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Tritium Focus Group (TFG) meeting
23-25 Sept. 2014, Energy Innovation Laboratory
Idaho National Laboratory, Idaho Falls, ID

Advanced Polymers for Tritium Service

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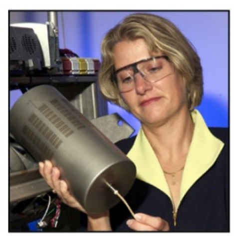
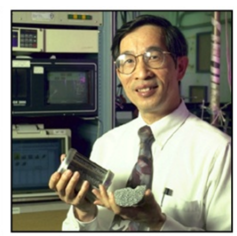
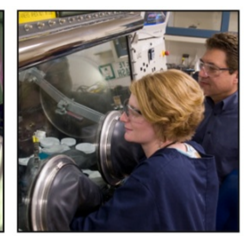
Tritium Engineer: Louis Boone

September 24, 2014

1 Savannah River National Laboratory, Aiken, SC
2 Clemson University, Clemson, SC
2 NanoTechLabs, Inc., Yadkinville, NC

Plant Directed R&D

Project Team

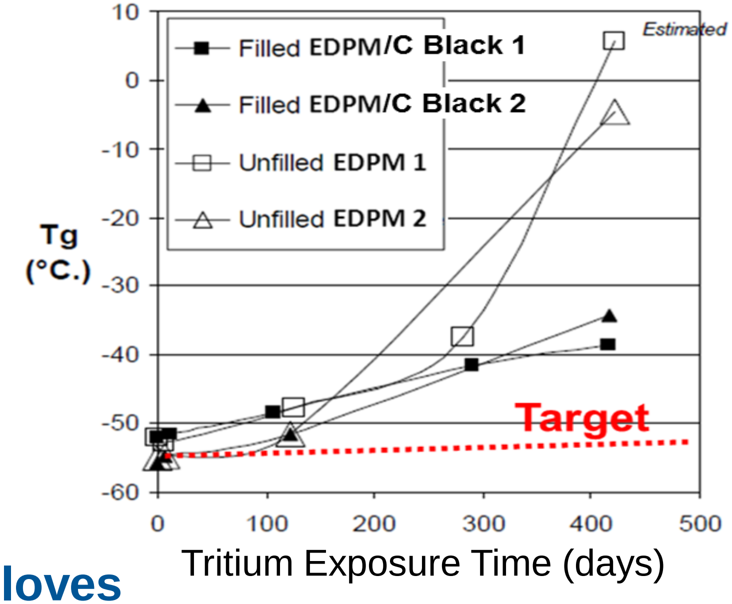
- **Jay Gaillard – SRNL/Material Science & Engineering**
  - *PI: Project coordination, polymer development, beta simulations*
- **Hector Colon-Mercado – SRNL/Renewable Energy**
  - *PI: Development of polymer composites, TGA, and DMA*
- **Steven Serkiz – SRNL/Nuclear Nonproliferation**
  - *Lead: Project coordination*
- **Brent Peters – SRNL/Material Science & Engineering**
  - *Lead: Mechanical testing and electron microscopy*
- **Elise Fox – SRNL/Material Science & Engineering**
  - *Lead: Tritium/SRNL interface for tritium exposure studies*
- **Timothy DeVol – Clemson University/Environmental Engineering Dep.**
  - *Collaboration: Beta radiation exposures with Sr90 source*
- **Richard Czerw – NanoTechLabs, Inc./CEO – Small Business**
  - *Collaboration: Production of nanomaterial/polymer composites*

Improving Polymers in Tritium Service

Radiation resistant elastomers in tritium service

- **Goal ➔ Extend lifetime of elastomer seals (o-rings, valve seals) in Tritium service**
  - Achieve >400 hrs service
- **Approach ➔ Investigate <u>nanotubes</u> and <u>graphene</u> as conductive fillers to impart conductivity (radiation resistance) in the polymers and graphene coatings as a permeation barrier.**

Increase in T_g leads to loss in "rubbery" behavior.

