A Novel Methodology for Self-Healing at the Nanoscale in CNT/Epoxy Composites

Elizabeth Quigley, Siddhant Datta, Aditi Chattopadhyay

School for Engineering of Matter, Transport and Energy

Research supported by the Office of Naval Research, Program Manager: William Nickerson

AIMS ADAPTIVE INTELLIGENT MATERIALS & SYSTEMS CENTER

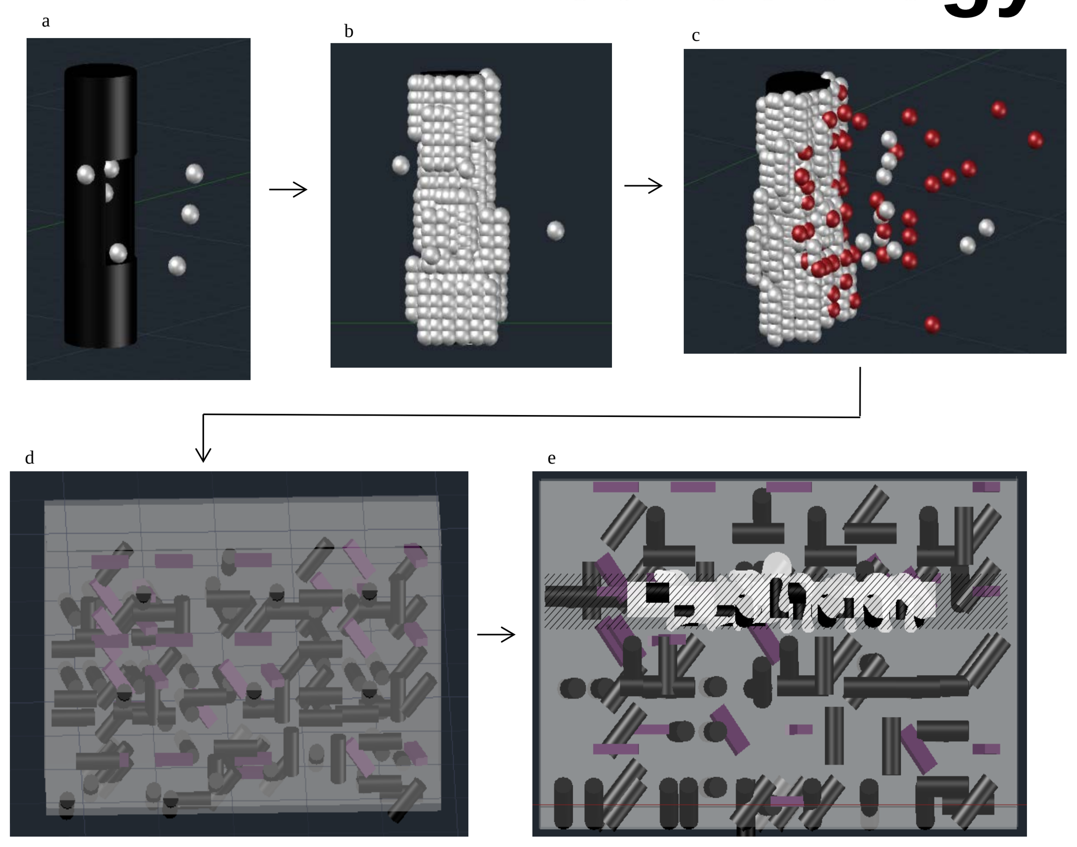
Objective:

- Develop a novel technique for filling carbon nanotubes (CNTs) with a healing agent, dicyclopentadiene (DCPD), to provide self-healing at the nanoscale
- Determine efficiency of CNT self-healing mechanism versus traditional microcapsule self-healing

Self-Healing and its Significance

- Self-healing materials: ability to repair damage caused by cracks
- Extend serviceable life as well as prevents catastrophic failure -> safer implementation in aircraft and civil platforms
- Current plane inspection methods cannot detect nano- or microscale cracks
- Microcapsules release the healing agent when a stress or load applied to the material causes the material to fracture at the nano- or micro-scale
- Carbon nanotubes (CNTs) enhance mechanical properties that polymeric nanocapsules cannot impart.

