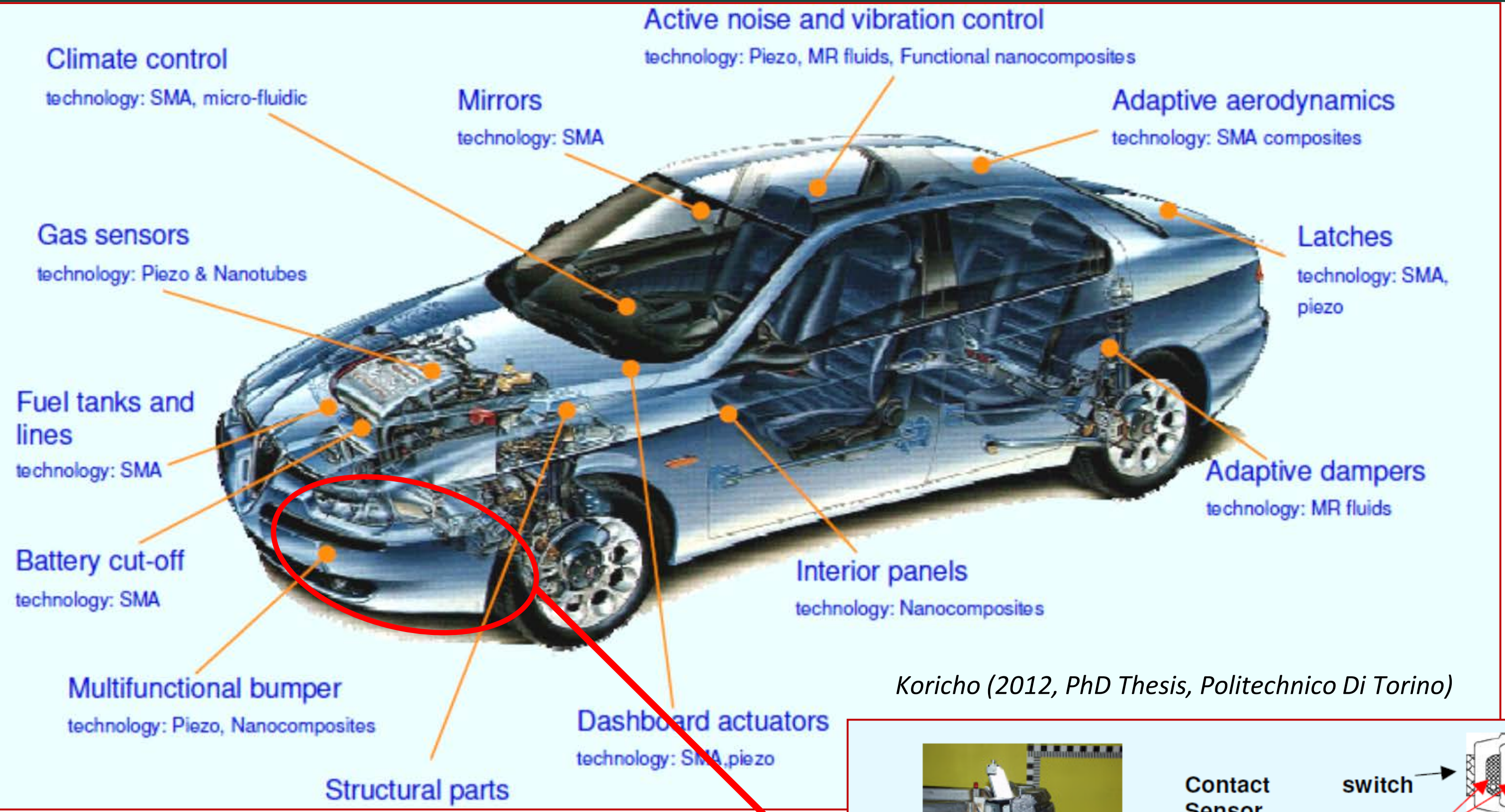
Schematic of the concept shown for in-plane joints

- **APPROACH**
  - An integrated experimental and numerical approach that would eliminate costly trial-and-error, instead use a rational computational materials (materials by design) based approach. Multi-use, Repair & Reassembly?
  - Synergistic use of Non-Destructive Evaluation Tools for joining efficiency and health monitoring.

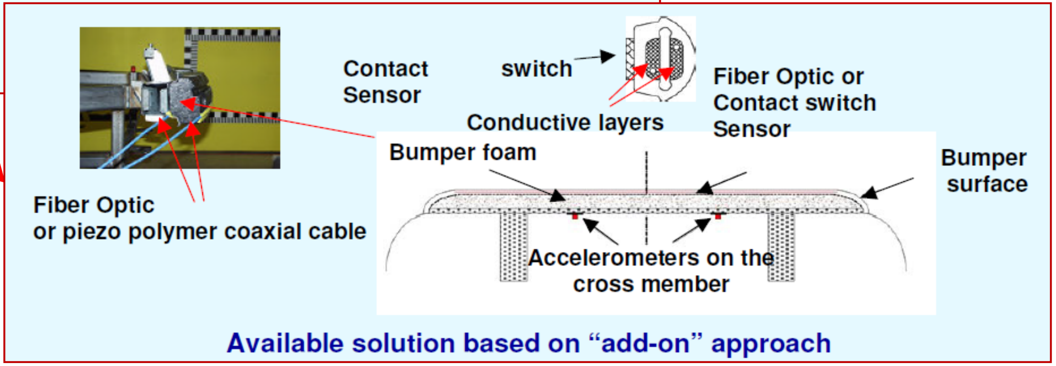
Objective(s) & Approach -I

- **OBJECTIVE :** The overall objective of 'active adhesive' development will be achieved by following sub-tasks:
- **A. Processing, Material Development and Optimization of Active Adhesive**
  - Processing Parameters, Optimal GnP Content, Synergy in multiple properties (stiffness-toughness balance), selective activation, re-assembly and repair
- **B. Lab-Scale Evaluation and Detailed Material Characterization**
  - "Design Validated by Experiments": Experimental testing of adhesives + substrates, structural joints, incorporation of NDE tools and efficient manufacturing.
- **C. Development of Design Tools and Database**
  - Develop "Experimentally Validated Simulations (EVS)": (i) to extrapolate experimental matrix rationally, & (ii) to use as design / database generation tool for new joint designs.
- **D. Large-scale Structural Joining & Industrial Applications**
  - To experimentally evaluate the behavior (performance, re-assembly and repair) of large-scale (realistic/industry-relevant) multi-material joints in:
    - (a) in-plane mode (lap-joints), b) out-of- plane mode (Pi/T-joints), c) Rotational or torsional mode (super-charger rotor, collaboration at Eaton).
- **E. Dissemination of results**

Summary of Progress : Relevance, Milestones and Accomplishments



Koricho (2012, PhD Thesis, Politechnico Di Torino)



Some known composites and plastics materials in Automotive sector:

- ***GFRP***
- ***CFRP***
- ***GMT***
- ***SMC***
- ***PA***
- ***PA 66***
- ***PP***

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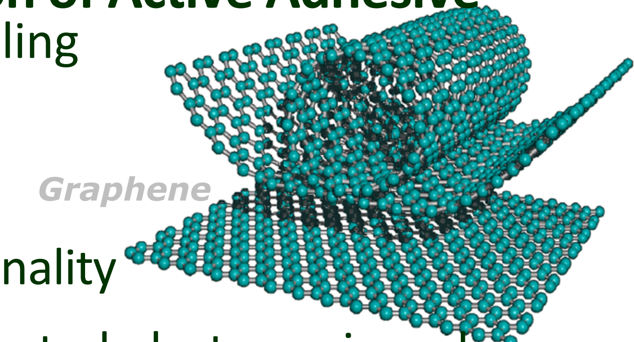
Summary of Progress : Relevance, Milestones and Accomplishments

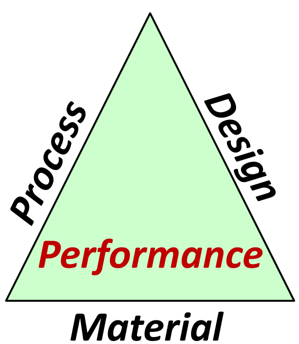
	Milestone	Type	Description	Status
FY 14	Activation and Bonding	Technical	The novel active adhesive couples with microwave radiations to activate, bond/un-bond resulting similar joints	SUCCESS!!
FY 14	Structural Properties Defined	Go / No-Go	The novel active adhesive structural properties (lap-shear) pre- and post- exposure to corrosive environments is better or equal to requirements in industrial practices with conventional bonding techniques	SUCCESS! GO ☑
FY 15	Demonstration of Structural Properties	Technical	The structural properties (lap-shear) pre- and post- exposure to corrosive environments is better or equal to requirements in industrial practices with conventional bonding techniques	SUCCESS!!
FY 15	Proven Efficiency	Technical	The NDE techniques used can prove the efficiency of the activation and re-assembly/bonding of the resulting joints	SUCCESS / In-Progress
FY 15	Characterization of Material Properties	Go / No-Go	The experimental characterization of material properties of the adhesive and adherend can be successfully performed to provide input to robust simulations (next phase)	SUCCESS / In-Progress GO ☑
FY16	Model Using Simulations	Technical	The simulations developed model the behavior and failure phenomena accurately without making crude assumptions and successfully agree with a wide range of experimental tests. <u>NOTE: Experimentally Validated Simulations!</u> An effort of 50% or more will be on experiments to validate and increase the robustness of the models, and to create reliable databases.	Future Work

Progress : Graphene Nanoplatelets (GnP) , Functionalization & Design Methodology

- **Processing, Material Development and Optimization of Active Adhesive**
  - ➢ GnP in Thermoplastic matrix (e.g. nylon) acts as a coupling agent with microwave energy to heat the matrix.