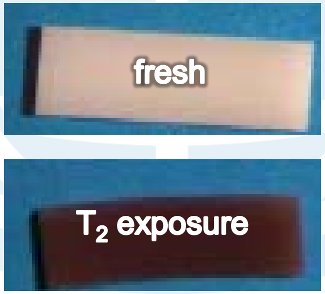


Graphene permeation barriers for glovebox gloves

- **Our goal is to produce graphene/butyl rubber composites with significantly lower permeability of water and oxygen as compared to current Tritium facility glovebox gloves.**
- **Approach ➔ i) a layered/durable graphene coating on the glove surface or interlaminate layer and ii) graphene as a filler in the butyl rubber matrix.**

Motivation

- **Elastomer seals (O-rings, valve seals) lack stability for tritium service**
  - Ionizing radiation creates *broken bonds* in the polymer
  - Results in damage of the seal and process performance
    - Mechanical degradation of the seal, particulate contamination, and off-gassing of volatile compounds



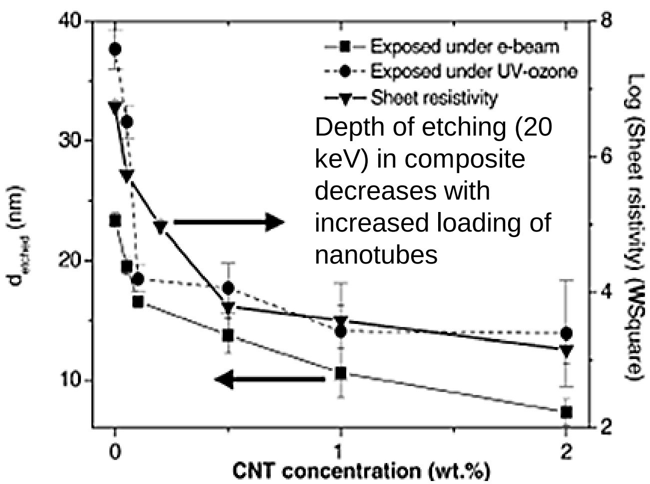
Teflon

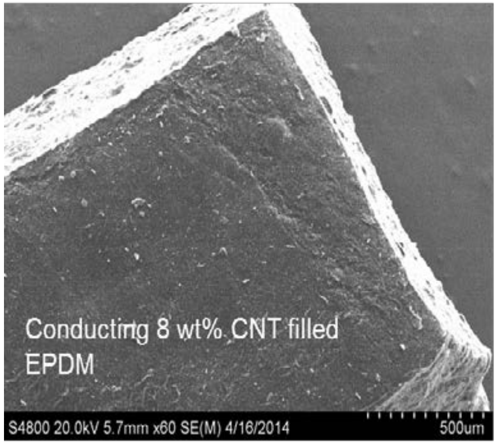
- **Current glovebox gloves lack sufficient impermeability to T_2, O_2 and H_2O**
  - O_2/H_2O permeation through glovebox gloves contributes to consumption of Mg beds: represents a material cost savings.
  - Gloves with high puncture resistance displayed higher tritium permeation than Site approved gloves. *Butyl gloves are used in the facility because of their low permeability; however, butyl rubber is not a particularly tough, puncture resistant, or abrasion resistant material.*

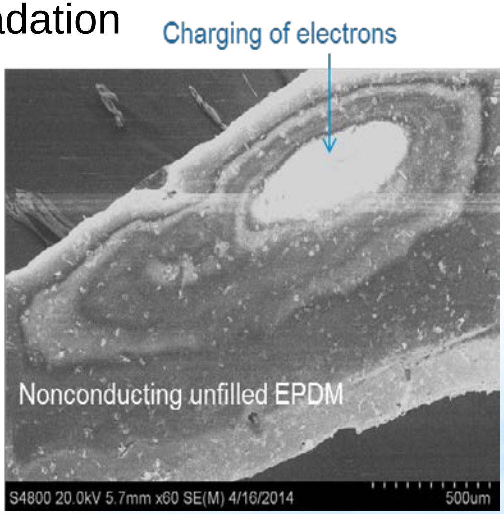
Radiation resistant elastomers for tritium service