Methodology for Filling CNTs

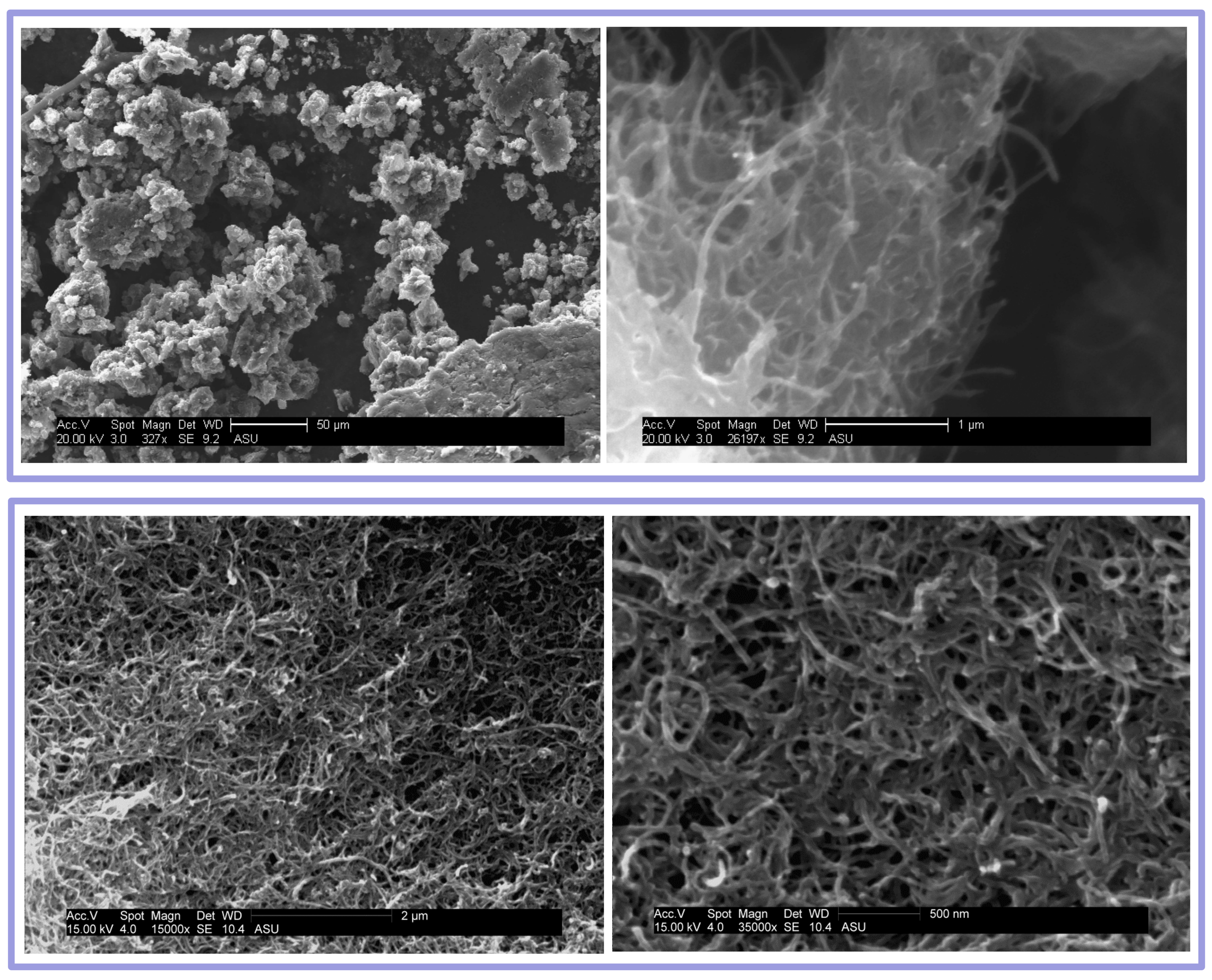


(a) open CNT being filled with DCPD (represented by silver spheres); (b) CNT with an excess of DCPD on the surface. (c) shows methanol (red spheres) removing the excess DCPD; (d) filled CNTs and Grubbs' catalyst (purple) dispersed in an epoxy matrix. Thin films of varying weight fractions of CNTs and catalyst were fabricated; (e) crack (black diagonal lines) starting to heal (white regions).