- **Functionalization of GnP:**
  - ➢ Improve mechanical properties+Toughness+Multifunctionality
  - ➢ Based on our studies: a) aliphatic epoxy, b) phase separated elastomeric carboxy terminated butadiene nitrile rubber (CTBN), and c) styrene-butadiene-methyl-methacrylate (SBM) triblock polymer have shown the greatest potential. (Results discussed in the following accomplishment section.)
- **Design Factors Considered to Achieve "Active Adhesives"**



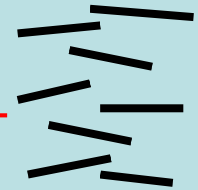
- **Thermomechanical properties and Multi-functional enhancements**
- **Geometry Factors (bond area, adhesive thickness, etc.)**
- **Substrate type, Surface Prep, etc.,**
- **Influence of loading and environmental conditions**
- **GnP concentration on processing: Activation, Re-assembly and Repair**

Progress: Active Adhesives – Film & Joint Production

Nylon/6	
Chemical base	*PA 6 Extrusion grade*
Cure mechanism	*Physical hardening*
Application temperature	*220 – 260°C*
xGnP-5	
Chemical base	*Graphene*
Diameter : 5 μm	*Thickness : ~ 10-20 nm*

Nylon-6

+

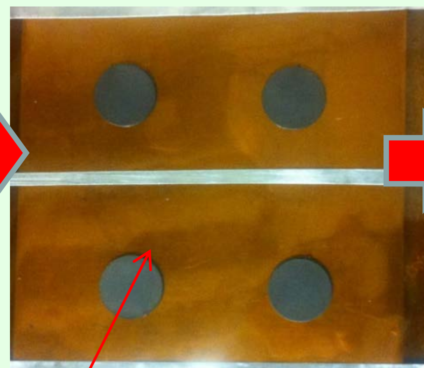


GnP

=

Active Adhesive Pellets ready for film production or injection dispensing

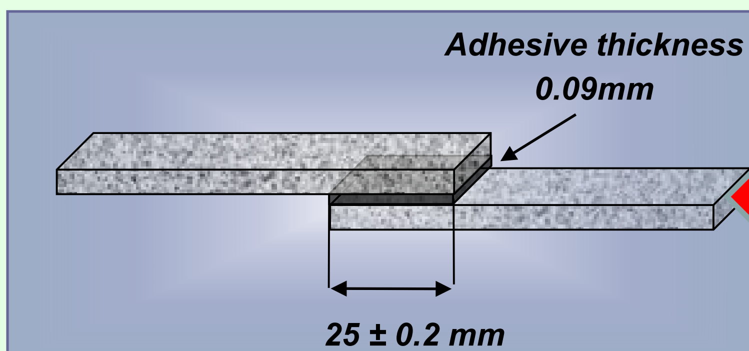
a) Micro Compounder & Injector



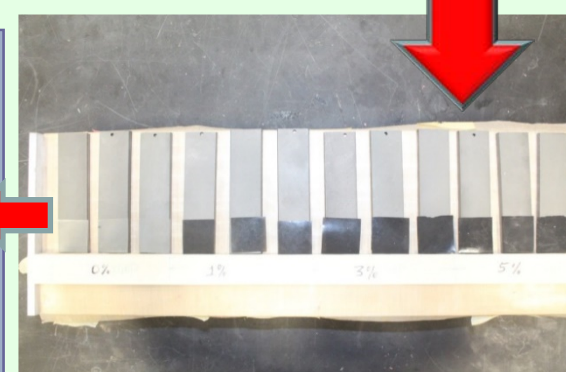
b) Manufactured Disks

c) Pressing Machine

d) GnP film + spacers

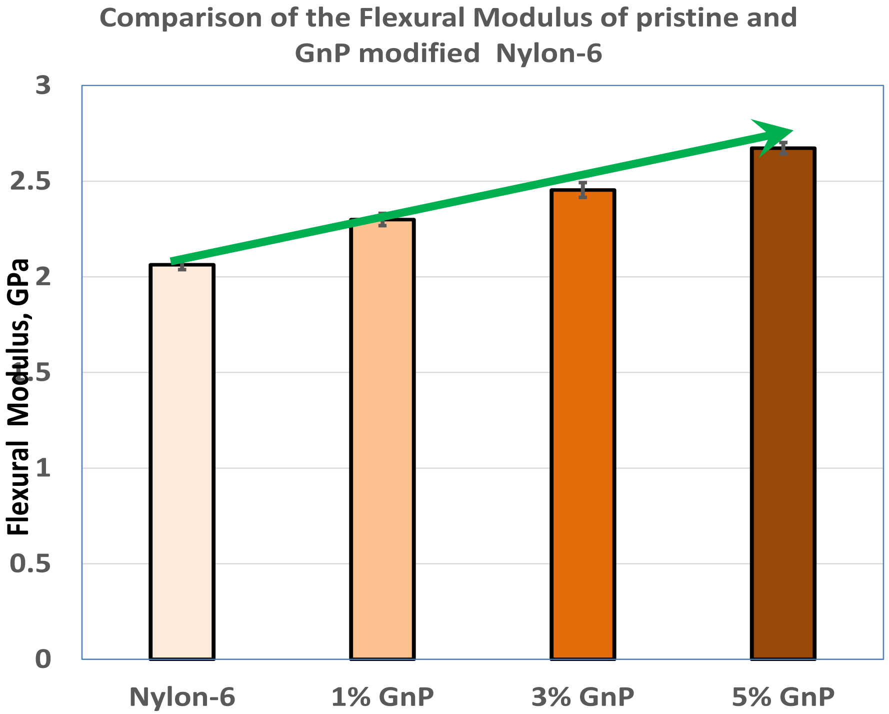


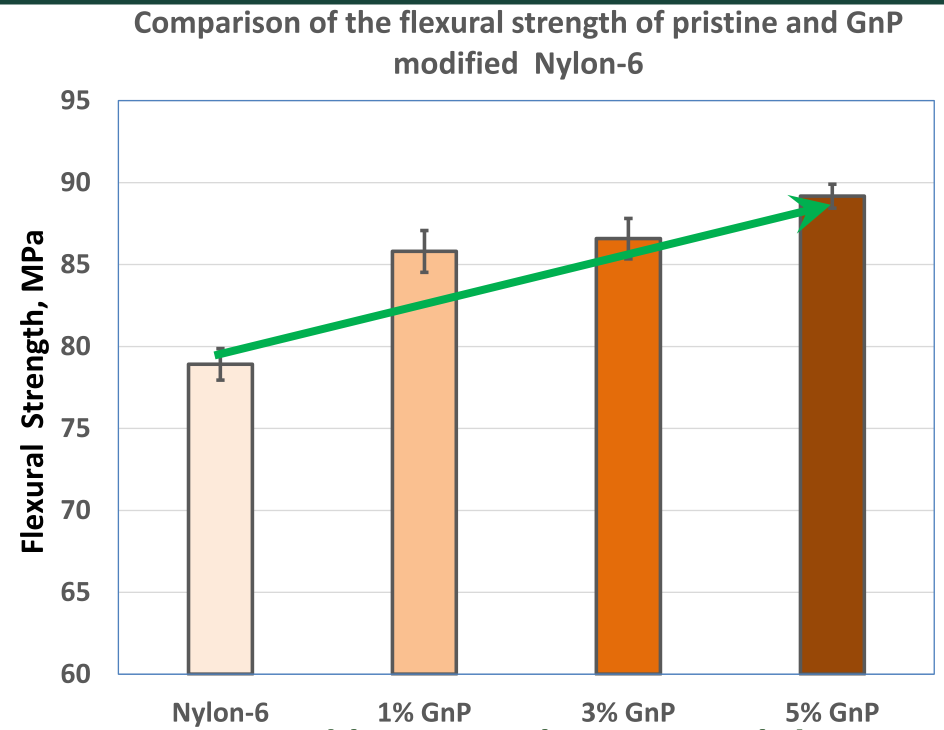
e) Schematic of a joint



e) Manufacturing of a Joint

Progress: Technical Accomplishments/Results

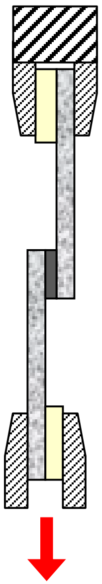




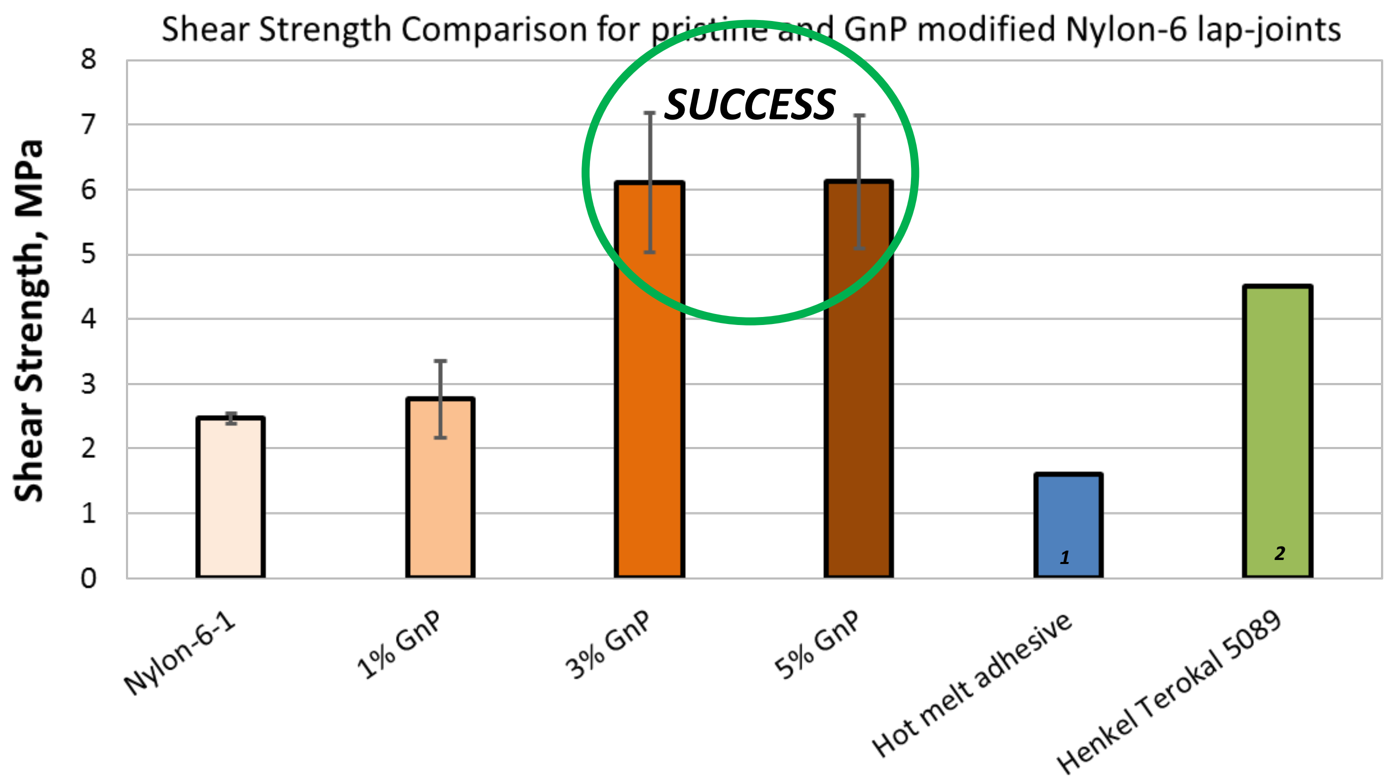
- ***For 5% of xGnP, the flexural modulus, nylon-6 was improved by more than 30% while strengths were improved by more than 10%.***
- ***STRAIN RATE PROPERTIES: GnP based adhesives performed better at high-strain rates. (Presented at last AMR meeting)***