Radiation Resistant Elastomers for Tritium service

- **Radiation damage is higher in *e*⁻ insulating materials**
  - Insulating material-β interactions generate an excited energy state that becomes stored as potential energy resulting in the *creation of radicals* or *"broken bonds"*
  - Conductive material- β induced vacancies are localized to the valence band, which is filled very rapidly and release as thermal energy *with no permanent damage*
- **Carbon nanotube (CNT) fillers have already shown resistance to β radiation**
- **Graphene also acts as a conductive filler and permeation barrier**
  - Resistance up to 80-300 keV of accelerated electrons based on e⁻ beam experiments (beta energy from tritium ~5.8 keV)
  - Act as radiation sink and radical scavenger to impede degradation





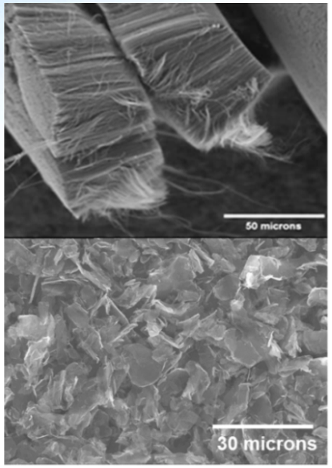


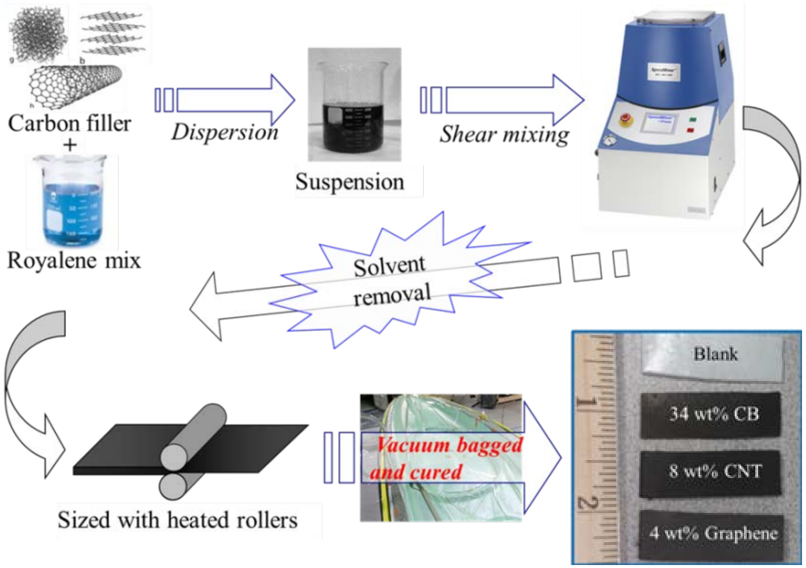
SRNL

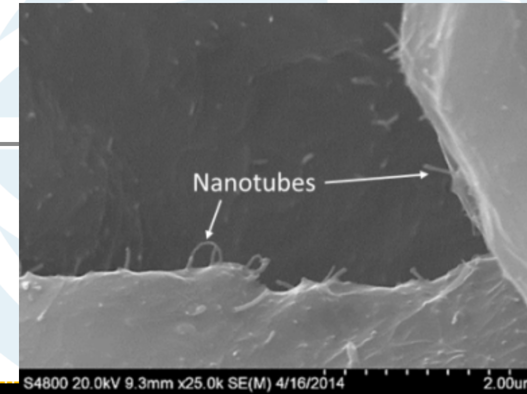
E Najafi, K Shin, "Radiation resistant polymer–carbon nanotube nanocomposite thin films", Colloids and Surfaces A: Physicochem. Eng. Aspects, 257–258, 333–337 (2005).

