Multifunctional Thermoset Polymer Matrix with Self-Sensing and Self-Healing Capabilities

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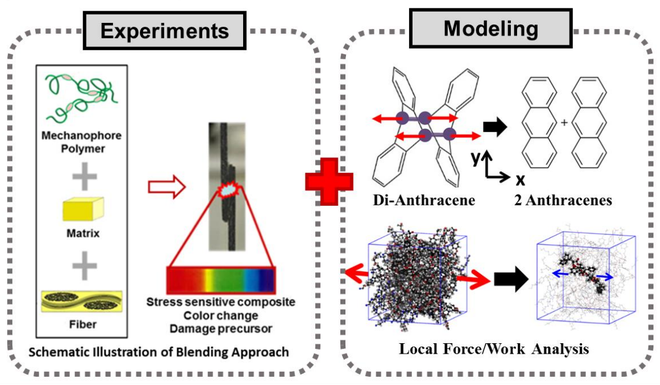
Objectives:

- **Identification of damage precursors in polymer matrix composite structures**
- **Synthesis and characterization of mechanophore embedded thermoset polymer (self-sensing/self-healing)**
- **Development of a novel modeling framework to simulate mechanochemical reaction of mechanophores**
- **Validation of the modeling framework with experimentally observed responses**

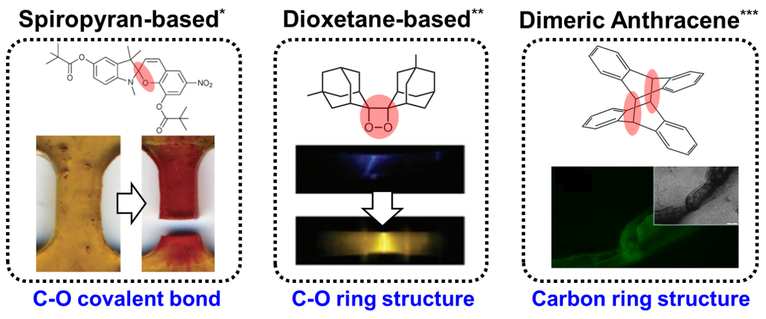
Motivation for Research

Motivation: **Urgent need for novel materials for damage precursor detection in polymer matrix composites**



Research Outcomes
- **Mechanophoric polymers with damage detection capability**
- **Simulation framework for mechanochemistry**
- **Integration of experiments and simulations for materials by design**

Mechanophores



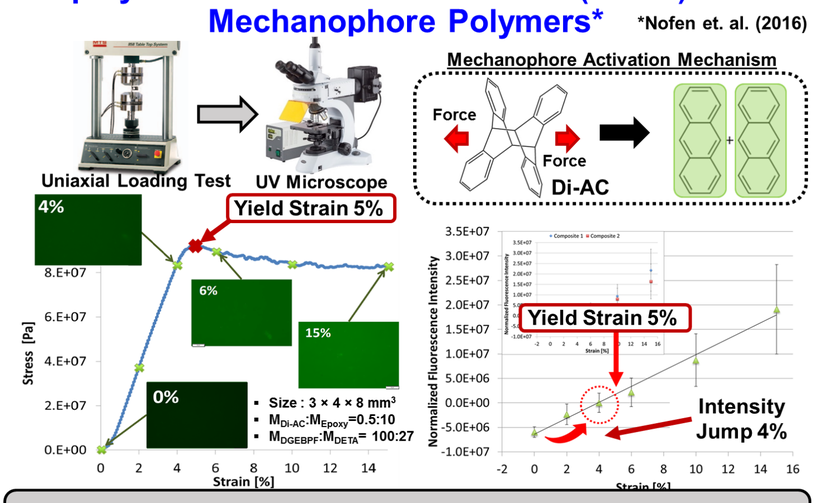
"A stress or strain activated molecular unit providing a molecular-scale reading of the local mechanical state or to transform materials properties *in response to the local mechanical environment*."

*Davis et al. *Nature* (2009). **Chen et al. *Nature chemistry* (2012)
***Nofen et. al. *Mat. Res. Exp.* (2016)

Dimeric-Anthracene (Di-AC) mechanophore used in *thermosets for aerospace applications*

Employment of Dimeric Anthracene (Di-AC)-based Mechanophore Polymers*

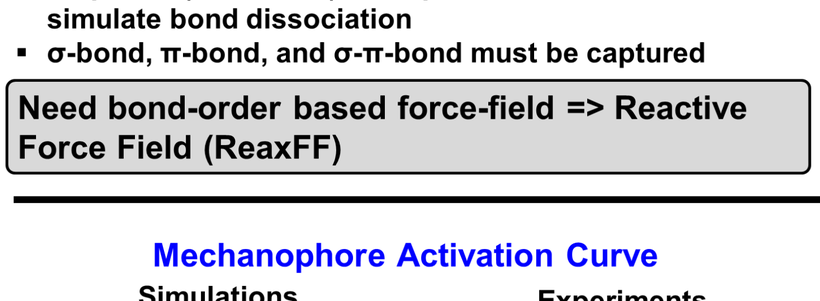
*Nofen et. al. (2016)