- ***Functionalization (three to four different types in progress) will further enhance the modulus, strengths, impact, strain-rate dependent properties along with processing (activation and microwave interaction) properties.***

Progress: Technical Accomplishments/Results

➢ ***Comparison of Shear Strength for similar class of adhesives***



Lap-shear test



[1]Elena Verna, Ermias Gebrekidan Koricho, Irene Cannavaro, Valentina Brunella, Giovanni Belingardi, DavideRoncato, BrunettoMartorana, Vito Lambertini, Vasilica Alina Neamtu, Romeo Ciobanu, Adhesive joining technologies activated by electro-magnetic external trims, International Journal of Adhesion and Adhesives, 2013:46;21-25

[2]X.Yang, L. Yao, Yong Xia, Qing Zhou, Effect of base steels on mechanical behavior of adhesive joints with dissimilar steel substrates, International Journal of Adhesion and Adhesives, 2014;51:42-53

Progress: Technical Accomplishments/Results
Selective Activation – Bonding and Disbonding

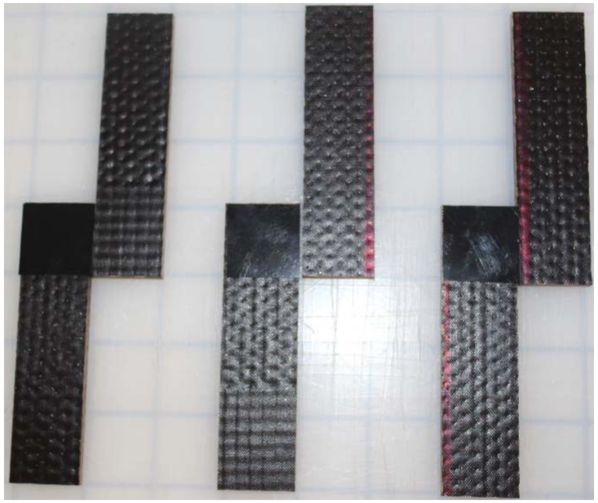
✓ *Objective:*

- ***Apply Variable Frequency Microwave (VFM) for effective bonding and de-bonding of Glass Fiber Composite by specifically targeting and coupling to the GnP reinforced Nylon material which is sandwiched between two similar composite specimens; without causing damage or burning of the composites.***

✓ *VFMW Heating Trials: (ALL COMPOSITE SPECIMENS)*

- ***Six (6) specimens:, 3 for bonding and 3 for de-bonding were tried in the initial evaluation***
- ***The GnP material, had a film thickness of ≈ 0.127 mm***
- ***Composite/material assembly was ≈ 25.4 x 100 mm; with a total thickness of ~ 10.33 mm***

GFRP substrates and 'Active Adhesive bonding/dis-bonding'



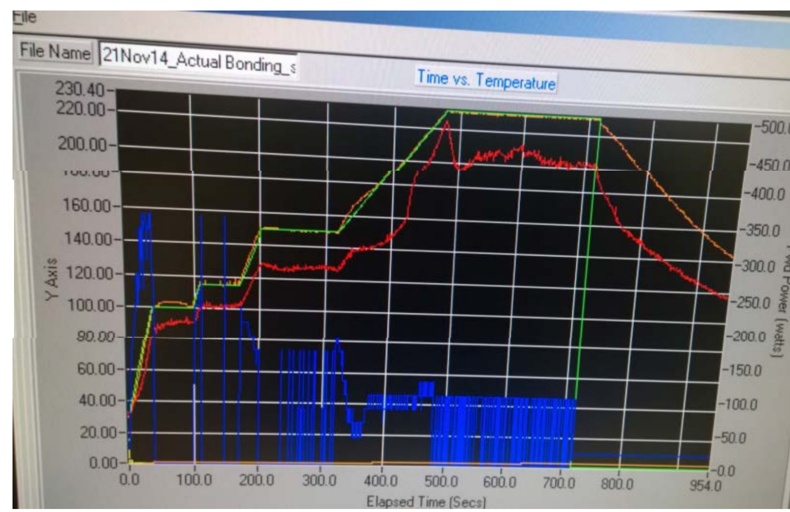
(a) Dis-assembled joints with Active Adhesive film for BONDING / ASSEMBLY

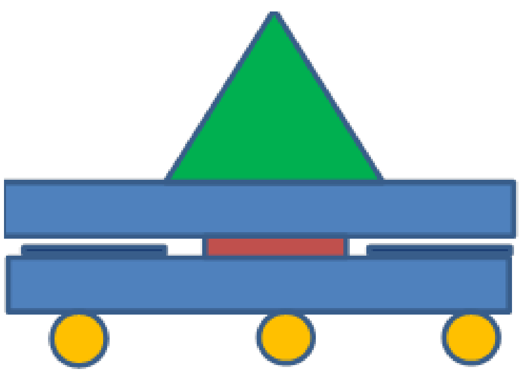
(b) Bonded joints with Active Adhesive for DIS-ASSEMBLY

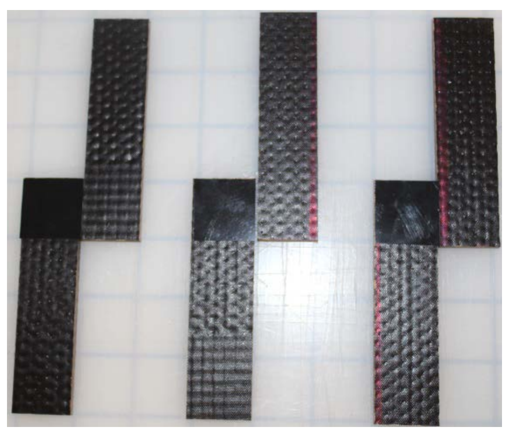
Progress: Technical Accomplishments/Results