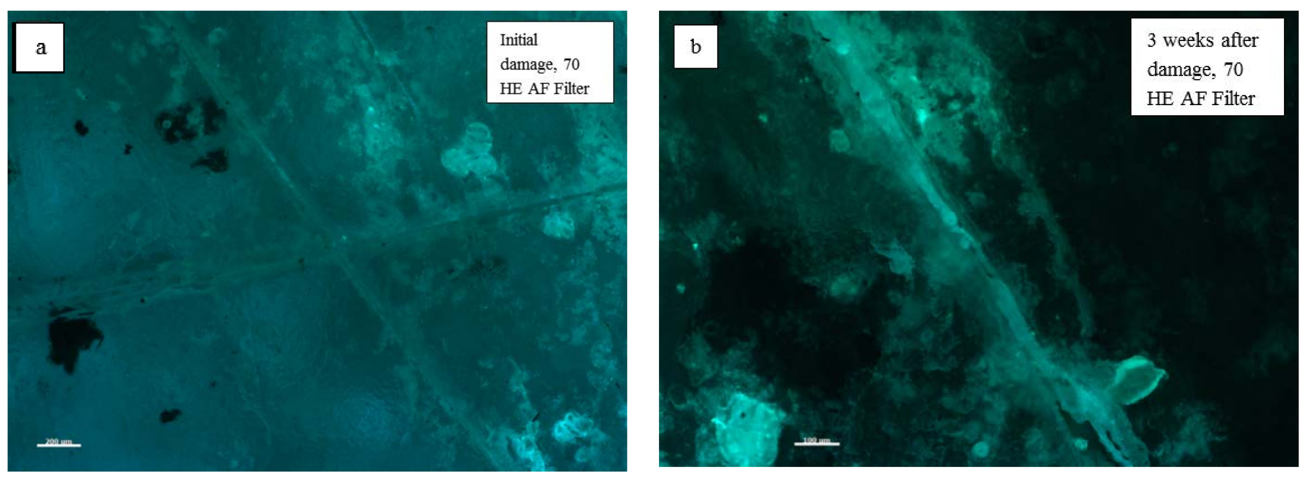
Below: Scanning electron images of two methods to extract the filled CNTs from excess DCPD.
Top row: acetone extraction at two different magnifications. Filled CNTs are heavily agglomerated with the acetone extraction method; therefore, acetone is not effective in removing DCPD.
Bottom row: methanol extraction method at two different magnifications. Filled CNTs are more separated and less DCPD is present on the surface; therefore, methanol is effective at removing DCPD from the surface of CNTs.