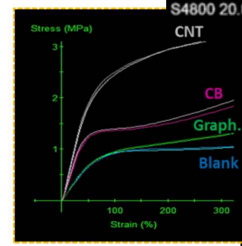
Plant Directed R&D PDRD

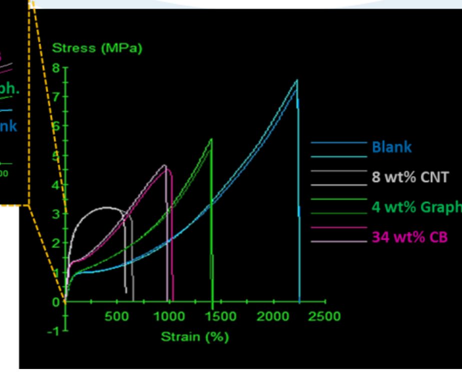
Radiation Resistant Elastomers







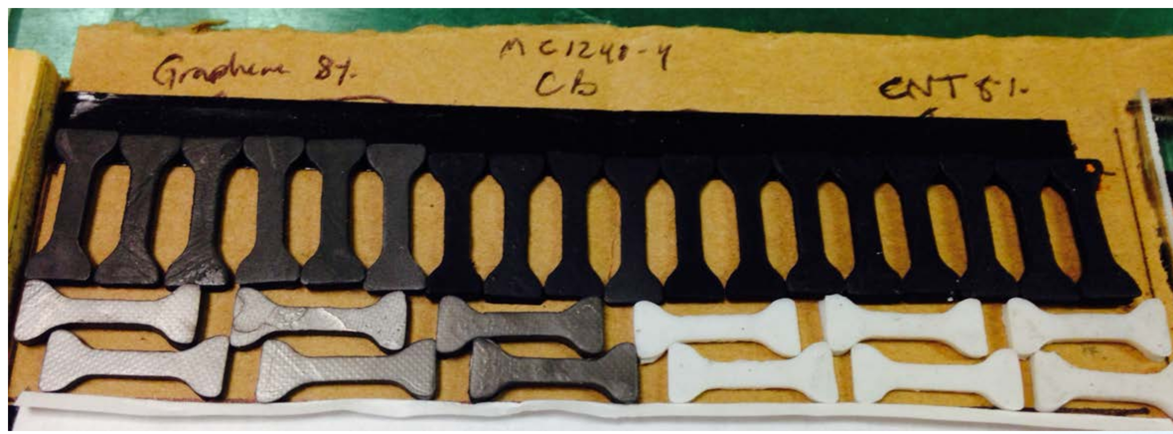




- **In FY14, CNT- and graphene- EPDM composites were produced at NanoTechLabs, Inc.** Seven different large coupons were produced that included EPDM blanks and different concentrations of CNTs and graphene loaded EPDM.
- **Stress-strain and SEM showed good dispersion and mechanical performance.** Nanotubes had increase in modulus (stiffer) while graphene showed same modulus (stayed rubbery) as the unfilled EPDM.
- **6 total sample sets (6 each) were put into SAS (June 2014):** 6 and 12 month tritium exposure planned. Mass spectrometry (measures off gassing) and DMA when taken out.