➢ *Reversible Bonding of Single Lap-Joint with Nylon6 + xGnP*

- ➢ ***FOR BONDING**, each individual sample was placed inside the MC2100 VFM cavity on a quartz stand.*
- ➢ ***A fiber optic contact probe was attached to the bond-line region of assembly.***
- ➢ ***Quartz rods weighing ≈125 g each, were used to provide process hold down weight.***
- ➢ ***Four step VFM recipe of: Ramp 2 °C/s to 100°C - 1min; Ramp 1.5 °C/s to 115°C -1 min; Ramp 1 °C/s to 150 °C-2 min, and Ramp 0.5 °C/s to 230 °C - 4min***







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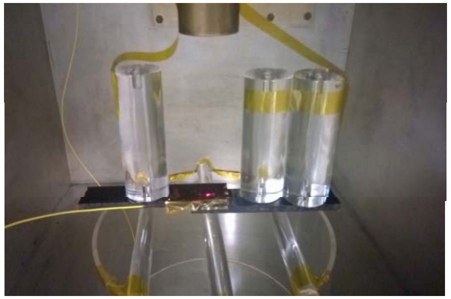
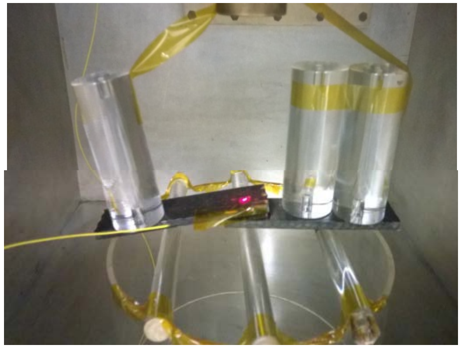
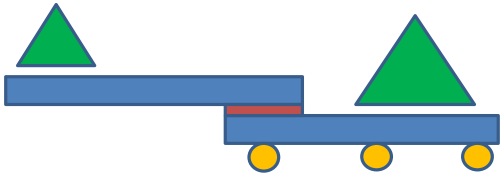
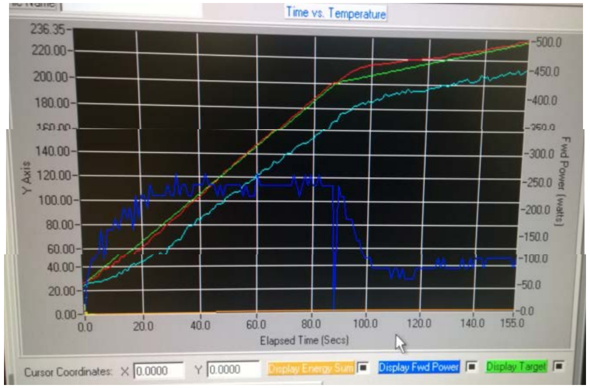
Progress: Technical Accomplishments/Results

- ***Reversible Dis-Bonding of Single Lap-Joint with Nylon6 + xGnP***
  - ***FOR DIS-ASSEMBLY,* the samples were placed inside the MC2100 VFM cavity on a quartz stand.**
  - ***A fiber optic contact probe was attached to the bond-line region of assembly.***
  - ***Three quartz rods weighing ≈125 g each, were used to provide counter weight.***
  - ***Two-step VFM recipe of: Ramp 2 °C/s to 200 °C -1s Ramp 0.5°C/s to 240°C - 1min., however, in all three cases, de-bonding appeared to have occurred as temperature approached Approximately 235 °C***

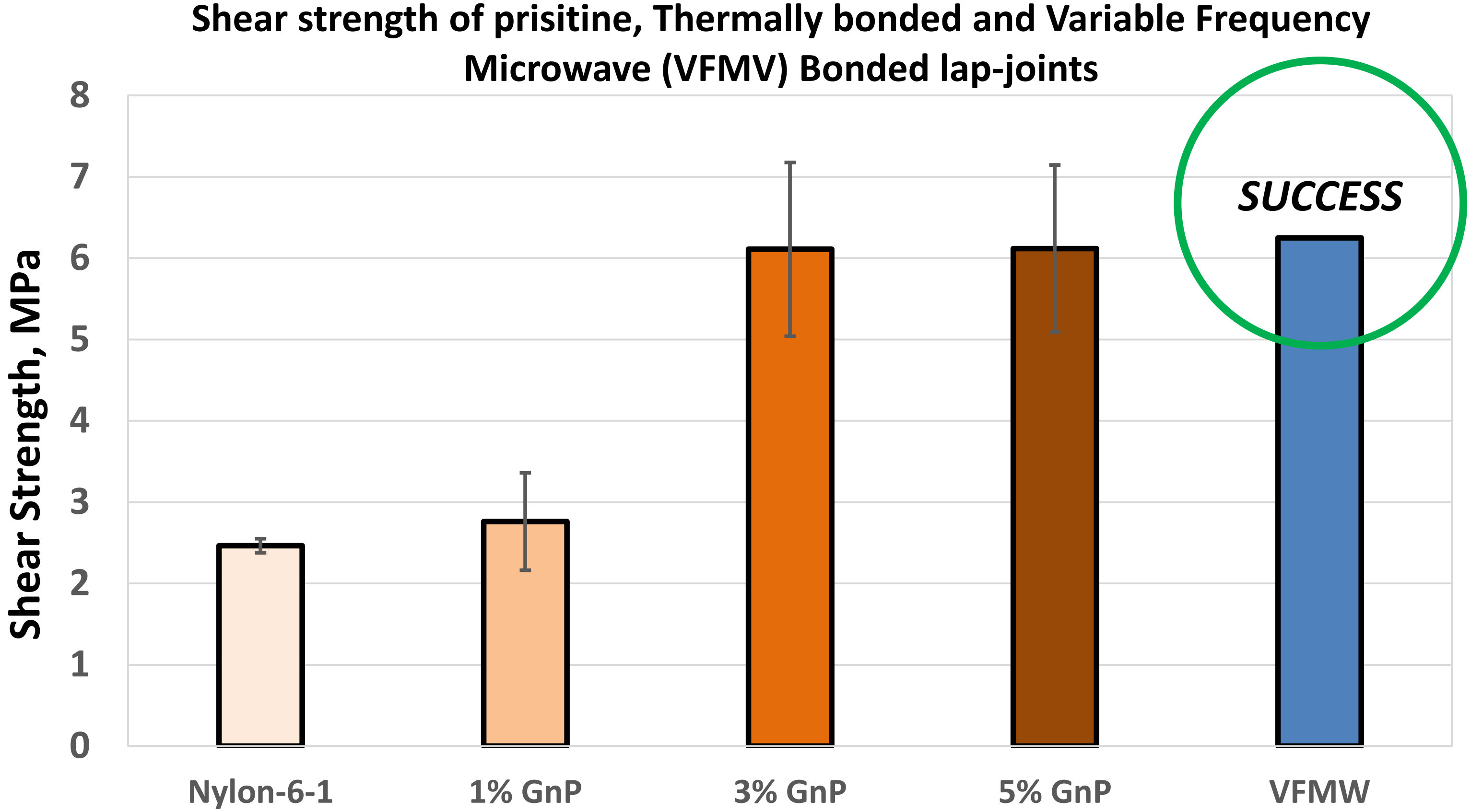








Progress: Technical Accomplishments/Results



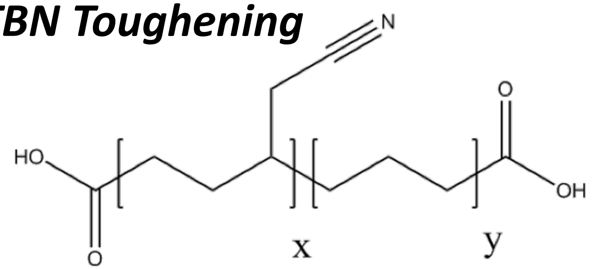
- ***Preliminary results reveal adhesive joint strength of Variable Frequency Microwave (VFMW) heated joints had similar shear strengths of that of thermally bonded joints.***
- ***Milestone Achieved!***
- ***Further progress on statistically significant experimental tests in progress***

Progress: Functionalization of GnP

- **Functionalization of GnP:**

- Improve mechanical properties + Toughness + Multi-functionality
- a) aliphatic epoxy (AE), b) phase separated elastomeric carboxy terminated butadiene nitrile rubber (CTBN) , and c) styrene-butadiene-methyl-methacrylate (SBM) triblock polymer have shown the greatest potential.