Di-AC nanocomposite successfully shows early signal detection capability

Modeling of Di-AC based Mechanophore Thermoset Polymers

- **Develop a new method to generate epoxy network (epoxy curing) and simulate mechanophore activation (covalent bond breakage)**
- **Physics-based modeling approach provides information to mechanophore design enhancement**



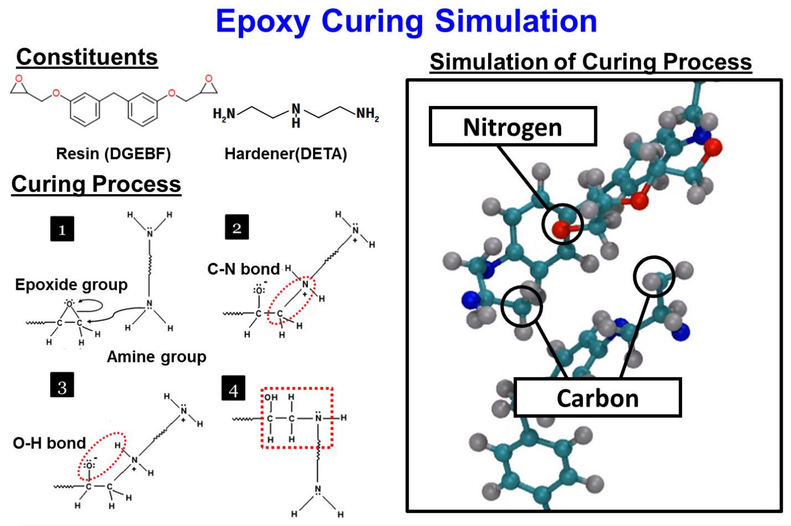
Quantum Mechanics + Molecular Dynamics => Hybrid MD Simulation Framework

Hybrid MD Simulation Framework

Key elements

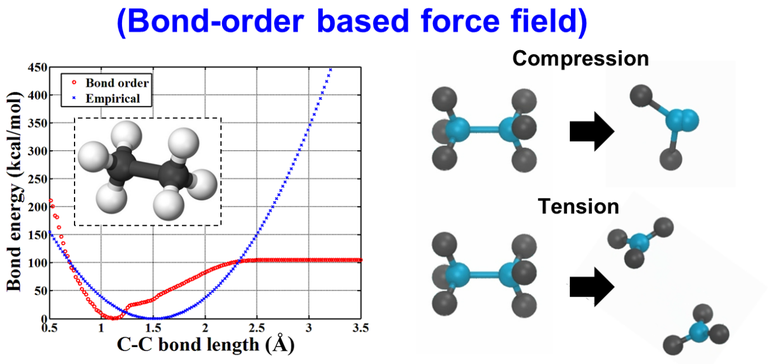
- **Epoxy network**
  - **Perform covalent bond generation method**
- **Covalent bond dissociation**
  - **Implement bond-order based force field**
- **Mechanical loading test in MD**
  - **Develop a quasi-continuum deformation method**
- **Characterization of Di-AC (mechanophore)**
  - **Calculate bond dissociation energy**

Epoxy Curing Simulation



Epoxy-based thermoset matrix (host) generated

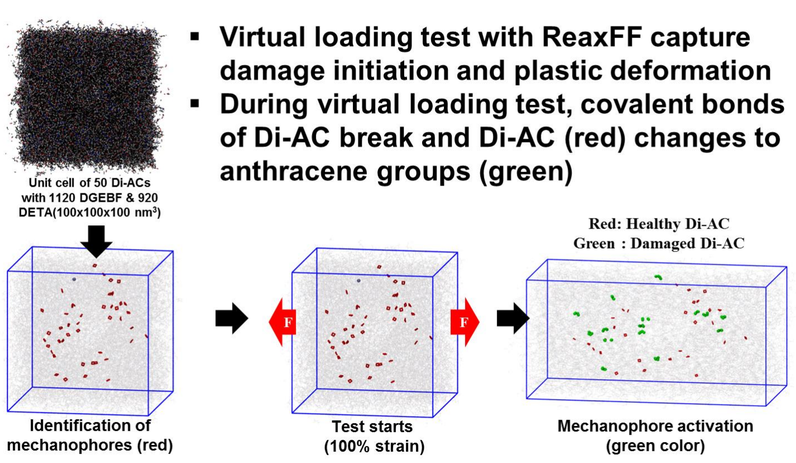
Covalent Bond Dissociation (Bond-order based force field)



- **Empirical (traditional) bond potential in MD does not simulate bond dissociation**
- **σ-bond, π-bond, and σ-π-bond must be captured**

Need bond-order based force-field => Reactive Force Field (ReaxFF)