Radiation Resistant Elastomers

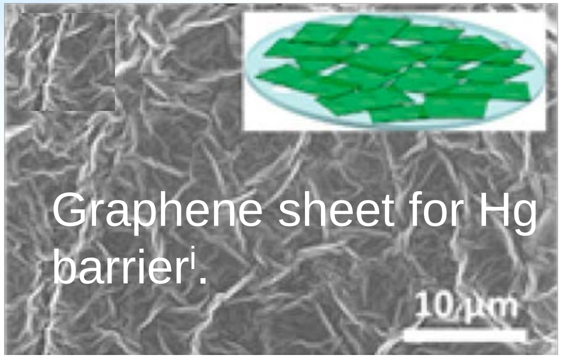
- **We plan to down select tritium exposed composites** by the end of year 2 (FY15) and start final tritium exposure tests that will continue into year 3 (FY16) for final recommendations.
- **For quicker feedback, downselect composites using high energy beta experiments**: we are currently performing beta exposure with 5.5" x 1" $^{90}Sr/^{90}Y$ ~20 mCi (546 keV) at Clemson University. Six and nine week exposures have finished – currently taking mechanical measurements for preliminary results. In FY15, we plan to calibrate the source using a dosimeter and investigate the downselected materials.

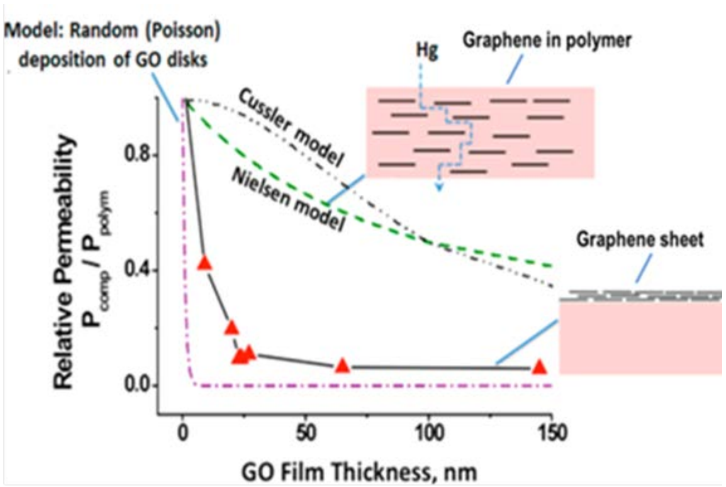


Sr-90 (10 mCi) exposed dogbones at Clemson University

Graphene permeation barriers for glovebox gloves

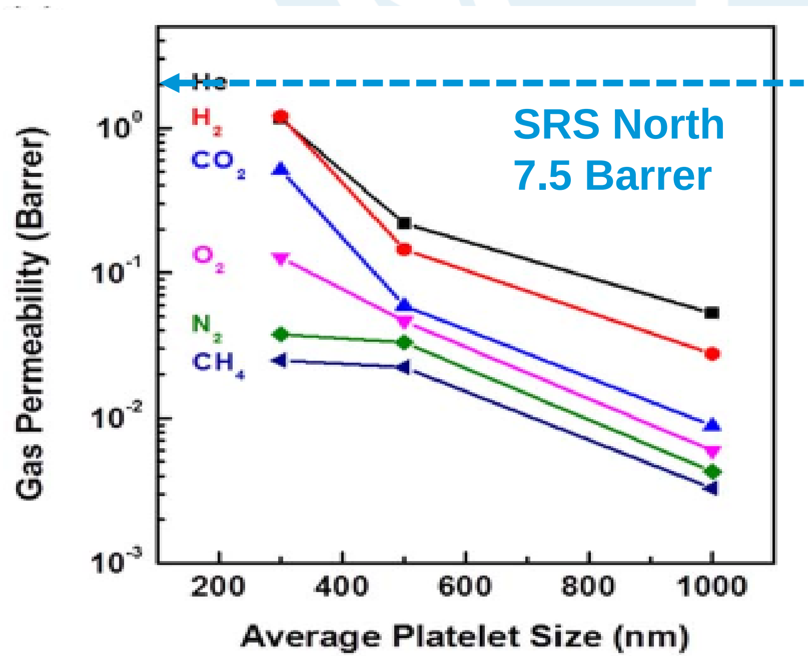
Graphene Permeation Barriers: Coatings





A graphene/polymer composite at several microns thick would approach similar relative permeability as the sheet.