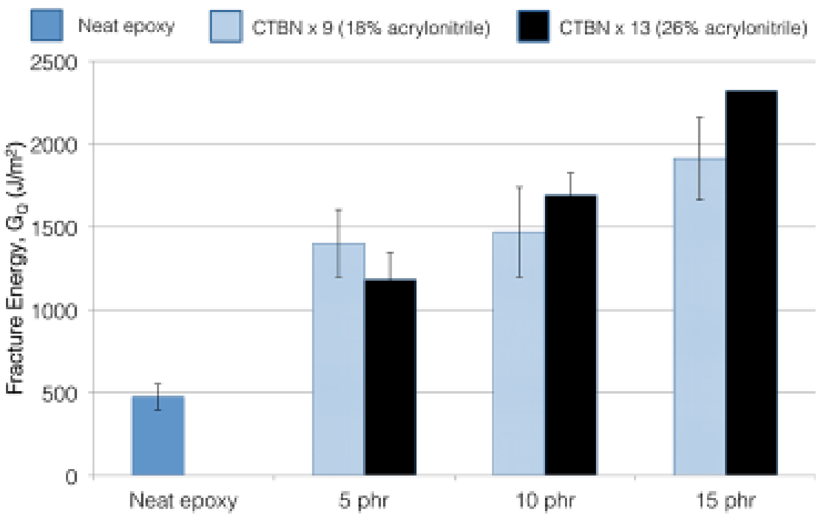
CTBN Toughening



CTBN-carboxyl terminated butadiene acrylonitrile

- For brevity, only CTBN shown here.
- Functionalization of GnP with all three types of grafting (AE, CTBN, SBM) has been completed.
- Experimental characterization of multiple properties in progress.

CTBN (18 and 26% acrylonitrile) in Epoxy: Fracture Energy (J/m^2)

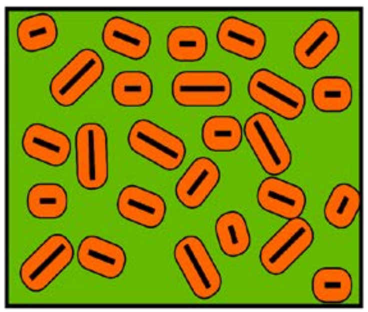


- G_{Ic} increases with increasing concentration of CTBN
- Maximum increase (400%) in G_Q was observed at 15 phr CTBNx13
- Increased acrylonitrile in the rubber additive leads to smaller particles and larger increases in fracture energy

Progress: Tailoring Damage Properties ? Modeling/ Numerical Simulations

- **Need & Approach for Modeling**

Factors governing microstructure:



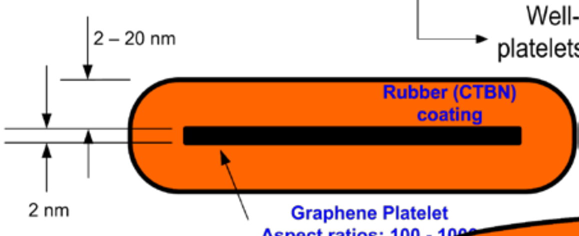
FACTORS GOVERNING EFFICIENCY OF xGnP / CTBN HYBRID SYSTEM

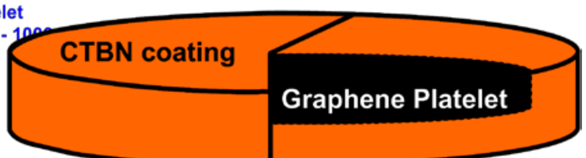
GRAPHENE (xGnP) CONTENT
Three weight fractions of xGnP will be sought, e.g. 1%, 2% and 3%

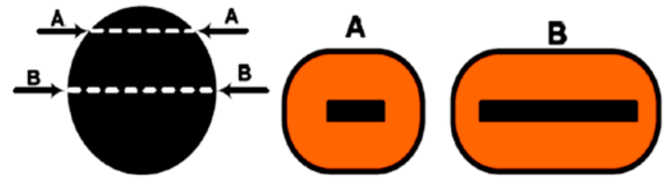
RUBBER (CTBN) CONTENT
Amount of CTBN is controlled by the thickness xGnP coating. Three thickness, namely 2 nm, 5 nm and 10 nm will be attempted

ASPECT RATIO
(Constant diameter of xGnP platelet will be attempted, aspect ratio will vary depending on CTBN coating)

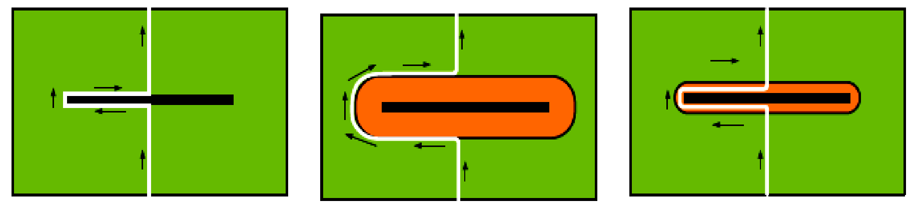
ORIENTATION & DISTRIBUTION
Well-Dispersed xGnP/CTBN platelets with Random Orientation will be used





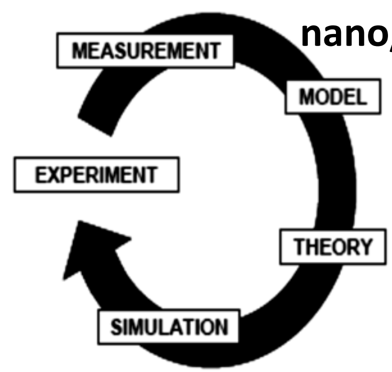


Observed aspect ratios in 2D, due to cutting of platelet at various locations. Also, the same variation is shown with respect to CTBN coated platelets.



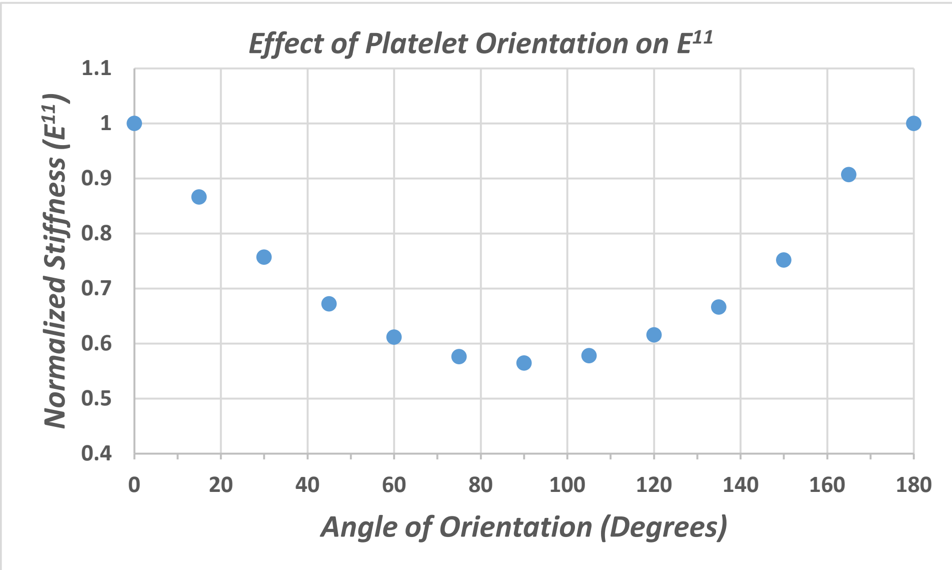
Crack-blunting & tailorable xGnP/CTBN interface, a) no CTBN coating, b) thick CTBN coating revealing delamination around rubber, and c) thin rubber coating revealing debonding of xGnP.

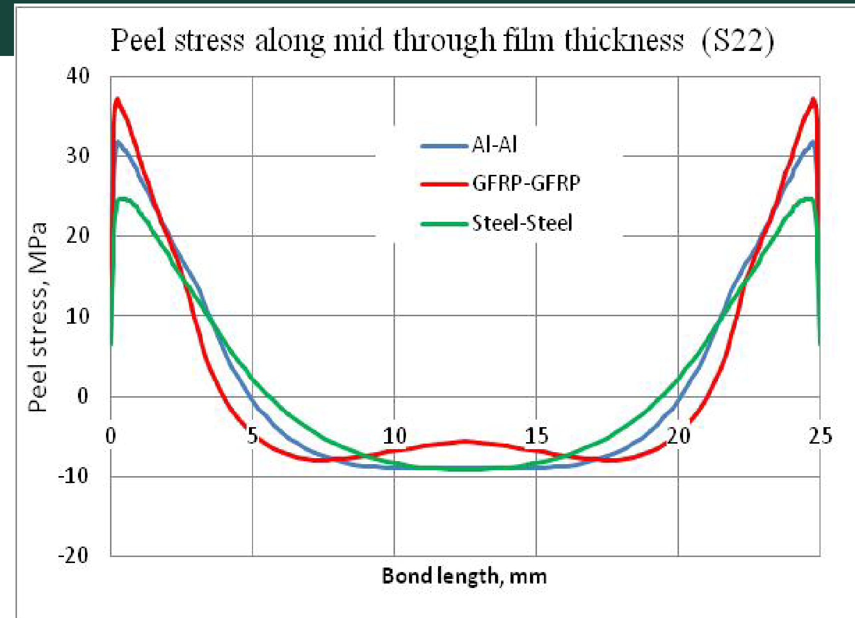
Tailoring at nano/microscale

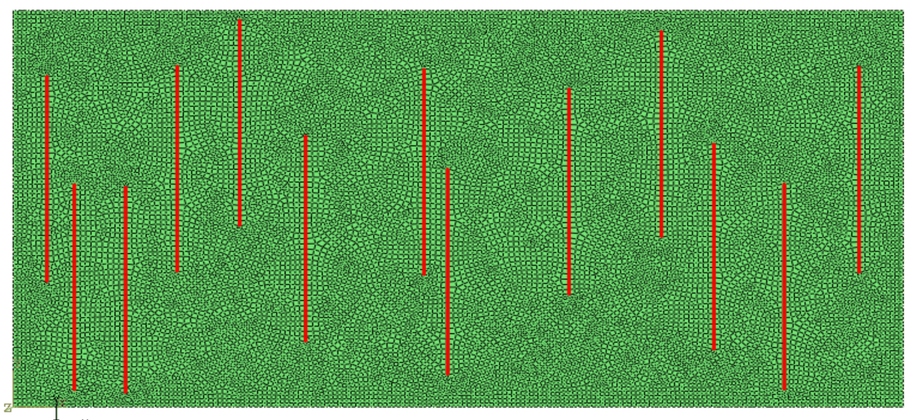


Computational Materials : Material by Design
Adapted from Gates et al (2005)