Acetone extracted CNTs

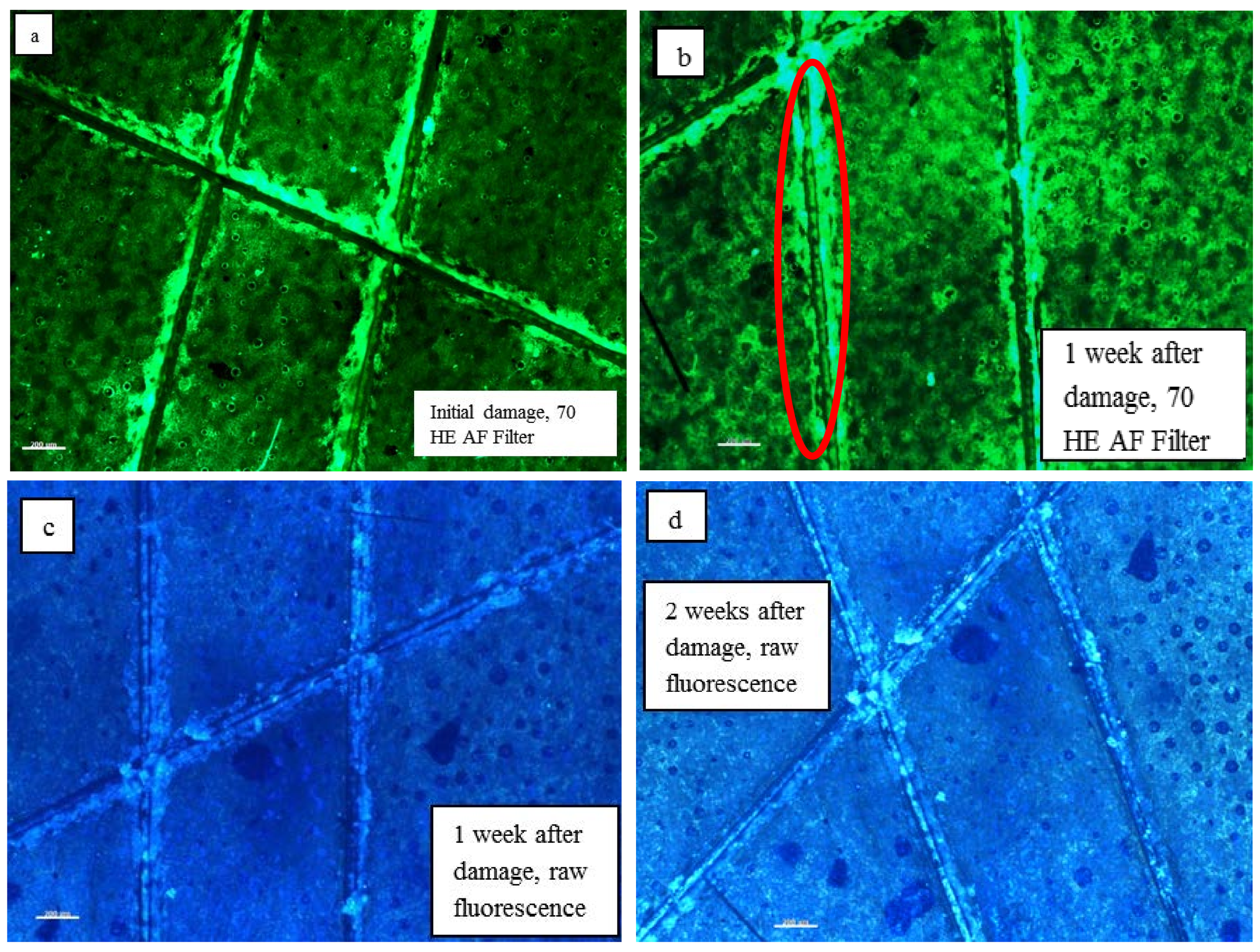
Methanol extracted CNTs



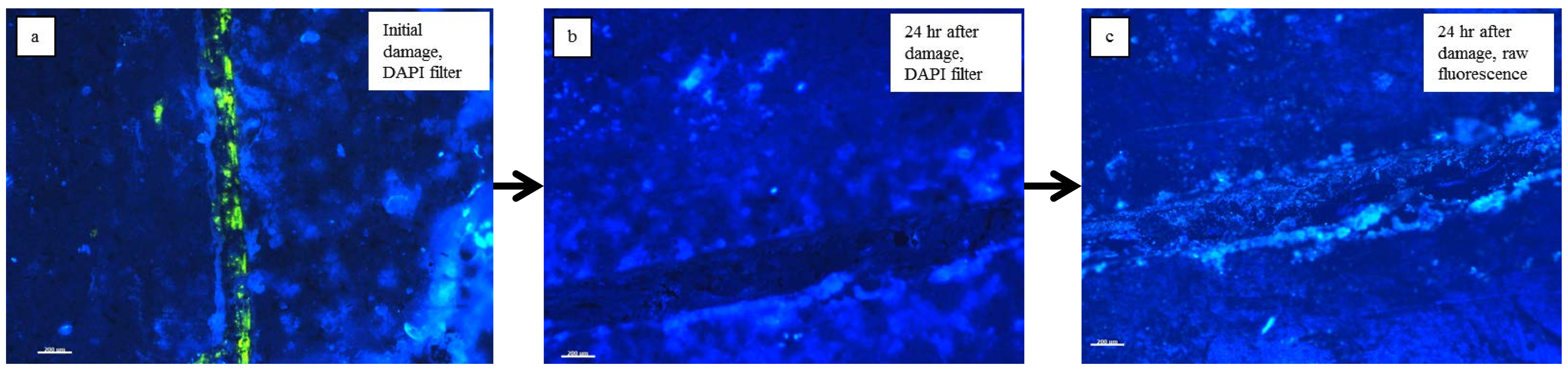
Below: Results of Film-1 fabricated with 0.4 wt% CNTs and 0.4 wt% Grubb's catalyst. CNTs were agglomerated to have concentrated areas of healing for identification purposes. a) Initial damage shown under 70 HE AF filter, 430-460 nm. Dark regions are agglomerated CNTs within an epoxy matrix. b) region with complete healing of the cut shown. All scale bars are 200 μm.



Below: Progression of healing shown with different fluorescent filters. a) initial damage shown with 70 HE AF (430-460 nm). b) 1 week after damage with same filter. Healing is evident (red circle) but not clear. c) Also 1 week after damage but with raw fluorescent light (320-650 nm). Healing is more evident and seen in all damaged areas except for lower right cut. d) 2 weeks after damage with raw fluorescent light. Healing more pronounced due to more complete healing. All scale bars are 200 μm.



Below: Evidence of healing due to disappearance of catalyst. a) film initially damaged and imaged under DAPI filter (350-390 nm). Green regions are fluorescent catalyst. b) Similar region imaged 24 hrs after damage under DAPI filter. Green regions no longer visible, i.e. catalyst optical properties have changed due to DCPD polymerizing. c) white/light blue regions within cut are healed regions. All scale bars are 200 μm.



Summary of Results

- CNTs were <u>successfully extracted</u> from excess DCPD using methanol
- All thin films showed <u>evidence of healing</u>
- Different weight fractions had different amounts of healing
  - Film-1 had most complete healing
  - Film-2 had more regions healed
- Evidence for healing supported by <u>disappearance of catalyst</u> after 24 hours
- Highest healing rate: 71.4 μm $\pm$ 1.8 μm per day
  - High enough to <u>completely or partially heal</u> the crack
- CNTs one to two orders of magnitude lower than the wt% of microcapsules reported in literature
  - Healing was observed → <u>CNTs more efficient at self-healing</u> than their microcapsule counterparts
- Healing of crack continued to progress over several days
  - Occurred slower than expected

Future Work

- Understanding optimal healing environment
- Investigating mechanical recovery of CNT/epoxy composites
- Using single walled CNTs vs multi-walled CNTs
- Exploring the effect of different healing agents
- Finding the optimal weight fraction of CNTs and catalyst

ASU Ira A. Fulton school of engineering

ADAPTIVE INTELLIGENT MATERIALS & SYSTEMS CENTER