Guo et al. *Environ Sci Technol.* 46(14): 7717–7724. (2012)



Gas permeability of thick graphene films (0.5 µm)

Yoo et al., *J. Appl. Polym. Sci.* 39628 (2014)

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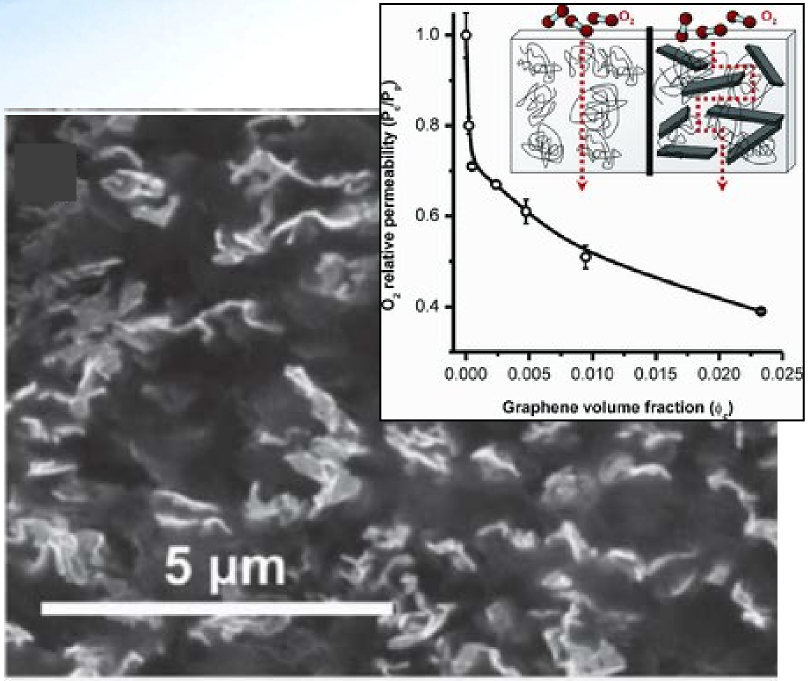
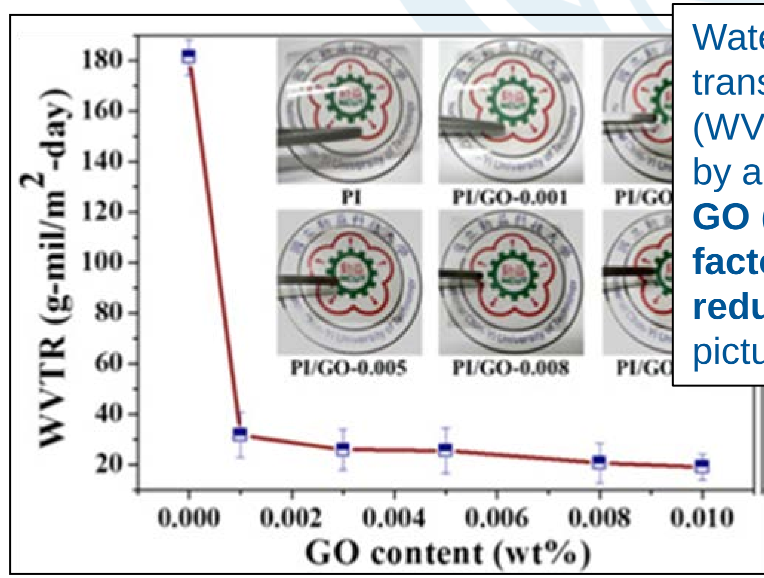
Graphene Permeation Barriers: Polymer composites