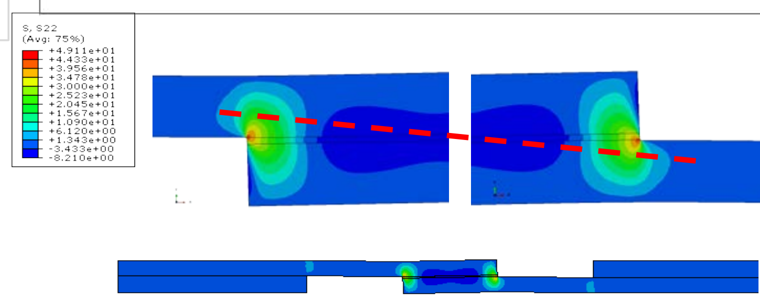
Progress : Key Results from Simulations





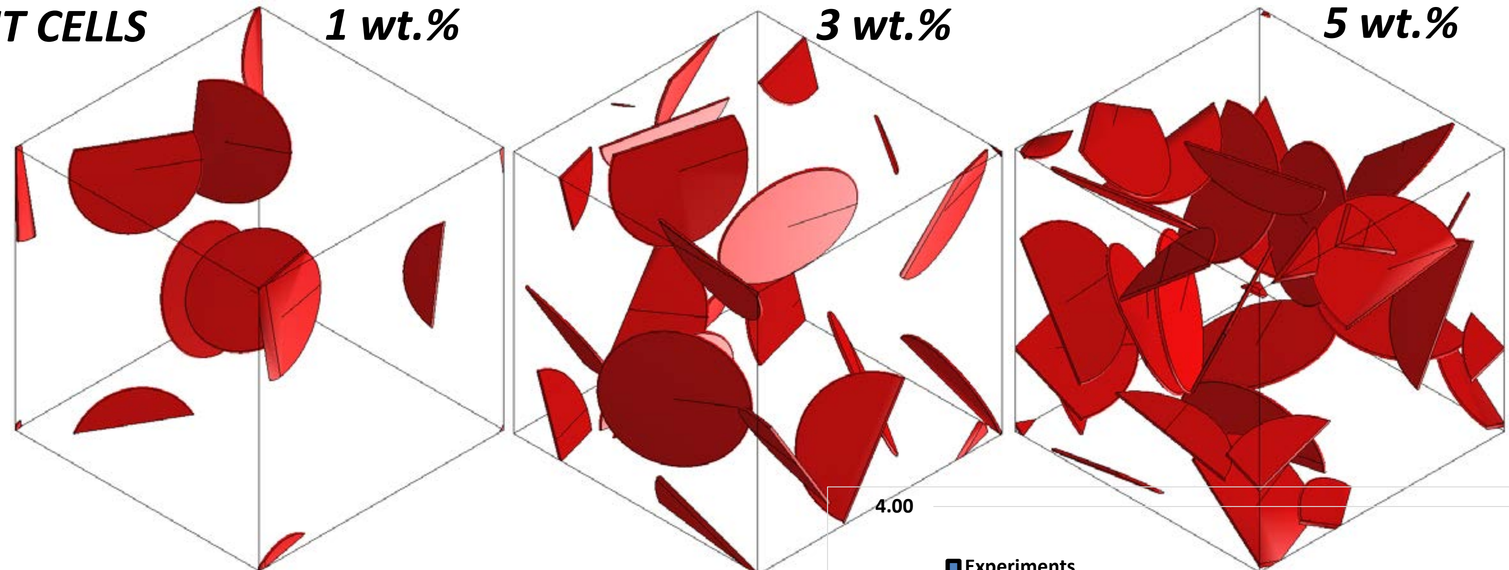


Study on Effect of Orientation



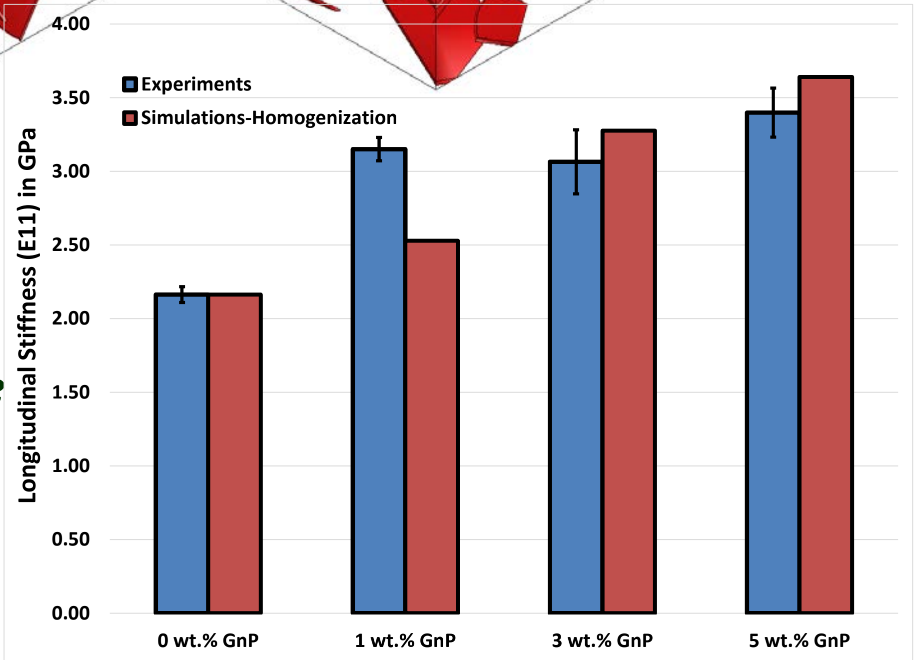
- *Manufacturing of films with varying GnP orientation possible.*
- *Can place desired orientations at ‘designed’ locations to exploit the full benefits of GnP films in bonded joints*

Progress : Key Results from Simulations



- E_{GnP}=1000 GPa; E_{Nylon}= 2.17 GPa
- Morphology: Platelet, Aspect ratio= 0.02
- Commercial Software Digimat® used

- Accurate extrapolation of experimental matrix
- Modeling of thermal and damage propagation properties in progress
- Development of Design Tools and Databases



Response to Previous Year Reviewers' Comments

Reviewer's Comment	Action Taken and Results
#1 - The reviewer stated that the approach to proving the **concept is generally sound**; however, the reviewer saw no mention of **baseline comparison to conventional adhesives.** The reviewer also did not have a clear vision of **what materials this project wanted to focus on.** The reviewer added that most of the information seemed to focus on polymer composites, but the test pieces cited were aluminum-steel couples.	✓ Baseline comparison with similar class of adhesives commonly used in automotive applications was performed and presented. The active adhesives in this work performed much better than similar class of automotive adhesives. ✓ The project aims at multi-material/dissimilar material joints. Last year metals to metals were initially studied. This year all composites and metal to composite were attempted. Activation studies were performed on only composite-composite joints. All metal-composite combinations will be studied in a) in-plane, b) out-of-plane and c) rotational joints
#2 - The reviewer stated that thus far this seems like it is primarily an independent project. **It is not obvious that Eaton has contributed to the effort,** because this project covers an array of technology gaps (e.g., adhesive bonding, NDE, development of a "reusable" adhesive), **it would be good to get some appropriate suppliers involved as well.**	✓ Eaton was not involved in the first year of the project. This was 'by design' as the objective/ milestone for the first year was to develop the 'active adhesives' and the proof-of-concept. Eaton brings in the use of 'light-weighting' and multi-material joining using the materials in this work for high-speed, torsional applications such as supercharger rotors. Eaton is active in 2nd and 3rd years, and has already en-route for testing on composite to metal rotors. ✓ The investigators are also working with OakRidge National Lab (ORNL) and its Carbon Fiber Technology Facility for using low-cost carbon-fiber for 'adherends' in joining. ✓ Additionally, interest from automotive material suppliers such as 3M, Henkel, BASF, DuPont and others, has led to incorporation of automotive relevant materials. The investigators have the choice of using the relevant materials without losing the focus on deliverables.
#3 - The reviewer stated that **if the structure of the project remains as is, the resources are probably sufficient.** However, if the **participation is increased (i.e., adding car makers), it will be grossly insufficient.**	✓ With the help from program managers from DOE, presentations were made to USCAR and associates. Significant interest from many big auto companies (OEM), Tier I suppliers and other auto-part manufacturers received. The reviewer is 'correct,' addressing all the needs of all the parties is infeasible and impractical as the resources will become 'grossly insufficient.' The attention received is being channeled as positive feedback to this project.