Mechanophore Activation using Virtual Loading Test

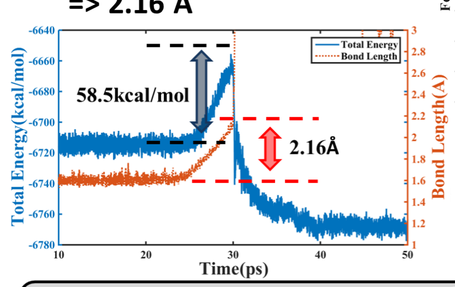


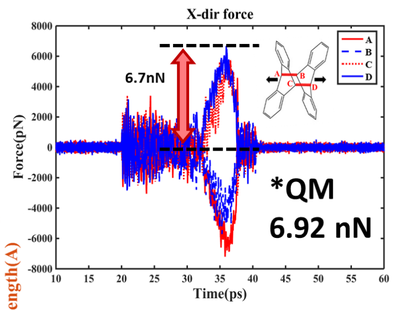
- **Virtual loading test with ReaxFF capture damage initiation and plastic deformation**
- **During virtual loading test, covalent bonds of Di-AC break and Di-AC (red) changes to anthracene groups (green)**

Covalent bond dissociation successfully simulated

Characterization of Di-AC

- **Bond dissociation energy of Di-AC => 58.5 kcal/mol**
- **Critical bond length => 2.16 Å**





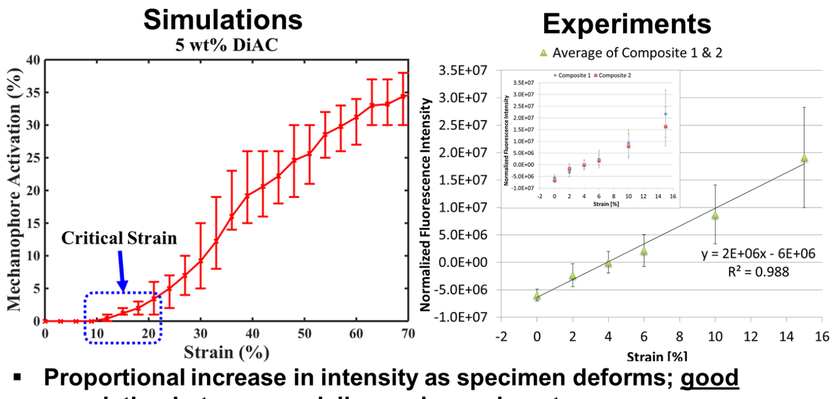
- **Bond rupture force of Di-AC (6.7nN)**
- ***QM – 6.92nN**

*Beyer et al. JCP (2000): 7307-7312.

- **BDE : 58.5 kcal/mol**
- **BRF : 6.7 nN**

Thresholds

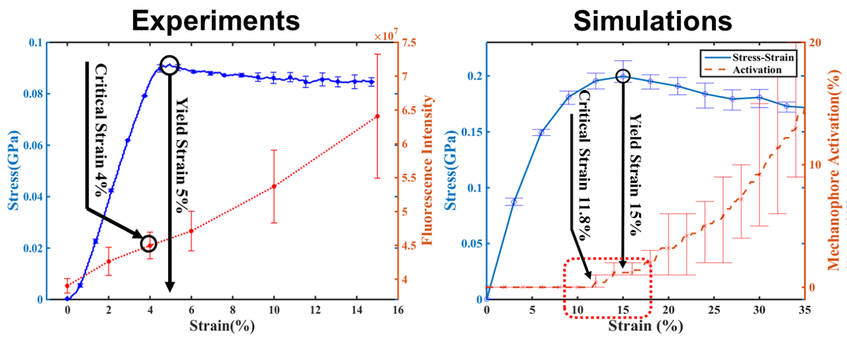
Mechanophore Activation Curve



- **Proportional increase in intensity as specimen deforms; good correlation between modeling and experiments**
- **Critical strain values representing the onset of mechanophore activation are estimated**

Mechanophore activation can represent intensity curve

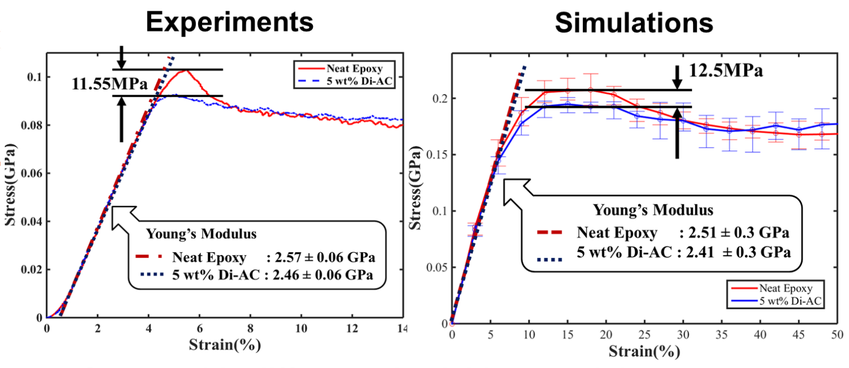
Early Signal Detection



- **Early signal detection of Di-AC was observed in experiments**

Early signal detection is captured computationally through the comparison of stress-strain curve and mechanophore activation

Yield Strength Comparison Neat Epoxy vs. 5 wt% Di-AC



- **Comparable difference in yield strength between simulations and experiments**

Captures experimentally observed responses

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