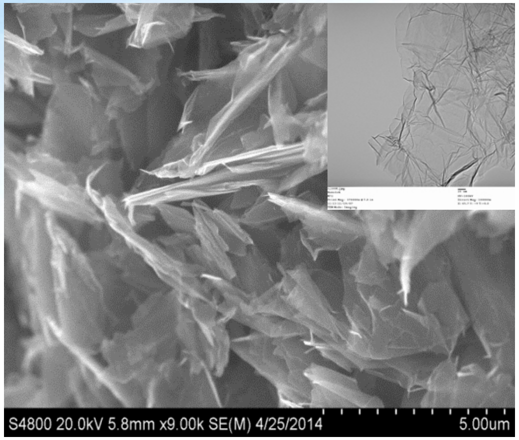
Water-vapor-transmission-rate (WVTR) decreased by a **factor of 9 for GO** (above) and a **factor of 11 for reduced GO** (not pictured).

- Polystyrene/graphene composite drastically inhibited the permeation of oxygen molecules at very low volume fraction[i].

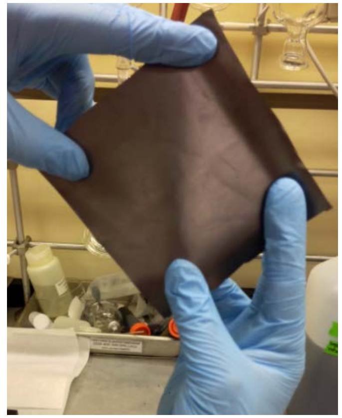
- Moisture barrier from thin (2 µm) polyimide/ graphene composite film at different loadings[ii].

i) Compton et al. *Advanced Materials* **22** p. 4759–4763 (2010)
ii) Tsai et al. *Polymer International* 62 p. 1302–1309 (2013)

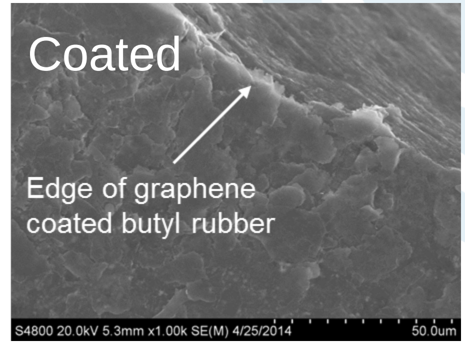
Graphene permeation barriers for gloves



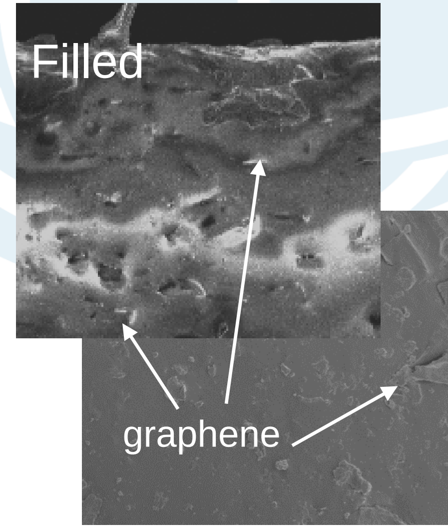
Graphene N006P (Angstron Materials, Inc.)



Graphene coated 15 mil Piercan butyl rubber glove.



SEM of graphene coated (above) and filled (right) butyl rubber



- **Graphene coatings:** Large platelet (~15µm) graphene was solution drop-casted onto the surface of butyl rubber coupons. In addition, we mechanically exfoliated/coated graphene onto butyl rubber surface. We are currently developing the capabilities to coat the butyl rubber by dip-coating.
- **Graphene filled butyl rubber has been produced at NanoTechLabs** using solution processing of exfoliated graphene mixed with isobutylene isoprene (IIR) (uncured butyl rubber) matrix followed by heat rolling and vacuum molding.
- **O_2 and H_2O Permeation testing** is currently being performed at Illinois Instruments Inc.
- **Industrial collaboration has been established with Guardian gloves.** They have agreed to produce graphene filled butyl coupons by added our recipe to their glove formulation.

Questions?