Collaborations & Coordination

Collaborators / Partners	Details
Eaton Corporate Research and Technology **(PARTNER)**	✓Low-inertia, light-weight, supercharger applications ✓High-speed rotational/torsional testing ✓Non-destructive Evaluation at high speeds ✓Metal – to- metal and Metal to composite Bonding ✓In-situ repair, assembly and disassembly
U.S. Army TARDEC **(In-kind Collaborator)**	✓Periodic review of progress and guidance on relevant materials for automotive applications and path forward.
OakRidge National Laboratory **(ORNL)**, Carbon Fiber Technology Facility **(CFTF):** **(In-Kind Collaborator)**	✓Low-cost, Large-Tow Carbon Fiber. ✓Guidance of possible automotive applications

Barriers and Solutions + Future Work

- **CHALLENGES / BARRIERS:**
- **Composite Substrates that can withstand high temperatures (beyond melting points of thermoplastic adhesives) for repeatable bonding. *ADDRESSED: a) High-Temperature epoxies used to make composite adherends and Tier-I suppliers' materials used, b) thermoplastics with lower melting points and desired mechanical properties.***
- **Microwave Equipment: Efficient microwave oven/applicator to explore all parameters needed. *ADDRESSED: Collaboration with Lambda Technologies has led to a purchase of a microwave to explore all possible material combinations.***

- **FUTURE WORK (Current Budget-Period):**
- **Determine Optimal GnP content for multi-property enhancements and synergies.**
- **Corrosion Analysis followed by structural testing.**
- **Structural Behavior of Multi-material Joints: a) In-plane, b) Out-of-plane, and c) Torsion**
- **Selective Activation Studies: Re-assembly and In-situ Repair (post-fatigue)**
- **Non-Destructive Evaluation: a) Guided Waves, b) IR Thermography, & c) Fiber-optic sensors.**

- **Budget Period-3 (01/16- 09/16)**
- **Development of Robust Simulations (multi-scale Analysis) and Design Tools**
- **Proof-of-Concept with Large-scale Industrial Applications and Dissemination of Results**

Summary

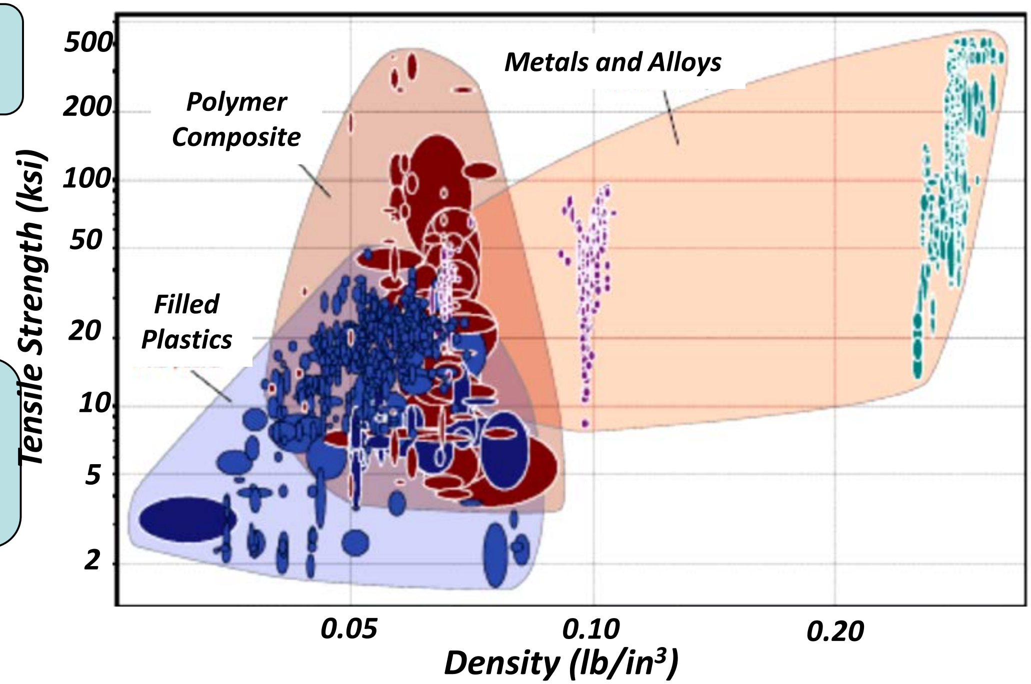
- **RELEVANCE:**
  - Joining & Assembly: Multi-material Joints that inherit the benefit of both bonded (lightweight) & bolted (re-assembly+repair) joints through 'active,' 'reversible,' adhesives.
- **APPROACH:**
  - Reinforcement of thermoplastic adhesive with novel graphene nano-platelets (GnP) and to use GnP/microwave-interaction for 'targeted heating of adhesive' thereby allowing ease of repair and re-assembly
  - An Integrated Experimental & Simulations based approach that eliminates the trial-and-error approach is adopted. Robust design tools are also developed.
- **TECHNICAL ACCOMPLISHMENTS**
  - Successful Development of Novel GnP reinforced TP Adhesives.
  - Proof-of-concept Successful : Targeted heating of adhesive, dis-bonding and re-assembly done.
  - Structural Properties of Resulting Multi-material Joints better than similar class of materials
  - Dissemination of Results: (1) Conference, (1) journal, and an invited presentations to OEMs and Tier I suppliers made. Also, (1) provisional patent filed.
- **Partners / Collaborations:** Eaton Innovation Center, MI.
- **FUTURE WORK:**
  - Activation/Re-Assembly Studies
  - Proof-of-Concept on Large-scale Industrial Applications
  - Multi-property Enhancements and Optimization
  - NDE + Modeling +Development of Design Tools

Active, Tailorable Adhesives for Dissimilar Material Bonding, Repair and Assembly

TECHNICAL BACKUP SLIDES

RELEVANCE / MOTIVATION : WHY COMPOSITES?

- **Offer Unparalleled Weight Savings**
- **Low Density, Improved Strength Better energy Absorption and Increased Safety.**
- **Create Value through Consolidation of Parts - JOINING**
- **U.S. Department of Energy is putting considerable efforts in light-weighting technologies.**



Tensile strength versus density for filled plastics, polymer composites, and metals and metal alloys
Courtesy: Granta Design / ACC RoadMap - 2014

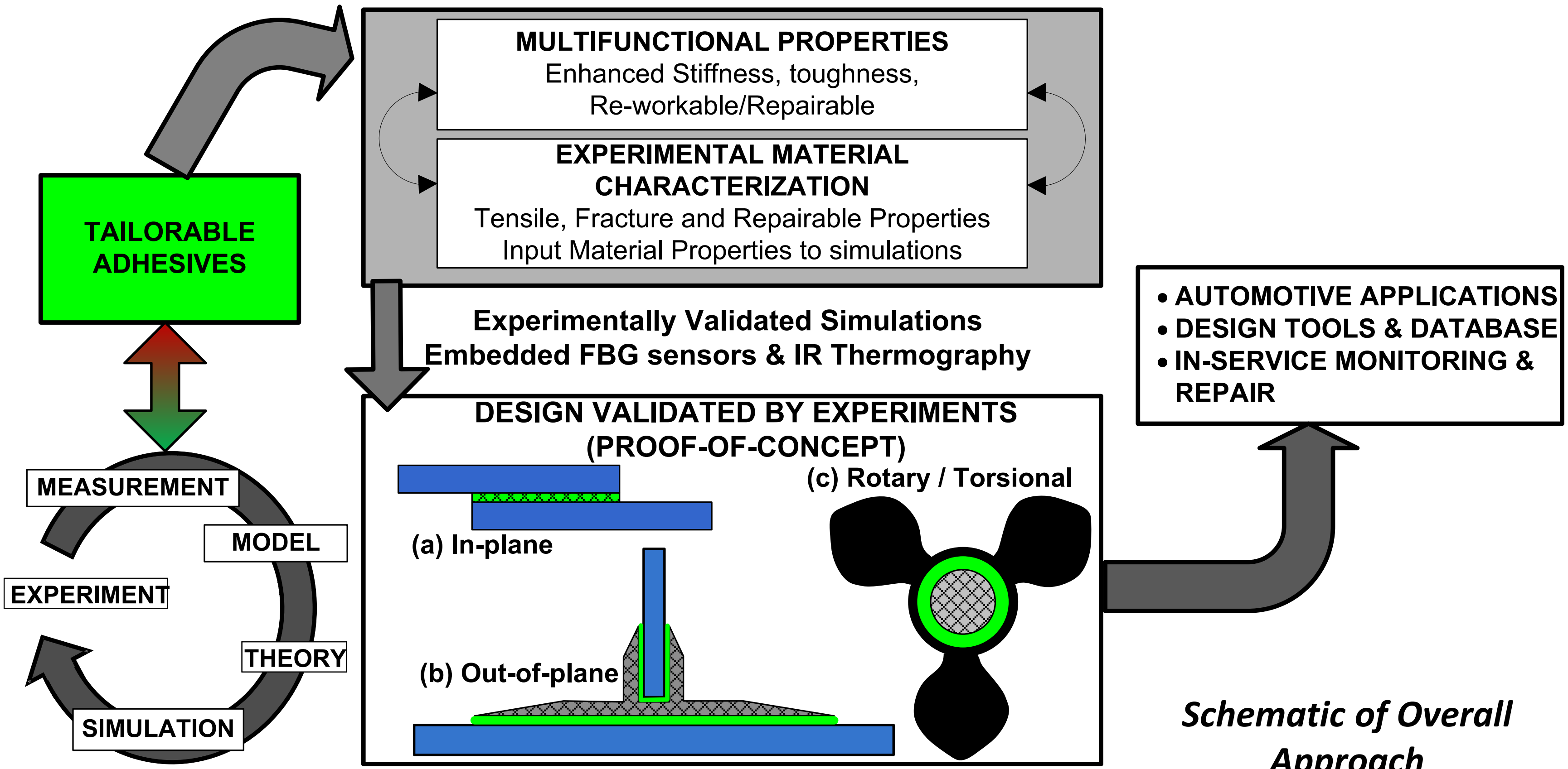
- ***U.S. DOE has identified four key challenges for use of composites for light-weighting technologies***
  - **Cost of Materials**
  - **Cost of Manufacturing**
  - **Dissimilar Material Joining**
  - **Modeling/Simulations and Database Creation**

MICHIGAN STATE UNIVERSITY | Composite Vehicle Research Center

- **This project addresses all the above-mentioned challenges!**

Objective(s) & Approach

- **GLOBAL APPROACH**

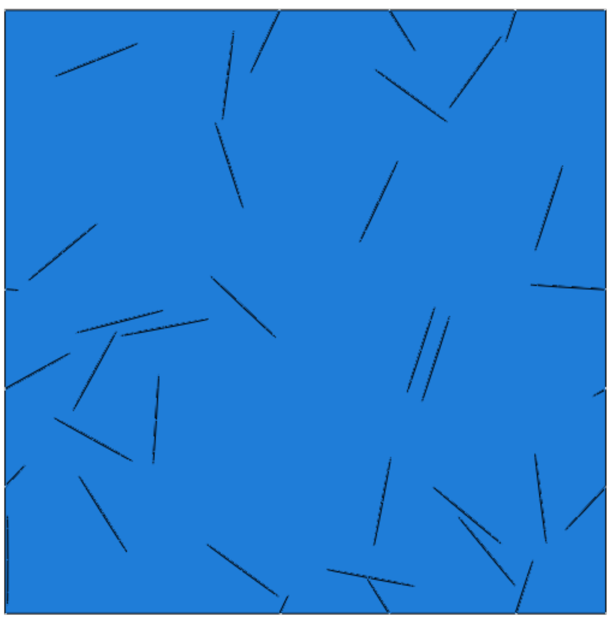


Schematic of Overall Approach

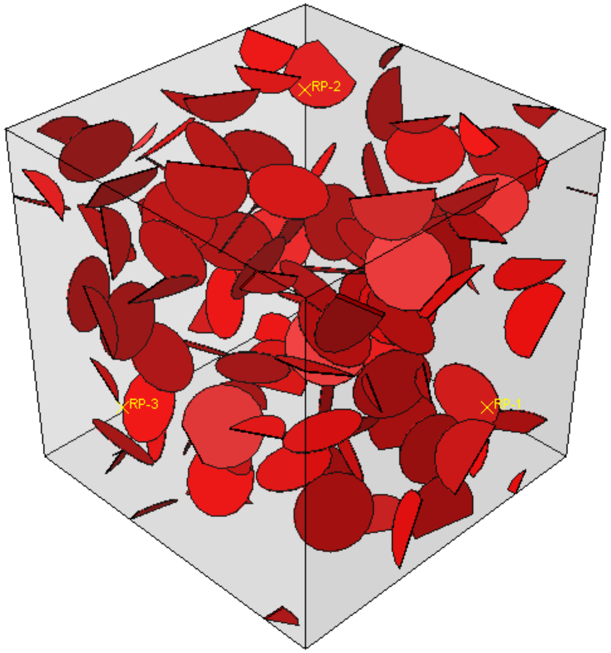
➢ Most structural joint development focuses solely on in-plane behavior. This work evaluates a) in-plane, b) out-of-plane and c) rotary/torsional joint

Nano-scale Simulations and Homogenization:

- ***Nanoscale modeling allows the possibility of understanding and designing materials considering the nanoscale and upwards.***
- ***One of the main advantages of a computational approach as the one taken in this work is that it eliminates costly trial and error experiments, and provides extrapolation of key experimental data with confidence and in a rational manner.***

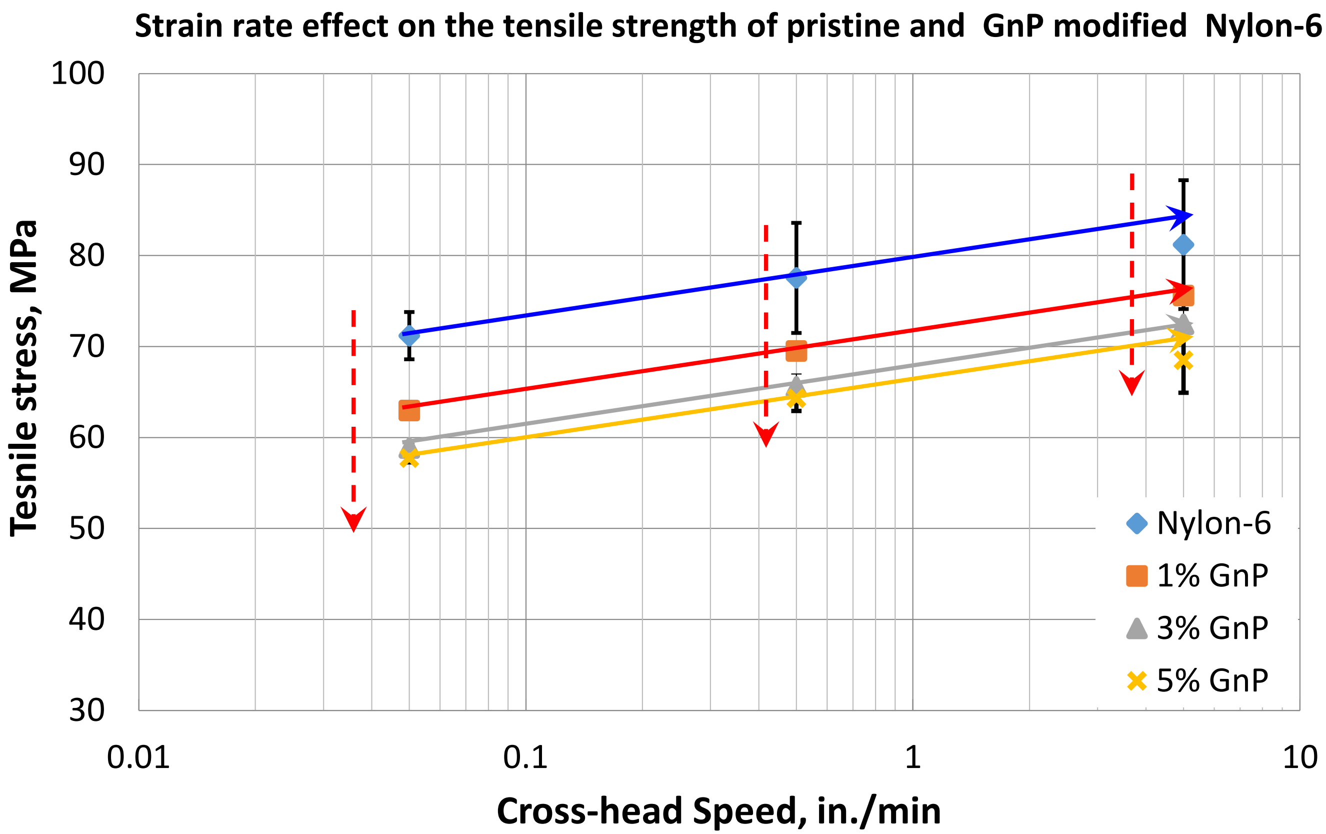


2D Representative Volume Element (RVE)



3D Representative Volume Element (RVE)

Progress: Technical Accomplishments/Results Strain-Rate Effects and Enhancements by GnP



- ***Generally, presence of GnP in Nylon-6 was found to decrease tensile strengths.***
- ***GnP based adhesives performed better at high-strain rates.***
- ***Functionalization of GnP in progress to increase chemical compatibility with host polymer will increase the tensile properties***